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# Fire-retardant unsaturated polyester thermosets: The state-of-the-art, challenges and opportunities

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## ABSTRACT

The increasing demands placed upon structural thermosets, such as epoxy and unsaturated polyester (UP), and ever-increasing regulations for fire safety, have driven the development of high-performance ecofriendly fire-retardant thermoset polymers. This review provides a historical overview of fire-retardant UP that aims to review the state-of-the-art design and efficiency of fire-retardant strategies developed in the last decade, and pave the way for developing next-generation fire-retardant UP materials in the future. In general, there are three approaches for creating fire-retardant UP with reactive and additive fire-retardants (FRs). One promising strategy is to develop intrinsically fire-retardant UP resins by using FRs monomers. Another favorable approach is the copolymerization of UP resin with reactive FRs comonomers. The last but encouraging method is the hybridization of phosphorus additive FRs with metal hydroxides. Recently, the design of polymeric, nanostructured and core–shell structured FRs has emerged as a subject of enormous scientific interest. Although advantages of current fire-retardant systems, there have remained some key challenges with them, such as their adverse impacts on the processability, curing behavior, and mechanical properties of UP. This work reviews the state-of-the-art, design, performance, and applications of fire-retardant UP thermosets. Also, additive FRs are classified according to the fire-retardant index (FRI) and the required level of FRs to achieve a UL-94 V-0 rating. Finally, we discuss current challenges and possible directions for future research on the promising fire-retardancy strategies for UP thermosets.

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*Abbreviations:* AA, Acrylic acid; ADP, Aluminium diethylphosphinate; AHP, Aluminium hypophosphite; APP, Ammonium polyphosphate; ATH, Aluminium trihydrate; BAHEE, Bisphenol A bis(2-hydroxyethyl)ether; BADPS, Bis(acryloxyethyldiphenylphosphate) sulfone; CB, Carbon black; ClA, Cl-containing anhydride; DASPP, Di(allyloxybisphenol sulfone) phenoxy phosphonate; DHP, 2-((((6-oxidodibenzo [c, e] oxaphosphinin-6-yl)methoxy)(phenoxy)phosphoryl)oxy) ethyl acrylate; DMPY, Dimelamine pyrophosphate; DMVBP, Dimethyl-vinylbenzylphosphonate; DT, Phosphaphenanthrene and triazine-trione groups; DTAP, Diethylene glycol modified tetra-allyl phosphate; EP, Epoxy resin; EACGP, Ethyl acrylate cyclic glycol phosphate; FA, Fumaric acid; FGI, Fire Growth Index; FRI, Flame Retardancy Index; GO, Graphene Oxide; IPhA, Isophthalic acid; Kao, Kaolinite; KUIC, Kaolinite-urea intercalation complex; MA, Maleic anhydride; MCA, Melamine cyanurate; MCC, Microscale combustion calorimetry; MDH, Magnesium hydroxide; MEL, Melamine; MPDIOL, 2-Methylpropane-1,3-diol; MPP, Melamine pyrophosphate; MVDOS, Methyl vinyl di (1-thio-2,6,7-trioxal-1-phosphabicyclo [2.2] octane-4-methoxy) silane; ODOPB-AC, 10-(2,5-diacrylic ester phenyl) 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide; PDAP, 1-oxo-2,6,7-trioxa-1- phosphabicyclo-[2.2.2]octane-methyl diallyl phosphate; PER, Pentaerythritol; PhA, Phthalic anhydride; PHRR, peak heat release rate; PPG, Propylene glycol; PPAP, Piperazine pyrophosphate; PPISP, Poly(hydroxyphenyl imino methyl phenol spirocyclic pentaerythritol diphosphonate); Si-APP, Silane-coated ammonium polyphosphate; THR, Total Heat Release; TTI, Time To Ignition; TAOPO, Tris (allyloxymethyl) phosphine oxide; TAP, Triallyl phosphate; TDCAA-DOPO, 1,4-phenylene-bis((6-oxido-6H-dibenz [c,e] oxaphosphorinyl) methylene) diacrylate; TGIC-AA-DOPO, Acrylate [1,3,5-triglycidyl isocyanurate–acrylic acid-DOPO; TRIPOD-DOPO, 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine-DOPO; UP, Unsaturated polyester; ZnPi, Zinc diethylphosphinate.

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## 1. Introduction

### 1.1. *Background of unsaturated polyester (UP)*

The modern world continues to place increasing demands upon materials through emerging applications and more stringent regulatory regimes. Nowhere is this more relevant than for polymers and polymer composites to be more fire-retardant, to keep people safe and the built environment secure [1,2]. Thermoset polymers are ideally suited for structural applications due to their mechanical strength [3–5], with unsaturated polyesters being the most commonly used resin for everyday applications in the construction, maritime, transportation and wind energy industries [6–8]. Their low cost, ease of processability combined with excellent mechanical and thermal stability, and chemical resistance means they are in demand, particularly in applications close to human activity.

The high flammability of UP therefore is a major problem [6–8] and indeed the flammability of UP is the worst of the most common commercially available resins as follows: phenolic < bismaleimide < epoxy < UP [9]. This review will focus on the state of the art for fire-retardants (FRs) used over the last decade in UP thermosets and its composites. In addition, it will discuss the effect of the FR additive upon the flow behaviour, curing mechanism, thermal decomposition and mechanical properties of UP. Finally, this review presents some key challenges associated with different FRs and proposes future development directions and opportunities.

### 1.2. *Curing reaction and thermal decomposition of UP*

UP is produced by the condensation reaction of a diol with a mixture of saturated and unsaturated diacids and anhydrides with the reaction being driven to completion through the continuous removal of water [10]. With the addition of vinyl monomers such as styrene as a processing aid, reactive diluent and crosslinker, a catalyst and accelerator, a three-dimensional network is produced via free radical chain growth polymerization. UP resins are generally categorized based on their prepolymer starting materials as follows: ortho resins, *iso*-resins, bisphenol-A, chlorendic, and vinyl ester as depicted in the Figure S1 [11].

Much work has shown the thermal stability of UP [13–15] was impacted by several parameters, such as styrene content, the chemical structure of the prepolymer and final network structure [16]. The degradation initiates through homolytic cleavage of the bonds nearest the ester group (C—O) to form two free radicals (reaction-1 in Fig. 1). Then, subsequent reaction with hydrogen, phthalic anhydride (at about 330 °C [15]) and hydroxyester compounds (at about 390 °C [17]) are produced. The oligostyrene cross-links then depolymerize via weaker aliphatic carbon–carbon bonds (bond A) adjacent to the polyester backbone which ultimately form styrene monomers and oligomers as illustrated in reaction-2 (bond B) in Fig. 1 [12]. The crosslinked polystyrene can also decompose to the styrene, styrene dimer, styrene trimer, toluene, phenylacetaldehyde, benzaldehyde, α-methylbenzene and ethylbenzene [18,19]. By depolymerisation of styrene (about 380 °C [15]), linear polyester sequences forming and further chain scission occurring by thermal degradation as presented in Reactions 3 and 4 in Fig. 1. The last step is the oxidation of carbonaceous char [20].

### 1.3. *Evaluation methods of fire-retardant performance(s)*

The most comprehensive analysis of a materials combustion profile is cone calorimetry [21,22] by measuring the time to ignition (TTI), the peak heat release rates (PHRR) and total heat released (THR). Table 1 represents the equations have been used to evaluate the flame retardants performance by cone calorimetry. Herein, ΔPHRR, ΔTHR and flame retardancy index (FRI) are used for comparing fire performances of different fire-retardant systems.

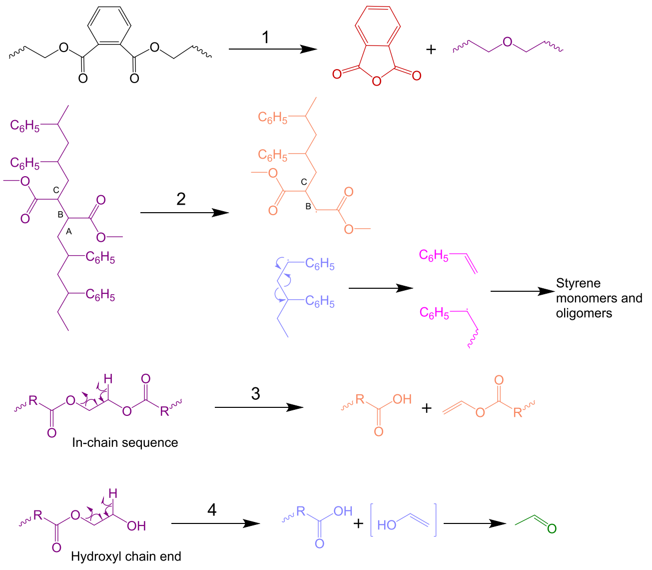

**Fig. 1.** Proposed thermal degradation mechanism of UP. Reactions (1 to 4) represent the main decomposition stages, reproduced with permission from [12] copy right 2014 Elsevier Ltd.

**Table 1**
Evaluation methods of flame retardants performance by cone calorimetry.

| No. | Equation | Evaluation | Reference |
|---|---|---|---|
| 1 | $\Delta PHRR = \dfrac{PHHR_c - PHHR_p}{PHHR_p} \times 100$ | Higher values indicate better fire retardancy. | [21] |
| 2 | $\Delta THR = \dfrac{THR_c - THR_p}{THR_p} \times 100$ | Higher values indicate better fire retardancy. | [21] |
| 3 | $FGI = \dfrac{PHHR}{T_{PHHR}}$ | Fire growth index (FGI): lower FGI indicates better fire retardancy. | [27–29] |
| 4 | $FPI = \dfrac{TTI}{PHHR}$ | Fire performance index (FPI): higher FPI indicates better fire retardancy. | [30,31] |
| 5 | $FRI = \dfrac{[THR \times \frac{PHHR}{TTI}]p}{[THR \times \frac{PHHR}{TTI}]c}$ | Flame retardancy index (FRI): FRI < 1 (Poor), 1 < FRI < 10 (good), and 10 < FRI (excellent) | [23–26] |

*c and p represents composite and polymer, respectively.

## 2. Fire-retardants for UP

There are three main approaches for making fire-retardant UP. One promising strategy is to develop intrinsically fire-retardant UP resins by using fire-retardants (FR) as monomers. Typically, these monomers contain chlorine, bromine, phosphorus, nitrogen, silicon, and sulphur in their structure. Another favorable approach is the copolymerization of UP resin with reactive fire-retardant comonomers. The last is additive FRs which are just physically mixed into the resin. The additive FRs are classified as organic and inorganic. Halogenated, charring resins, oligomeric and polymeric FRs are organic FRs types while P-N complexes, ATH, nanostructured, and core–shell structured FRs are inorganics. Fig. 2 illustrates the classification of FRs for UP in this review.

### 2.1. *Reactive fire-retardants*

There are attempts to modify the molecular backbone of UP to fabricate an intrinsic fire-retardant UP, in which monomers containing halogen, phosphorus, and recently magnesium introduce during the polycondensation reaction. This approach has some advantages including better durability and a less deleterious impact on the

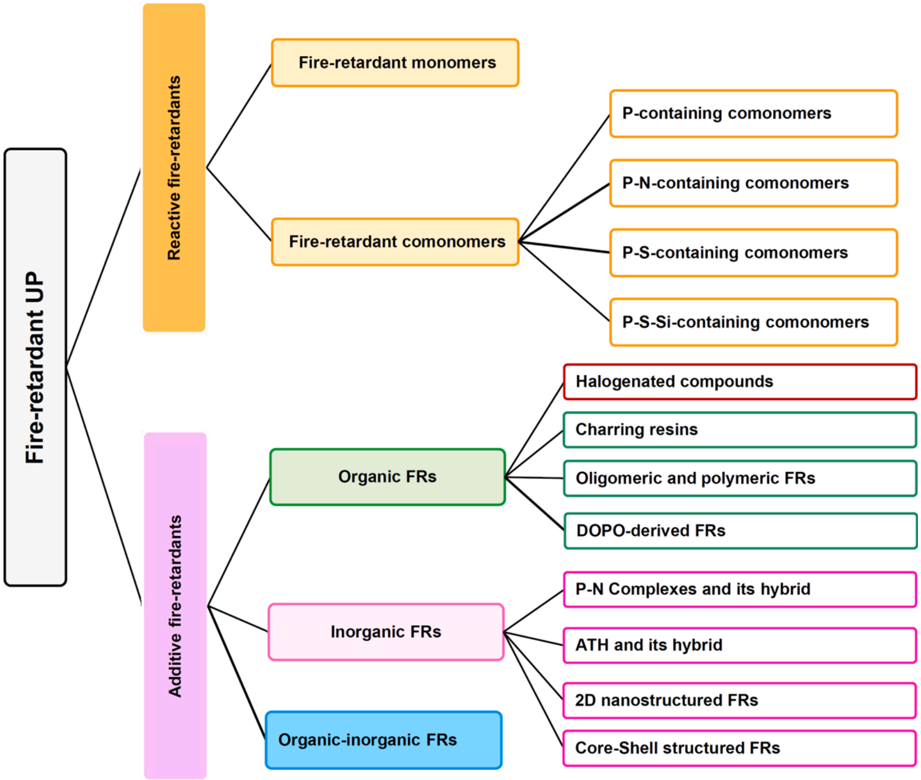

**Fig. 2.** The classification of FRs for UP thermosets.

mechanical and physical properties of the thermoset. Fig. 3 shows the chemical structure of FR monomers were used to synthesis an intrinsic fire-retardant UP.

