The application of ammonium polyphosphate in unsaturated polyester resins: A mini review

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ABSTRACT

Ammonium polyphosphate (APP) is a common and commercially available flame retardant for various polymeric materials due to its low cost, ease of proccessing, low toxicity, and environmental friendliness. This mini review focuses on the application of APP in unsaturated polyester resin (UPR) and outlines the flame retardancy, thermal stability, and mechanical properties of the APP-containing UPR composites. As an effective acid source, APP can facilitate the dehydration and carbonization of the UPR matrix during combustion, forming a graphite char layer on the matrix surface to slow down heat exchange and volatile release, thus suppressing the burning reaction. Due to the inorganic properties of APP, microencapsulation and surface decoration are usually conducted on it to enhance its compatibility with UPR and its flame-retardant efficiency. Moreover, different flame-retardant synergists are also applied to strengthen the flame-retardant performance of APP in UPR. In this review, we briefly summarized the influences of microencapsulated APP, surface-decorated APP, and APP/synergist on the properties of UPR, respectively. Then, the advancement and challenges of these APP systems are highlighted, and future research opportunities are also proposed.

1. Introduction

Unsaturated polyester resin (UPR) has emerged as one of the most important thermosetting resins globally due to its exceptional mechanical properties, corrosion resistance, heat resistance, and cost-effectiveness [1-4]. UPR is mainly composed of UPR prepolymers and vinyl diluents. UPR prepolymers are synthesized through the polycondensation of saturated and unsaturated acids with diols. The raw materials of UPR prepolymer include maleic anhydride, isophthalic anhydride, and ethylene glycol [5]. For vinyl diluents, styrene is the most common one, and its content in UPR can vary from 30 to 50 wt% [6]. The properties of the cured UPR can be altered by adjusting the crosslinking density and diluent addition amount [7,8].

With the frequent occurrence of fires and increasing concerns about safety issues, engineers and researchers have begun to pay attention to the high flammability of UPR. According to previous research, the limiting oxygen index (LOI) of the common UPR is only 19.0 % and it cannot achieve any ratings in the vertical burning (UL-94) test [5,9-11],

and thus it is a typical flammable polymer. During combustion, UPR will produce abundant molten drippings and toxic smoke, *e.g.,* styrene, phthalic anhydride, and toluene, which will greatly promote the spread of fires and reduce escape opportunities [12,13]. In recent years, there has been a huge demand in various industries for self-extinguishing materials with a LOI > 28.0 % and an UL-94 V-0 rating. Hence, it is necessary to develop flame-retardant UPR with self-extinguishing characteristics. Initially, researchers tended to develop fire-retardant UPR by employing halogenated monomers to synthesize UPR prepolymer due to their high flame-retardant efficiency. This method can be traced back to 1954, and P. Robitschek et al. synthesized a halogen-based monomer, 1,4,5,6,7,7-hexachlorobicyclo(2,2,1)−5-heptene-2,3-dicar-boxylic anhydride (HCHDA), from the reaction of hexachlorocyclopentadiene and maleic anhydride, and applied it in the fabrication of self-extinguishing UPR [14]. Although using halogenated monomers is a valid way to improve the flame resistance of UPR, they have been banned in many countries and deemed as contaminants since their burning products will lead to serious harm to humans and

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environment [15]. One of the main burning products of halogen-containing UPR is halogenated hydrocarbons, which are associated with many health issues in animals and humans, such as endocrine and thyroid disruption, respiratory diseases, and cancer [16]. Therefore, it has become a trend to seek environmentally friendly alternatives to halogenated flame retardants (FRs) in the manufacture of flame-retardant UPR. Among them, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives [17-21], oligomeric P-containing flame retardants [20,22-25], and P-N complexes were prevalently investigated [26-30].

Ammonium polyphosphate (APP) is a halogen-free, environmentally friendly flame retardant, which is rich in phosphorus (P) and nitrogen (N) elements. During combustion, the phosphorus-containing groups in APP will promote matrix carbonization, and the nitrogen-containing groups will decompose to release inert N-based gases to dilute combustible gases. Additionally, the joint action of P- and N-containing groups will lead to the formation of an intumescent char layer on the matrix surface, which inhibits heat release and smoke generation, thus improving flame retardancy [31-35]. As previously reported, about 20–30 wt% of APP endowed UPR/APP composite with a UL-94 V-0 rating [36-39]. Obviously, APP is a proven flame retardant for UPR, but its shortcomings should not be ignored and need to be addressed. The migration, moisture sensitivity, and aggregation issues of APP caused by its polarity and inorganicity impact not only its flame-retardant effect but also its practical value [40,41]. Enhancing the interfacial interaction between APP and polymer matrix is an effective way to address these issues and thus endow the APP-containing polymer with better flame retardancy and comprehensive performances. In the past decades, many efforts have been devoted to enhancing the compatibility between APP and polymer, and two main methods have been developed: surface decoration and microencapsulation. In addition to these methods, introducing synergists into the UPR/APP system is also effective in reducing APP loading levels and improving flame retardancy. This mini review discusses the research progress of the APP-containing, flame-retardant UPR composites. Flame-retardant properties, thermal stability, and mechanical performances of these UPR composites are probed to provide a comprehensive understanding of the influences of APP and its derivatives on the overall properties of UPR composites. Finally, the advantages and shortcomings of these APP-based flame-retardant systems are summarized, and their potential development direction is proposed.

2. Microencapsulated APP for UPR

Microencapsulation technology is applied in APP frequently, and it allows APP to be encapsulated inside a microsphere/microcapsule to construct core-shell, APP-based flame retardant. This method has been proven to be effective in improving interface compatibility and reducing water absorption of APP. Based on microencapsulation technology, many APP-based flame retardants were developed and applied to different polymeric materials [42-46]. In this section, the advance of the microencapsulated APP for UPR is introduced.

Fig. 1 shows the synthesis routes and microstructures of three microencapsulated APP derivatives for UPR. Zhang et al. synthesized a microencapsulated APP (MAPP, see Fig. 1a) with a Schiff base shell and investigated its effects on the thermal, mechanical, and flame-retardant properties of UPR [47]. Before microencapsulation, the APP surface was smooth and regular, while the MAPP surface became uneven and rough due to the existence of the Schiff base shell (see Fig. 1d). Compared with the neat UPR, the UPR composite containing 17 wt% MAPP (UPR/MAPP) showed a LOI of 28.6 % and an UL-94 V-0 level, with 30.6 % and 39.5 % reductions in peak heat release rate (PHRR) and total heat release (THR). In addition, the flame propagation index (FGI) of UPR/MAPP composite was much lower than that of UPR, further
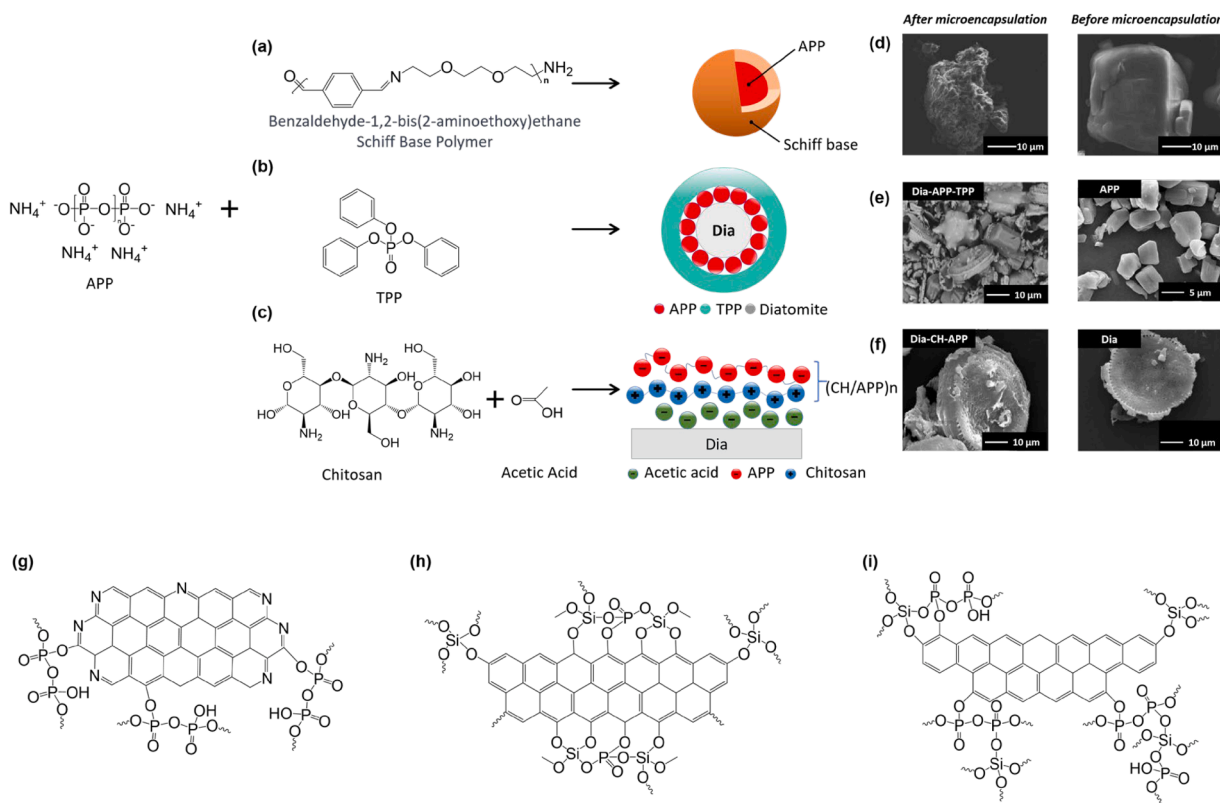

