# Bio-based flame retardants to polymers: A review

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A B S T R A C T

Due to environmental concerns, some of the conventional halogenated flame retardants have been banned. In this context, both the industrial and academics have made efforts to develop more eco-friendly and sustainable flame retardant materials. Among new flame retardants, bio-based groups have attracted plenty of attention. In this review, varied types of bio-based flame retardants are systematically described, including the structural characteristics, flame retardant behaviors, and an overview of flame retardant mechanism. Recent research progress on various bio-based materials such as flame retardants (e.g., chitosan, lignin, phytic acid, polydopamine, Tannic acid, β-cyclodextrin, etc.) applied to different polymers are adequately summarized. Finally, the opportunities and challenges for the future development of bio-based flame retardants are briefly outlooked.

## 1. Introduction

With the limited use of halogenated flame retardants, the development of environmentally friendly flame retardants with novel, efficient, and low toxicity have become vital area for current research [1]. Bio-based material shall be understood as a kind of natural material with rich reserves and a wide variety. They have attracted extensive attention due to their low price, wide source and easy access [2]. Natural structures such as chitosan [3], lignin [4], cyclodextrin [5] and starch [6] contain polyhydroxy groups. They can be used as carbon sources for intumescent flame retardants (IFR) because they are cross-linked to carbon through

esterification during combustion. Phytic acid and dopamine can also chelate with transition metals, thus showing excellent flame retardancy and smoke suppression [7,8]. In addition, DNA is a natural three-source integrated IFR [9]. Because the pentose, phosphoric acid, and nitrogen base in its structure can be used as carbon source, acid source, and gas source, respectively. Many bio-based materials can be used as flame retardants in a wide range of biological, construction, and other applications [10–14]. There are also many scopes for the design of bio-based flame retardants. However, how to select and design appropriate schemes to produce composites with flame retardant properties is a research focus.

As known, most polymer materials are easy to burn, in order to ensure the safe use of materials, they are mostly combined with flame retardants. Bio-based flame retardants are widely used in the polymer systems, such as polypropylene (PP), polyethylene (PE), polylactic acid (PLA), epoxy resin (EP), ethylene vinyl acetate copolymer (EVA), polyurethane (PU) foam, fabric and so on. Aiming to make the polymer achieve the flame retardant effect, destroying the inevitable combustion conditions is necessary. There are two common theories about the flame retardant mechanism of polymer materials. One is based on the condensed phase flame retardant, while the other is supported by vapor phase flame retardant. The

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## Abbreviations

| | | | |
|---|---|---|---|
| ABS | Acrylonitrile butadiene styrene | OS | Oxidized starch |
| APP | Ammonium polyphosphate | PA | Phytic acid |
| ATH | Aluminum hydroxide | PA 11 | Polyamide 11 |
| β-CD | β-Cyclodextrins | PA 6 | Polyamide 6 |
| BN | Boron nitride | PBS | Polybutylene succinate |
| CCT | Cone calorimeter test | PDA | Polydopamine |
| CNT | Carbon nanotubes | PE | Polyethylene |
| EG | Expandable graphite | PEI | polyethyleneimine |
| EP | Epoxy resin | PER | Phenolic epoxy resin |
| EVA | Ethylene vinyl acetate copolymer | PET | Polyethylene glycol terephthalate |
| FPUF | Flexible polyurethane foam | pHRR | Peak heat release rate |
| HDI | Hexamethylene diisocyanate | PLA | Polylactic acid |
| HNT | Halloysite nanotubes | PP | Polypropylene |
| IFR | Intumescent flame retardant | PS | Polystyrene |
| GO | Graphene oxide | PUF | Polyurethane foam |
| LBL | Layer-by-layer | PVA | Polyvinyl alcohol |
| LDH | Layered double hydroxides | PVC | Polyvinyl chloride |
| LOI | Limiting oxygen index | $SiO_2$ | Silica |
| MCC | Microcrystalline cellulose | SPR | Smoke production rate |
| MDH | Magnesium hydroxide | TA | Tannic acid |
| MOF | Metal organic framework | THR | Total heat release rate |
| OMMT | Montmorillonite | tris | Tris(hydroxymethyl)methyl aminomethane |
| | | TPU | Thermoplastic polyurethane |
| | | TSR | Total smoke release |

flame retardant mechanism of the condensed phase mainly occurs in polymer pyrolysis. Due to the dehydration and carbonization of flame retardant, a carbon layer protective film will be formed to cover the surface of the polymer. The carbon layer plays a critical role in the flame retardant of polymers. At the same time, the addition of flame retardant makes the carbon layer denser and improves the graphitization degree of the composite. The existence of a carbon layer not only blocks the transfer of heat but also prevents the supplement of external oxygen. Therefore, the flame extinction speed is greatly accelerated, and the flame retardant performance of polymer materials is improved. Gas phase flame retardancy refers to the fact that flame retardants can act as free radical inhibitors or release small particles to combine with free radicals during combustion to terminate the chain reaction. In the process of the combustion reaction, the composite will release a large amount of non-combustible gas to dilute the oxygen concentration to extinguish the flame [15–17]. Most bio-based materials can realize the joint action of both the condensed and gas phases to promote the flame retardant effect of polymers.

The typical one of the previous reviews already comprehensively summarized the flame retardant polymeric nanocomposites through the combination of nanomaterials and conventional flame retardants [18]. While under the guidance of sustainable development needs, more and more bio-based flame retardant materials based on both bio-based polymer matrix, such as PLA [19,20] or biobased flame retardant additives. Fig. 1a shows the number of peer-reviewed journal articles (found on the Web of Science) describing (a) biobased flame resistant (s) per year between 2010 and 2022 (April), which indicates the application research of biobased materials is still booming at present.

As shown in Fig. 1b, the mainstream biomass flame retardants include chitosan, DNA, lignin, phytic acid, dopamine hydrochloride, cyclodextrin, tannic acid, etc. European and American scientists have tried to apply DNA as a flame retardant to the surface of cotton fabrics, polyester foam, ethylene vinyl acetate, polyurethane and other materials, all of which have achieved good flame retardant effects. However, due to its poor heat resistance, it cannot meet the

melt processing of polymer materials. And DNA is expensive, three orders of magnitude higher than current commercial flame retardants, which will significantly limit its industrial application [21,22]. In addition, Cardanol is widely used as an intrinsic flame retardant [23,24], which is not the focus of this review. Therefore, this article will review the most detailed research progress of biomass flame retardant additives, which are mainstream and have broad application prospects. Specifically, in the following, we will sort out the research progress in related fields with Chitosan, Lignin, PA, PDA, TA, and CD as the core objects. This review focuses on the flame-retardant properties of bio-based flame-retardant composite materials. Finally, the opportunities and challenges in applying and developing bio-based flame retardants will also be discussed.

## 2. Progress in the typical biobased flame retardants as additives

### 2.1. Chitosan

#### 2.1.1. The application strategies of chitosan-containing flame retardants

In Table 1, we list the core composition and relevant research data on flame retardant components containing chitosan in recent years. We can see that chitosan is widely used in the flame retardant modification of PLA, thermoplastic polyurethane (TPU), Epoxy resin (EP), cotton fabric and other substrates. However, chitosan is not used as a flame retardant alone but is usually used with other flame retardants. Typically, it can be applied as (1) a component combined with other functional fillers; (2) surface functionalization of flame retardant particles; and (3) surface coating modification of polymeric materials by layer-by-layer self-assembly.

(1) As a component combined with other functional fillers

Chitosan is generally used with other flame retardant functional components, such as APP, aluminum hypophosphite (AHP),
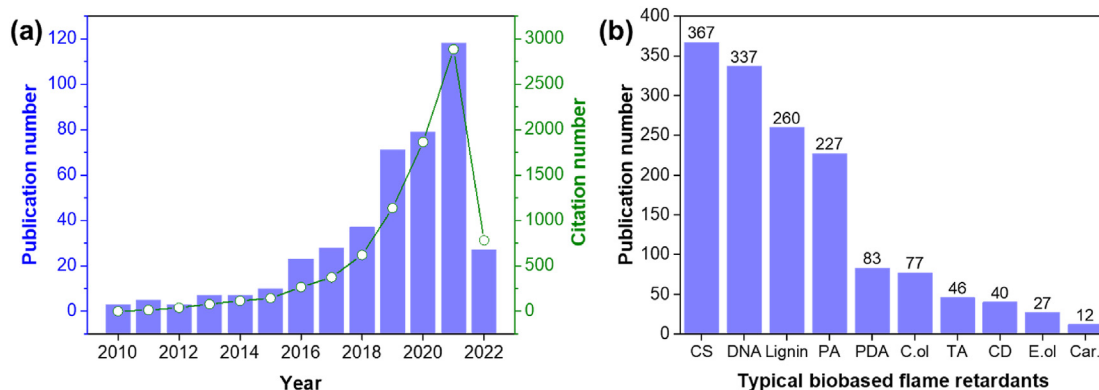
**Fig. 1.** Graph representing the number of peer-reviewed journal articles (found in Web of Science) describing (a) biobased flame resistant (s) per year between 2010 and 2022 (April) and (b) typical biobased flame retardants. C.ol is Cardanol, E.ol is Eugenol and Car. is Carrageenan.

**Table 1**
The formulation and core index of the functional composites with Chitosan as a typical flame retardant filler.