### 2.1.1. *Fire-retardant monomers*

Early efforts to develop fire-retardant UP focussed upon the use of halogenated monomers, because of their high levels of efficiency [6]. In this regard, chlorine/bromine-containing anhydrides or phenols were used to prepare FR-UP [11]. In 1954, a fire-retardant UP system based on hexachlorocyclopentadiene was reacted with maleic anhydride to synthesise 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-5-heptene-2,3-dicarboxylic anhydride (HCHDA) under the commercial name of HET acid [32]. The most important halogenated FRs for UP prepolymer in order are tetrabromophthalic anhydride (TBPA), then tetrachlorophthalic anhydride (TCPA), and finally dibromoneopentyl glycol (DBNPG) [50]. Generally, bromine-containing compounds are more effective fire-retardants compared to chlorine [50]. It has been demonstrated that to achieve self-extinguishing behaviour, at least 12% bromine is required [51]. However, due to environmental concern their use has become increasingly restricted.

9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) is a well-known fire-retardant which has been used widely for epoxy thermoset as a reactive fire-retardant where the DOPO easily reacts with epoxide groups [52–54]. However, DOPO cannot react with UP directly, so it has been first reacted with dicarboxylic acid or maleic anhydride. Reacting DOPO with itaconic acid (ITA) has been shown to form 9,10-dihydro-10[2,3-di(hydroxy carbonyl)propyl]-10-phosphaphenanthrene-10-oxide (DDP) [37], which can then be used as a monomer to prepare the UP. Thus a fire-retardant UP with LOI value of 29% and V-0 rating was prepared by incorporation of 1.62% phosphorus content (17.4 wt% of DDP). Also, cone calorimetry results revealed a reduction of about 43% in PHRR and THR. DOPO can also react with maleic anhydride to form 2-[10-(9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide-10-yl)]-maleic acid (DOPO-MA), and used as a reactive monomer to synthesise UP [36]. A UP sample with 2.24 % P-content was prepared by 23.3 wt% of DOPO-MA in the synthesised recipe. The LOI of 25.4% and V-1 rating was reported for this system. Comparison of these two system [36,37], indicating that reactive incorporation of DOPO using a dicarboxylic acid is more effective than maleic anhydride. It should be noted that the introduction of DOPO in the backbone of UP can reduce the viscosity of the entire system, which facilitates its processing for composite manufacturing. However, the phosphine oxide particularly the P-O groups, can have a retarding effect on the curing reactivity of the UP, which will be discussed later.

Recently, magnesium hydroxide (MH) has been modified with maleic acid (MA) to form a reactive organic magnesium hydroxide (OMH) compound which can be involved in the polycondensation of UP [55]. It has been presented that 1 wt% of OMH with 8 wt% expandable graphite (EG) resulted in a V-0 class of UL94 and LOI of 28.5%. Moreover, it was shown that UP with 6% of EG and 1% of OMH significantly reduced PHRR and THR to 281 (kW $m^{-2}$) and 57.4 (MJ $m^{-2}$), respectively. However, the flexural strength of UP/6EG + 1OMH declined significantly by 41%. Hence, the incorporation of a metal hydroxide in polymer backbone during polymerization is a promising strategy to overcome the difficulty of processing. Nevertheless, it is essential to further characterize the viscosity and rheological behaviors of these fire-retardant systems.

### 2.1.2. *Fire-retardant comonomers*

Another approach to fabricate a fire-retardant UP is using FR vinyl comonomers to reactively incorporate to UP thermoset during curing reaction. Fig. 3b shows vinyl comonomers for fire-retardant UP systems. Comparing Fig. 3b with Fig. 3a somewhat illustrates the comparative degree of research into development of FR comonomers in recent years.

*2.1.2.1. Phosphorus-containing comonomers.* Replacement of styrene by phosphorous-based monomer as a comonomer is a more attractive strategy than modification of the polyesters itself due to the complexity of the polycondensation process. As a result, efforts have been

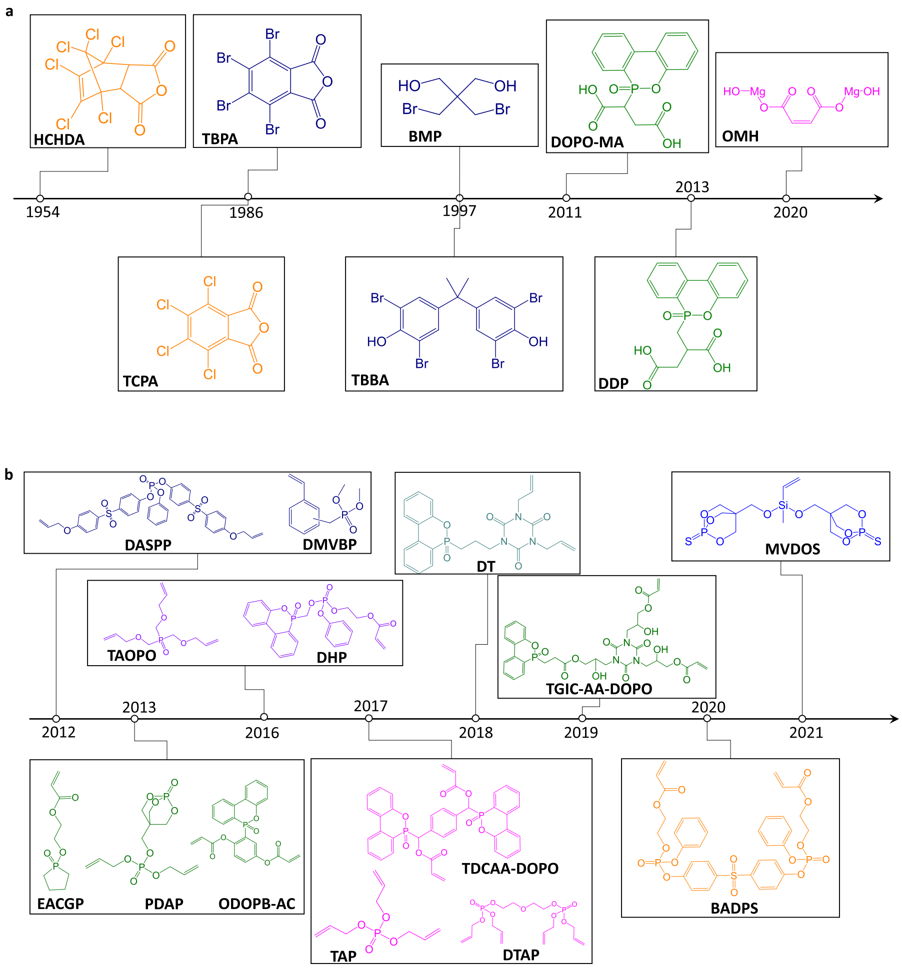

**Fig. 3.** a) Chemical structure of FR monomers were used to synthesise an intrinsic fire-retardant UP: HCHDA [32], TBPA [33], TCPA [33], TBBA [34], BMP [35], DOPO-MA [36], DDP [37]; b) Chemical structure of vinyl comonomers for fire-retardant UP systems: DASPP [38], DMVBP [39], EACGP [40], PDAP [41], ODOPB-AC [42], TAOPO [43], DHP[43], TAP [44], TDCAA-DOPO [45], DTAP [44], DT [46], TGICAA-DOPO [47], BADPS [48], MVDOS [49].

concentrated on developing a new family of phosphorous-containing vinyl monomers and replacing or reducing the use of styrene. As an example, the diallyl ester, di(allyloxybisphenol sulfone) phenoxy phosphonate, (DASPP) was developed as a fire-retardant for UP. When the composition of DASPP increased to 20 wt% (UPR20), the LOI increased from 20.5% to 26% and dripping during combustion stopped when the concentration of DASPP was 15% or more [38]. The cone calorimetry results indicated that for UPR20, the PHRR reduced by about 45 % and the THR declined significantly for UPR20, from 76 MJ/m$^2$ (unmodified sample) to 59 MJ/m$^2$. The mechanical properties showed that addition of 15 wt% of the DASPP actually improved tensile strength and Young's modulus by 27% and 8.7%, respectively. Evaluation of $T_g$ also pointed to an increase of 7.1 °C (135.8 to 142.9°) for UPR20, due to the increased crosslinking, aromaticity and the thermally stable sulfone group in the network. The toughness (area under the stress–strain curve) for UPR20 was increased more than four times, likely due to the aryl–ether linkage in the structure of DASPP facilitating rotation of O–C links.

A phosphonated styrenic monomer, Dimethyl-vinylbenzylphosphonate (DMVBP) was explored as a comonomer for an UP system [39]. DMVBP reduced the thermal stability and the decomposition temperature ($T_d$) from 262 °C to 211 °C for UP networks containing 38% DMVBP. However, faster formation of the char via a catalytic effect, slowed down decomposition, increasing the char residue at 800 °C (under nitrogen) from 0.2% to 29.8%. Similarly, ethyl acrylate cyclic glycol phosphate (EACGP) decreased the $T_d$ and also improved char yield [40]. The LOI increased from 20.5% for unmodified UP to 26.5% for modified UP at 20 wt% of EACGP (EACGP20). Also, the cone calorimetry results indicated that the PHRR of EACGP20 reduced from 408 W/g to 183 W/g (55.1%). Again, 1-oxo-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane-methyl diallyl phosphate, (PDAP) [41] when used as a FR for UP reduced the $T_d$ at 10% weight loss, from 348 °C to 273 °C (under nitrogen). At 20 wt% of PDAP (PDAP20), the char residue at 800 °C (under nitrogen) increased from 3.5% to 13.1%. In this work, the THR of the control UP was 21.5 KJ/g which was reduced to 15.8, 13.5, 13.1 KJ/g, for PDAP10, 15, and 20, respectively, while the LOI increased significantly from 20% to 27.5% for PDAP20. TG-FTIR analysis suggested that less gaseous products were emitted, although pyrolysis products were produced faster in the presence of PDAP compared with unmodified UP, validating the catalysing impact of PDAP on decomposition.

The reactive phosphorus-containing acrylate, 10-(2,5-Diacrylic ester phenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (ODOPB-AC) was also synthesised as a comonomer for UP [42]. The LOI increased from 20.5% to 28% at 20 wt% of ODOPB-AC in UP and the PHRR decreased from 412.7 to 288.7 W/g. The higher residual char indicating that ODOPB-AC acted in the condensed phase which is primarily due to the presence of oxygen and highly aromatic structures. The synthesis of tris (allyloxymethyl) phosphine oxide (TAOPO) used at 25.5 wt% in a UP resin system (phosphorus content increased to 3%), improved the LOI value to 27% and reduced PHRR and THR significantly by 45.7% and 45.5%, respectively [43]. It was described that the fire retardancy of TAOPO is primarily based on the formation of a compact carbonaceous char which hinders the transfer of heat through the polymer and subsequently reduces the intensity of gaseous products.

Another fire-retardant containing multivalent phosphorus was synthesised for the UP system namely, 2-((((6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)methoxy)(phenoxy)phosphoryl)oxy)ethyl acrylate (DHP) [20]. UP containing 20 wt% of DHP, passed the UL 94 with a V-0 rating, increased the LOI to 29% and the PHRR was reduced by 37.2% to 284 W g − 1. DHP can act as radical scavenger in the gaseous phase during combustion and also DHP catalysed the char formation of UP. Triallyl phosphate (TAP) was synthesised for a UP system containing 35 wt% of styrene and up to 15 wt% was used to replace the styrene [44]. Incorporation of 15 wt% of TAP increased tensile strength from 22.79 to 28.18 MPa, while flexural strength reduced from 24.21 MPa to 19.24 MPa. The UL94 fire test showed that samples containing 10 wt% of TAP can achieve a V-0 rating while LOI was 28%. Also, diethylene glycol modified tetra-allyl phosphate (DTAP) was also investigated for a UP system containing 35% of styrene, and again replaced by 15% of the DTAP. The UL94 fire test showed that samples containing 10 wt% of DTAP achieved V-0 with a LOI of 29%. Again, the mechanical properties exhibited improved tensile strength from 22.79 to 29.5 MPa, while reduced flexural strength from 24.21 MPa to 18.34 MPa. Comparing DTAP with TAP, suggested that both comonomers are effective FRs for UP but TAP had the better mechanical properties. It is worth pointing out however, that the $T_g$ of UP in this study was quite low 34.22 °C and was also increased by addition of TAP and DTAP to about 50 °C.