Fig. 1. The synthesis of (a) MAPP, (b) Dia-APP-TPP, and (c) Dia-CH-APP; the SEM images of (d) MAP, (e) Dia-APP-TPP, and (f) Dia-CH-APP; and the possible residual char structures of (g) UPR/MAPP, (h) UPR/Dia-APP-TPP, and (f) UPR/Dia-CH-APP. Reprinted from [47,50,51], Copyright (2023, 2019, and 2020), with permission from Elsevier.

demonstrating enhanced fire safety [48]. The tensile and flexural strengths of UPR/MAPP were both lower than those of UPR, but higher than those of the UPR/APP composite with 17 wt% of unmodified APP. All these results indicated that MAPP enhanced the flame retardancy of UPR obviously, and the Schiff base coating reduced the adverse effect of APP on the mechanical performance of UPR by increasing the interfacial interaction between APP and UPR. Furthermore, the Schiff base shell will form pyridine and its derivatives due to its rearrangement and cyclizing reaction during combustion, and these compounds will react with phenyl fragments, which are the main source of soot [49]. Obviously, it may lead to most of the phenyl compounds being trapped in the condense phase and participating in the formation of char layer, thus enhancing flame retardancy and smoke suppression. The condensed-phase action of the Schiff base coating reinforced the flame-retardant effect of MAPP (see Fig. 1g).

Chen et al. developed a microencapsulated flame retardant (Dia-APP-TPP) *via* using triphenyl phosphate (TPP) as shell material and diatomite/ammonium polyphosphate (Dia/APP) as core material (see Fig. 1b and e) [50]. With the addition of 30 wt% of Dia-APP-TPP, the obtained UPR/Dia-APP-TPP composite showed a much higher char yield than UPR in thermogravimetric analysis (TGA) (see Table 1), indicative of its flame retardancy to some extent. In Dia-APP-TPP, the Dia and APP parts mainly functioned in the condense phase during combustion, which facilitated the formation of a compact and continuous char layer on the UPR surface by generating Si-O-P and Si-O-C bonds (confirmed by the X-ray spectroscopy, see Fig. 1h). The TPP part mainly took action in the gas phase to release P-derived radicals to quench the active H· and OH· radicals produced by the combustion chain reaction of the UPR matrix [52]. Due to the dual-phase effect of Dia-APP-TPP, the UPR/Dia-APP-TPP composite showed superior flame retardancy to UPR, and its PHRR, THR, and FGI were reduced by 54.1 %, 34.0 %, and 64.3 % respectively compared with those of the neat UPR. However, the total smoke release of the UPR/Dia-APP-TPP composite was higher than that of UPR, indicating that Dia-APP-TPP could not suppress the smoke generation during combustion and may mainly function in the gas phase. Moreover, the introduction of Dia-APP-TPP also led to the decreased tensile and flexural strengths of UPR/Dia-APP-TPP. Thus, Dia-APP-TPP endowed UPR with flame retardancy at the expense of mechanical properties.

In addition to the above work, Chen et al. reported another microencapsulated, APP-based flame retardant (Dia-CH-APP, see Fig. 1c and e) using chitosan (CH), APP, and Dia as raw materials, and also applied it in the fabrication of flame-retardant UPR composite [51]. Like MAPP, Dia-CH-APP exhibited a rough and irregular surface (see Fig. 1e). After introducing 25.0 wt% of Dia-CH-APP, the resultant UPR/Dia-CH-APP composite showed improved thermal stability and flame retardancy, with a LOI of 25.7 % and an UL-94 V-0 rating (see Table 2). Furthermore, compared with pure UPR, the PHRR, THR and TSR of UPR/Dia-CH-APP decreased by 40.8 %, 18.1 %, and 52.4 %, respectively. Obviously, the enhanced flame retardancy and smoke suppression of the UPR/Dia-CH-APP composite was mainly due to the joint flame-retardant action of Dia, CH, and APP. Under heat radiation, the CH will undergo dehydration and carbonization under the catalysis of APP and its derivatives. Meanwhile, the Dia will decompose to generate plenty of silicone compounds, which will cooperate with the phosphorous-containing fragments from APP to promote the formation of a dense and continuous char layer, which can isolate heat transfer and volatile release (See Fig. 1i). Notably, the addition of Dia-CH-APP effectively maintained the tensile and flexural strengths of UPR, which made it superior to its counterpart (Dia-APP-TPP).

These above three microencapsulated APP-based flame retardants all show good flame retardancy towards UPR and can effectively improve the char-forming ability of UPR. Additionally, these works demonstrate that the microencapsulation technology can enhance the interfacial interaction between APP and UPR, and thus reduce the adverse effect of APP on the mechanical performance of UPR. However, some

Table 1
TGA data of UPR composites.

Ref.	Flame retardant system (condition)	ΔT_i-U (°C)	ΔT_i-A (°C)	ΔT_{max}-U (°C)	ΔT_{max}-A (°C)	ΔCY-U (%)	ΔCY-A (%)
[47]	MAPP (N_2)	+1	−4	−73	−3	+22.1	+1.1
[50]	Dia-APP-TPP (N_2)	+11	/	−52	/	+27.6	/
[51]	Dia-CH-APP (N_2)	+16	+36	+2	+13	+28.1	+6.9
[53]	APP-BIM (N_2)	+17	/	−77	/	+33.8	/
[39]	STAPP/PER/MEL (N_2)	−48	−14	−51	−1	+21.9	−1.1
[54]	APP/Fe_2O_3 (N_2)	−1	+1	−67	−1	+28.2	+5.2
[54]	APP/Sb_2O_3 (N_2)	−3	−1	−72	−6	+30.5	+7.5
[54]	APP/Al_2O_3 (N_2)	+4	+6	−67	−1	+37.5	+14.5
[55]	APP/DMMP (N_2)	−93	−85	−70	−5	+23.4	−6.6
[56]	APP/ATH/DMMP (N_2)	+15	/	−62	/	+20.5	+8.2
[57]	APP/AHP (Air)	−11	+2	−23	0	+17.1	+2.6
[58]	APP/AlPi (N_2)	+6	−18.1	−10	+1	+12.2	+0.9
[59]	APP/PER/MEL/PA-MMT (N_2)	−35	−4	−38	+8	+18.8	−1.6
[60]	APP/KUIC (N_2)	−11	+5	+19	+27	+15.4	+2.4
[61]	APP/BPCNT (N_2)	−23	−11	−71	+2	+21.8	−0.3
[62]	APP/INTs-PF6-Ils (Air)	+12	−4	−30	−3	+19.5	+1.1
[63]	APP/I-Mxene (Air)	+34	+22.8	−46	+5	+11.3	+7.7

[a] ΔT_i-U: Variation in initial decomposition temperature (T_i) compared with UPR.
[b] ΔT_i-A: Variation in T_i compared with the APP-containing UPR.
[c] ΔT_{max}-U: Variation in maximum weight loss temperature (T_{max}) compared with UPR.
[d] ΔT_{max}-A: Variation in T_{max} compared with the APP-containing UPR.
[e] ΔCY-U: Variation in char yield (CY) compared with the UPR.
[f] ΔCY-A: Variation in CY compared with the APP-containing UPR.