| Polymer | Flame Retardant Additives | UL-94 | LOI (%) | pHRR decrease (%) | FRI | Ref |
|---|---|---|---|---|---|---|
| PU | 8 wt%5BL chitosan/P—CNF | / | / | 31.0 | 1.22 | [25] |
| TPU | 15 wt% MCMPP | V0 | 29.4 | 65.9 | 2.37 | [26] |
| PUF | 8BL chitosan/Ti$_3$C$_2$ | / | / | 57.2 | 6.79 | [27] |
| PUF | 9BL HAP-SA/HAP- chitosan | / | / | 77.7 | 25.8 | [28] |
| UPR | 9BL chitosan@APP@ diatomite | V0 | 25.75 | 40.8 | 2.21 | [29] |
| Silk fabric | 10BL chitosan/VB2 | / | 32.8 | / | / | [30] |
| Cotton | 6BL chitosan/APP | / | / | 75.0 | 12.29 | [31] |
| Cotton | C$_{15}$APP/AM/chitosan | | 31.5 | 39.2 | / | [32] |
| Cotton fabric | 5.2 wt% chitosan/PA/Ba/PA | / | 22 | 61.2 | / | [7] |
| Polyester/cotton | 20BL chitosan/PA | / | 29.2 | 29.0 | / | [33] |
| Jute fabric | 3 wt% chitosan/7 wt%SA | / | 27 | 48.2 | / | [34] |
| PLA | 10 wt% APP@ chitosan@PA-Na | V0 | 30.5 | 33.0 | 1.85 | [35] |
| PLA | 10 wt%APP@ chitosan@SA-3BL | V0 | 30.6 | 23.0 | 1.49 | [36] |
| PLA | Core-shell graphene oxide hybrid | V0 | 30.0 | 21.0 | 4.9 | [37] |
| PLA | 5 wt% chitosan/TA@5 wt%HNT | / | 22.5 | 30.4 | 17.1 | [38] |
| PLA | chitosan-sepiolite-chitosan-APP quad-layer LbL deposition | / | 25.3 | 61.1 | 1.21 | [39] |
| PET | 15.1 wt%20BL chitosan/APP | / | 26.2 | / | / | [40] |
| PET | 6 wt% phosphorylated chitosan/nanosilver particles | / | 24.3 | / | / | [41] |
| BF/PP | chitosan/PA/HNT | / | / | 45.3 | / | [42] |
| PVC | 3 wt% BiOCl@ chitosan-PA | V0 | 29.8 | 39.6 | / | [43] |
| EP | 7 wt%RP@ chitosan/LS | V0 | 30.6 | 59.8 | 5.0 | [44] |
| EP | 15 wt % P-MCC@chitosan @PA-Na | V1 | 26.2 | 50.2 | 2.14 | [45] |
| EP | 15 wt% CEMP/3 wt% OMMT | V0 | 30.9 | 77.9 | 2.07 | [46] |
| EP | 10 wt% HNT@ chitosan@Fe$_3$O$_4$ | / | 31.3 | 32.0 | / | [47] |
| EP | 10 wt% CCD | V0 | 31.6 | 6.2 | 1.62 | [48] |
| TPU | 4.5 wt%APP/4.5%ACS/1%OMMT | V0 | 29 | 64.8 | / | [49] |
| TPU | 3 wt% PCS-MXene | / | / | 66.7 | 2.46 | [50] |
| TPU | 9 wt% AHP and 1% PMT | V0 | 28.4 | 82.1 | 10.91 | [51] |
| PUF | chitosan-G8 | / | 31 | 86.8 | 38.46 | [52] |
| PLA | 4 wt% PCS/Co | V1 | 22.5 | 23 | | [53] |
| PLA | 9 wt% PA@CHTM | V0 | 29.6 | 3.2 | / | [54] |
| PLA | 3 wt%CTSPA | V0 | 30.5 | 19.1 | 1.84 | [55] |
| PAN | FR-PAN | / | / | 20.7 | 2.11 | [56] |
| PA66 | chitosan-DOPA | / | 23.5 | 39.8 | / | [57] |
| PVC | Sn-chitosan | / | 30.5 | 30.5 | 0.97 | [58] |
| Cotton | 7.5 wt%PCS | / | 25.7 | 88.2 | / | [59] |

Note: *P—CNF* means phosphorylated cellulose nanofibrils, *MCMPP* means microencapsulation of melamine polyphosphate with toluene diisocyanate crosslinked carbox-ymethyl chitosan, *PUF* means flexible polyurethane foam, *HAP* means hydroxyapatite, *UPR* means unsaturated polyester resins, *VB2* means vitamin B2, C$_{15}$APP/AM/chitosan means 15BL APP/p-aminobenzene sulfonic acid modified melamine/chitosan, *PA-Na* means sodium phytate, *SA* means sodium alginate, *BiOCl* means bismuth oxychloride nanosheet, *RP* means red phosphorus, *LS* means lignosulfonate, *P-MCC* means phosphorylated-microcrystalline cellulose, *CEMP* means chitosan ethoxyl melamine phosphate, *CCD* means cinnamalde/chitosan/DOPO, *ACS* means crosslinking of chitosan with bis-(4-formylphenyl)-phenyl phosphonate (ABPO), *AHP* means aluminum hypophosphite, *PMT* means PCS modified OMMT, *G8* means 8 wt% expandable graphite, *PCS* means phosphorylation of chitosan, *CHTM* means self-assembly between bio-derived chitosan microspheres, *CTSPA* means complexation of chitosan with phytic acid, *FR-PAN* means phosphorylated GMA-g-chitosan/PAN, and *DOPA* means hydrogen peroxide treatment DOPO.

organically modified montmorillonite (OMMT) [49], etc. For ex-amples, Zhang et al. [21] prepared a new chitosan flame retardant, which is mainly obtained by cross-linking bis (4-formyl phenyl)-phenylpropionate with chitosan. Then the functional chitosan, OMMT and APP are mixed with TPU in a melt blending manner. The

pHRR dramatically decreased by 64.8% for the flame-retardant TPU composite.

It is also a common modification method that chitosan is phosphorylated and then mixed with other flame retardants. Using phosphorylation of chitosan (PCS) as raw material, organically

modified exfoliated montmorillonite (PMT) was prepared by ultrasonic catalysis. Then the AHP and PMT are processed using a twin-screw extruder to prepare TPU composite materials. When the composite material contains 9% AHP and 1% PMT, the limiting oxygen index (LOI) of the TPU composite material increases from 20.8% to 28.4%, and the UL-94 rating reaches V-0. After adding flame retardant, and the pHRR of the TPU sample decreased from 1090 kW/m$^2$ to 195 kW/m$^2$ [51].

Zhang [47] et al. used halloysite nanotubes (HNT), Fe$_3$O$_4$, and chitosan to create a three-dimensional network structure in EP matrix to improve the flame retardant properties of epoxy resins. Chitosan can act as a carbon-forming agent in this structure, promoting catalytic carbonization of the matrix. Fe$_3$O$_4$ on the surface of HNT can further enhance the composite's carbonization ability. The presence of HNT@chitosan@Fe$_3$O$_4$ reduces the toxic gases released from EP materials during combustion significantly. Similarly, as shown in Fig. 2a, in order to develop an environmentally benign flame retardant for bamboo/PLA composites (BPC), chitosan (CS) and tannic acid (TA) were used as cationic and anionic polyelectrolyte respectively to stabilize HNT on the surface of bamboo fiber and PLA [38]. LOI and cone calorimetry tests were used to study the flammability of BPC and the results showed that the addition of CS/TA complex and HNT had a synergistic effect on the flame retardant performance of BPC materials. The resulting BF/PP composites exhibited excellent flame resistance with a significant reduction in the peak heat release rate (45.3%) and total smoke production (58.8%) than the control [42].

(2) Surface coating modification of polymeric materials by layer-by-layer self-assembly

The implementation of layer-by-layer (LbL) self-assembly technology is usually to directly modify the surface of the target material by selecting appropriate anionic compounds and Chitosan with cationic nature. Chitosan usually has cationic properties and is often used as a surface functional additive for flame retardant modification. LbL is a typical preparation process for chitosan, which can be directly coated on the surface of the polymer for modification. The components commonly used as flame retardants combined with chitosan include APP, phytic acid, sodium alginate and sodium phytate, etc. The corresponding detailed structures are shown in Fig. 2f. We can further claim that the LbL technology here is mainly applied for the surface coating of foams of fabrics. We will list several typical research in the following section.

*PU foam*. Carosioa and colleagues [25] used layer-by-layer assembly to coat chitosan and phosphorylated cellulose nanofibers (P—CNF) on PU foam. Only adding 8 wt% chitosan/P—CNF can reduce the peak heat release rate (pHRR) of composites by 31%. Compared with PU without flame retardant, the presence of chitosan/P—CNF coating improves the flame retardancy of the composite and inhibits the droplet phenomenon.

*Fabrics*. i) The chitosan/PA coating assembled by LBL can catalyze carbon in the condensed phase to protect the matrix. In recent studies, chitosan/phytic acid (chitosan/PA) bio-based intumescent flame retardants material coatings were constructed on polyester/cotton blended fabrichitosan [33]. It is found that this bio-based IFR can make polyester cotton blended fabric to obtain better flame retardant properties, leading to inhibiting dripping. The LOI of uncoated fabric is 17.3%. However, the LOI increases to 29.2% as chitosan/PA reaches 20 BL. After adding 20BL chitosan/PA flame retardant, the pores, which are the surface of residual carbon of the composite, disappeared. ii) Cotton fabric were treated with phosphorylated chitosan to improve flame retardant properties [59]. In cotton fabric, phosphorylated chitosan can form covalent bonds with hydroxyl groups. Establishing a network structure can

significantly improve the flame retardant properties of cotton fabric. iii) The flame retardancy could also be significantly improved when chitosan and APP were coated on polyethylene glycol terephthalate (PET) fabric by LBL assembly method [40]. When chitosan/APP on PET fabric reached 20BL, the LOI of PET fabric increased from 21.1% to 26.2%. With the increase of LBL layers, the droplet phenomenon of PET fabric was also significantly inhibited. iv) Li et al. [34] applied 3 wt% chitosan and 7 wt% SA to jute fabric through LBL to improve the flame retardant properties of the composites. The LOI of jute composite increased to 21.4%, and the burn length was 3.8 cm with the addition of flame retardant. At the same time, the addition of flame retardant significantly improved the charring ability of jute fabric, and the carbon residue in the system increased significantly.

(3) surface functionalization of flame retardant particles

There is a group of works that use layer-by-layer self-assembly technology to modify the flame-retardant functional particles further. As a result, novel flame retardants with core-shell structures are obtained, and typical examples are shown in Fig. 2b—e. Specifically, for example:

*Fibers*. As shown in Fig. 2b [39], a quad-layer coating of chitosan-sepiolite-chitosan-APP was formed on fabrics by LBL technology. The existence of this layer significantly improves the flame retardancy of fabrics. The LOI value of fabric increased to 25.3%, and the pHRR value decreased by 32.6%. This quad-layer flame retardant coating enhances the carbonization of the fibre during the combustion process, forming a stable carbon layer structure. This improves the flame retardancy of fibre materials.

*Diatomite*. As shown in Fig. 2c, a novel flame retardant system was prepared by depositing chitosan and APP composite coatings on the surface of diatomite (Dia), which was applied in unsaturated polyester resin (UPR) [29]. The UPR with 9BL chitosan/APP@Dia composite coating has the best flame retardant performance. The LOI value of the composite material increased to 25.7%, and the UL-94 test reached the V0 level. Compared with pure UPR, the pHRR of UPR composites decreased from 450.9 kW/m$^2$ to 266.9 kW/m$^2$.

*RP*. As shown in Fig. 2d, with microencapsulated red phosphorus (RP) as the core and chitosan and lignosulfonate (LS) as the shell, a novel core-shell flame retardant (RP@chitosan/LS) was created [44]. When the flame retardant addition was 7 wt%, the LOI of the EP composite increased from 20.4% to 30.6%, while the UL-94 test achieved V0 rating. Compared to EP, the pHRR of EP composites decreased by 59.8%, and the THR decreased by 48.2%. In this core-shell structure, the RP acts as the acid source in the system, and the shell composed of chitosan/LS can serve as the carbon source and gas source. Core-shell flame retardants promote the catalytic formation of carbon in the combustion process of composite materials, producing inert gases and inhibiting combustion from proceeding.