Another phosphorus-containing acrylate comonomers investigated for UP was 1,4-phenylene-bis((6-oxido-6H-dibenz [c,e] oxaphosphorinyl) methylene) diacrylate (TDCAA-DOPO) [45]. The pyrolysis char at 700 °C, increased from 9.5% to 13.8% and the PHRR decreased from 794 kW/m$^2$ to 442 kW/m$^2$, while the LOI increased from 22% to 27.2% for UPR20. It appeared that the outer surface of UP char had a loose and porous structure, while UPR20 displayed a compact and continuous char structure on the outer surface. This kind of char layer effectively hinders the diffusion of the combustible gases from fire.

Fig. 4 shows the TG and DTG curves of UP and modified with 5–20 % of TDCAA-DOPO and modified with 15 wt% of TDCA-DOPO (1,4-phenylene-bis((6-oxido-6*H*-dibenz[*c*,*e*][1,2]-oxaphosphorinyl) carbinol) [45]. The thermal stability of UP improved significantly in the presence of TDCAA-DOPO, the $T_d$ increased from 278 to 307 °C for 20 wt% of TDCAA-DOPO (UPR20), and the char residue increased as well under

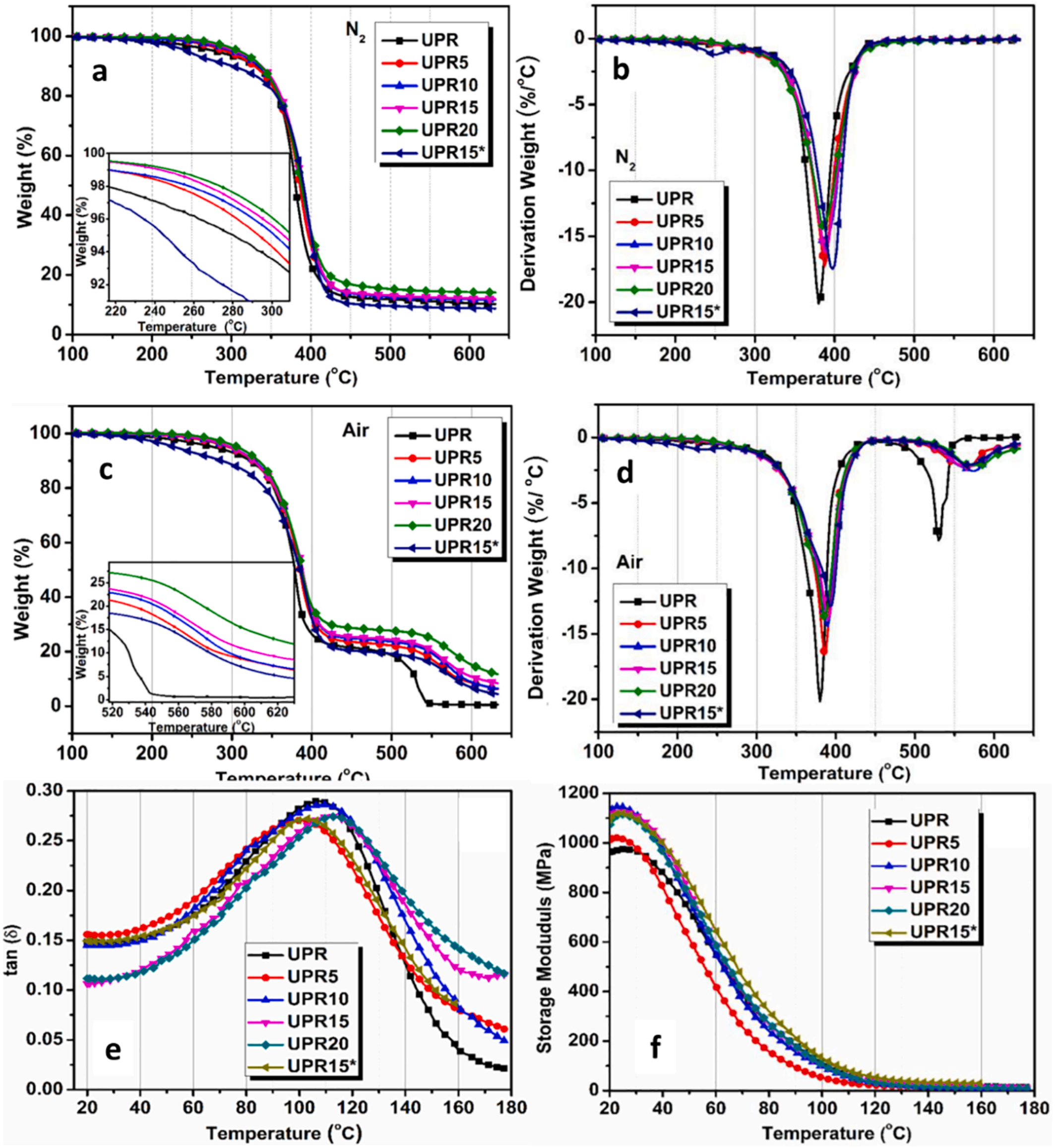

**Fig. 4.** (a) and (b) TG and DTG curves of UP and modified UP with 5–20 % of TDCAA-DOPO and modified with 15 % of TDCA-DOPO, in nitrogen and air atmosphere, respectively; (e) Tan δ and (f) storage modulus curves; reproduced with permission from [45] Copyright © 2017, American Chemical Society.

nitrogen and air. For the UP modified with 20 % of TDCAA-DOPO, the char residue increased from 0.7 to 8.3 wt% (air) and from 9.5 to 13.8 wt % (nitrogen). Fig. 4e shows the tan δ, where the maximum peak temperature represents $T_g$. The unmodified UP has a $T_g$ of 109.1 °C and by incorporation of FR, the $T_g$ decreased with 5 wt% and then increased to 115.7 °C for UPR20. Fig. 4f gives the storage modulus as a function of temperature, the modulus of FR-UP in the rubbery plateau is higher than unmodified UP, indicating a higher crosslinking density and a higher $T_g$. As such, the TDCAA-DOPO exhibits a great potential as a high-performance fire retardant for UP.

*2.1.2.2. Phosphorus-nitrogen-containing comonomers.* Compounds containing phosphaphenanthrene and triazine-trione groups were prepared and incorporated to UP to improve fire retardancy [46]. Although, incorporation of 20 wt% and 30 wt% increased the LOI significantly to 27.2% and 29.8 %, the UL-94 rating only reached V-1 with 30 wt% of modifier. Another comonomer trialled has been the phosphorus–nitrogen-containing acrylate, 1,3,5-triglycidyl isocyanurate (TGIC)–acrylic acid (AA)-DOPO (TGIC–AA–DOPO) [47]. When added to a vinyl ester resin at 40% a V-0 rating and LOI of 31.7% was achieved, despite a significant reduction in flexural and tensile strength.

*2.1.2.3. Phosphorus-sulfur-containing comonomers.* The phosphorus-sulphur containing reactive monomer bis (acryloxyethyldiphenylphosphate) sulfone, (BADPS) was synthesised for UP. BADPS increased the $T_g$, improved the tensile strength and also toughness of UP. Moreover, PHRR of sample containing of 20 % of BADPS reduced from 944 kW/m$^2$ to 657 kW/m$^2$ and THR reduced from 80 MJ/m$^2$ to 58 MJ/m$^2$. The LOI of BADPS at 20 wt% increased from 20.5% to 26.5% [48].

*2.1.2.4. Phosphorus-sulfur-silicon-containing comonomers.* Recently, Methyl vinyl di (1-thio-2, 6, 7-trioxal-1-phosphabicyclo [2.2] octane-4-methoxy) silane (MVDOS) was also investigated as a comonomer for UP thermoset (n). When the composition ratio of MVDOS reached 18 wt%, the vertical fire test passed V-0 rating with an LOI value of 29.1% [49]. The PHRR and THR reduced by 57% and 28% to 238.2 KW/m$^2$ and 85.9 MJ/m$^2$, respectively. It was shown that MVDOS significantly supressed the heat release, CO and smoke during combustion by intumescence and formed a dense char layer. Moreover, MVDOS modestly improved the tensile strength and elongation at break of UP.

Therefore, using reactive FRs (monomers or/and comonomeres) is an effective and promising approach to create fire-retardant UP without compromising mechanical performances of bulk UP. Among reactive FRs, the development of FRs comonomers is easier than FRs monomers from a perspective of real-world industrial productions. It is worth noting that the cost of reactive FRs are much higher than additive FRs.

## 2.2. *Additive fire-retardants*

Flame retardant can also physically mix with UP resin before the curing reaction without having a chemical bond with the UP network. These FRs can be organic, inorganic or organic–inorganic, wherein having a good fire-retardancy, good dispersion, and compatibility with UP matrix, are the challenges. Upon the incorporation of additive FRs, the glass transition temperatures ($T_g$) and mechanical properties of UP are often reduced due to their potential plastization effects. Another issue is the leaching/migration of the additive FRs owing to a poor interfacial compatibility.

### 2.2.1. *Organic FRs*

*2.2.1.1. Halogenated compounds.* Halogenated additive FRs have been regarded as one class of highly effective fire retardants for polymer because they act in the gas phase by releasing halogen radicals to scavenge the free radicals and interfering the chain reactions in the flame. However, using halogenated FRs are restricted because of the health and environmental concerns. These are including producing of highly toxic compounds such as dioxin derivatives during combustion [56], and contamination of the environments during recycling [57]. Moreover, halogenated additive FRs are able to leach out from the UP matrix over time which increases its health and environmental risks. To date, there are still several halogenated compounds that are still being used as additive FRs for UP, including tetrabromo-p-xylene, pentabromoethyl benzene, pentabromobenzyl bromide, decabromodiphenyl oxide, and pentabromotoluene [9].

*2.2.1.2. Charring resins.* One of the more cost-effective approaches to make a FR-UP is to blend the UP with char forming resins such as phenolic resoles [12,58], melamine–formaldehyde, novolac [59], and furan resins [12]. It is noting that phenolic resole and furan resins do not co-cure with UP resin, with furan resin plasticizing the network [12] while resole phase separates during cure [60]. Co-curing has been explored using a phenolic novolac (Ph-N) and UP [59] using a vinylbenzylated phenolic novolac (VB-Ph-N) synthesised through reaction of Ph-N and 4-vinylbenzyl chloride. The LOI results show that when styrene is replaced by VB-novolac, LOI increased by + 5.6 while PHRR and THR from cone calorimetry reduced by 47% and 35%, respectively. Comparing these results to an allyl-phenolic resole-UP network with no styrene, LOI increased by + 4.3 and PHRR and THR reduced by 24% and 39%, respectively [61]. The fire retardancy of UP/phenolic blend in the presence of APP, significantly improved, incorporating 10 wt% of APP in a UP/phenolic (90/10) blend [62] resulted in a V-0 rating. Table S1 summaries a range of literature fire retardancy results from UP-novolac blend resin systems, highlighting that FRI was between 1 and 2, with ΔPHHR and ΔTHR reduced by more than 30%. Blending char forming resins with UP can efficiently improve the char formation, but the lack of the gas-phase action often leads to a relatively low efficiency. Moreover, the curing profile of these blend systems are relatively complex as each resin needs a specific curing temperature and time.

*2.2.1.3. Oligomeric and polymeric FRs.* Recently developed FRs are the oligomeric and polymeric compounds which have more compatibility with the polymer matrix. A thermostable FR containing Schiff base and spirocyclic structures, namely, poly(hydroxyphenyl imino methyl phenol spirocyclic pentaerythritol diphosphonate) (PPISP), has been made and used in UP thermosets [63]. Incorporating 20 wt% of PPISP in UP resulted in an LOI of 28.2%, a V-0 rating and a sharp 60% reduction of PHRR. The PHRR and THR have been reduced from 756 kW m$^{-2}$ and 79.6 MJ/m$^2$ to 364 kW m$^{-2}$ and 53.9 MJ/m$^2$, respectively. The char surface of UP showed large holes, while the char surface of UP/PPISP showed small tunnels and bubbles. This FR contains rigid aromatic and spiral rings which can enhance the rigidity of FR-UP. As a result, both the $T_g$ and elastic modulus increase, but accordingly the tensile strength and elongation at break decrease. Meanwhile, the Schiff base and spirocyclic structures can significantly impact on carbonization and aromatization of char residues.