Table 2
Flame-retardant and mechanical performances of UPR composites containing microencapsulated or surface-decorated APP additives.

Ref.	FR content (wt%)	Variation (%) PHRR	Variation (%) THR	UL-94 rating	LOI (%)	Variation (%) Tensile strength	Variation (%) Flexural strength
[47]	17.0	−30.6	−39.5	V-0	28.6 %	−49.1	−36.5
[50]	30.0	−54.1	−34.0	V-0	27.8 %	−35.7	−22.5
[51]	25.0	−40.8	−18.1	V-0	25.7 %	+6.9	+3.4
[53]	20.0	−64.0	−55.7	V-0	34.0 %	–	–
[39]	15.0/5.0/5.0 (STAPP/PER/MEL)	−54.1	−15.7	V-0	41.5 %	−29.4	−55.2

shortcomings of these microencapsulated flame retardants cannot be ignored. Firstly, some of these microencapsulated flame retardants suffer from poor smoke suppression. Secondly, the incorporation of these FRs into UPR still leads to the deterioration of mechanical properties. Finally, these FRs are not efficient enough and generally require high loading levels to achieve desirable flame retardancy. Obviously, using some synergists of APP, to develop microencapsulated APP-based FRs is expected to increase flame-retardant efficiency and reduce the negative influence on mechanical properties. In addition, creating microencapsulated APP-based FRs with a smoke-suppressing effect is also an important research direction.

3. Surface-decorated APP for UPR

Many organic groups are used in the surface decoration of APP to increase its hydrophobicity, compatibility, and dispersity, and the resultant surface-decorated APP flame retardants have been applied in various polymers. Among various modifiers, the most popular are amines and silane coupling agents [64-66]. Synchronously, some research works focused on the surface-decorated APP for the fabrication of flame-retardant UPR composites and investigated their impacts on the thermal stability, flame retardancy, and mechanical properties of UPR.

Li et al. synthesized a benzimidazole-modified APP (APP-BIM) and investigated its application in UPR (see Fig. 2a) [53]. Unlike the microencapsulated APP, the as-synthesized APP-BIM showed similar microstructure and surface morphology to the unmodified APP (see Fig. 2c). The TGA results indicated that the obtained UPR/APP-BIM composite with 20 wt% of APP-BIM showed higher initial decomposition temperature (T_i) and lower maximum weight loss temperature (T_{max}) than pure UPR, indicative of improved thermal stability (see Table 1). In addition, the UPR/APP-BIM composite featured superior self-extinguishing ability, and it passed a UL-94 V-0 rating and achieved a LOI of 34.0 %. Additionally, the PHRR and THR values of the UPR/APP-BIM composite were 64.0 % and 55.7 % lower than those of UPR (see Table 2). APP-BIM also featured a great smoke-suppressing effect due to its benzimidazole groups, 20 wt% of which brought about 52.8 % and 64.3 % reductions in total smoke production (TSP) and peak smoke production rate (PSPR). During combustion, the N-containing decomposition products of APP-BIM (see Fig. 2e) accelerated the formation of large N-doped particles in the condensed phase, and the APP part converted into phosphates and adhered these spherical particles together in the condensed phase, thus forming a protective char layer (see Fig. 2f) on the UPR surface to inhibit the heat release and smoke generation.

Chen et al. applied (3-aminopropyl) triethoxysilane (KH-550) to modify APP and named the product as STAPP (see Fig. 2b) [39]. Like APP-BIM, the surface of STAPP did not change significantly after the modification of KH-550 (see Fig. 2d). With the incorporation of 15.0 wt % of STAPP, 5.0 wt% of pentaerythritol (PER), and 5.0 wt% of melamine (MEL), the resulting UPR/STAPP/PER/MEL obtained an UL-94 V-0 rating and a LOI of 41.5 %. However, the UPR/STAPP/PER/MEL showed a lower T_i in comparison to pure UPR and UPR (UPR/APP/-PER/MEL) composite with 15.0 wt% of unmodified APP, 5.0 wt% of PER and 5.0 wt% of MEL. Obviously, the KH-550 accelerated the decomposition of APP and led to the reduced initial decomposition temperature of UPR/STAPP/PER/MEL. Notably, the combination of KH-550 and APP endowed STAPP with superior promoting charring ability (see Fig. 2g), as confirmed by the higher char yield of UPR/STAPP/PER/MEL than those of UPR and UPR/APP/PER/MEL. In the cone calorimetry test, UPR/STAPP/PER/MEL showed much lower heat release than the neat UPR, with 54.1 % and 15.7 % decreases in PHRR and THR. Notably, the PHRR and THR of UPR/STAPP/PER/MEL were close to those of UPR/APP/PER/MEL, but the TSP of UPR/STAPP/PER/MEL was 17.2 % lower than that of UPR/APP/PER/MEL. Both UPR/STAPP/PER/MEL and UPR/APP/PER/MEL showed reduced mechanical performances relative to pure UPR. For instance, the tensile and flexural strengths of UPR/STAPP/PER/MEL were 29.4 % and 55.2 % lower than those of UPR. Thus, both STAPP/PER/MEL and APP/PER/MEL imparted flame retardancy to UPR at the expense of mechanical properties (see Fig. 3).

Overall, the surface decoration strategy provides a feasible way for APP to improve its interfacial interaction with the UPR matrix and flame retardancy. However, the efficiencies of these APP flame retardants are not high enough, and usually, their additions are higher than 20.0 wt%. In addition, due to their high addition, the resultant UPR composites
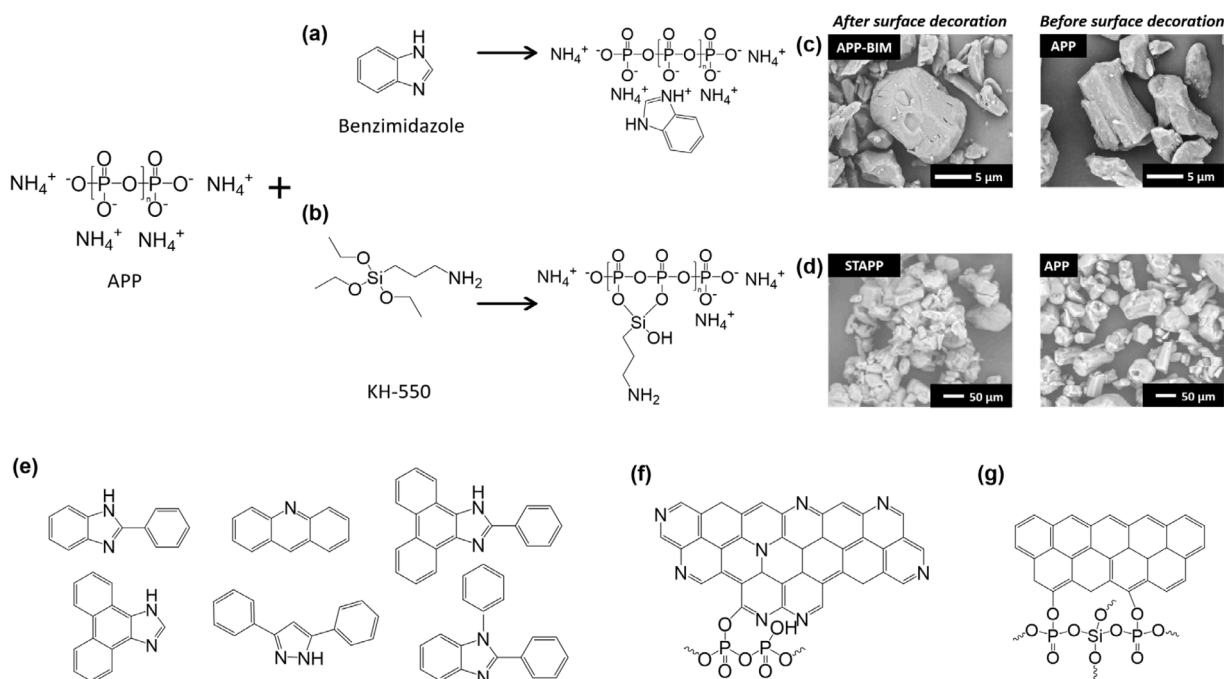