*Melamine polyphosphate*. As shown in Fig. 2e, a new flame retardant (MCMPP) was prepared with melamine polyphosphate (MPP) as the core and toluene diisocyanate cross-linked carboxymethyl chitosan as the shell to improve the flame retardant properties of TPU [26]. Compared with pure TPU, the addition of flame retardant significantly increased the carbon residue of the composite by 96.3%. MCMPP can be used as an acid source and carbonating agent. A large amount of non-combustible gas is released in the gas phase. An expanded carbon layer is formed in the condensed phase to improve the quality of the carbon layer.

*APP*. Xiong et al. [35] assembled sodium phytate (PA-Na) and chitosan on APP through the interaction of electric charges to form a green bio-based core-shell flame retardant. This core-shell flame
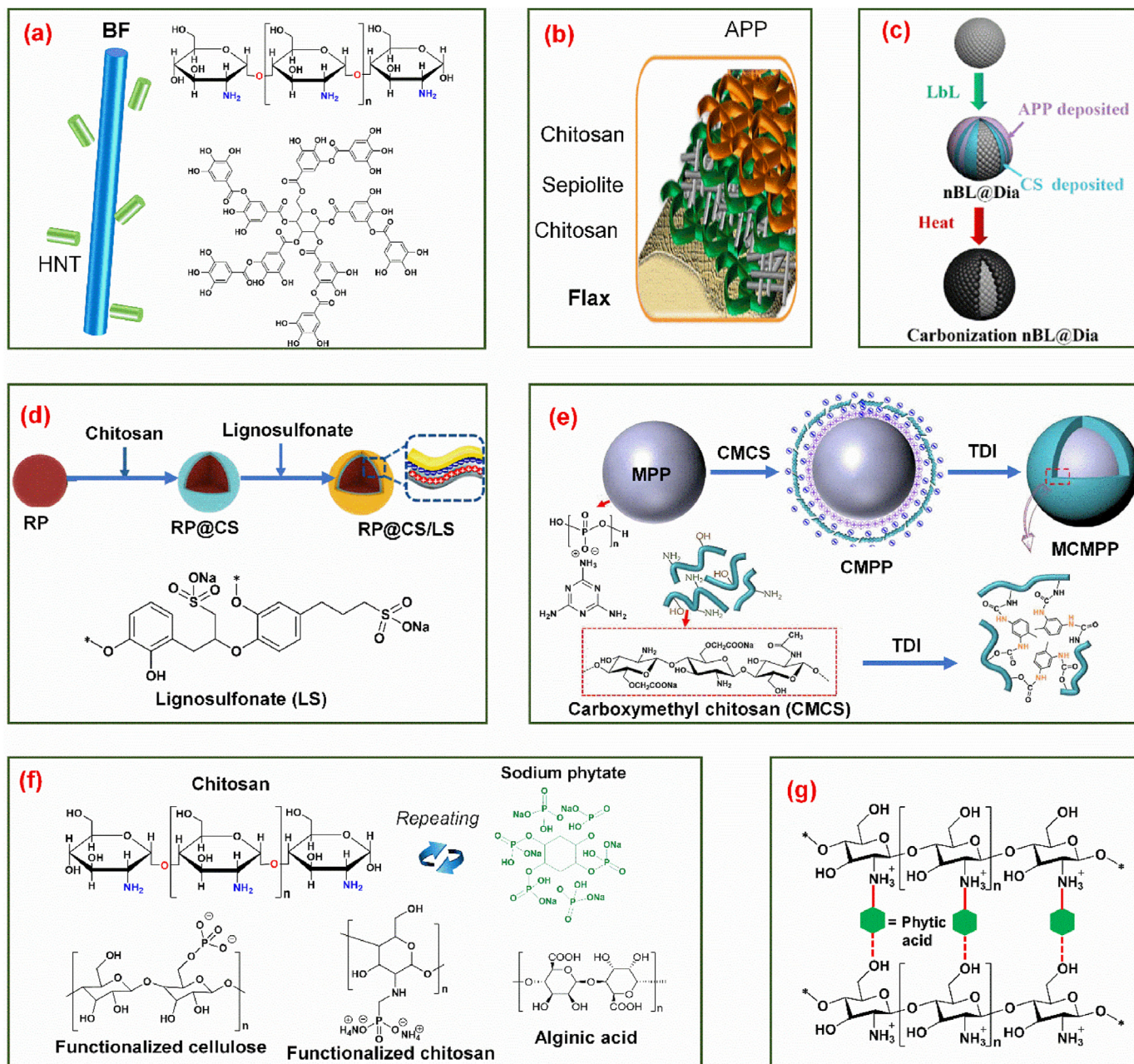
**Fig. 2.** (a) HNT/Chitosan/TA flame retardant system (Redrawn from Ref. [38] Copyright (2020) Wiley), (b) Fiber-based core-shell flame retardant containing Chitosan (Redrawn from Ref. [39] Copyright (2020) Elsevier) (c) Flame-retardant mechanism for nBL@Dia in flaming UPR composites (Redrawn from Ref. [29] Copyright (2020) Elsevier), (d) Red phosphorus-based core-shell flame retardant (Redrawn from Ref. [44] Copyright (2021) Elsevier), (e) MPP-based core-shell flame retardant, Schematic diagram for the preparation of MCMPP microcapsules (Redrawn from Ref. [26] Copyright (2019) Elsevier), (f) LbL technology realizes flame retardant modification of polymer materials, and (g) Novel Chitosan-based flame retardant [55].

retardant is prepared with APP as the core and chitosan and PA-Na as the shell. 10% chitosan/PA-Na/APP is added to PLA to make the composite material LOI reach 30.5%, UL-94 V-0 level. Experiments tested the effects of core-shell flame retardants and single-component flame retardants on the flame retardant properties of PLA. Compared with the individual results of each component, the increase of phosphorus-containing compounds in the chitosan/APP/PA-Na system leads to the improvement of the flame retardant properties of PLA composites. Zhang and his partner [36] made a flame retardant system similar to chitosan/APP/PA-Na. They assembled chitosan, sodium alginate (SA) and APP into a core-shell

structure coated on the surface of PLA. When 10% APP@chitosan@SA was added, the LOI of PLA increased from 20% to 30.6%, and the UL-94 test reached the V-0 level.

For another typical example, as shown in Fig. 2g [55], the study presents a facile and solvent-free fabrication of flame retardant (FR), UV protective, and reinforced PLA composite using two bio-based complexing couples: chitosan/phytic acid (CTSPA). The thermal and burning properties of PLA composites were evaluated by TGA, limited oxygen index (LOI), UL-94 test, and cone calorimetry. PLA/CTSPA showed earlier mass loss and higher char residue than pristine PLA. CTSPA (3 wt%) enhanced the LOI value of PLA

from 19.6% to 30.5%. PLA/CTSPA and PLA/TAFe/CTSPA achieved V-0 ratings in UL-94 test with slight melt dripping.

### 2.1.2. Flame retardancy index (FRI) analysis

FRI analysis is a key parameter to describe flame retardant efficiency. Its definition formula is as follows [60–63].

$$\text{Flame Retardancy Index (FRI)} = \frac{\left[ THR \times \frac{pHRR}{TTI} \right]_{Neat\ polymer}}{\left[ THR \times \frac{pHRR}{TTI} \right]_{Composite}}$$

where, the TTI (s) is time to ignition, THR ($MJ/m^2$) is total heat release, pHRR ($kW/m^2$) is peak of heat release rate. The corresponding parameter values are also summarized in Table 1. We can see from the data in Table 1, the FRI of the chitosan modified sample is between 0.97 and 38.46. In addition, we also found that when chitosan was compounded with the APP, HAP, AHP, etc., the FRI was as high as 12.29, 25.8 and 10.91, respectively, which proved that chitosan with phosphorus-containing compounds could achieve excellent modification effect. When chitosan is compounded with 8 wt% of expandable graphite, the FRI is as high as 38.46, which proves that when chitosan is compounded with graphene and other carbon-based materials, the flame retardant performance of the materials can be significantly improved, which has a good research prospect. Therefore, we can preliminarily speculate that when chitosan is mixed with carbon-based flame retardants, the flame retardant modification effect is more significant. For a comprehensive classification of nanoparticle performance using the flame retardancy index, please see the chapter elsewhere [64]. Notably, as a core flame retardant parameter, FRI will also be summarized in the following sections.

### 2.1.3. General flame retardant mechanism

Because chitosan is rich in nitrogen and hydroxyl, it is often used as a charring agent for flame retardant composites. At high temperatures, the amino group in the chitosan structure forms $NH_3$, thus diluting the oxygen concentration in the system. At the same time, combustion will promote the ring-opening reaction of chitosan, form an aromatic ring structure, and produce a compact carbon layer in the condensed phase. There are many experimental studies can confirm this view. For examples, Hafezeh Nabipour et al. [28] assembled hydroxyapatite (HAP), sodium alginate and chitosan on FPUF by using charge characteristics. The cone calorimetry experiment shows that the composite material's performance is the best when the 9-layer flame-retardant coating and the HAP addition amount in the system is 1 wt%. The pHRR of FPUF with 9-layer HAP-SA/HAP-chitosan flame retardant coating was significantly reduced by 77.7%, and the smoke production rate (SPR) was reduced by 53.8%. Chitosan and HAP as carbon and acid sources in the flame retardant promoted the catalytic carbonization of the polymer. The presence of the flame-retardant coating increases the carbon residue of the composite material, enhances the condensed phase flame-retardant, and improves the flame-retardant performance of the composite material.

### 2.2. Lignin

### 2.2.1. The application of lignin

Lignin is one of the three essential components of wood and one of the most abundant biopolymers next to cellulose and chitin. The illustrated chemical structure of lignin is complex and shown in Fig. 3a. It is referred as a three-dimensional amorphous polymer consisting of phenylpropane units based on the three monolignols as coniferyl, sinapyl, and p-coumaryl alcohol. lignin can be used as

an essential source of other compounds, namely, depolymerization of lignin to generate novel chemicals, e. g., acetophenones and phenolic compounds. Lignin can also be directly applied to the modification of polymers by blending. Lignin also used as a reactive component in various resins and polymers [93,94].

As listed in Table 2, we can see lignin was widely used for fire safety functionalization of PA, PBS, ABS, Cotton, EP, PLA, PP, and PU [95] etc. Its typical main indicators, such as UL-94 rating, LOI, pHRR decrease and THR decrease, and FRI are all summarized in Table 2. We can further find that lignin is often applied for flame retardant modification of polymer in the following two forms.

(1) Conjunction with other flame retardants

Lignin intercalated montmorillonite (LM) can be used with intumescent flame retardant as a synergist to polybutylene succinate (PBS) [66], as shown in Fig. 3b. When 22 wt% IFR and 3 wt% LM are added to the composite material, the LOI value of the sample reaches 36.5%. Since LM is added to PBS as a synergist, the PBS composite shows excellent mechanical properties when 3% of LM is added to the system. Montmorillonite and lignin produce an expanded silicate carbon layer in the presence of APP, and lignin generates a large amount of inert gas during the combustion process. The combined effect of LM and IFR significantly improves the flame retardant performance and efficiency.