Poly(piperazine methylphosphonic acid neopentylglycol ester) (PPMPNG) was synthesised and incorporated into UP at a concentration of 15 wt%, achieving a V-0 rating and LOI of 32.1% [64]. Moreover, the cone calorimetry results showed significant reduction of PHRR from 734.1 kW m$^{-2}$ for UP reducing by 60.8% to 287.7 kW m$^{-2}$ for the 15 wt % PPMPNG modified UP (at 167 s). The THR also reduced dramatically from 107.9 MJ/m$^2$ to 63.1 MJ/m$^2$. The flame retardant mechanism displayed in Figure S2 shows that PPMPNG acts in both the gas and condensed phases. In the gaseous phase, it decomposes and generates the phosphine oxygen radical which scavenges free radicals, while in the condensed phase it decomposes to vinylidene, diene, and piperazine derivatives which promote cross-linking and hence charring. As a monocomponent intumescent flame retardant (IFR) containing three different sources (acid, carbon, and gas), the PPMPNG IFRs clearly shows a good fire performance in UP. Unfortunately, more investigations are still needed to determine the mechanical and rheological properties of the system.

*2.2.1.4. DOPO-Derived FRs.* DOPO based derivatized fire-retardants have also been synthesised for epoxy [1,46,52,53,65,66] or thermoplastics [54,67]. DOPO containing triazine group, namely, 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine (TRIPOD)-DOPO was synthesised for a UP system [68]. When loaded with 30 wt% of TRIPOD-DOPO, a V-0 rating was achieved and a LOI of 30.5%. Moreover, a reduction in PHRR and THR by 52% and 27%, respectively was observed. The fire retardancy mechanism of TRIPOD-DOPO lies in the fire inhibition in the gas phase and the char formation in the condensed phase. The TRIPOD-DOPO reduces significantly the production of volatilized substances, such as carbon monoxide, carbon dioxide, styrene, esters, and hydrocarbons. In addition, the DOPO-based moiety accelerates polymer degradation that facilitates the production of an oxidative char residue due to the phosphoric acid formation. The formed char layer can protects the underlying polymer matrix by serving a physical thermal barrier.

### 2.2.2. Inorganic FRs

*2.2.2.1. Phosphors-Nitrogen complexes and its hybrids.* Phosphorous containing and phosphorus and nitrogen synergistic FRs have been increasing in importance for more than two decades. In broad terms these modifiers interrupt the exothermic process by scavenging free radicals in the gaseous phase while at the same time, promoting degradation which increases the char residue in the condensed phase [42,53,69]. Ammonium polyphosphate (APP) is a polymeric compound containing P and N elements. It is low cost and widely available and highly effective FR. Due to low compatibility of APP with UP, surface modification of APP is however, necessary. For this reason, the APP is modified using coupling agents [70] or microencapsulation [71].

Recently, Jiang et al. [71], first prepared a composite of UP containing 50 wt% APP, then used a pulverizer to prepare a microencapsulated APP (UP coated APP) with diameter of 15 µm. Then, a formulation of 34 wt% of modified APP (which contains 17 wt% of APP), 10 wt% of dimethyl methyl phosphonate (DMMP), 1 wt% of montmorillonite (MMT) and 2 wt% of zinc borate (ZB) in UP was prepared. The resulting thermoset achieved a V-0 rating and an LOI of 31.3%. The PHRR and THR reduced significantly from 357.5 (kW/m$^2$) and 113.1 (MJ/m$^2$) to 179.8 (kW/m$^2$) and 62.7 (MJ/m$^2$), respectively. Similarly, an intumescent formulation (IFR) was prepared based on a UP coated with APP, melamine (MEL), and pentaerythritol (PER) with the following ratio MAPP: PER: Mel = 6:1:1 [72]. Incorporation of MMT was needed to improve thermal stability and achieve a V-0 rating using UL-94. The intumescent formulation consisting of 29.6 wt% of IFR and 1.5 wt% of MMT achieved V-0 and LOI of 28.3%, and when the MMT was treated with phytic acid the LOI increases to 29.2%.

To reach a V-0 rating of UP by APP, high loading is typically required which has a negative impact on the processability and properties [38], although there is some disagreement in the literature. In references [73–76], UP containing 20 wt%, 25 wt%, 28 wt%, and 40 wt% APP, respectively, could not achieve a V-0 rating. While in [77] the APP composition ratio ≥ 17.6 wt%, and in [73] showed that 25 wt% reached a V-0 rating. It is worth mentioning that the type of APP, surface modification, and particle size, all have a significant impact on its fire retardancy. Also, the type of UP, styrene content and curing condition all impact overall performance.

Attempts to reduce the loading level of APP in UP, via a hybrid strategy includes the use of aluminum hypophosphite (AHP). By using just 1.5 wt% of AHP, it was found that the APP content could be reduced to 10.3 wt% while still achieving a V-0 rating and a LOI of 31.0% [77]. Hybrid blends of APP/AHP, display a significant improvement in the efficiency of char formation compared with APP. Furthermore, AHP can acts in the gas phase where AHP releases $PH_3$ which subsequently produces phosphorus radicals which can scavenge the H and OH radicals. It was demonstrated that incorporation of 20 wt% of APP resulted in a V-2 rating, but when 9 wt% of dimethyl methylphosphonate (DMMP) was added, a V-0 rating was obtained [78]. Using 3 wt% kaolinite (Kao) or kaolinite-urea intercalation complex (KUIC) in combination with APP, was another strategy to successfully reduce the APP loading level to 12 wt% [79]. The UP system containing APP 12 wt%, and 3 wt% of Kaolinite increased the LOI to 27.3%, PHRR and THR of 226 (kW m$^{-2}$) and 67.2 (MJ m$^{-2}$), respectively. Also, it has been shown that modification of Kaolinite by urea can increase LOI to 28%, and reduce THR and PHRR slightly. KUIC promotes the formation of strong char layers which thermally insulate and shield the oxygen from the fire.

Table S2 summarises the fire test results of P-N complexes fire-retardants, including APP and hybrid APP. In regard to the FRI, the UP containing 35 wt% silane-coated APP, 35 wt% APP, and 15 wt% APP + 50 wt% ATH were found to be highly fire-retardant, showing a FRI value of 17.3, 14.5, and 14.4, respectively. Fig. 5a presents the LOI of UP/APP systems which achieved a V-0 rating with different FR loading. Meanwhile, the UP with 10.3 wt% APP and 1.5 wt% AHP has the lowest FR conent but exhibits a V-0 rating and an LOI of 31%. Fig. 5b presents the FRI values of UP/APP systems achieving a V-0 rating with different FR loading levels. The FRI values for all of the presented system in Fig. 5b are between 1 and 10. The UP system with 30 wt% of APP has the highest FRI (8.3) with V-0 rating. It was demonstrated that APP in combination with inorganic FRs is more efficient than pure APP in UP matrix. Piperazine pyrophosphate (PPAP) is a common FR for UP and when 18 wt% is incorporated into the UP matrix, a UL94 V-0 rating was achieved with LOI of 29.8% [81]. Incorporation of 16 wt% of PPAP reduces the THR and PHHR by 31% and 49% while incorporation of 18 wt% of PPAP reduces THR and PHHR by 42% and 61 %, respectively. The FRI of UP with 18 wt% of PPAP is 2.5, indicating a high fire retardancy.

Fig. 6 showing timed digital photographs of unmodified UP and modified with 18 wt% of PPAP during UL-94 tests. As shown in Fig. 6a, unmodified UP is ignited quickly and burned violently for about 96 s after ignition, along with continuous melt drippings. With 18 wt% of PPAP, the fire retardancy of UP thermosets is enhanced, reaching a UL-94 V-0 rating. Fig. 6b depicts the timed phots of UP-18 wt% PPAP samples which self-extinguished in 1 and 4 s after twice ignitions [81]. This clearly shows that the presence of PPAP can remarkably reduce the flammability of UP and makes it more difficut to ignite the latter.

The melamine polyphosphate (MPP) was examined for UP system and shown achieved a V-0 rating with LOI of 35% at a concentration of 30 wt% [73]. At 20 wt% MPP the PHRR and THR were 424 kW/m$^2$ and 85.1 MJ/m$^2$ with 35 wt% of MPP reducing to 360 kW/m$^2$ and 87.3 MJ/m$^2$, respectively. This represents a significant reduction compared to the neat resin which had a PHRR and THR of 773 kW/m$^2$ and 113.2 MJ/m$^2$ [82]. The combined effect of MPP, APP and ATH, in three different formulations based on 40 wt% of MPP:APP:ATH:EG displayed a very large reduction in PHRR and THR going from 870.3 kW/m$^2$ and 141.6 MJ/m$^2$ to 145.8 kW/m$^2$ and 101.8 MJ/m$^2$, respectively [83].

The ammonia (gas phase), and phosphoric acid (condensed phase) are generated by decomposition of MPP [85] as shown in the Fig. 7a. The ammonia dilutes the oxygen and other combustible gases and produces thermally stable compounds such as melon, melam, and melem. Phosphoric acid catalyses the dehydration of polymer during thermal degradation and promotes formation of char layer [86,87].

Liu et al. [84] applied DMPY in combination with ADP as a synergistic system for UP. Fig. 7b presents the synergistic fire retardancy mechanism of dimelamine pyrophosphate (DMPY) and ADP for UP. During thermal degradation of ADP, free radicals such as P and PO are generated through cleavage of the P-C bond which then act as radical scavengers to obstruct the free radical chain reactions in the gas phase. Also, the phosphoric and polyphosphoric acids produced by

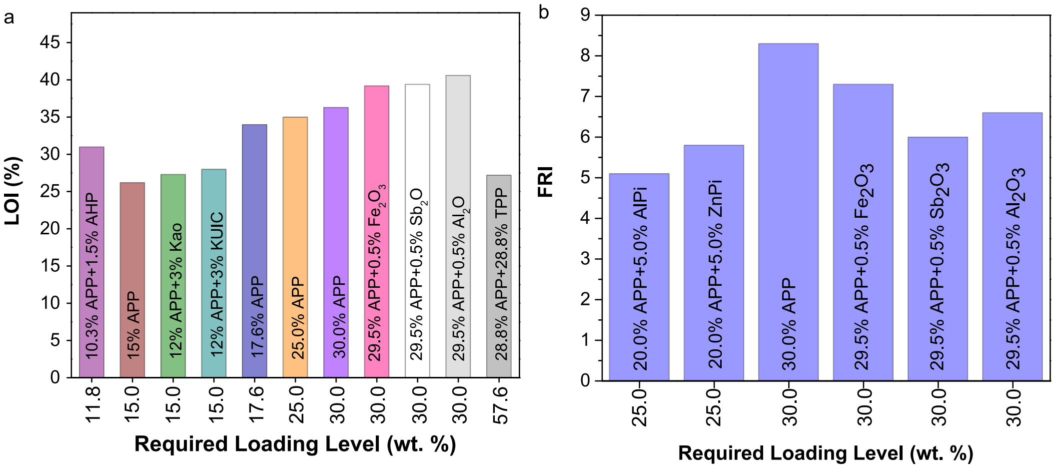

**Fig. 5.** Comparing UP/APP systems with V-0 rating: a) LOI versus required loading level of FR; b) FRI versus required loading level of FR. The data are collected form the literature: 17.6% APP [77], 25% APP [73], 28.8%APP + 28.8% TPP [75], 30% APP [80], 29.5%APP + 0.5%$Fe_2O_3$ [80], 29.5%APP + 0.5%$Sb_2O_3$ [80], 29.5% APP + 0.5% $Al_2O_3$ [80], 15% APP [79], 12% APP + 3% Kao [79], 12% APP + 3% KUIC [79], 20% APP + 5% ADP [74], 20% APP + 5% ZnPi [74].