Fig. 2. The synthesis routes of (a) APP-BIM and (b) STAPP; the SEM images of (c) APP-BIM and (d) STAPP; the gas-phase products of (e) APP-BIM during combustion; and possible residual char structures of (f) UPR/APP-BIM, and (g) UPR/STAPP/PER/MEL. Reprinted from [39,53], Copyright (2021, and 2023), with permission from Springer Nature and Elsevier.
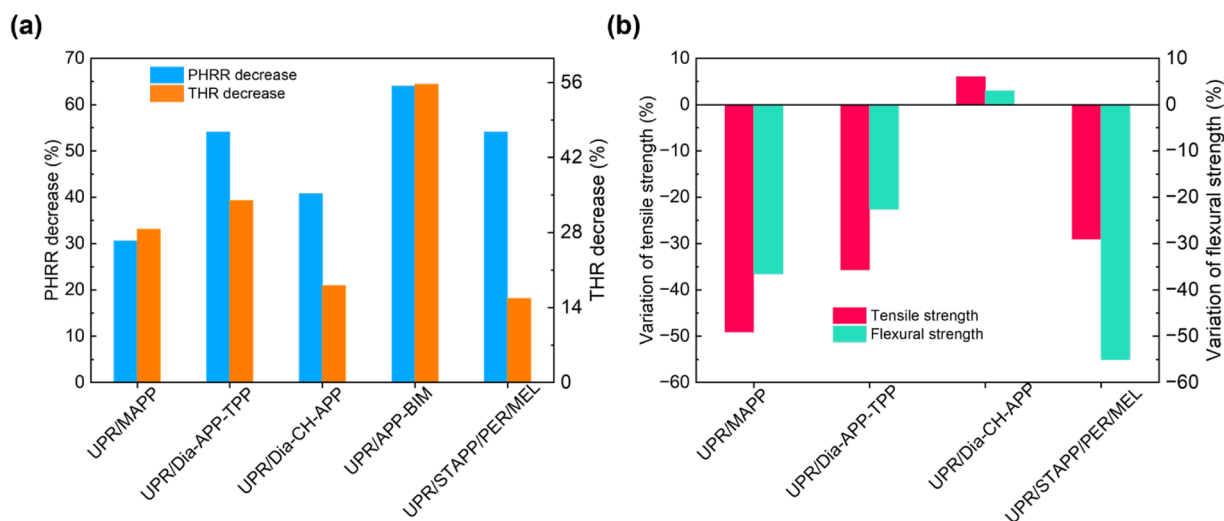
Fig. 3. (a) PHRR and THR reductions, and (b) variations of tensile and flexural strengths of previous APP-containing UPR composites relative to virgin UPR [39,47, 50,51,53].

showed poor mechanical properties (see Fig. 3), which limit their practical application. Clearly, how to seek suitable modifiers to decorate APP and increase its efficiency is still a huge challenge. Hence, more work should be conducted on the development of highly effective surface-decorated APP flame retardants.

4. APP/synergist for UPR

The flame-retardant performances of the UPR/APP composite can be improved by introducing an additional flame retardant that can serve as a synergist of APP. The synergist of APP can be simply divided into three categories. The first type is metallic oxide (MO)/metal hydroxide (MHO), the second one is organic phosphorous flame retardant, and the third one is mineral-derived and nanomaterial. To investigate and compare the flame retardancy and mechanical properties of different UPR/APP/synergist systems, their corresponding data are listed in Table 3.

In 2009, Hapuarachchi et al. combined APP and aluminium tri-hydroxide (ATH) in the fabrication of flame-retardant UPR [67]. In this work, the addition amount of ATH was set as 50.0 wt%, and that of APP was 5.0, 10.0, and 15.0 wt%, respectively. With 50.0 wt% of ATH and 15.0 wt% of APP, the obtained UPRAPP/ATH composite exhibited the best flame retardancy, but this synergistic system suffers from poor smoke-suppressing effect.

Gao et al. investigated the flame-retardant synergism between APP

and different metallic oxides (Fe_2O_3, Sb_2O_3, Al_2O_3) in UPR [54]. In this work, the loading level of metallic oxide ranged from 0.5 to 5.0 wt%, and that of APP was between 25 and 30 wt%. Their result indicated that replacing part of APP with metallic oxides could increase the LOI of the resultant UPR composite. The LOI of UPR/APP composite with 30 wt% of APP was 36.3 %, while those of UPR/APP/Fe_2O_3 (with 29.5 wt% of APP and 0.5 wt% of Fe_2O_3), UPR/APP/Sb_2O_3 (with 29.5 wt% of APP and 0.5 wt% of Sb_2O_3), and UPR/APP/Al_2O_3 (with 29.5 wt% of APP and 0.5 wt% of Al_2O_3) increased to 39.2 %, 39.4 %, and 40.6 %, respectively (see Table 3). In addition, UPR/APP/Fe_2O_3, UPR/APP/Sb_2O_3, and UPR/APP/Al_2O_3 all passed the UL-94 V-0 rating. In the cone calorimetry test, UPR/APP/Fe_2O_3, UPR/APP/Sb_2O_3, and UPR/APP/Al_2O_3 showed much lower PHRR and THR than UPR. For instance, the PHRR and THR of UPR/APP/Fe_2O_3 reduced by 63.2 % and 49.2 %, and those of UPR/APP/Al_2O_3 decreased by 62.9 % and 49.5 % relative to those of UPR. Obviously, the superior flame-retardant performances of UPR/APP/Fe_2O_3, UPR/APP/Sb_2O_3, and UPR/APP/Al_2O_3 were attributed to the synergism between APP and Fe_2O_3/Sb_2O_3/Al_2O_3. The TGA result confirmed that the APP and Fe_2O_3/Sb_2O_3/Al_2O_3 synergistically functioned in the char formation, leading to significantly increased char yields. In addition, the char layers of UPR/APP/Fe_2O_3, UPR/APP/Sb_2O_3, and UPR/APP/Al_2O_3 obtained from the cone calorimetry tests were more compact than those of UPR and UPR-APP, further indicating the condensed-phase synergism of APP and Fe_2O_3/Sb_2O_3/Al_2O_3. Although the tensile and flexural strengths of UPR/APP/Fe_2O_3, UPR/APP/Sb_2O_3,

Table 3
Flame-retardant and mechanical properties of UPR/APP/Synergist composites.

Ref.	Flame retardant system	APP addition (wt %)	Synergist addition (wt %)	Variation (%)			UL-94 rating	LOI (%)	Variation (%)	
				PHRR	THR	TSP			Tensile strength	Flexural strength
[67]	APP/ATH	15.0	50.0	−73.6	+12.5	+82.0	–	–	–	–
[54]	APP/Fe_2O_3	29.5	0.5	−63.2	−49.2	–	V-0	39.2	−48.3	−43.5
[54]	APP/Sb_2O_3	29.5	0.5	−58.1	−45.8	–	V-0	39.4	−42.2	−30.5
[54]	APP/Al_2O_3	29.5	0.5	−62.9	−49.5	–	V-0	40.6	−46.1	−30.8
[56]	APP/ATH/DMMP	8.8	18.2	–	–	–	V-0	30.1	–	–
[57]	APP/AHP	10.3	1.5	−49.3	−22.0	–	V-0	31.0	–	–
[58]	APP/AlPi	20.0	5.0	−68.5	−35.8	−53.3	V-0	–	–	–
[59]	APP/PER/MEL/PA-MMT	22.2	8.9	−63.2	−19.5	–	V-0	29.2	−28.5	−20.8
[60]	APP/KUIC	12.0	3.0	−43.1	−36.3	−38.4	–	28.0	–	–
[61]	APP/BPCNT	18.0	2.0	−61.8	−58.6	−11.1	V-0	30.6	–	−37.3
[62]	APP/INTs-PF6-Ils	16.6	0.4	−41.1	−34.2	–	V-0	28.0	–	–
[63]	APP/I-Mxene	16.9	0.1	−64.7	−52.6	+8.1	V-0	29.1	−2.7	–

and UPR/APP/Al$_2$O$_3$ were both lower than those of UPR, they were higher than those of UPR/APP, indicating that the introduction of Fe$_2$O$_3$/Sb$_2$O$_3$/Al$_2$O$_3$ contributed to reducing the negative effect of APP on the mechanical property.

The MO/MHO plays an important role in promoting the carbonization of the UPR matrix. During combustion, the MO/MOH can catalyse the degradation of APP, leading to the formation of the phosphoric acids and the removal of NH$_3$ and H$_2$O. Then, the phosphoric acids can dehydrate the UPR matrix to form chars. Besides, the phosphoric acids can also react with the MO/MHO to form metal/phosphorous-containing compounds to strengthen the char layers. Moreover, the molten vitreous MO/MOH can cover on the UPR surface, effectively suppressing the burning reaction in the condensed phase and thereby improving flame retardancy.