In Fig. 3c, alkali lignin was copolymerized with polyacrylamide and then chelated with $Fe^{3+}$, which was added to intumescent flame retardant (containing APP and ML) to improve the flame retardancy of polybutylene succinate (PBS) [67]. Adding 23 wt% IFR and 2 wt% lignin chelate to PBS, the LOI value of the composite increased to 36.2%. Compared with pure PBS, the pHRR of the composite decreased from 854 $kW/m^2$ to 454 $kW/m^2$, and the amount of carbon residue increased significantly. The presence of metal ions in lignin will catalyze the esterification reaction in the system and produce a large amount of carbon residue. APP will decompose non-combustible gases such as $NH_3$ at high temperatures and dilute the oxygen concentration in the matrix. At the same time, the generated phosphate can promote the formation of a more stable carbon layer structure. The synergistic effect of the two makes the flame retardancy of PBS improved.

Furthermore, Shu et al. [79] prepared lignin-APP flame retardant from phosphoric acid, lignin and urea, then applied it to thermoplastic polyvinyl alcohol (TPVA). When the amount of flame retardant was 20 wt%, the composite UL-94 reached the V0 level, and the LOI value increased to 33.1%. The presence of lignin and APP enhanced the composites' carbon forming ability and carbon layer stability. In order to improve the flame retardancy of PLA, APP, lignin and OMMT were added as flame retardants [81]. When 17 wt%APP/3 wt%lignin/1 wt%OMMT was added, the LOI value of the composite reached 39%, and the pHRR decreased by 53%.

Wu et al. [83] prepared the flame retardant of layered double hydroxide (LDH) modified by sodium lignosulfonate (SLS) by the coprecipitation method. Then PP and LDH-SLS composites were prepared. Compared with pure PP, the pHRR and TSR of PP/LDH-SLS composites decreased by 62.9% and 43.3%, respectively. In addition, the LOI value of PP/LDH-SLS is 29.4%, and the vertical combustion test reaches the level of V-0, which is much higher than that of PP/LDH. The uniform dispersion of LDH-SLS and the synergistic flame retardant between LDH and SLS effectively improve the flame retardant properties of the composites.

(2) Chemically functionalized lignin

In the previous review focuses on the flame-retardancy effects of pristine lignin and lignin chemically modified by introducing the
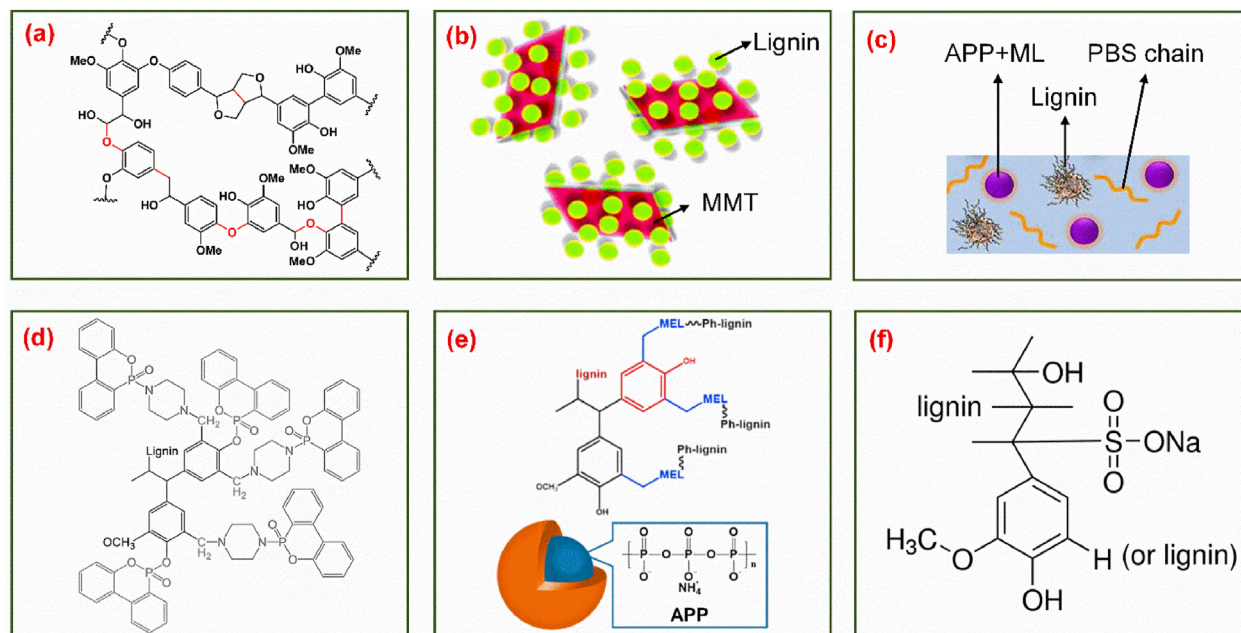
**Fig. 3.** (a) Illustration of Lignin chemical structure; (b) Schematic of the steps involved in the intercalation, exfoliation of Montmorillonite (MMT) (Redrawn from Ref. [66] Copyright (2021) Wiley). (c) Lignin as synergistic component for PBS flame retardancy functionalization (ML is melamine, PBS is polybutylene succinate), (Redrawn from Ref. [67] Copyright (2021) Wiley). (d) Synthetic routes of DOPO-functionalized Lignin [74]. (e) The synthesis route of Functionalized-lignin@APP (Redrawn from Ref. [75] Copyright (2021) Elsevier), and (f) Structure illustration of the lignosulfonate [83].

**Table 2**
The formulation and core index of the functional composites with Lignin as a typical flame retardant filler.

| Polymer | Flame Retardant Additives | UL-94 | LOI (%) | pHRR decrease (%) | THR decrease (%) | FRI | Ref |
|---|---|---|---|---|---|---|---|
| PA11 | 10 wt%LSL/10 wt%ZnP | V1 | / | 50.9 | 14.5 | 1.94 | [65] |
| PA11 | 10 wt%LSL/10 wt%AlP | V1 | / | 53 | 15.6 | 1.63 | [65] |
| PBS | 22 wt% IFR/3 wt% LM | V0 | 36.5 | 57.5 | 28.7 | 2.88 | [66] |
| PBS | 24 wt%IFR/1 wt% lignin chelate | V0 | 36.2 | 58.9 | 1.45 | / | [67] |
| PBS | 10 wt%PN-Zn-lignin | / | / | 50 | 67 | 6.14 | [68] |
| PBS | 30 wt% CP-lignin (halogen-free flame retardant) | / | / | 27.2 | 31.1 | 1.44 | [69] |
| ABS | Lignin-N/red phosphorus | / | / | 67.9 | 77.5 | / | [70] |
| ABS | 25 wt% lignin/aluminum phosphate@RP | V0 | 26.5 | 64.6 | / | / | [71] |
| Cotton | 1 wt% lignin/1 wt% carbon nanotubes/1 wt% K$_2$CO$_3$ | / | 38.5 | 27.8 | 61.9 | 2.60 | [72] |
| Cotton | 30 wt%SLS | / | 29.5 | 25.5 | 57.9 | 1.28 | [73] |
| EP | 10 wt% Lig-F | V0 | 34.2 | 45.2 | 51.4 | 1.64 | [74] |
| EP | 20 wt%F-lignin@APP | V0 | 36.1 | 45.2 | 51.3 | 1.93 | [75] |
| EP | PHMS-lignin-TCP | V1 | 25.3 | 37.5 | 18.4 | 1.58 | [76] |
| EP | 7 wt%PEI-g-poly phosphoric acid@lignin | V0 | 31.4 | 39.0 | 2.7 | 1.64 | [77] |
| Lignin/phenol/glyoxal@EP | bi-hydroxyl-bi-DOPO | V0 | 35.2 | 11.6 | 15.2 | 1.21 | [78] |
| TPVA | 20 wt% Lignin-APP | V0 | 33.1 | / | / | / | [79] |
| PLA | APP/LHP | / | / | 31.5 | 33.7 | 1.82 | [80] |
| PLA | 17 wt%APP/3 wt%lignin/1 wt%OMMT | V2 | 39 | 52.5 | 21.1 | 2.39 | [81] |
| PLA | 10 wt%TP-g-lignin | V0 | 26.6 | −23.2 | 1.36 | / | [82] |
| PP | 20 wt%LDH-SLS | V0 | 29.4 | 62.9 | 25.1 | / | [83] |
| PP | 25 wt%TiO$_2$/lignin | / | / | 34.4 | 35.5 | / | [84] |
| Wood/PP | 15 wt%functionalized lignin | V1 | / | 21 | 25.2 | / | [85] |
| PP | 30 wt%PN-lignin | / | / | 73.3 | 21.2 | 3.74 | [86] |
| PP | 20 wt%PN-lignin-Ni | / | 26 | 75.6 | 20.4 | 3.25 | [87] |
| RPU | APP/MEL/Lignosulfonate (3:1:4) | / | 24.5 | 11 | 3.5 | / | [88] |
| RPU | SLS/APP(1:5) | / | 30.5 | 34.3 | 4.1 | / | [89] |
| ALPG-NERs | 10 wt%SDB | V0 | 34.5 | 27.5 | 30 | 1.63 | [90] |
| P34HB | 30 wt%MAP-lignin/5 wt% RHA | / | / | 42.8 | 24.3 | / | [91] |
| VAE | M-AT/SLS | V0 | 32 | 48 | 50 | / | [92] |

Note: *LM* means lignin and montmorillonite nanocomposites, *lignin chelate* means Lignin and Fe$^{3+}$ chelate, *PN* means P,N modified lignin, *CP-lignin* means the reactant of cyanuric chloride (CNC) and 2,6,7-Trioxa-1-phosphabicyclo- [2,2,2]octane-4-methanol-1-oxide (PEPA) reacts with lignin to obtain the product, *SLS* means sodium lignin sulfonate, *PHMS* means polymethylhydrosiloxane, *TP* means phosphorus containing monomer, *PN-lignin* means P,N modified lignin, *ALPG-NERs* means alkali lignin-phenol-glyoxal novolac epoxy resins, *SDB* means N,S modified DOPO, *MAP-lignin* means melamine phosphate modified lignin, *RHA* means rice husk ash.

elements phosphorus and/or nitrogen, as well as their synergistic effects with existing flame-retardant additives [96]. In Fig. 3d, in order to improve the flame retardancy of lignin, DOPO was reacted with lignin by the Mannich method [74]. UL-94 of 10 wt% Lig-F/EP composite passed V0, and the pHRR value decreased by 45.2%. The FRI value of EP composite reaches 1.64, which has fire safety. In

combustion, the addition of lignin flame retardant makes the material produce more carbon residue. The flame retardancy and thermal stability of EP composites have been improved to a certain extent. As shown in Fig. 3e, Aluminum lignin and MEL were coated on the surface of APP by Mannich method to prepare a new flame retardant F-lignin@APP [75]. Add 20 wt% F-lignin@APP to EP. The flame retardancy and smoke suppression properties of the composite can be significantly improved. Compared with unmodified EP, the LOI value of EP composites increased by 36.1% from 26.7%. The pHRR and TSP of the composites decreased by 45.2% and 76.4%, respectively. In Fig. 3f, the APP is decomposed during the combustion process to produce non-combustible gas, which dilutes the oxygen concentration in the system and slows down the combustion reaction. Sodium lignosulfonate (SLS) is a commonly used lignin-based flame-retardant material [83]. The LOI of 30 wt% SLS cotton fabric composites reached 28.5%. SLS can produce a large amount of non-combustible gas during the combustion process to prevent the combustion from continuing. At the same time, the presence of sodium in the structure promotes the dehydration and decarboxylation of SLS to form a large amount of carbon residue. Furthermore, Hydroxyapatite modified lignin (LHP) can be added to PLA as a new flame retardant [80]. Compared with pure PLA, when PLA/APP/LHP was added, the pHRR decreased by 31.5%. Lu [88] et al. used lignosulfonate instead of pentaerythritol as a charring agent in intumescent flame retardant. With the addition of the lignosulfonate flame retardant system, the LOI value of the composite increased from 23.9% to 24.5%, and the pHRR value decreased by 11%.