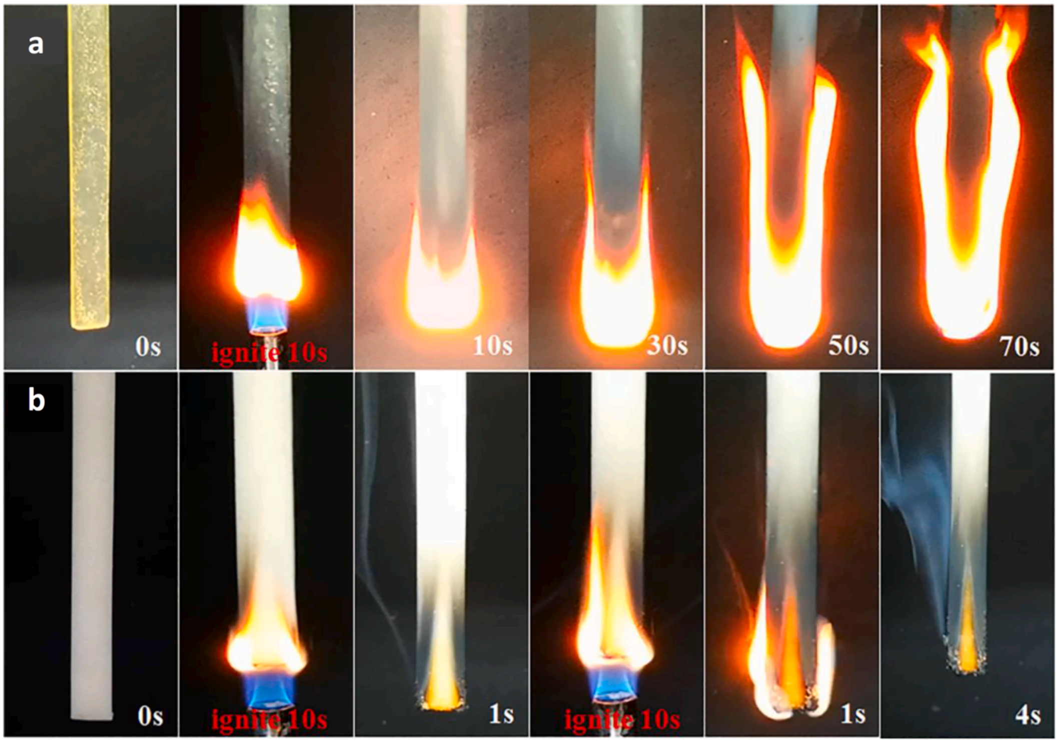

**Fig. 6.** Photographs of UL-94 tests of (a) unmodified UP and (b) UP containing 18 wt% piperazine pyrophosphate (PPAP), reprinted with permission from [81], copyright 2020 John Wiley & Sons Ltd.

decomposition of ADP are able to further catalyse char formation. Moreover, UP with mixture of DMPY and ADP has a larger, more uniform and coherent char residue than UP/DMPY. The DMPY molecule consists of two triazine rings and a pyrophosphate structure. DMPY contributes in both the gas and condensed phases through a fuel dilution mechanism and char formation.

An intumescent FR, pentaerythritol diphosphonate melamine-urea–formaldehyde, MIFR , was synthesised and incorporated into UP [88]. The UP containing 24 wt% of MIFR achieved a V-0 rating and had a LOI of 30.5%. It was demonstrated that loadings of<27% of MIFR had a modest effect on mechanical properties, with the tensile and impact strength decreasing by only 7% using 24 % of MIFR. MIFR acts in the condensed phase by improving the char residue by about 13%. Incorporation of MIFR reduced the initial degradation temperature from 224 °C to 204 °C which further assists char formation at lower temperature. Also, formation of nitrogen-containing gaseous by decomposition of MIFR, promotes the swelling of the carbonaceous layer, which insulate underlying polymers from the heat.

Incorporating 8 wt% of diammonium hydrogen phosphate (DAP) in UP, produced a UL-94 V-0 rating with LOI values of 28% [89]. Furthermore, the decomposition temperature decreased from 373 °C to 349 °C and the char yield at 600 °C increased from 11.5% to 23.3% (in Nitrogen). Ammonia, water, and pyrophosphoric acid are formed by decomposition of DAP. Subsequently the pyrophosphoric acid dehydrates to produce phosphorus pentoxide ($P_4O_{10}$) which has a melting of 340 °C, forming a viscous layer at higher temperature to protect

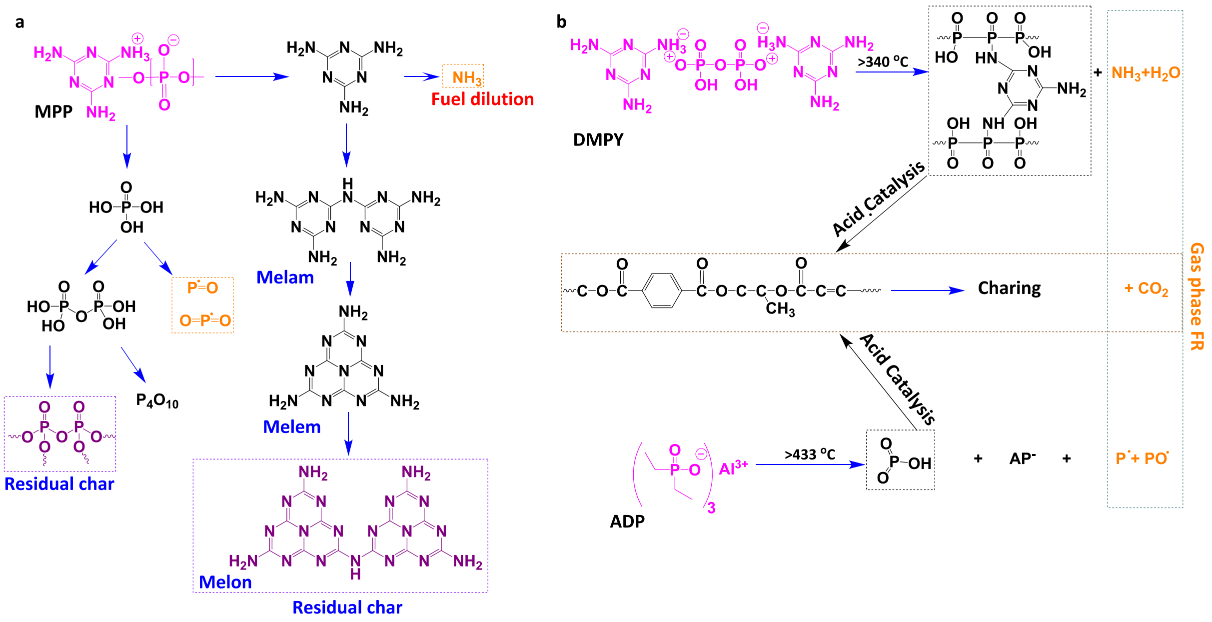

**Fig. 7.** a) Thermal decomposition of MPP; b) illustration of the fire-retardant mechanism of UP/ DMPY/ ADP thermosets, reproduced with permission from [84] copyright 2019 Elsevier Ltd.

samples during combustion. Aluminium methyl methylphosphonate (AMMP) has been formulated for UP as an additive fire-retardant with high reactivity [90]. Upon the addtion of 22.5 wt% of AMMP into UP, a UL-94 V-0 rating was achieved, and PHHR and THR decreased by 66% and 61%, respectively. Although the required weight fraction of AMMP is comparable with some other phosphorus-based FRs to pass a V-0 rating, unlike some phosphorus-based FRs, AMMP does not impact the curing of UP.

Fig. 8a compares the LOI versus the loading level of P-N FR required to achieve a V-0 rating. UP/30MPP reached the highest LOI of 36%, while UP/15PPMPNG reached the LOI of 32.1% with just half this loading level. UP with 15 wt% of PPMPNG has a higher LOI than UP with 18 wt% of PPAP and 20 wt% of PPISP. Fig. 8b compares the FRI versus required loading level of P-N FR to achieve a UL-94 V-0 rating. The UP/35MPP has the highest FRI of 6.6, while the UP/20PPISP has an FRI of 4.5 (32% lower) at a much lower loading level. All the presented systems show a FRI value between 1 and 10 which is classified as good fire retardancy.

*2.2.2.2. Aluminium hydroxide and its hybrid.* The most widely used fire-retardant is aluminium trihydroxide (ATH), or $Al(OH)_3$, because of its low cost and effectiveness. When the temperature reaches about 220 °C, ATH decomposes to aluminium oxide ($Al_2O_3$) and water. ATH therefore acts as a heat sink by releasing water vapour an endothermic process, which equates to about 35% of its weight. The major problem with mineral FRs is the necessity for high levels of addition, increasing the UP viscosity and reduce its processability. So, the focus on using ATH has been to combine it with other fire-retardants. For example, ATH tends to be used in a combination of carbon black (CB) and magnesium hydroxide (MDH) [94]. A sample of UP incorporated with Al(OH) of 40 wt %, MDH 10 wt% has reported a V-0 rating in UL-94 fire test. Incorporation of 5 % CB, makes the sample non-flammable with zero ignition time, where CB significantly improves the thermal stability of UP. Incorporation of MDH in UP reduces the PHRR significantly. Using 35%, 45% and 55% of Mg(OH) incorporated into UP, the PHRR reduced by 60.47%, 65.89% and 74.99%, respectively [92]. Unfortunately, a high loading level of ATH or MDH is required to reduce the flammability and smoke production of UP. This is unfavourable for processing as the viscosity increases significantly. Moreover, such a high loading level of ATH has negative effects on mechanical properties.

Aluminium diethylphosphinate (ADP) was applied in combination with ATH, using a mass ratio of 3:2, at 15 % ADP and 10 % ATH to UP. The LOI increased to 30% and a UL-94 V-0 rating was achieved [95]. MCC results displayed a 30.4 wt% and 24.4 % reduction of PHRR and THR in comparison to the pure UP, respectively. It was confirmed that 25 wt% of ADP (P content of 5.95%) increased the LOI to 29.5% with a V-0 rating. However, another study showed that incorporation of 10 wt % of ADP into UP was enough to reach a V-0 rating of the UL-94 test [89]. Although ADP has very good fire retardancy, the tensile and flexural strength for UP-25ADP reduced significantly by 65% and 52%, respectively [96]. The ADP mainly acts in the condensed phase promoting char formation during thermal degradation by the formation of crystallized aluminophosphates. Other mineral fire-retardants such as antimony oxide ($Sb_2O_3$) and ZB have also been used as synergists with other FRs. Smoke, a critical hazard during a fire, requires smoke suppressants in the resin formulation such as ZB, zinc hydroxystannate (ZHS), and zinc stannate (ZS) [13,58]. Synergistic effects are expected when ATH is combined with other fire-retardants.

Mixture of ATH with APP and talc, promote formation of a self-supporting ceramic layer. ATH and APP interacts through the reaction between the hydroxyl groups of ATH with protons of polyphosphoric acid to produce a thermally stable crystalline aluminium orthophosphate ($AlPO_4$) and long chain aluminium polyphosphates [97,98]. Moreover, magnesium-ammonium polyphosphates and silicon-ammonium tetrapolyphosphate were produced via reaction between talc and APP [97,99]. The self-supporting ceramic char has a high thermal stability and provides a shielding effect to protect the underlying polymer.

ATH (micron size) and nano size alumina oxide ($Al_2O_3$), have been shown to have a substantial influence on fire retardancy [93]. Table S3 summarises the fire results in UP/Mineral FR system in the literature. Fig. 8c presents the FRI for a range of UP/Mineral FR systems published in the literature. Two different types of systems are presented, ATH + minerals and ATH + P-FR where the ATH + P-FR systems were shown higher FRI values. ATH with different specific surface areas, 4.5 $m^2g^{-1}$ and 300 $m^2g^{-1}$ have also been used in UP system and its synergistic effect with different phosphorus-based fire-retardants (FRs), aluminium hypophosphite (AHP) or zinc diethylphosphinate (DEPZn), have been