Chen et al. combined APP with dimethyl methylphosphonate (DMMP) to prepare flame-retardant UPR composites and investigated the synergistic effect between APP and DMMP [55]. With the addition of 20 wt% of APP, the obtained UPR/APP sample only achieved a UL-94 V-2 rating, while the UPR/APP/DMMP sample with 18.5 wt% APP and 7.4 wt% DMMP passed a UL-94 V-0 classification. In addition, the LOI of the UPR/APP/DMMP sample reached about 31.0 %. Clearly, the introduction of APP and DMMP enabled UPR to achieve satisfied flame retardancy. Because of the catalytic decomposition effects of APP and DMMP, the initial decomposition temperature of UPR/APP/DMMP was lower than those of the neat UPR in nitrogen condition according to TGA result. The char yield (in N$_2$) of UPR/APP/DMMP increased from 1.7 wt % of UPR to 25.1 wt%. Notably, the char yield of the UPR/APP/DMMP sample in nitrogen condition was lower than that of the control UPR/APP sample containing 20 wt% of APP (see Table 1), demonstrating that DMMP did not participate in promoting carbonization. It has been reported that the flame retardants containing phosphorus with a high oxidation state mainly functions in condensed phase instead of gas phase [68,69]. Although DMMP did not promote carbonization, its addition led to the increased compactness of char layers, which contributed to suppressing heat release and smoke generation. During combustion, APP acted in the condensed phase to promote char formation. In another work, a flame-retardant UPR system containing ATH, DMMP, and APP was reported [56]. They reported that the incorporation of 8.7 wt% of APP, 10.9 wt% of ATH, and 7.3 wt% of DMMP allowed the UPR/APP/ATH/DMMP composite to pass an UL-94 V-0 rating and achieve a LOI value of 30.1 %. In this UPR system, both ATH and APP mainly functioned in the condense phase during combustion to promote the formation of a compact Al$_2$O$_3$-containing graphite char layer to retard the heat transfer between the fire zone and the UPR matrix. In addition to condense-phase effect, DMMP also exerted the gas-phase effect in this system.

Lin and Reuter et al. reported the application of aluminum hypophosphite (AHP) and aluminum diethylphosphinate (AlPi) as flame-retardant synergists for APP in UPR, respectively [57,58]. The UPR/APP/AHP sample containing 10.3 wt% of APP and 1.5 wt% of AHP achieved a LOI of 31.0 % with an UL-94 V-0 rating, and the UPR/APP/AlPi sample containing 20 wt% of APP and 5 wt% of AlPi also passed an UL-94 V-0 classification. In cone calorimetry, both UPR/APP/AHP and UPR/APP/AlPi samples showed lower heat release than the neat UPR and the APP-containing UPR samples, indicative of the synergism between APP and AHP/AlPi. Obviously, these APP/synergist systems showed similar flame-retardant mechanisms. AlPi and AHP all participated in the condense phase during combustion, which promoted the matrix to form a P/Al-containing protective char layer on the surface to suppress heat release. Therefore, these two works demonstrate that the combination of APP and AHP or AlPi can endow UPR with superior flame retardancy, and it is an effective method to reduce the addition amount of APP and thus reduce its negative effects on the mechanical property of UPR.

In addition, Yu et al. developed a montmorillonite-containing phytic acid (PA-MMT) and introduced it, APP, MEL, and PER into UPR to prepare flame-retardant UPR/APP/PA-MMT/MEL/PER samples [59]. In this work, the compatibility of MMT with the UPR matrix was enhanced after modifying with PA. When the contents of APP, MEL, PER, and PA-MMT were 22.2, 3.7, 3.7, and 1.5 wt%, respectively, the obtained UPR/APP/PA-MMT/MEL/PER sample showed an UL-94 V-0 rating and a LOI of 29.2 %, with 63.2 % and 19.5 % decreases in PHRR and THR relative to those of UPR sample, demonstrating superior flame retardancy. In addition, the total smoke release (TSR) of the UPR/APP/PA-MMT/MEL/PER sample was lower than that of the UPR sample, indicative of enhanced smoke suppression. However, the tensile and flexural properties of the UPR/APP/PA-MMT/MEL/PER sample were decreased compared with those of the UPR sample. Such results indicated that simultaneously adding PA-MMT, APP, MEL, and PER enhanced the flame retardancy and smoke suppression of UPR, but their introduction reduced the mechanical performance.

The organic phosphorous synergists can act in the gas phase during combustion by releasing PO· and HPO· radicals. In addition, the P-containing decomposition products of organic phosphorous synergists can also catalyse the carbonization of the UPR matrix. APP mainly functions in the condense phase to promote carbonization during combustion, and it will produce some inert gases, such as NH$_3$ and N$_2$, to disturb the burning reaction in the gas phase. The introduction of organic phosphorous synergists can strengthen the gas/condensed-phase flame-retardant effects by trapping radical and promoting carbonization during combustion. Hence, the combination of APP and organic phosphorus flame retardants can realize bi-phase flame retardancy, significantly enhancing the flame retardancy of UPR.

In addition to the above works, the application of the mineral-derived and nano FRs as synergists of APP in UPR has also attracted great interest. Yue et al. developed an organic modified kaolinite-urea intercalation complex (KUIC) using dimethyl sulfoxide (DMSO) as the precursor of kaolinite intercalation and applied it as a synergist of APP to fabricate flame-retardant UPR [60]. With the addition of 12.0 wt% of APP and 3.0 wt% of KUIC, the obtained UPR/APP/KUIC sample showed a LOI of 28.0 %, and its PHRR, THR, and TSP were 43.1 %, 36.3 %, and 38.4 % lower than those of UPR, demonstrating superior flame retardancy and smoke suppression. Clearly, KUIC endowed APP with improved smoke suppression. During combustion, the decomposition products of KUIC can react with the P-rich char layer to increase the char compactness and integrity, thus effectively suppressing the heat release and smoke generation and protecting the underlying matrix.

Besides the mineral-derived FRs, the nano FRs have also been applied in the UPR/APP system to strengthen flame retardancy. For instance, Chen et al. synthesized a graphitic carbon nitride-modified, boron/phosphorus-doped multi-walled carbon nanotube (BPCNT), and combined it with APP to flame retardant UPR [61]. With the addition of 20.0 wt% APP, the LOI and UL-94 rating of the resultant UPR/APP sample were up to 29.0 % and V-0, respectively. When 2.0 wt% APP was replaced by BPCNT, the obtained UPR/APP/BPCNT sample showed a higher LOI of 30.6 %, with a UL-94 V-0 rating. In addition, the PHRR, THR, and TSP of the UPR/APP/BPCNT sample reduced by 61.8 %, 58.6 %, and 11.1 % compared with those of the UPR sample, and they were all lower than those of the UPR/APP sample. All these results demonstrated that there was a flame-retardant synergism between APP and BPCNT, which enhanced the flame retardancy and smoke suppression of UPR. In the burning process, the P and B elements of BPCNT functioned in the condensed phase to form a compact char on the UPR surface to suppress the heat and smoke release, and the graphitic carbon nitride and carbon nanotube both increased the char compactness. Moreover, the graphitic carbon nitride degraded to release the inert N-containing gases to exert a diluting effect. In general, BPCNT cooperated with APP to retard the burning of the UPR matrix in both condensed and gas phases. However, the UPR/APP/BPCNT sample showed deteriorative mechanical properties in comparison to the virgin UPR sample, but fortunately, it was much better than that of the UPR/APP sample. Thus, BPCNT also reduced the adverse effect of APP on the mechanical

property of UPR.