### 2.2.2. General flame retardant mechanism of lignin

Lignin has many functional groups, such as methoxyl, carbonyl, benzene ring and so on. It is often used as the carbon source of intumescent flame retardant. In the process of combustion, the methoxyl group in the lignin structure may decompose to produce a free radical trapping agent that captures free radicals and terminates the combustion reaction. The non-combustible gas will also be produced during combustion, diluting the system's oxygen concentration [66,67]. However, the benzene ring and carbonyl will produce a large amount of residual carbon during combustion, forming a stable carbon layer structure. The carbon layer barrier effectively protects the polymer matrix from flame burning. Therefore, lignin can be a flame retardant in gas and condensed phases, and it is a green bio-based flame retardant. Lignin decomposes at high temperatures and is continuously esterified and dehydrated to produce much residual carbon. The carbon layer interacts with the polybasic acid in the system, which makes it closer. The carbon layer effectively isolates the EP matrix and heat source, so the flame retardant performance of EP has been improved [75]. Lignin contains many hydroxyl groups in its structure and has a high carbon content, so it has a better effect when used as a charring agent. The reaction of lignosulfonate with APP will produce aromatic ether compounds and a cross-linked carbon layer, forming a stable carbon layer barrier. The non-combustible gases such as $NH_3$ and $H_2O$ produced during combustion dilute the oxygen concentration in the system to prevent further combustion of the foam matrix [88].

### 2.3. Phytic acid

#### 2.3.1. Application of PA

As a green bio-based flame retardant, PA contains 6 phosphate groups in its structure, and the phosphorus content is as high as 28% [78,128]. As shown in Table 3, PA and its derivatives or composite modifiers are widely used to improve the fire safety of EP, cotton, PLA, PP, EVA, etc. For example, Gong et al. [121] prepared a new intumescent flame retardant to improve the flame retardancy of

PLA. After adding 4 wt% PA-Ni and 11 wt% IFR to PLA, the pHRR of PLA composites decreased by 62% and UL-94 reached V-0. As an acid source, PA can promote the cross-linking reaction of IFR and form a more compact three-dimensional network carbon layer structure in the reaction stage. The presence of phosphorus compounds promoted the catalytic carbonization of the system and created a carbon layer barrier in the condensed phase to protect the matrix. The existence of PA-Ni can also capture free radicals to achieve the effect of gas-phase flame retardancy. In addition, PA can be combined with piperazine melamine through electrostatic interaction to form a bio-based intumescent flame retardant (PIMEPA) [127]. Flame retardant ethylene-vinyl (EVA) acetate copolymer with aluminium hydroxide (ATH). The EVA composite with 30 wt% flame retardant UL-94 reached V0, and the LOI increased to 26.5%.

It is further found that the use forms of PA mainly include the following aspects:

(1) Forming salts with metal ions for use with other flame retardants

**$Zn^{2+}$**. Using zinc phytate (PA-Zn) and two-dimensional graphite $C_3N_4$ (g-$C_3N_4$) as raw materials, a new core-shell flame retardant was prepared by layer assembly method [112] (Fig. 4a). EP/g-$C_3N_4$/PA-Zn composites were formed by blending flame retardant with EP. The specific assembly is shown in Fig. 4a. The presence of PA-Zn can promote the degradation of EP and form more carbon residue in the combustion process. Therefore, the existence of g-$C_3N_4$/PA-Zn makes EP composites have better flame resistance and smoke suppression in the combustion process.

**$Mg^{2+}$**. The addition of PA-Mg (Fig. 4b) to EP resins at 10 wt% improves the flame retardant properties of EP [113]. It was found that there was an excellent synergistic effect between agricultural waste rice husk ash (RHS) and PA-Mg. When 5 wt% PA-Mg and 5 wt% RHS were added to EP, the pHRR of EP composites decreased by 28.6%. When 10 wt% PA-Mg was added to EP, the pHRR of the composite material dropped by 17.5%. At the same time, when PA-Mg and RHS act synergistically, the THR, SPR, and TSR values of the composite material are also significantly reduced.

**$Ba^{2+}$**. As shown in Fig. 4c, Zhang et al. [7] prepared IFR system (CS/PA/Ba/PA) composed of barium ion ($Ba^{2+}$), PA and CS. The flame retardancy of cotton fabric was enhanced by adding flame retardants. The addition of flame retardant reduced the pHRR of the composites by 61.2% and increased the carbon residue rate to 29.7%. Due to the existence of phytic acid metal salt, the composites' thermal stability and carbon residue rate were improved. Phytic acid as an acid source in the system can promote the formation of catalytic carbonization. At the same time, the existence of metal ions inhibits the formation of combustible gases. The flame retardants act simultaneously in the condensed phase and gas phase, and the flame retardancy of the composites is significantly improved. More examples of the LbL assembly of chitosan and phytic acid has been described in section 2.1. In addition, Barium phytate (PA-Ba) was prepared by mixing phytic acid with barium carbonate in an aqueous solution [110]. It was mixed with IFR to improve the flame retardancy of EP. When 14 wt% IFR and 2 wt% PA-Ba are flame retardants, the flame retardant performance of EP composite is the best. The LOI reached 30.7%, and the pHRR decreased by 69.1%. The intumescent carbon layer produced by the combustion of this proportion of flame retardant is the most obvious, and the quality of the carbon layer is better than that of other proportions of EP composites. As an acid source, PA-Ba can also partially replace the carbon source in IFR flame retardant system to promote the catalytic carbonization of the system.

**$Ni^{2+}$**. Gong et al. [121] added nickel phytate (PA-Ni) to PLA containing intumescent flame retardant to enhance the flame

**Table 3**
The formulation and core index of the functional composites with Phytic Acid (PA) as a typical flame retardant filler.

| Polymer | Flame Retardant Additives | UL-94 | LOI (%) | pHRR decrease (%) | THR decrease (%) | FRI | Ref |
|---|---|---|---|---|---|---|---|
| Cotton | 7BL SiO$_2$-PEI/PA | / | 33.7 | 75.4 | / | / | [97] |
| Cotton | 4BL PEI-g-C$_3$N$_4$/PEI-PA | / | 30.5 | 76.9 | 77.1 | / | [98] |
| Cotton | 16 wt%TEOS:PA (7:3) | / | / | 74.7 | / | 4.5 | [99] |
| Cotton | 8 wt%PA@BC | V0 | / | 49.5 | 9.5 | 1.39 | [100] |
| Cotton | QM/PA | / | 43.0 | 88.4 | 87.4 | / | [101] |
| Cotton | 5 wt% GPA | / | 29.0 | 46.2 | 58.1 | 1.94 | [102] |
| Cotton | 20 wt% APA | / | 43.2 | 94.5 | 58 | | [103] |
| Wool fiber | HPPHBTCA | / | 30.3 | / | / | / | [104] |
| Silk | PA/TiO$_2$/BTCA | / | 36.8 | 56.3 | / | / | [105] |
| EP | 10 wt% EHPP@PA | / | | 64 | / | 1.95 | [106] |
| EP | 5 wt%PAD/DOT | V0 | 29.0 | 42.9 | 18.8 | 2.10 | [107] |
| EP | 8 wt%APP/4%CP@PA | / | / | 82.4 | 76.8 | 26.2 | [108] |
| EP | 15 wt%PIPT | V0 | 35.5 | 51.4 | 35.9 | / | [109] |
| EP | EP/14IFR/2 PA-Ba | / | 30.7 | 69.1 | 71.55 | / | [110] |
| EP | 6 wt% PA/MEL | V0 | 29.7 | 62.3 | 1 | 2.87 | [111] |
| EP | 5 wt% g-C$_3$N$_4$/PA-Zn | / | 28.3 | 71.4 | 58 | 5.0 | [112] |
| EP | 5 wt% PA-Mg/5 wt%RHS | / | / | 28.6 | 10.6 | 1.73 | [113] |
| EP | 5 wt% PA-UiO66-NH$_2$ | V1 | 29.1 | 41 | 40.6 | / | [114] |
| PLA | 20 wt% f-BNNSs | / | 27.5 | / | / | / | [115] |
| PLA | 19 wt% CaMg-PA/1 wt% CNT | | | 35.3 | 11.7 | 1.35 | [116] |
| PLA | 23 wt%TPA | / | 26.5 | 30.2 | / | 1.75 | [117] |
| PLA | 20 wt%MPAZn | / | 27.5 | 45.1 | 21.0 | 1.62 | [118] |
| PLA | 10 wt% rGO/MEL/PA | V0 | 25 | 35.3 | 20.9 | 1.56 | [119] |
| PLA | 4 wt%PF | V0 | 28.5 | 8.14 | 2.14 | 0.93 | [120] |
| PLA | 4 wt% PA-Ni/11 IFR | V0 | 31 | 70.5 | 10.2 | 2.96 | [121] |
| PLA | 3 wt% PA-THAM | V0 | 25.8 | 10.7 | 8.6 | 1.42 | [11] |
| PLA | 5 wt% HACP-PA | V0 | 24.2 | 15.3 | 25.1 | 0.99 | [122] |
| PP | 2 wt%APP/PA-LDH | V0 | 27 | 78 | 6.42 | 2.66 | [123] |
| PP | PaLys | V0 | 26.0 | 70.7 | 10.6 | 2.12 | [124] |
| TPU | 5 wt%SW-Si$_3$N$_4$ | / | / | 40.8 | 35.2 | 5.96 | [125] |
| FPUF | 5 wt% APA/5 wt%OMMT | V0 | 22.6 | 69.3 | 34.3 | / | [126] |
| EVA | 30 wt% PIMEPA@ATH | V0 | 26.5 | 78.9 | 13.7 | 3.84 | [127] |