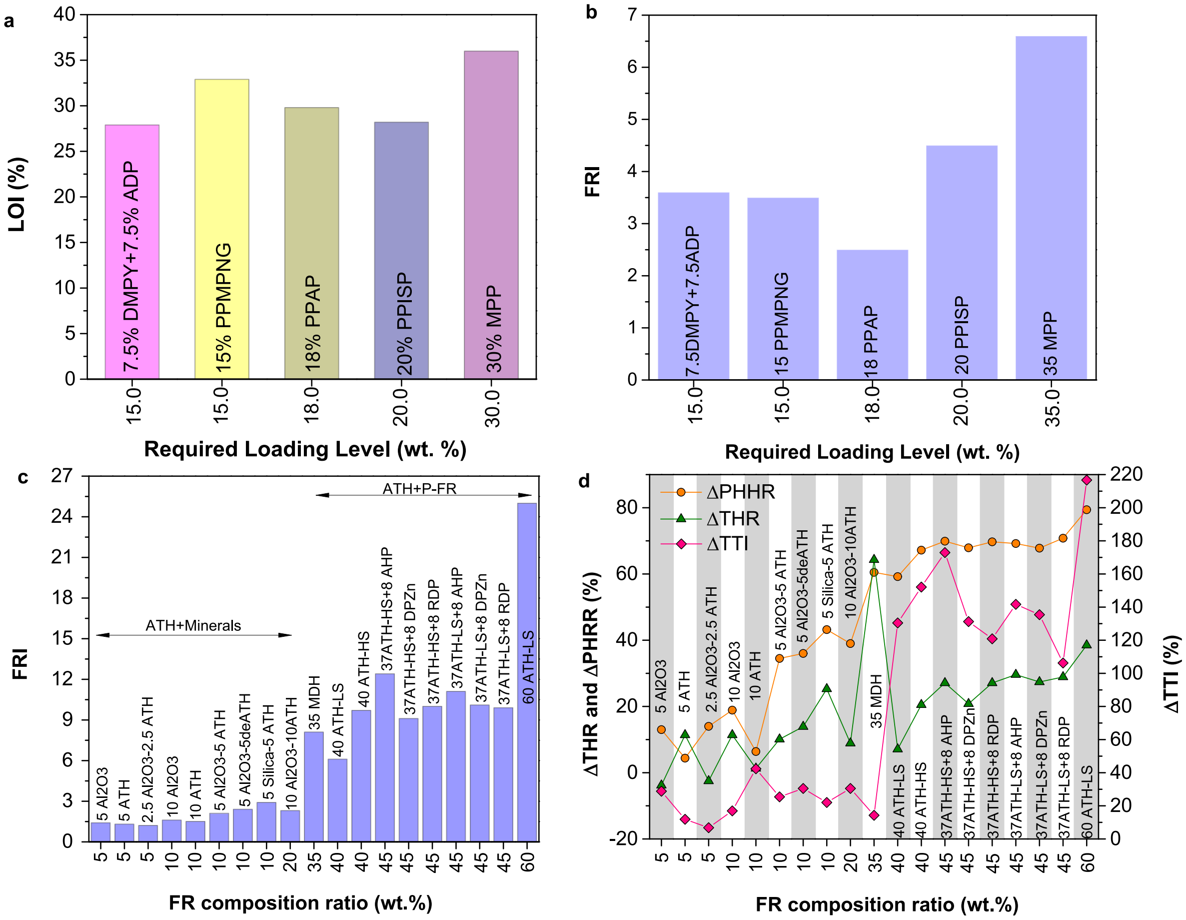

**Fig. 8.** a) Comparing LOI versus required loading level of UP/P-N FR systems with V-0 rating; b) FRI required loading level of UP/P-N FR systems with V-0 rating FR. The data are collected form the literature: 7.5%DMPY + 7.5% ADP [84], 15PPMPNG [64], 18% PPAP [84], PPISP20 [63], 30% MPP [73], 35% MPP [82]; c) FRI versus required loading level of UP/Mineral FR systems; d) ΔTHR, ΔPHHR, and ΔTTI versus required loading level of UP/Mineral FR systems. The data are collected from the literature: UP-60 ATH-LS (ATH with specific surface area of 4.5 $m^2 g^{-1}$) [91] , UP-40 ATH-LS [91] , UP-40 ATH-HS (ATH with specific surface area of 300 $m^2 g^{-1}$) [91] , UP-37 ATH-HS-8% AHP [91] , UP-37 ATH-HS-8% DEPZn [91] , UP-37 ATH-HS-8% RDP [91] , UP-37 ATH-LS- 8% AHP [91] , UP-37 ATH-LS- 8% DEPZn [91] , UP-37 ATH-LS- 8% RDP [91] , UP-35 MDH [92] , UP-45 MDH [92] , UP-55 MDH [92] , UP-5 Alumina [93] , UP-5ATH [93] UP-2.5 $Al_2O_3$-2.5 ATH [93] }, UP-10 $Al_2O_3$ [93] UP-10ATH [93], UP-5$Al_2O_3$-5ATH [93] , UP-10 $Al_2O_3$-10ATH [93], UP-5 $Al_2O_3$-5deATH [93], UP-5Silica (fumed silica treated with a methacrylsilane)-5ATH [93].

studied [91]. The specific surface area and the crystalline or amorphous state of a filler clearly had a profound impact on the fire retardancy of the modified UP. With 60 wt% of crystalline ATH (4.5 $m^2 g^{-1}$), the UP achieved a V-0 rating, while 60 wt% amorphous ATH (300 $m^2 g^{-1}$) was entirely not processable. It was found that 37 wt% ATH and 8 wt% AHP or DEPZn in the UP system improved the fire retardancy performance to V-0 while the cone calorimetry results, PHRR and THR reduced significantly from 825 (kW $m^{-2}$) and 131 (MJ $m^{-2}$) to 265.3 (kW $m^{-2}$) and 95.1 (MJ $m^{-2}$), respectively. Thermal analysis showed that crystalline ATH (4.5 $m^2 g^{-1}$) had a $T_d$ of 251 °C and was more thermally stable compared with amorphous ATH (300 $m^2 g^{-1}$) which had a $T_d$ of 235 °C. Therefore, crystalline ATH with lower specific surface area (4.5 $m^2 g^{-1}$) proposed better fire retardancy performance in comparison with amorphous and higher specific surface area (300 $m^2 g^{-1}$). Therefore, an excellent synergy can be achieved by combining crystalline ATH with a low specific surface area and DEPZn or AHP.

Fig. 8d shows the ΔPHHR, ΔTHR, and ΔTTI versus different amount of mineral FR in UP thermosets. The resulting hybrid FRs consisting of ATH and $Al_2O_3$ blends demonstrated a synergistic effect [93]. Incorporating 10 wt% of FRs (ATH + $Al_2O_3$/Silica) in a 50/50 ratio, reduced PHHR significantly in comparison with the single FR in the UP. However, THR declined slightly, while TTI slightly decreased. The synergistic effect can be assigned to the arrangement of both kinds of particles with different size on composite surface during combustion. Combination of ATH with 300 nm with nano particles ($Al_2O_3$ with 13 nm, or silica with 12 nm) produced a compact protective layer. Also, promotion of a catalytic effect resulting from a high surface area of alumina oxide. The presented results in Fig. 8d confirmed that the THR is relatively unaffected by the change in composition ratio of mineral FR, while TTI increases significantly, when the FR is over 40 wt%.

*2.2.2.3. Core-Shell structured FRs.* Core-shell particles has been used recently as additive fire-retardant for UP thermosets with different materials as a core such as APP [100,101], AHP [102], Diatomite (Dia) [103], $TiO_2$ [104]. An example being that of Gao et al. who developed a new core–shell FR, namely TA-MAPP, by applying tannic acid–iron complexes (TA–$Fe^{3+}$) as the second shell layer of melamine resin-coated ammonium polyphosphate (MAPP). By incorporation of just 10 wt% of TA-MAPP in UP, a LOI of 27.8% and a UL-94 V-0 rating were achieved while 10 wt% of MAPP only received a V-2 rating [101]. The fire retardancy, smoke suppression, and mechanical properties of UP are enhanced by the incorporation of TA-MAPP. The reduction in the smoke release can be attributed to the formation of TA–$Fe^{3+}$ coating layer on the MAPP surface. Moreover, the coating layer of TA–$Fe^{3+}$ improves the compatibility of MAPP to UP matrix, which is advantageous to improve the mechanical performance of fire-retardant UP.

It was demonstrated that a UP composite with 30 wt% of CP@AHP microencapsulated (AHP as a core and chlorinated paraffin (CP) as a shell with mass ratio of CP and AHP 1:2), achieved a V-0 rating from the UL-94 test and a LOI of 28.5%. Also, PHHR and THR of such system decreased by 58.4% and 46.1%, respectively [102]. Core–shell hybrid nanosphere (BL@Dia), with core of Diatomite and a shell of APP + chitosan (bi-layer) has been fabricated for UP through layer-by-layer assembly [103]. Incorporation of 25 wt% of the 9BL@Dia (containing 9 bilayer), produced an LOI of 25.7% and a V-0 rating. The results also produced PHRR and THR of 266.9 (kW $m^{-2}$) and 94.4(MJ $m^{-2}$), which represented a significant reduction by 40.8% and 18.1%, respectively.

By incorporation of 20 wt% of Dia-APP-TPP (triphenyl phosphate (TPP) as the capsule or top shell, and APP as a shell for diatomite as a core material) in UP matrix, a V-0 rating and LOI of 26.6% was achieved [105]. Moreover, the results for 30 wt% of Dia-APP-TPP in UP matrix, exhibited a PHRR and THR of 344.9 (kW $m^{-2}$) and 118.4 (MJ $m^{-2}$), respectively. Another core–shell particles was phosphorylated chitosan-coated carbon microspheres (PCH@CMS) [106] in which 3 wt% of PCH@CMS in UP matrix, displayed PHRR and THR of 419.0 (kW $m^{-2}$) and 126.9 (MJ $m^{-2}$), respectively. However, the LOI of UP with 10 wt% of PCH@CMS was 22.2, which is close to unmodified UP.

Fig. 9a shows the fabrication process of a hierarchical core–shell structured FR with the core of $TiO_2$ and shell of LDH@$Ni(OH)_2$ for UP matrix [104]. $TiO_2$-LDH@$Ni(OH)_2$ increased modestly the mechanical and fire retardancy properties of UP. By incorporation of 3 wt% of $TiO_2$-LDH@$Ni(OH)_2$ in UP, the PHRR and THR declined slightly, however, the LOI just increased 1% achieving no rating during UL-94 testing. $TiO_2$-LDH@$Ni(OH)_2$ core–shell structured has been shown to have a catalytic charring effect to form a thermally stable carbonaceous layer. Although this core–shell structured FR fails to make UP reach a UL-94 V-0 rating, the high specific surface area of FR caused a significantly reduced toxic smoke.

By incorporating 25 wt% of DMPPD (diatomite (DIA) as a core, melamine pyrophosphate (MPP) as the first shell and DOPO as second shell layer as shown in Fig. 9b) the LOI increased to 29.5% and achieved V-0 rating using the UL-94 test [107]. While incorporating 25 wt% of DMCAD (diatomite (DIA) as a core, melamine cyanurate (MCA) as the first shell and DOPO as second shell layer as shown in Fig. 9b), an LOI of 26.5% and V-1 rating was achieved. The proposed fire-retardant mechanism of DMPPD presented in Fig. 9c. By thermally decomposition of UP/DMPPD system, first, DOPO melted and promoted DMPPD to migrate to the surface of the UP thermoset pyrolysis zone. Then, DOPO was pyrolysed to aromatic molecules which promoted char formation in the condensed phase and phosphorus radicals were volatilised and were scavenged free radicals ($OH^{\bullet}$) to effectively hinder the chain reactions. MPP and melamine act in both condensed and gas phases as described

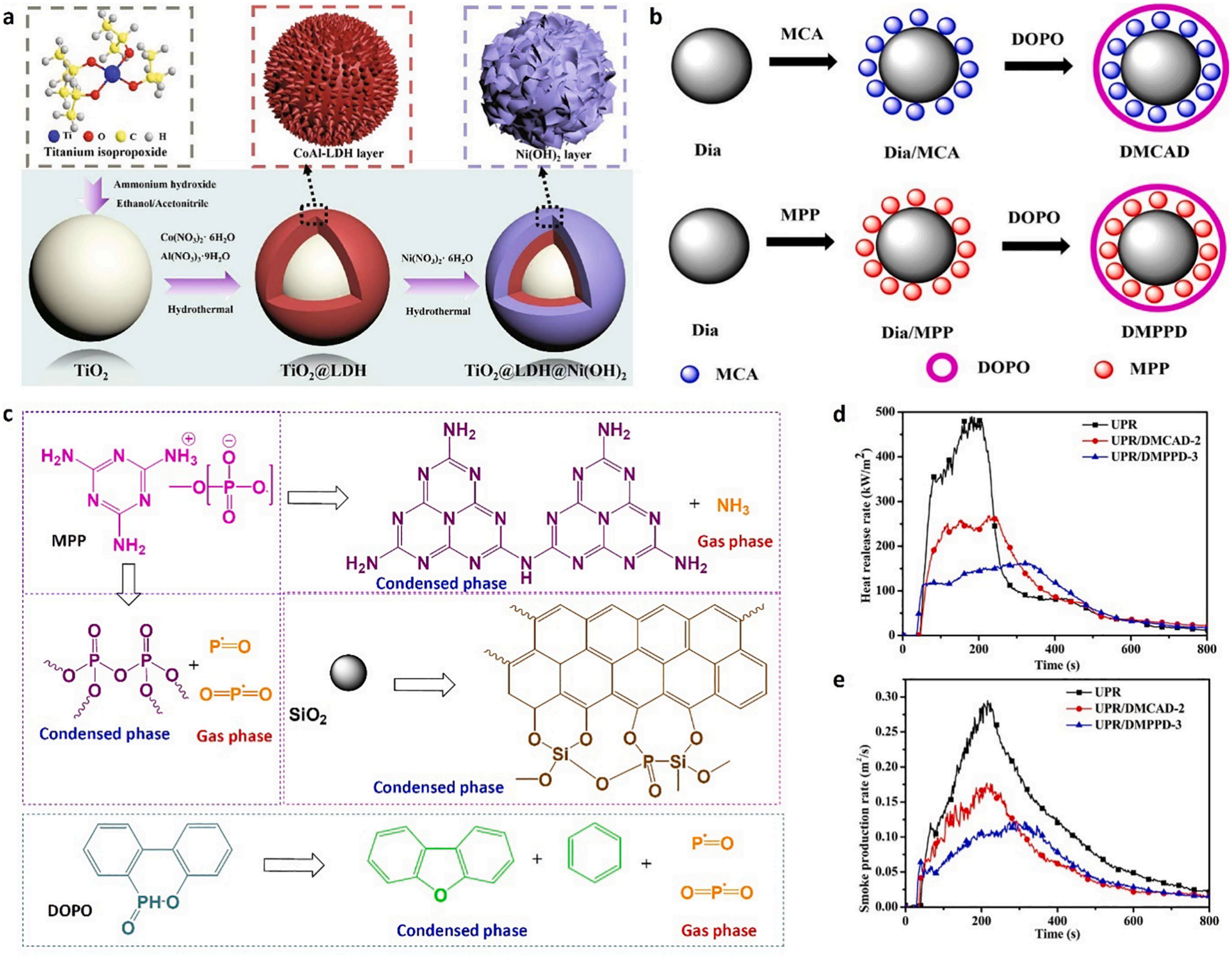

**Fig. 9.** a) Fabrication process of hierarchical core–shell $TiO_2$@LDH@$Ni(OH)_2$, reproduced with permission from [104], copyright 2020 Elsevier B.V.; b) DIA-DOPO-melamine core–shell bilayer FR; c) Fire-retardant mechanism of UP/DMPPD, reproduced with permission from [107], copyright 2019 John Wiley & Sons Ltd; d-e) HRR and smoke production rate curves of pure UP and UP modified with core–shell structured (DMCAD-2 and DMPPD-3 represent two core–shell structured Dia: MCA:DOPO 1:2:1 and Dia:MPP:DOPO 0.75:2.25:1, respectively), reproduced with permission from [107], copyright 2019 John Wiley & Sons Ltd.