Zhu et al. investigated the synergistic effect between modified imogolite nanotubes (INT) and APP in flame-retardant UPR [62]. The imogolite nanotubes were modified with 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF$_6$) and 3-aminopropyltriethoxysilane (KH550) to increase its dispersity within the UPR matrix, and the obtained nanotubes were named as INTs-PF6-ILs. APP demonstrated an obvious flame-retardant synergism with INTs-PF6-IL. The UPR/APP sample containing 17.0 wt% of APP showed a LOI of 25.8 % and an UL-94 V-2 rating, while the UPR/APP/INTs-PF$_6$-ILs sample with 16.6 wt % of APP and 0.4 wt% of INTs-PF$_6$-ILs achieved a LOI of 28.0 % and an UL-94 V-0 rating, indicative of improved flame retardancy due to the synergism between APP and INTs-PF$_6$-ILs. Furthermore, the cone calorimetry results indicated that the PHRR and THR of the UPR/APP/INTs-PF$_6$-ILs sample were 41.1 % and 34.2 % lower than those of the UPR sample, demonstrating that APP and INTs-PF$_6$-ILs effectively suppressed the heat release of the UPR matrix during combustion. In addition, the TGA results showed that the introduction of APP and INTs-PF$_6$-ILs increased the initial decomposition temperature and char yield of UPR in air condition (see Table 1). The enhanced flame retardancy of the UPR/APP/INTs-PF$_6$-ILs sample was probably because APP and INTs-PF$_6$-ILs both facilitated the generation of a compact and continuous char layer on the matrix surface to inhibit heat and oxygen transfer.

Gao et al. chemically grafted [BMIM]PF$_6$ onto the surface of MXene to develop an MXene-based flame retardant (I-MXene), which was used as a synergist of APP in UPR [63]. At the same FR content, the UPR/APP sample containing 17.0 wt% of APP showed a LOI of 25.8 % and an UL-94 V-1 rating, while the UPR/APP/I-MXene sample containing 16.9 wt% of APP and 0.1 wt% of I-MXene showed higher LOI value and UL-94 rating (29.1 % and V-0). In addition, the PHRR and THR of the UPR/APP/I-MXene sample were reduced by 64.7 % and 52.6 % relative to those of the virgin UPR sample, and both were lower than those of the UPR/APP sample. Hence, APP and I-MXene exerted synergistic flame-retardant effects during the combustion of UPR, therefore improving flame retardancy. I-MXene could cooperate with APP to facilitate the UPR matrix to generate a compact and dense char layer, which suppressed the heat release and protects the underlying matrix. However, the introduction of APP and I-MXene increased the TSP and reduced the tensile strength of UPR, which limited the practical application of this UPR/APP/I-MXene system.

The mineral-derived and nano synergists can exert barrier effect to retard the heat and oxygen exchange during combustion, and it can also catalyse the carbonization of the UPR matrix. Hence, their introduction can strengthen the condensed-phase flame retardancy of the APP-containing UPR. In addition, the mineral-derived and nano synergists usually feature superior high-temperature stability, which can improve the thermal stability of char layers. Obviously, the synergistical flame retardant effect between APP and mineral-derived or nano FRs mainly occurs in the condensed phase.

To sum up, the combination of APP and synergists can endow UPR with great flame retardancy at a relatively low FR (APP + synergists) addition amount. For instance, introducing 16.6 wt% of APP and 0.4 wt % of INTs-PF6-Ils (FR addition: 17.0 wt%) can increase the UL-94 classification and LOI value of UPR to V-0 and 28.0 %, respectively. Besides the flame-retardant effect, some APP/synergist systems feature an obvious smoke-suppressing effect towards UPR. However, introducing APP/synergist systems usually reduces the mechanical performances of UPR, and their loading levels are still high, which is over 17.0 wt%. Thus, searching for highly effective synergists for APP is critical, and fortunately, the nano FRs show relatively obvious flame-retardant synergism with APP, which offers a guideline for researchers and engineers.

5. Conclusion and prospect

In this mini review, the research progress of three different modification methods of APP is summarized, and their advantages and weaknesses are shown in Table 4. The microencapsulation method can effectively strengthen the interfacial compatibility of APP and UPR, prevent the migration of APP in long-term usage, and reduce the water absorption of APP. The surface modification method can effectively maintain the morphology and size of APP, and it also contributes to enhancing the interfacial interaction. Both microencapsulation and surface modification methods can increase the flame-retardant efficiency of APP. However, the microencapsulated and surface-decorated APP flame retardants both suffer from the high addition amount ($\geq$17 wt%) and adverse effect on the mechanical performances of UPR. Moreover, they are ineffective in suppressing smoke generation during the combustion of UPR. Obviously, the APP/synergist-containing flame-retardant UPR composites are easy to prepare, and some of them show high flame retardancy and smoke suppression. However, these APP/synergist systems also suffer from a negative effect on the mechanical properties and high FR addition, and the high water absorption of APP cannot be addressed by introducing synergists.

In sum, more effort should be devoted to the development of high-performance APP derivatives for the flame-retardant UPR. For the microencapsulation and surface decoration methods, using the synergists as the shell materials or surface modifiers to prepare microencapsulated or surface-decorated APP may be able to increase the flame-retardant efficiency and reduce the loading level. In addition, developing microencapsulated or surface-decorated APP with reinforcing/toughening and smoke-suppressing effects is an important research direction. Considering sustainable development strategy, using biobased raw materials as synergists of APP should also receive attention. Finally, combining microencapsulation/surface decoration with the incorporation of synergists may be an effective approach to developing high-performance, APP-based flame-retardant systems for UPR.

CRediT authorship contribution statement

Tao Chu: Writing – original draft, Investigation, Conceptualization. **Yixia Lu:** Investigation. **Boyou Hou:** Data curation. **Pooya Jafari:** Formal analysis. **Zhezhe Zhou:** Validation. **Hong Peng:** Writing – review & editing. **Siqi Huo:** Writing – review & editing, Supervision, Funding acquisition. **Pingan Song:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

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.

Table 4
Advantages and shortcomings of different APP modification methods.

Methodology	Advantages	Shortcomings
Microencapsulation	ü Enhanced interfacial compatibility ü Reduced sensitivity to water ü Improved flame retardancy	² Poor smoke suppression ² Reduced mechanical properties ² High FR addition
Surface decoration	ü Maintained particle size and morphology ü Enhanced interfacial compatibility ü Improved flame retardancy	² Poor smoke suppression ² Reduced mechanical properties ² High FR addition
Incorporating synergist	ü Ease of processibility ü High flame retardancy ü Good smoke suppression	² High FR addition ² Reduced mechanical properties ² High water absorption

Data availability

Data will be made available on request.

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References

[1] M. Malik, V. Choudhary, I. Varma, Current status of unsaturated polyester resins, J. Macromol. Sci. Phys. 40 (2–3) (2000) 139–165.

[2] M. Davallo, H. Pasdar, M. Mohseni, Mechanical properties of unsaturated polyester resin, Int. J. Chemtech Res. 2 (4) (2010) 2113–2117.

[3] Y. Gao, H. Zhang, M. Huang, F. Lai, Unsaturated polyester resin concrete: a review, Constr. Build. Mater. 228 (2019) 116709–1167021.

[4] F. Chu, S. Qiu, S. Zhang, Z. Xu, Y. Zhou, X. Luo, X. Jiang, L. Song, W. Hu, Y. Hu, Exploration on structural rules of highly efficient flame retardant unsaturated polyester resins, J. Colloid Interface Sci. 608 (2022) 142–157.

[5] S. Tawfik, J. Asaad, M. Sabaa, Effect of polyester backbone structure on the cured products properties, Polym. Test. 22 (7) (2003) 747–759.

[6] E. Sanchez, C. Zavaglia, M. Felisberti, Unsaturated polyester resins: influence of the styrene concentration on the miscibility and mechanical properties, Polym. (Guildf.) 41 (2) (2000) 765–769.

[7] B. Cherian, E.T. Thachil, Synthesis of unsaturated polyester resin—Effect of sequence of addition of reactants, Polym.-Plast. Technol. Eng. 44 (5) (2005) 931–938.

[8] G. D'auria, M. Malinconico, E. Martuscelli, L. Paolillo, M.G. Volpe, Characterization of cured rubber modified polyester resins by nuclear magnetic resonance methods, Int. J. Polym. Mater. 12 (2) (1988) 125–133.

[9] W. Hu, Y. Li, S. Hu, Y. Li, D. Wang, The design of the nano-container to store the highly efficient flame retardants toward the enhancement of flame retardancy and smoke suppression for the unsaturated polyester resins, Colloid. Surf. A Physicochem. Eng. Asp. 658 (2023) 130708–130717.

[10] F. Chu, W. Wang, Y. Zhou, Z. Xu, B. Zou, X. Jiang, Y. Hu, W. Hu, Fully bio-based and intrinsically flame retardant unsaturated polyester cross-linked with isosorbide-based diluents, Chemosphere 344 (2023) 140371–140380.

[11] B. Yang, Z. Chen, Y. Yu, T. Chen, Y. Chu, N. Song, Q. Zhang, Z. Liu, J. Jiang, Construction of bimetallic metal-organic frameworks/graphitic carbon nitride hybrids as flame retardant for unsaturated polyester resin, Mater. Today Chem. 30 (2023) 101482–101495.