Note: *PEI* means polyethyleneimine, *TEOS* means tetraethoxysilane, *BC* means biochar, *QM* means laccase, *GPA* means the reaction between (3-piperazinylpropyl) methyl-dimethoxysilane and phytic acid, *HPPHBTCA* means the reaction of phytic acid, pentaerythritol, and 1,2,3,4-butanetracarboxylic acid, *BTCA* means 1,2,3,4-Butane tetra-carboxylic acid, *EHPP* means phenylphosphonate-based compound, *PAD* means the combination of PA and DOPO, *DOT* means borate, *APA* means ammonium phytate, *CP* means polyaniline coupled graphite carbon nitride, *PIPA* means piperazine phytate, *g-C$_3$N$_4$* means graphitic carbon nitride, *RHS* means rice husk ash, *UiO-66-NH$_2$* means metal-organic framework, *f-BNNSs* means boron nitride nanosheets and phytic acid, *CaMg-PA* means calcium magnesium phytate, *TPA* means phytic acid reacts with tris (hydroxymethyl) methylaminomethane, *MPAZn* means melamine zinc phytate, *PF* means the reactant of PA and furfurylamine (FA), *PA-Ni* means nickel phytate, *THAM* means trometamol, *HACP-PA* means phytic acid and hexakis (4-Aminophenoxy) cyclotriphosphazene, *PaLys* means phytic lysine salt, *SW-Si$_3$N$_4$* means sandwich-like melamine/phytic acid/silicon nitride hybrid sheets, and *PIMEPA* means piperazine-melamine phytate complex.

**Table 4**
The formulation and core index of the functional composites with polydopamine (PDA) as a typical flame retardant filler.

| Polymer | Flame Retardant Additives | UL-94 | LOI (%) | pHRR decrease (%) | FRI | Ref |
|---|---|---|---|---|---|---|
| EP | 5 wt%HNT@PDA@Fe(OH)$_3$ | V1 | 33.9 | 41 | 1.36 | [129] |
| EP | 5 wt% Fe-PDA | V0 | 31.6 | 40.9 | / | [130] |
| EP | 30 wt%MDH/MDH@Fe-PDA | V0 | 29.3 | 57 | / | [8] |
| EP | 6 wt% BN@PDA@Fe | V0 | 34.2 | 38.9 | 2.13 | [131] |
| EP | 7.0 wt% RP@PDA/MEL | V0 | 30.9 | 65.1 | 6.72 | [132] |
| EP | 5 wt% PZS@PDA@Ni(OH)$_2$ | V0 | 31.8 | 69.8 | 2.49 | [133] |
| EP | 3 wt% RMH@PDA@PBA | V0 | 32.3 | 43.1 | 2.34 | [134] |
| EP | 2 wt% nano-PDA | / | / | 53.6 | 2.30 | [135] |
| EP | 4 wt% DOPO/PDA | V0 | 35.4 | 40.0 | 2.11 | [136] |
| EP | 3 wt% UiO66-PDA-PBA | V1 | 27.5 | 45.4 | / | [137] |
| EP | 5 wt%PDA/TA@Ni@β-FeOOH | V0 | 27.8 | 28.4 | / | [138] |
| EP | 2 wt% h-BN@PDA@MoS$_2$ | V1 | 27.8 | 32.1 | 2.04 | [139] |
| SMEP | 20 wt%PDA@APP/WEP | / | 32.6 | 63.4 | / | [140] |
| PU foam | 3 wt% MCC and 12 wt% EG | / | 25.3 | / | / | [141] |
| FPUFs | PDA-rGO | / | / | 49.3 | / | [142] |
| TPU | 5 wt%APP-Cu@PDA | V0 | 28 | 82.6 | 7.11 | [143] |
| Cotton | APP@PDA | / | 28.5 | 59.6 | 3.02 | [144] |
| Cotton | 8 BL PDA/PHA/APTES | / | 31.4 | 36.4 | 4.97 | [145] |
| PLA | 10 wt% AZA/PDA | V0 | 23.7 | 18.8 | / | [146] |

Note: *MEL* means melamine, *PZS* means polyphosphazene microspheres, *RMH* means magnesium hydroxide rods, *PBA* means prussian blue analogue, *UiO66* means MOF, *SMEP* means shape memory epoxy, *WEP* means water-borne epoxy, *rGo* means reduced graphene oxide, *PHA* means phenylphosphonic acid, *APTES* means 3-aminopropyltriethoxysilane, and *AZA* means azo-boron-2,2-bis(4-hydroxyphenyl) propane.

retardancy of PLA further (Fig. 4d). When 4 wt% PA-Ni and 11 wt% IFR were added to PLA, the flame retardancy of the composites was the best. The LOI value of PLA composites reached 31% and

successfully passed the UL-94 test V0. At the same time, the addition of flame retardant significantly reduced the pHRR value of PLA composites by 62.4%. The existence of PA-Ni in the system
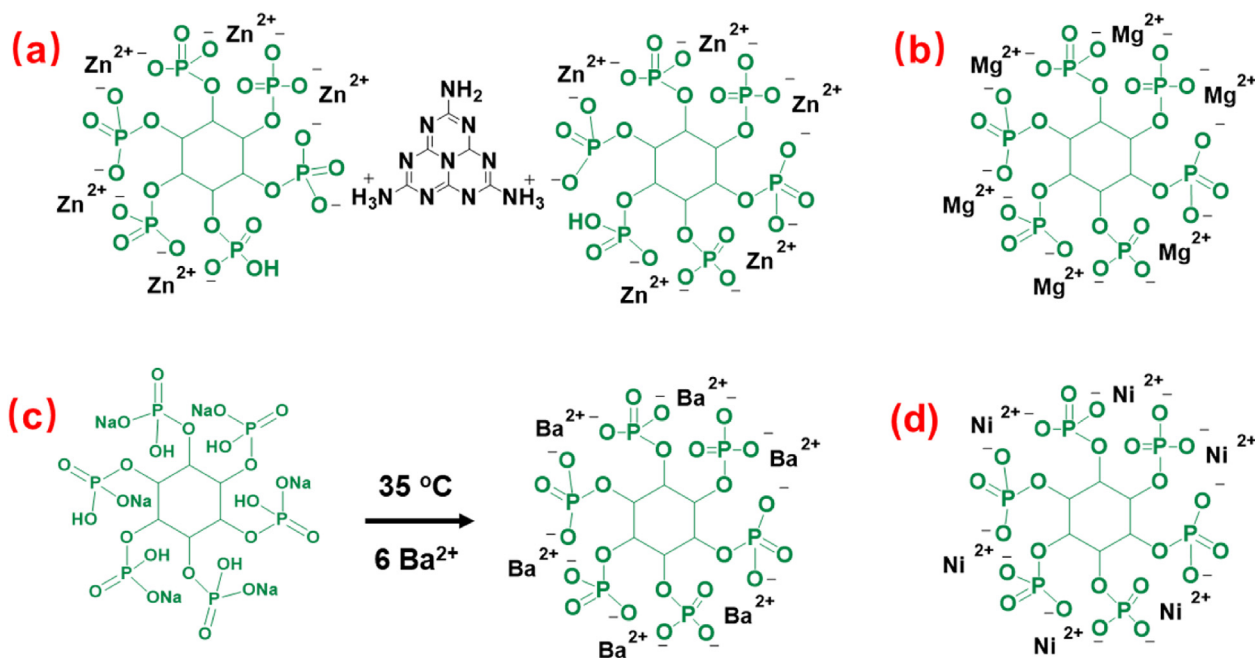
**Fig. 4.** (a) The formation mechanism of g-C$_3$N$_4$/PA-Zn [112], (b) The molecular structure of PA-Mg (Redrawn from Ref. [113] Copyright (2020) Springer), and (c) Synthesis route of PA-Ba [110], (d) Chemical structure of PA-Ni$^{2+}$ [121].

promotes the production of carbon residue and forms a physical barrier to protect the matrix from flame damage. At the same time, due to a large amount of phosphorus in PA, free radical scavengers are produced during the combustion process to stop the combustion reaction.

(2) Compounding with some other fillers

Usually, PA is compounded with some other fillers, such as BN [115], CNT [116], MOF [114], Graphene [119], LDH [123], Si$_3$N$_4$ [125], etc. The schematic diagram of the core structure of each composite flame retardant is shown in Fig. 5.

**BN.** As shown in Fig. 5a, Rosely et al. [115] synthesized boron nitride nanosheets and phytic acid with a silane coupling agent to form a new flame retardant f-BNNSs. When 20 wt% f-BNNSs was added to PLA, the LOI value of the composite reached 27.5%. Due to a large amount of phosphorus, nitrogen, silicon, and other elements in the new flame retardant f-BNNSs, the charring ability of the composites is greatly improved. A dense carbon protective layer is formed in the condensed phase, preventing the entry of oxygen and heat transfer. Therefore, the flame retardancy of PLA composites has been improved.

**CNT.** A new bio-based flame retardant calcium magnesium phytate (CaMg-PA) and acid-treated carbon nanotubes (CNT) were used to synergistically flame retardant PLA (Fig. 5b) [116]. When 19 wt% CaMg-PA and 1 wt% CNT were added to PLA, the pHRR of the composite decreased from 385 kW/m$^2$ of pure sample to 249 kW/m$^2$. The addition of flame retardant reduces the smoke emission during the combustion of the composite and increases the carbon residue. When the two flame retardants are used together, the flame retardancy of the composite is better than that of the two alone.

**Si$_3$N$_4$.** Si$_3$N$_4$ sheet is used as a template and covered with two-dimensional phytic acid/melamine (PAMA) coating to form a flame retardant material with a sandwich structure (Fig. 5c) [125]. Applying 5 wt% flame retardant to TPU can significantly improve the flame retardant properties of the composites. Compared with pure TPU, the addition of flame retardant reduced the pHRR of the

composite from 1252 kW/m$^2$ to 741 kW/m$^2$. At the same time, the existence of PAMA/Si$_3$N$_4$ inhibits the smoke release during combustion and achieves a pronounced smoke suppression effect. In the combustion process, the presence of phosphorus, nitrogen, silicon and other elements in the flame retardant promotes the catalytic carbonization of the matrix, forms a dense carbon layer barrier, and effectively prevents the release of smoke and heat transfer.

**Protein.** As shown in Fig. 5d, Laccase (QM) and phytic acid (PA) coatings were constructed on cotton fabrics [101]. Due to flame retardant coatings, the LOI value of cotton fabrics increased significantly from 18.8% to 43%. At the same time, both pHRR and THR decreased significantly. According to the Raman test findings, the graphitization degree of the QM/PA coating is higher. And the higher the graphitization degree, the better the flame retardant performance of the carbon layer. The joint action of QM and PA promotes the catalytic carbonization of the matrix, forms a dense carbon layer and produces non-combustible gas. Therefore, the flame retardancy of cotton fabric has been significantly improved.