before. The stable char layer structures contained Si—O and Si—P, formed by $P_4O_{10}$ and aromatic hydrocarbons associating with $SiO_2$ of DIA. Although increasing the thickness (or weight fraction) of the MCA or MPP shell improves the mechanical properties (flexural strength) to some extent, which are still lower than the control UP sample. While the compatibility of DIA with UP matrix is improved by applying these types of shells, the interactions of the outer shell with the UP matrix need to be further examined.

The cone calorimetry results revealed 67.1 % and 26.4% reduction of PHRR and THR for UP with 25% of DMPPD while UP/25 DMCAD produced a lower reduction of PHRR and THR of 45.4% and 14.5%, respectively [107] (Fig. 9d). Moreover, by incorporation of DMCAD-2 and DMPPD-3 into UP network, the SPR peaks significantly reduced by 37.9% and 58.6%, respectively (Fig. 9e). Table S4 summarises the fire test results for core–shell FR system in the literature. The FRI values are between 1 and 4, and ΔPHHR significantly increased for UP/25DMPPD to 67.1%. The ΔPHHR of UP/10TA-MAPP reduced by 62.4 % with FRI of 3.4 which classified it as a good FR. Comparing the FRE results of Table S4 indicates that TA-MAPP has the most efficient core–shell FR for UP thermoset.

*2.2.2.4. 2D nanostructured FRs.* 2D nanostructured materials have developed as a promising new class of FRs for thermoplastic and thermosets [109] due to their physical barrier effect during combustion. Nanomaterials, in addition to fire retardancy are well known to improve a range of advantageous thermal and mechanical properties. MXene and MAX, as new class of 2D nanomaterial [108,110–112] can also improve the fire retardancy of UP. Fig. 10a shows the preparation of MXene from MAX and their UP nanocomposites thermoset schematically. Fig. 10b displays the SEM image of MXene, the interlayer spacing indicate the removal of Al layers removed from MAX. The results confirm the effectiveness of MXene by reduction of PHRR. The PHHR and THR of UP with 2 wt% of MXene reduced by 29.6% and 14.8%, respectively, while for with 2 wt% of MAX reduced by 11% and 2.8%, respectively (Fig. 10c) [108]. The 2D structure of MAX and MXene plus the $TiO_2$ nanoparticles on the surface acting as physical barrier during combustion process, which disrupts the supply of oxygen and heat and reduces the release rate of combustible gases [113]. Finally, higher thermal stability of MXene and MAX improved thermal stability of modified UP.

It was shown that a UP with 0.1 wt% of B-Si@GO (functionalized GO by boron silicon network), 10 wt% of MMT and 4.9 wt% of APP , achieved an LOI of 28.5% and a V-0 rating using UL-94 [114]. Moreover, the PHRR and THR reduced to 138 (kW $m^{-2}$) and 31 (MJ $m^{-2}$), respectively. Zirconium phosphate (α-ZrP), was explored for UP, in which 10 wt% of modified α-ZrP in UP result to UL-94 V-0 rating with LOI of 27.1% [115]. Hybridisation of nanoparticles is another strategy, for example using Metal–organic framework (MOF) and graphite carbon nitride (g-C3N4) as a FR system, namely MFeCN for UP [116]. It was revealed that 4 wt% of MFeCN, has a LOI of 21.8% and MFeCN reduced PHRR and THR significantly, form 520.1 (kW $m^{-2}$) and 131.9 (MJ $m^{-2}$) to 313.0 (kW $m^{-2}$) and 118.4 (MJ $m^{-2}$), respectively. These 2D nanostructured FRs are not much effective in increasing the char, but they can create a protective layer as a thermal barrier in the condensed phase.

A decorated GO nanosheet with $Cu_2O$ and $TiO_2$ was developed for a UP system (Fig. 11a) to improve the barrier effect and catalytic activity of UP by reducing pyrolysis and hence volatiles [117]. The PHRR and THR declined from 897 (kW $m^{-2}$) and 59.2 (MJ $m^{-2}$) for neat UP to 631 (kW $m^{-2}$) and 47.9 (MJ $m^{-2}$) for $Cu_2O$-$TiO_2$-GO/UP. The explanation of the fire retardancy mechanism of $Cu_2O$-$TiO_2$-GO, consists of absorbing the long chain pyrolysis compounds onto acid sites of graphene surface

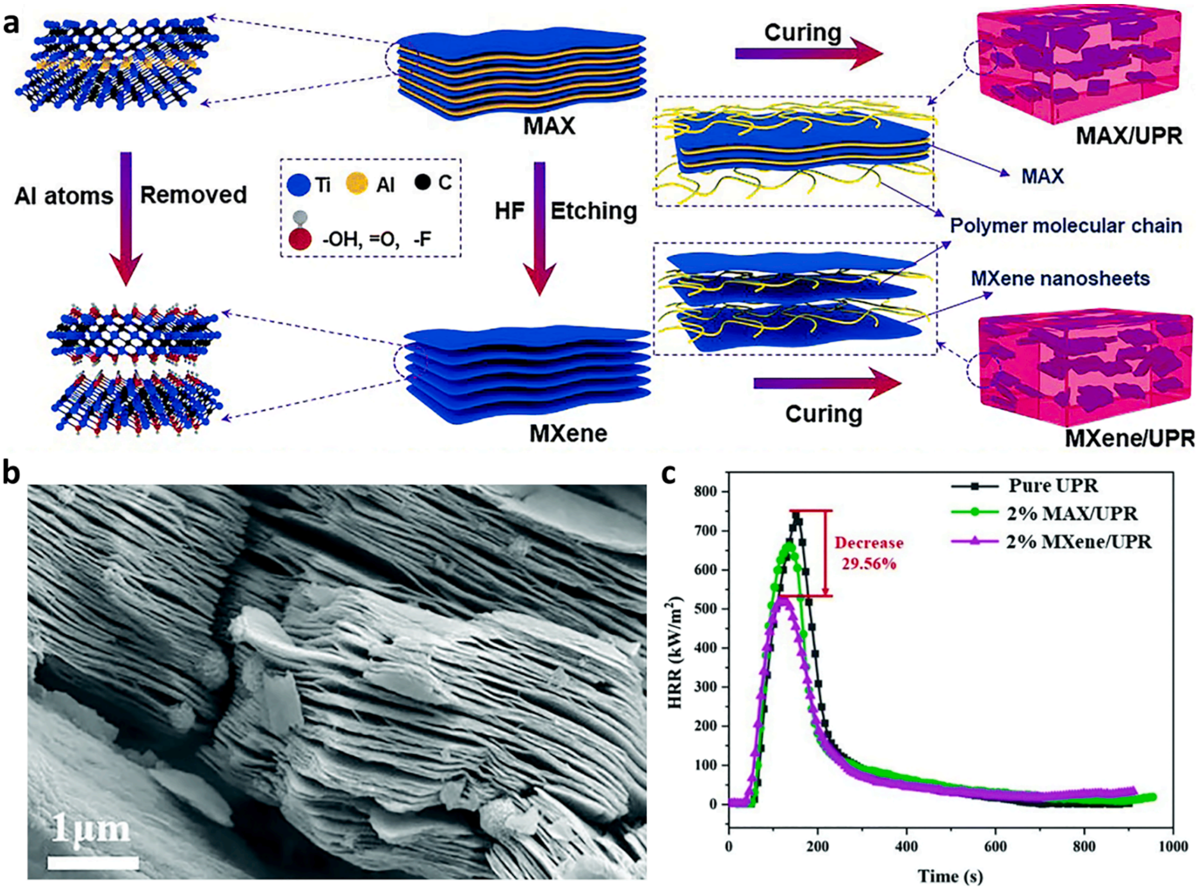

**Fig. 10.** a) Schematic preparation of MXene from MAX and the fabrication of nanocomposites thermosets; b) SEM image of MXene; c) The HRR graph of MXene and MAX nanocomposites thermosets reproduced with permission from [108] copy right 2020 The Royal Society of Chemistry.

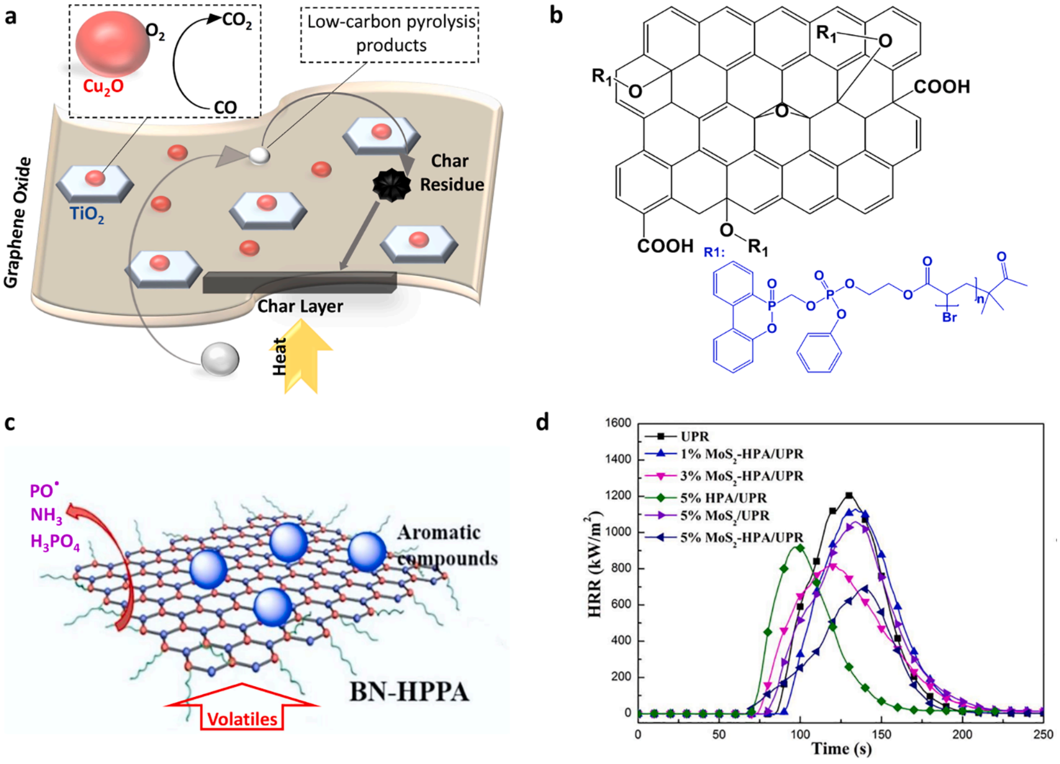

**Fig. 11.** a) illustration of nano-barrier effect and catalytic activity of the flaming $Cu_2O$-$TiO_2$-GO/UP nanocomposite, reproduced with permission from [117], copyright 2016 Elsevier B.V; b) GO functionalized by phosphorus oligomer, reproduced with permission from [118], copyright 2018 Wiley Periodicals, Inc.; c) schematic presentation of the proposed fire-retardant mechanism of BN-HPPA, reproduced with permission from [119], copyright 2018 Elsevier Ltd; d) HRR results of pure UP and its composite with $MoS_2$-HPA, with permission from [104], copyright 2020 Elsevier B.V.

with $TiO_2$ subsequently broken into lower-carbon products. It was demonstrated that the $Cu_2O$ could covert the CO toxic gases to non-toxic $CO_2$ and the $TiO_2$-GO nanosheets could delay the catalytic reaction time of pyrolysis and inhibit the transferring of oxygen and heat.