[12] B. Mortaigne, S. Bourbigot, M.Le Bras, G. Cordellier, A. Baudry, J. Dufay, Fire behaviour related to the thermal degradation of unsaturated polyesters, Polym. Degrad. Stab. 64 (3) (1999) 443–448.

[13] S. Seraji, P. Song, R. Varley, S. Bourbigot, D. Voice, H. Wang, Fire-retardant unsaturated polyester thermosets: the state-of-the-art, challenges and opportunities, Chem. Eng. J. 430 (2022) 132785–132802.

[14] P. Robitschek, C.T. Bean, Flame-Resistant Polyesters from Hexachlorocyclopentadiene, J. Ind. Eng. Chem. 46 (8) (1954) 1628–1632.

[15] E. Weil, S. Levchik, Commercial flame retardancy of unsaturated polyester and vinyl resins, J. Fire Sci. 22 (4) (2004) 293–303.

[16] S. Shaw, Halogenated flame retardants: do the fire safety benefits justify the risks? Rev. Environ. Health 25 (4) (2010) 261–306.

[17] Y. Cao, X. Wang, W. Zhang, X. Yin, Y. Shi, Y. Wang, Bi-DOPO structure flame retardants with or without reactive group: their effects on thermal stability and flammability of unsaturated polyester, Ind. Eng. Chem. Res 56 (20) (2017) 5913–5924.

[18] C. Zhang, J. Huang, S. Liu, J. Zhao, The synthesis and properties of a reactive flame-retardant unsaturated polyester resin from a phosphorus-containing diacid, Polym. Adv. Technol. 22 (12) (2011) 1768–1777.

[19] Z. Bai, S. Jiang, G. Tang, Y. Hu, L. Song, R.K. Yuen, Enhanced thermal properties and flame retardancy of unsaturated polyester-based hybrid materials containing phosphorus and silicon, Polym. Adv. Technol. 25 (2) (2014) 223–232.

[20] S. Hu, Y. Li, W. Hu, J. Hobson, D. Wang, Strategic design unsaturated polyester resins composites with excellent flame retardancy and high tensile strength, Polym. Degrad. Stab. 206 (2022) 110190–110200.

[21] Z. Bai, L. Song, Y. Hu, X. Gong, R.K. Yuen, Investigation on flame retardancy, combustion and pyrolysis behavior of flame retarded unsaturated polyester resin with a star-shaped phosphorus-containing compound, J. Anal. Appl. Pyroly. 105 (2014) 317–326.

[22] Z. Zhu, L. Wang, L. Dong, Influence of a novel P/N-containing oligomer on flame retardancy and thermal degradation of intumescent flame-retardant epoxy resin, Polym. Degrad. Stab. 162 (2019) 129–137.

[23] M. Zhang, W. Ye, Z. Liao, Preparation, characterization and properties of flame retardant unsaturated polyester resin based on r-PET, J. Polym. Environ. 30 (2022) 1984–1994.

[24] S. Huo, T. Sai, S. Ran, Z. Guo, Z. Fang, P. Song, H. Wang, A hyperbranched P/N/B-containing oligomer as multifunctional flame retardant for epoxy resins, Compos. Part B Eng. 234 (2022) 109701–109712.

[25] F. Chu, S. Qiu, Y. Zhou, X. Zhou, W. Cai, Y. Zhu, L. He, L. Song, W. Hu, Novel glycerol-based polymerized flame retardants with combined phosphorus structures for preparation of high performance unsaturated polyester resin composites, Compos. Part B Eng. 233 (2022) 109647–109660.

[26] D. Wang, X. Mu, W. Cai, L. Song, C. Ma, Y. Hu, Constructing phosphorus, nitrogen, silicon-co-contained boron nitride nanosheets to reinforce flame retardant properties of unsaturated polyester resin, Compos. Part A Appl. Sci. Manuf. 109 (2018) 546–554.

[27] M. Ribeiro, S. Sousa, P. Nóvoa, C. Pereira, A. Ferreira, Fire retardancy enhancement of unsaturated polyester polymer resin filled with nano and micro particulate oxide additives, IOP Conf. Ser.: Mater. Sci. Eng. 58 (2014) 012020–012028.

[28] X. Qiu, Z. Li, V. Chevali, P. Song, X. Li, Z. Zhang, Functionalized mesoporous silica fire retardant via hierarchical assembly for improved fire retardancy of unsaturated polyester, ACS Appl. Polym. Mater. 5 (3) (2023) 2203–2212.

[29] Y. Hai, S. Jiang, C. Zhou, P. Sun, Y. Huang, S. Niu, Fire-safe unsaturated polyester resin nanocomposites based on MAX and MXene: a comparative investigation of their properties and mechanism of fire retardancy, Dalton Trans. 49 (18) (2020) 5803–5814.

[30] Y. Hai, S. Jiang, X. Qian, S. Zhang, P. Sun, B. Xie, N. Hong, Ultrathin Beta-Nickel hydroxide nanosheets grown along multi-walled carbon nanotubes: a novel nanohybrid for enhancing flame retardancy and smoke toxicity suppression of unsaturated polyester resin, J. Colloid Interface Sci. 509 (2018) 285–297.

[31] H. Li, Z. Wang, X. Chen, M. Sun, X. Zhang, L. Tang, Synergistic flame retardancy of 4A-zeolite/MF-THEIC/ammonium polyphosphate in PP, Polym. Test. 129 (2023) 108276–108287.

[32] S. Zhang, Z. Chen, M. Ding, T. Yang, M. Wang, Reducing the fire toxicity of wood composites using hierarchically porous 4A (H4A) zeolite modified ammonium polyphosphate (APP) synthesized by a facile in-situ method, Constr. Build. Mater. 262 (2020) 120754–120765.

[33] M. Wang, X. Wang, L. Li, H. Ji, Fire performance of plywood treated with ammonium polyphosphate and 4A zeolite, Bioresources 9 (3) (2014) 4934–4945.

[34] Z. Yuan, Z. Shu, L. Qi, W. Cai, W. Liu, J. Wang, M. Derradji, Y. Wang, Curing behavior, mechanical, and flame-retardant properties of epoxy-based composites filled by expandable graphite and ammonium polyphosphate, J. Appl. Polym. Sci. 140 (1) (2023) 53267–53275.

[35] Y. Sun, S. Sun, L. Chen, L. Liu, P. Song, W. Li, Y. Yu, L. Fengzhu, J. Qian, H. Wang, Flame retardant and mechanically tough poly (lactic acid) biocomposites via combining ammonia polyphosphate and polyethylene glycol, Composit. Commun. 6 (2017) 1–5.

[36] L. Pan, G. Li, Y. Su, J. Lian, Fire retardant mechanism analysis between ammonium polyphosphate and triphenyl phosphate in unsaturated polyester resin, Polym. Degrad. Stab. 97 (9) (2012) 1801–1806.

[37] T. Nguyen, D. Hoang, J. Kim, Effect of ammonium polyphosphate and melamine pyrophosphate on fire behavior and thermal stability of unsaturated polyester synthesized from poly (ethylene terephthalate) waste, Macromol. Res. 26 (2018) 22–28.

[38] F. Chu, X. Yu, Y. Hou, X. Mu, L. Song, W. Hu, A facile strategy to simultaneously improve the mechanical and fire safety properties of ramie fabric-reinforced unsaturated polyester resin composites, Compos. Part A Appl. Sci. Manuf. 115 (2018) 264–273.

[39] Z. Chen, Y. Yu, Q. Zhang, Z. Chen, T. Chen, C. Li, J. Jiang, Surface-modified ammonium polyphosphate with (3-aminopropyl) triethoxysilane, pentaerythritol and melamine dramatically improve flame retardancy and thermal stability of unsaturated polyester resin, J. Therm. Anal. Calorim. 143 (2021) 3479–3488.

[40] H. Qu, W. Wu, J. Hao, C. Wang, J. Xu, Inorganic–organic hybrid coating-encapsulated ammonium polyphosphate and its flame retardancy and water resistance in epoxy resin, Fire Mater 38 (3) (2014) 312–322.

[41] X. Wang, Y. Li, W. Liao, J. Gu, D. Li, A new intumescent flame-retardant: preparation, surface modification, and its application in polypropylene, Polym. Adv. Technol. 19 (8) (2008) 1055–1061.