**MOF.** UiO-66-NH$_2$ is a metal-organic framework (MOF) that can be used as a flame retardant (Fig. 5e) [114]. It is functionalized with phytic acid to form a new type of high-efficiency flame retardant (PA/UiO-66-NH$_2$) to improve the flame retardant performance of EP. After adding 5 wt% PA/UiO-66-NH$_2$, the pHRR of the EP material was reduced by 41%, and the TSP was reduced by 42%. During the combustion process, EP and the PA/UiO-66-NH$_2$ work together to cross-link to form more carbon and establish a physical barrier. Also, the escape of toxic and harmful gases during the combustion of EP composites is significantly reduced.

**GO.** Yang et al. [119] assembled PA and melamine onto the surface of graphene oxide (rGO) for flame retardant PLA (Fig. 5f). When the amount of flame retardant was 10 wt%, the LOI of the composite was increased to 25%, and UL-94 passed V0 successfully. According to the CCT test results, the flame retardant can delay the ignition time of the material, and the pHRR value is reduced by 35.3%. In the flame retardant system, PA acts as an acid source, and phosphorus in the structure promotes the catalytic carbonization of rGO and melamine.
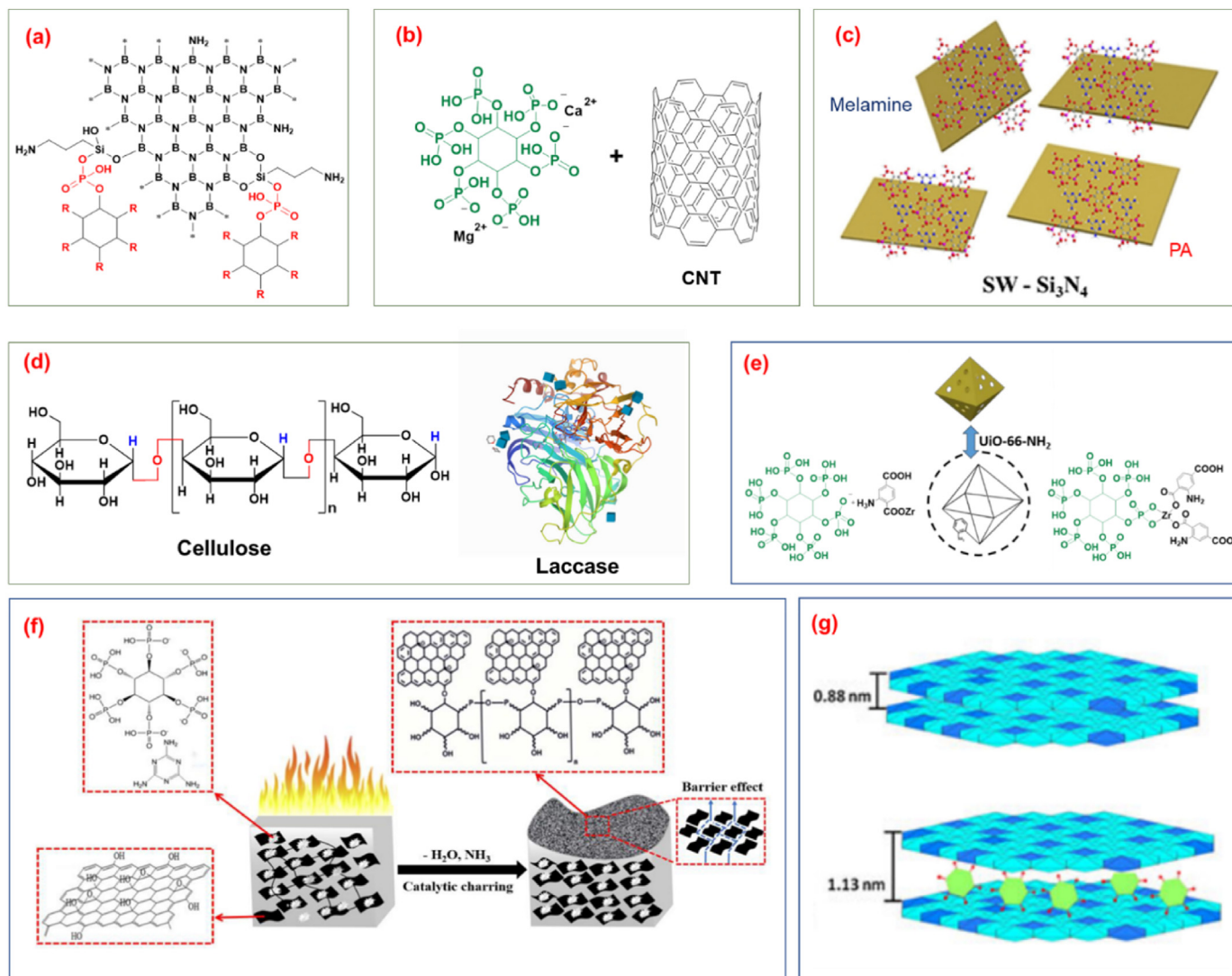
**Fig. 5.** (a) PA functionalized BN nanosheet [115], (b) PA derivatives and CNT [116], (c) Si$_3$N$_4$ (Adapted the permission from Ref. [125] Copyright (2021) Elsevier), (d) The scheme of the flame-retardant action of cotton/QM/PA [101], (e) The PA-UiO66-NH$_2$ and the two possible connections between PA and MOF [114], (f) GO and PA derivatives as synergistic flame retardant (Adapted the permission from Ref. [119] Copyright (2021) MDPI), and (g) PA as intercalation agent for LDH (Adapted the permission from Ref. [123] Copyright (2017) Wiley).

***LDH**. PA is introduced into LDH by coprecipitation to produce phytic acid-modified layered double hydroxide (PA-LDH) (Fig. 5g) [123]. It is added to PP together with APP in melt blending. The combination of PA-LDH and APP produces a positive flame retardant effect. This makes the carbon residue rate of PP composite increase instantaneously. Composite is compared with PP, adding 2 wt% APP/PA-LDH flame retardant reduces the pHRR value of the composite by 78%. Adding PA-LDH can effectively inhibit the generation of smoke, and the TSP value decreases by 31%. When APP/PA-LDH is added to 2 wt%, the composite carbon residue shows a compact and continuous structure.

Biochar (BC) and PA are uniformly mixed in water at a ratio of 1:1 and loaded on cotton [100]. When the amount of PA added is 8 wt%, the fabric achieves a self-extinguishing effect, and the carbon residue reaches 53%. Then replace PA with 4% BC and increase the carbon residue to 85%. This demonstrates the synergistic flame retardancy of PA and BC. Phytic acid-functionalized cotton and nylon blends also exhibit self-extinguishing properties.

(3) *Form other organic derivatives*. The specific example is shown in Fig. 6.

In Fig. 6a, PA reacts with furfuryl amine (FA) in water to form a new flame retardant substance PF [120]. When 4 wt% PF was added to PLA, the oxygen index of the composite increased to 28.5%, and UL-94 reached V0. The existence of PF can inhibit the exothermic and incomplete combustion of PLA composites. At the same time, the free radicals produced by matrix combustion are captured during the combustion process, and a graphitized carbon layer is formed to protect the matrix.

In Fig. 6b, Yang et al. [122] combined phytic acid with hexakis (4-Aminophenoxy) cyclotriphosphazene to prepare a green and environmentally friendly three sources one intumescent flame retardant (HACP-PA). The LOI value of PLA/5 wt% HACP-PA composite reaches 24.2%, and UL-94 reaches V0 level. Compared with pure PLA, the pHRR value of the composite added with 5 wt% flame retardants decreased by 15.3%. The cone calorimetry test showed
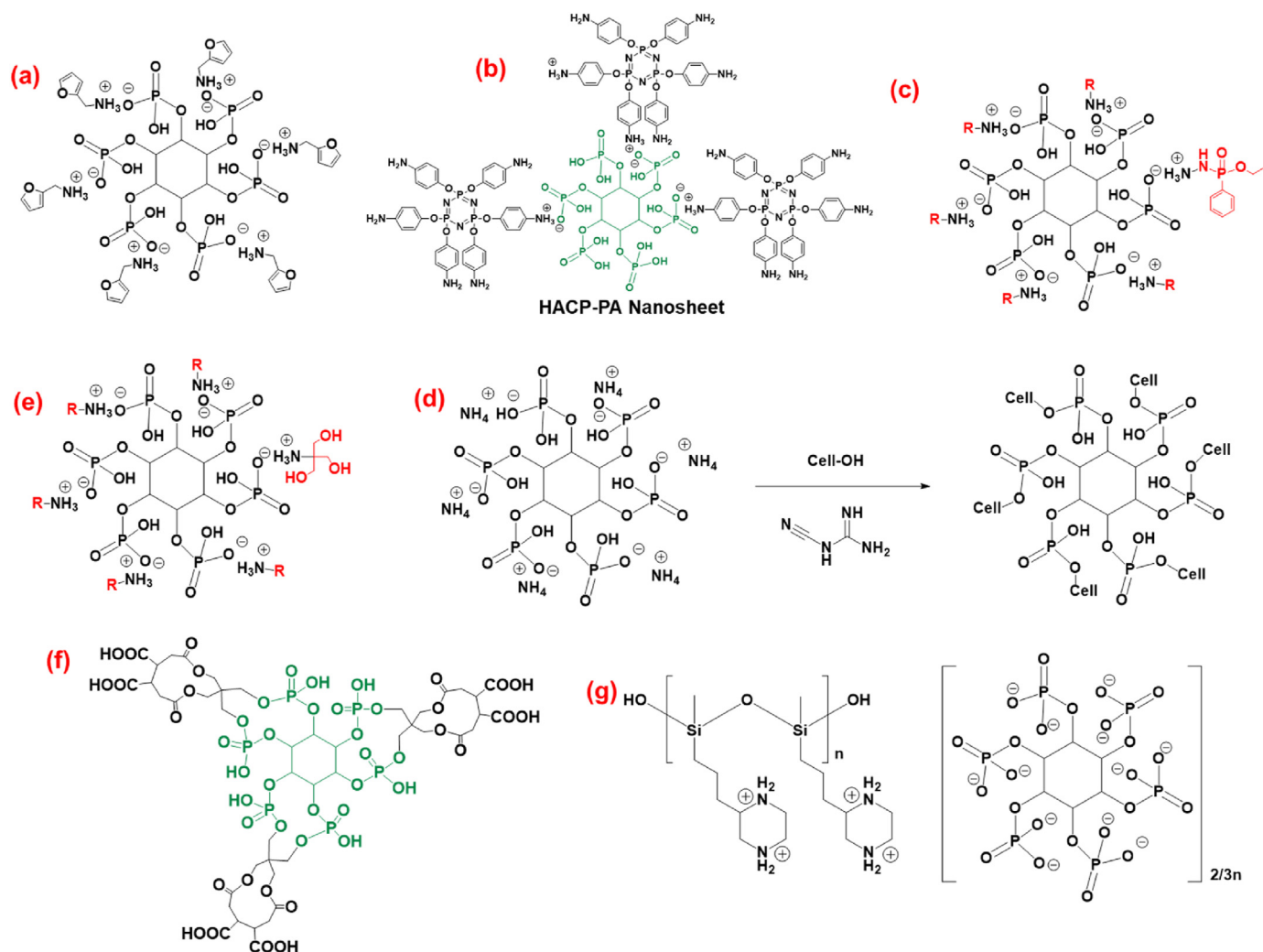
**Fig. 6.** (a) Structural diagram of reaction products of Furfurylamine and phytic acid [120], (b) Synthetic route of hexakis (4-aminophenoxy) cyclotriphosphazene-phytic acid (HACP-PA) microporous nanosheet [122], (c) Schematic illustration of the preparation of EHPP@PA [106], (d) Crosslinking reaction between cotton fibers and APA [103]; (e) Scheme of possible reaction route between PA and THAM [11], (f) HPPHBTCA structural formula (HPPHBTCA was synthesized using phytic acid, pentaerythritol and 1,2,3,4-butanete-tra-carboxylic acid) [104]; (g) GPA structural formula (GPA is the reactant of (3-piperazinylpropyl)methyldimethoxysilane and phytic acid) [102].