### 2.2.3. *Organic-inorganic FRs*

To improve the compatibility of inorganic FRs with UP matrix, surface modifications with organic compounds have been considered. Bautista et al. reported a highly fire-retardant UP that achieved an LOI of 51% by combining 5 wt% of caged silsesquioxane oligomers and 55 wt% of ATH because of the high thermal stability of the compound containing Si–O type bonds in the structure [120]. Jiang et al. [118] used an organophosphorus oligomer to functionalize GO (Fig. 11b), and only 2 wt% of functionalized GO reduced the PHHR of UP by 42%. However, there are several disadvantages with these systems, such as increased resin viscosity, significantly decreased crosslinking density and $T_g$ values.

In another work, incorporating 3 wt% boron nitride nanosheets modified by hyperbranched polyphosphate acrylate (BN-HPPA) into an UP matrix resulted in a significant reduction in both PHRR and THR, 28.2% and 38.0%, respectively [119]. The proposed fire retardant mechanism of BN-HPPA is presented schematically in Fig. 11c, where physical barrier effects of BN sheets retard heat and mass transfer between the combustion zone and the underlying UP matrix. As shown in Fig. 11d, molybdenum disulfide ($MoS_2$) nanosheets functionalised by hyperbranched polyphosphate acrylate ($MoS_2$-HPA) significantly reduced PHHR and THR of UP/5% $MoS_2$-HPA by 43.2% and 39.6%, respectively [121]. Dynamic mechanic analysis illustrates that incorporation of 5% $MoS_2$-HPA increases $T_g$ (Tan δ) from 97 °C for pure UP to 147 °C for modified UP. Interestingly, when $MoS_2$-HPA was incorporated to UP matrix, the $T_g$ was significantly increased due to covalent bonding of sulfydryl groups and functiontalized HPA with the UP matrix, and improved crosslinking density.

## 3. Effects of FRs on curing behaviours of UP

Addition of FR to UP system impacts the curing process. Increasing the gel time reduces the production rate which is a commercial disadvantage. Generally, the gel time of UP containing vinyl monomers reduced in presence of a vinyl phosphonate FR [122]. It was shown that UP containing DOPO-MA had a higher initially curing temperature ($T_i$) and peak curing temperature ($T_p$) compared with the unmodified UP [36]. For example, by introducing 20 wt% of DOPO-MA into the UP, the $T_i$ and $T_p$ increased by 45% and 34%, respectively. To address this retarding effect, suggestions included increasing the amount of initiator, higher temperature, or changing the initiator system. Also, it has been shown that 20 wt% APP increases the gelation time, while 5 wt% clay and 20 wt% ATH could reduce the gelation time of UP [123]. Moreover, it was shown that incorporation of ADP into UP makes the exothermic curing peak, flatter and wider with higher $T_i$ and $T_p$ compare with pure UP which indicates the lower curing rate [96]. Oligomeric phosphonates are regarded as good reactive FR candidates for fabrication of FR-UP without affecting the curing reaction (gel time<10 min) [124].

## 4. Effects of FRs on mechanical properties of UP

Generally, addition of FR reducing the mechanical properties of polymer matrix. Fig. 12 shows the effect of additive FR on the mechanical properties of UP thermosets. The FRI of presented UP/FR systems are between 1 and 10, indicative of good fire retardancy. Clay is the most promising modifier which has been shown to improve mechanical properties. It was shown that surface chemistry of clay is a determining factor in improving mechanical properties of UP [125]. It was demonstrated that the vinyl organic modifier such as vinyl triphenyl

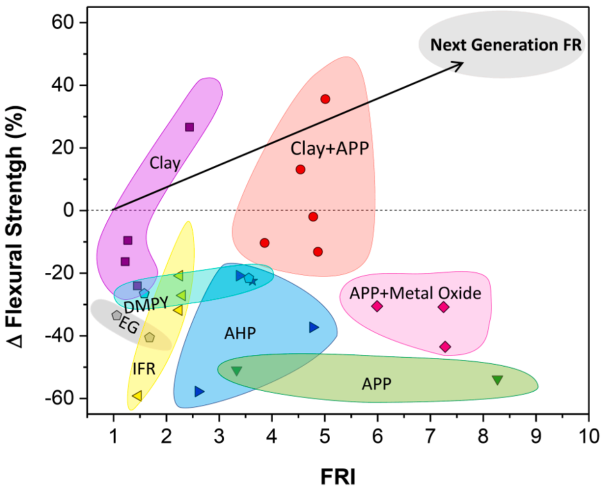

**Fig. 12.** Comparing the change of flexural strength versus the FRI values. The data are collected from the following references: (■)5%Na-MMT-Vinyl triphenyl phosphonium bromide modifier, 5%Na-MMT-Vinyl benzyl trimethyl ammonium chloride modifier, Na-MMT Hexadecyl trimethyl ammonium chloride, 5%Na-MMT Dodecyl ethyl dimethyl ammonium bromide [125]; (●) 5% Na-MMT-Vinyl triphenyl phosphonium bromide modifier/20%APP, 5%Na-MMT-Vinyl benzyl trimethyl ammonium chloride modifier/20%APP, 5%Na-MMT-Hexadecyl trimethyl ammonium chloride/20%APP, 5%Na-MMT-Dodecyl ethyl dimethyl ammonium bromide/20%APP [125], 1% MMT-2% ZB/17%APP [71]; (▼) 20%APP [125], 30% APP [80]; (▯) 4% Expandable graphite (EG)/1% OMH [55], 6%EG/1%OMH [55]; (⬠) Dia-APP-TPP-30 [105]; (⬟)15% DMPY, 7.5%DMPY/7.5% ADP [84]; (◆) 29.5%APP + 0.5%$Fe_2O_3$ [80], 29.5%APP + 0.5%$Sb_2O_3$ [80], 29.5%APP + 0.5% $Al_2O_3$ [80]; (▶) 30 %AHP, 30 %CP@AHP [102]; (◀) 24.5% intumescent fire-retardant (IFR) by APP/ PER/ MEL (APP-PER-MEL) (3:1:1) [70], 32% IFR (APP-PER-MEL)(6:1:1) [72], 29.6% IFR (APP-PER-MEL)(6:1:1) (6:1:1)/1.5% MMT [72], 29.5%IFR IFR (APP-PER-MEL) (6:1:1)/1.5%MMT-containing phytic acid (PA-MMT) [72].

phosphonium bromide (VTPB) and vinyl benzyl trimethyl ammonium chloride (VBTAC) showing better flexural properties. APP is the best fire-retardant but has significant negative impact on the flexural strength. The results suggest that a hybridized formulation of 20 wt% of APP and 5 wt% of modified Clay (Na-MMT-VTPB) can find a balance between good fire retardancy (FRI = 5.0) and improved flexural strength (36% APP increase).

Other FRs reduced the flexural strength more than 20%. So, it is essential to consider the effect of FR addition on the mechanical properties of UP thermosets. The mechanical properties suggest that the modified UP with DMPY/ADP had a higher tensile and impact strength than the UP modified with DMPY only [84]. Mixtures of DMPY and ADP are more compatible with the UP matrix, due to the high concentration of non-polar alkyl group from the ADP compared with the polar groups (amino and hydroxyl) of DMPY. Incorporation of AHP reduced the flexural strength by 37%, however, core–shell structured AHP with chlorinated paraffin (CP) as a shell just reduced the flexural strength by 20 % [102]. This is attributed to the improvement in the compatibility of AHP with the UP matrix. Therefore, a strong interfacial interaction between additive FRs and UP matrix is key to improving the mechanical properties.

## 5. Applications of Fire-Retardant UP

Fire-retardant UP applications are including wind turbine, electronics (such as insulation varnish, cable trays and switch boxes), transportation (in subway, interior of air plane, and automotive), chemical plants (cooling tower, pipes, tanks, ducts, ..) and building (artificial stone, fascia, …). For all these applications, some structural mechanical strength is necessary. Also, for some application such as ducts, pipe, tanks, cooling towers chemical resistance is additionally required. Another important application of UP is its use as a gelcoat for providing a high-quality finish to fibre reinforced composites. A suitable FR gelcoat requires some other properties beside flame retardancy, such as comparable coefficient of thermal expansion to the composite, low thermal conductivity, high interfacial adhesion to matrix resin, high weather and wear resistance [126]. Intumescent gelcoats based on APP are a good candidate for glass fibre reinforced UP resin laminates for applications in railway and aerospace [127]. Moreover, fabrication of fire-retardant laminated composites with UP based on acrylic modified resin blends have been developed with high fire retardancy relative to conventional ATH-loaded UP [128]. Another important application which recently patented is battery pack housing for electric vehicles [129].

## 6. Conclusions, challenges, and opportunities

### 6.1. Conclusions

There are three strategies for making fire-retardant UP. One promising strategy is to develop intrinsically fire-retardant UP resins by using FRs as monomers. Another favorable approach is the copolymerization of UP resin with reactive fire-retardant comonomers. Last one is the additive FRs, which categorized according to organic and inorganic compounds. Organic additive FRs are including halogenated, charring resins, and oligomeric-polymeric FRs. Inorganic additive FRs are consist of P-N complexes, ATH, nanostructured FR, core–shell structured FR, and their hybrid. It was found that blending with char forming resins can be an excellent method to reduce the flammability of UP. One of the most effective FR for UP is APP and its hybrid with nano-clay. Moreover, core–shell structured FR are a promising new class of FR in which disclosed promising results display a synergistic performance for UP.

Most of these FRs act through promoting char formation in the condensed phase and disrupting radical reaction in gas phase. These FRs strategies have inherent strengths and weaknesses, which have been discussed in this review. The effort to make FR-UP which circumvent the weaknesses without sacrificing strengths should be pursued. Hybridization of FRs such as P-containing and nanoparticles, P-containing and minerals, or UP blend with char forming resins with P-containing FRs are promising options. Oligomeric and polymeric FR are new types of additive FRs for UP in which encouraging findings have been revealed and make them as a promising candidate in the future. Good FRs for UP have been presented in this work by comparing cone calorimetry results of different FRs with their required loading level to pass UL-94 V-0 rating. In addition, it is worth noting that a good FR should be of low-cost and environmentally friendly from a perspective of practical applications.

### 6.2. Key challenges

Although additive ecofriendly FRs have demonstrated substantial advances in the last few years, there are still challenges that should be addressed.

(1) Curing behaviour: Understanding the effect of FR on the gel time and temperature of UP is crucial particularly for composite manufacturing. The effect of fire-retardants on the curing process has not been explored widely for the most of FR-UP systems. It has been discussed in this review some of these UP/FR system, have a prolonged gel time which is not desirable.
(2) Efficiency: The loading level of FRs in UP, in which most cases the required FRs to pass all requirement is about 15 wt%. The high loading severely weakens the processability, curing behaviour and mechanical performance. Also, most of additive FRs have a plasticization effect on UP matrix which deteriorate the mechanical performance. So, developing new FRs with lower

loading level (<10 wt%) would be highly desirable to maintain processability, curing behaviour and mechanical properties.

(3) Environment: Most of reported FRs for UP system are synthesised from petroleum-based resources and their synthesis procedures required large amounts of organic solvent which bring significant environmental challenges.

(4) Selection of UP matrix: There are different UP structures which have different properties, processability, and cost which enable the user to choose the right molecular structure for target applications. Comparing the fire retardancy of different strategies required the attention to the UP backbone structure, and cross-linking agent (St, MMT, or etc.) and content. Also, it is important to note that the static properties should not be sacrificed in the pursuit of improved fire performance.

### 6.3. *Opportunities*

The following research opportunities are proposed to develop next generation FRs for UP thermosets. (i) Research on the curing behaviour and chemo-rheological behaviour of UP resin containing FR is indispensable (examples [3,52] for epoxy/FR system) which poorly understood to date. This enable researchers to evaluate the side processability of UP system modified with FR. (ii) One important strategy would be hybridization, along with optimize formulation of UP is an opportunity which could meet these requirements. (iii) Further efforts are needed to develop oligomeric and polymeric FRs which can have good compatibility with UP matrix. Also, there are many more chances to achieve FR requirements with lower loading level. (iv) Recently, there is much attention to bio-based UP, by replacing traditional monomers such as isophthalic acid with bio-based monomers such as itaconic acid. Again, there are many opportunities to develop bio-based FR UPs.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.132785.

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