[42] W. Wang, W. Zhang, S. Zhang, J. Li, Preparation and characterization of microencapsulated ammonium polyphosphate with UMF and its application in WPCs, Constr. Build. Mater. 65 (2014) 151–158.

[43] M. Shen, W. Chen, C. Kuan, H. Kuan, J. Yang, C. Chiang, Preparation, characterization of microencapsulated ammonium polyphosphate and its flame retardancy in polyurethane composites, Mater. Chem. Phys. 173 (2016) 205–212.

[44] K. Wu, Z. Wang, Y. Hu, Microencapsulated ammonium polyphosphate with urea–melamine–formaldehyde shell: preparation, characterization, and its flame retardance in polypropylene, Polym. Adv. Technol. 19 (8) (2008) 1118–1125.

[45] Y. Zhang, Z. Xiong, H. Ge, L. Ni, T. Zhang, S. Huo, P. Song, Z. Fang, Core–shell bioderived flame retardants based on chitosan/alginate coated ammonia polyphosphate for enhancing flame retardancy of polylactic acid, ACS Sustain. Chem. Eng. 8 (16) (2020) 6402–6412.

[46] X. Bi, H. Di, J. Liu, Y. Meng, Y. Song, W. Meng, H. Qu, L. Fang, P. Song, J. Xu, A core–shell-structured APP@ COFs hybrid for enhanced flame retardancy and mechanical property of epoxy resin (EP), Adv. Composit. Hybrid Mater. 5 (3) (2022) 1743–1755.

[47] J. Zhang, Y. Fang, A. Zhang, Y. Yu, L. Liu, S. Huo, X. Zeng, H. Peng, P. Song, A Schiff base-coated ammonia polyphosphate for improving thermal and fire-retardant properties of unsaturated polyester, Prog. Org. Coat. 185 (2023) 107910–107919.

[48] Q. Yang, J. Wang, X. Chen, S. Yang, S. Huo, Q. Chen, P. Guo, X. Wang, F. Liu, W. Chen, P. Song, H. Wang, A phosphorus-containing tertiary amine hardener enabled flame retardant, heat resistant and mechanically strong yet tough epoxy resins, Chem. Eng. J. 468 (2023) 143811–143823.

[49] A. Yang, C. Deng, H. Chen, Y. Wei, Y. Wang, A novel Schiff-base polyphosphate ester: highly-efficient flame retardant for polyurethane elastomer, Polym. Degrad. Stab. 144 (2017) 70–82.

[50] Z. Chen, M. Jiang, Z. Chen, T. Chen, Y. Yu, J. Jiang, Preparation and characterization of a microencapsulated flame retardant and its flame-retardant mechanism in unsaturated polyester resins, Powder Technol. 354 (2019) 71–81.

[51] Z. Chen, J. Jiang, Y. Yu, Q. Zhang, T. Chen, L. Ni, Layer-by-layer assembled diatomite based on chitosan and ammonium polyphosphate to increase the fire safety of unsaturated polyester resins, Powder Technol. 364 (2020) 36–48.

[52] M. Thirumal, N. Singha, D. Khastgir, B. Manjunath, Y. Naik, Halogen-free flame-retardant rigid polyurethane foams: effect of alumina trihydrate and triphenylphosphate on the properties of polyurethane foams, J. Appl. Polym. Sci. 116 (4) (2010) 2260–2268.

[53] Z. Li, T. Fu, D. Guo, J. Lu, J. He, L. Chen, W. Li, Y. Wang, Trinity flame retardant with benzimidazole structure towards unsaturated polyester possessing high thermal stability, fire-safety and smoke suppression with in-depth insight into the smoke suppression mechanism, Polym. (Guildf.) 275 (2023) 125928–125937.

[54] W. Gao, Y. Yu, T. Chen, Q. Zhang, Z. Chen, Z. Chen, J. Jiang, Enhanced flame retardancy of unsaturated polyester resin composites containing ammonium polyphosphate and metal oxides, J. Appl. Polym. Sci. 137 (38) (2020) 49148–49156.

[55] Z. Chen, M. Jiang, Q. Zhang, Y. Yu, G. Sun, J. Jiang, Synergistic effect of combined dimethyl methylphosphonate with aluminum hydroxide or ammonium polyphosphate retardant systems on the flame retardancy and thermal properties of unsaturated polyester resin, Int. J. Polym. Anal. Charact. 22 (6) (2017) 509–518.

[56] Y. Zhang, Y. Yu, Q. Zhang, Effects of dimethyl methylphosphonate, aluminum hydroxide and ammonium polyphosphate on the flame retardancy and thermal properties of unsaturated polyester resin, IOP Conf. Ser.: Mater. Sci. Eng. 394 (2018) 022029–022034.

[57] Y. Lin, S. Jiang, Y. Hu, G. Chen, X. Shi, X. Peng, Hybrids of aluminum hypophosphite and ammonium polyphosphate: highly effective flame retardant system for unsaturated polyester resin, Polym. Compos. 39 (5) (2018) 1763–1770.

[58] J. Reuter, L. Greiner, P. Kukla, M. Döring, Efficient flame retardant interplay of unsaturated polyester resin formulations based on ammonium polyphosphate, Polym. Degrad. Stab. 178 (2020) 109134–109141.

[59] Y. Yu, Z. Chen, Q. Zhang, M. Jiang, Z. Zhong, T. Chen, J. Jiang, Modified montmorillonite combined with intumescent flame retardants on the flame retardancy and thermal stability properties of unsaturated polyester resins, Polym. Adv. Technol. 30 (4) (2019) 998–1009.

[60] L. Yue, J. Li, X. Zhou, Y. Sun, M. Gao, T. Zhu, X. Zhang, T. Feng, Z. Shi, Y. Liu, Flame retardancy and thermal behavior of an unsaturated polyester modified with kaolinite–urea intercalation complexes, Molecules 25 (20) (2020) 4731–4744.

[61] Z. Chen, W. Zhang, Y. Yu, T. Chen, Q. Zhang, C. Li, J. Jiang, Multi-walled carbon nanotubes encapsulated by graphitic carbon nitride with simultaneously co-doping of B and P and ammonium polyphosphate to improve flame retardancy of unsaturated polyester resins, Mater. Chem. Phys. 277 (2022) 125594–125604.

[62] T. Zhu, G. Guo, W. Li, M. Gao, Synergistic flame retardant effect between ionic liquid-functionalized imogolite nanotubes and ammonium polyphosphate in unsaturated polyester resin, ACS Omega 7 (51) (2022) 47601–47609.

[63] M. Gao, J. Wang, Y. Gao, J. Chen, L. Qian, Z. Qiao, Ionic liquids modified MXene as a flame retardant synergist for the unsaturated polyester resin, J. Vinyl Addit. Technol. 30 (2) (2024) 530–542.

[64] Z. Shao, C. Deng, Y. Tan, L. Yu, M. Chen, L. Chen, Y. Wang, Ammonium polyphosphate chemically-modified with ethanolamine as an efficient intumescent flame retardant for polypropylene, J. Mater. Chem. A. 2 (34) (2014) 13955–13965.

[65] C. Kuan, H. Kuan, C. Ma, C. Chen, Flame retardancy and nondripping properties of ammonium polyphosphate/poly (butylene succinate) composites enhanced by water crosslinking, J. Appl. Polym. Sci. 102 (3) (2006) 2935–2945.

[66] X. Xu, J. Dai, Z. Ma, L. Liu, X. Zhang, H. Liu, L.-C. Tang, G. Huang, H. Wang, P. Song, Manipulating interphase reactions for mechanically robust, flame-retardant and sustainable polylactide biocomposites, Compos. Part B Eng. 190 (2020) 107930.

[67] T. Hapuarachchi, T. Peijs, Aluminium trihydroxide in combination with ammonium polyphosphate as flame retardants for unsaturated polyester resin, Express Polym. Lett. 3 (11) (2009) 743–751.

[68] M. Velencoso, A. Battig, J. Markwart, B. Schartel, F. Wurm, Molecular firefighting—how modern phosphorus chemistry can help solve the challenge of flame retardancy, Angew. Chem. Int. Ed. 57 (33) (2018) 10450–10467.

[69] S. Huo, P. Song, B. Yu, S. Ran, V. Chevali, L. Liu, Z. Fang, H. Wang, Phosphorus-containing flame retardant epoxy thermosets: recent advances and future perspectives, Prog. Polym. Sci. 114 (2021) 101366–101401.