that the weight of carbon residue in the composite added with flame retardant increased significantly. This is attributed to the fact that HACP-PA promotes the formation of a high-quality carbon layer during combustion, forms a protective barrier, and plays an essential role in condensed phase flame retardation.

In Fig. 6c, PA reacts with phenyl phosphonate compound (EHPP) to form a new high-efficiency flame retardant [106]. Add 10 wt% EHPP@PA to EP, the pHRR and SPR of the composites decreased significantly. And the flame retardant efficiency is higher than when EHPP acts on EP alone. The flame retardant system can simultaneously be flame retardant in the condensed and gas phases. The existence of phytic acid mainly promotes the dehydration and carbonization of the matrix during combustion and forms an expansive carbon layer. The presence of a carbon layer reduces heat transfer and the continuous transport of oxygen. EHPP plays a crucial role in gas-phase flame retardant, producing quenching free radicals to prevent the reaction from continuing.

In Fig. 6d, cotton fabric was soaked in ammonium phytate (APA) solution to improve its flame retardancy [103]. The LOI value of cotton fabric treated with 20% APA solution can reach 43.2%. The pHRR value of treated cotton fabric decreased by 94.5%. Compared with untreated cotton fabric, the carbon residue increased significantly from 1.31% to

36.24%. The cotton fabric treated with APA contains many phosphate groups, which promote the carbonization of the cotton fabric and play a role in the condensed phase flame retardant.

Yang et al. [11] used the salt-forming reaction of phytic acid to react PA with trometamol (THAM) and add it to PLA (Fig. 6e). The new flame retardant synthesized is PA-THAM. Added only 3% PA-THAM, the LOI of PLA composite reached 25.8%, and UL-94 got V0. PA-THAM has excellent flame retardancy and mainly promotes the formation of a carbon layer in the condensed phase.

In Fig. 6f, Cheng et al. [104] reacted phytic acid, pentaerythritol, and 1,2,3,4-butanetracarboxylic acid to develop a new flame retardant named HPPHBTCA. The flame retardant will react with wool fiber to enhance the flame retardancy of wool. The LOI value of wool fabric treated with HPPHBTCA reached 30.3%, and the smoke produced by combustion was significantly reduced. Due to a large amount of phosphorus in its structure, this green flame retardant can promote the matrix's catalytic charring and inhibit the combustion process.

In Fig. 6g, Li et al. [102] prepared a new flame retardant GPA by reacting (3-piperazinylpropyl) methyldimethoxysilane with phytic acid. The flame retardant was successfully deposited on the surface of cotton fabric by soaking. When cotton fabric contains 5 wt% GPA,

its LOI value is 29%. In the vertical combustion test, the existence of GPA coating makes the scorch length of the composite only 11 cm and can achieve self-extinguishing, which has a good flame retardant effect. 5 wt% flame retardant reduced the pHRR value of cotton material by 46.2%, and the amount of carbon residue in the system increased significantly.

### 2.3.2. General flame retardant mechanism of PA

In the combustion process, PA is often used as the acid source in the intumescent flame retardant system. Metaphosphoric acid and other substances are produced by thermal decomposition to promote the catalytic carbonization of carbon sources in the flame retardant system. In addition, the PA produces many non-combustible gases, produces phosphorus-containing free radicals, and captures the free radical ions in the system in the gas phase to stop the combustion. At the same time, a large amount of phosphorus in its structure can be used as a charring agent to promote the formation of more stable carbon residue in the system. The more compact and continuous the carbon layer, the better the protection of the substrate. The carbon layer can be a physical barrier to reducing heat transfer and oxygen. PA will also produce phosphorus-containing compounds during the thermal decomposition process, which will cover the PLA surface during the decomposition process. Form a physical barrier to protect the substrate.

### 2.4. Polydopamine

PDA is an environment-friendly bio-based flame retardant material inspired by mussels (Fig. 7a). It is an environment-friendly bio-based material. PDA is known as a "molecular glue" [145]. It can be used as an interfacial compatibilizer while providing synergistic flame retardant properties. As an interfacial compatibilizer, it is widely used in the surface coating modification of functional particles. For example, it can be used for introduction of inorganic components on the surface of polymer microspheres or some other particles. Typically, biomimetic PDA was coated on polyphosphazene microspheres and then assembled with $Ni(OH)_2$ to synthesize $PZS@PDA@Ni(OH)_2$ flame retardant [134]. Only adding 5 wt% of flame retardants in EP can increase the LOI value of the composite to 31.8%. The pHRR value of the EP composite was reduced by 69.8%. And the composite material can successfully pass the UL-94 test to reach the V0 level. Due to the presence of nitrogen and phosphorus in the new flame retardant, elements such as phosphorus can be co-catalyzed with $Ni(OH)_2$ to form carbon, making the EP material's carbon layer more stable. As shown in Fig. 7b, Fe-PDA is formed by chelating iron ions with PDA and then adding EP resin to form a green system [130]. The flammability of the obtained EP nanocomposite is significantly reduced. Fe-PDA shows the LOI value of 31.6% under a load of 5 wt%, and UL-94 reaches V-0. The peak heat release rate dropped from 1285 kW/$m^2$ to 760 kW/$m^2$. This kind of flame retardant imparts excellent flame retardant properties to EP materials. Fe-PDA eliminates free radicals during the combustion process and plays a role in gas phase flame retardancy. At the same time, its existence can promote the formation of a more stable and dense carbon layer and inhibit combustion.

*Surface modification of APP.* To improve the flame retardant properties of TPU, an intumescent flame retardant APP-Cu@PDA was prepared [143]. Adding 5 wt% flame retardant to TPU, the LOI of the composite material can reach 28%, UL-94 V0 level. At the same time, the addition of flame retardant significantly reduced the pHRR and THR of the composites by 82% and 25%, respectively. The improvement of the flame retardant properties of TPU composites

is mainly because $Cu^{2+}$ in the flame retardant system can chelate PDA and promote the catalytic carbonization of the system.

*Surface modification of RP.* Cheng et al. [132] used PDA to coat red phosphorus (RP) to prepare microencapsulated red phosphorus (RP@PDA) and then compound it with melamine (MA) (Fig. 7c). This new core-shell flame retardant is applied to epoxy resin to improve its flame retardancy. The synthesis schematic diagram of the flame retardant is shown in Figure. When the addition amount of RP@PDA/MA is 7.0 wt%, the flame retardant performance of the composite is the best. The LOI value was increased to 30.9%, and UL-94 reached the V0 level. Compared with EP/RP@PDA, the pHRR value of EP/RP@PDA/MA is reduced from 583.3 kW/$m^2$ to 412.6 kW/$m^2$. RP@PDA/MA constitutes an intumescent flame-retardant system, with more phosphorus elements in the structure.

PDA has good adhesion and can be self-polymerized directly in an aqueous solution. It can also use its adhesion properties to form a flame retardant coating on the polymer surface. The catechol group in its structure can interact with the hydrogen bond in the polymer, significantly improving the flame retardant performance of the composite. Therefore, PDA can also be coated on the surface of fabric or PU foam as an interface coating. Then flame retardants of other components can be introduced to increase the adhesion of the flame retardant on the surface of the fabric, thereby improving the washability of the coating. Typically, on cotton coated with PDA, phenylphosphonic acid (PHA) and 3-aminopropyltriethoxysilane (APTES) LbL coatings were applied [145]. The LOI of cotton coated with eight layers of the flame retardant coating increased from 17.4% to 31.4%, while the pHRR decreased from 140 kW/$m^2$ to 89 kW/$m^2$. During burning, the flame retardant cotton fabric produced a substantial volume of non-combustible gases and trapped free radicals in the system, thus ending the process. The presence of PDA as a char-forming agent aided the substrate's dehydration and charring.

In Table 4, we have listed the core data of research reports on using PDA as a flame retardant functional component in recent years. Through comparative analysis, it is found that PDA has been widely used in the flame retardant modification of EP, TPU, polyester, cotton, PU, etc. Among them, it is the most extensive in EP research.

PDA is often used in combination with phosphorus nitrogen compounds or carbon-based materials, and the LOI of the composites has increased by different degrees. At the same time, according to the data in Table 4, it can be seen that the FRI of modified materials is generally in the same order of magnitude, ranging from 1.36 to 7.11. The addition of PDA flame retardant in the composites significantly reduces the flame propagation speed and the fire risk.

As shown in Fig. 7d, Bi et al. [8] prepared organic functionalized magnesium hydroxide by one pot method (MDH@Fe-PDA). The synthesis of the flame retardant mainly utilizes the catechol-based metal chelating properties and the self-polymerization properties of dopamine hydrochloride. Apply this new flame retardant to EP. The results showed that the flame retardancy of EP composites was significantly improved. The LOI value was increased from 20.5% of pure EP to 29.3%, and UL-94 was increased to V0. When the loading of MDH/MDH@Fe-PDA is 30 wt%, pHRR is reduced by 57%. During PDA combustion, H· and OH· in the system will be captured to cut off the continuation of the combustion reaction.

PDA is coated with other flame retardants, such as red phosphorus, boron nitride, graphene, etc. Li et al. [131] modified boron nitride nanosheets (BN) by thermal stripping. Then mixed BN with PDA loaded with iron ions to form a new type of nano-hybrid flame-retardant material BN@PDA@Fe (Fig. 7e). This flame retardant is used in EP to improve its flame retardant properties. When 6 wt% BN@PDA@Fe flame retardant is added to EP, the thermal conductivity of the composite material increases, and the pHRR of
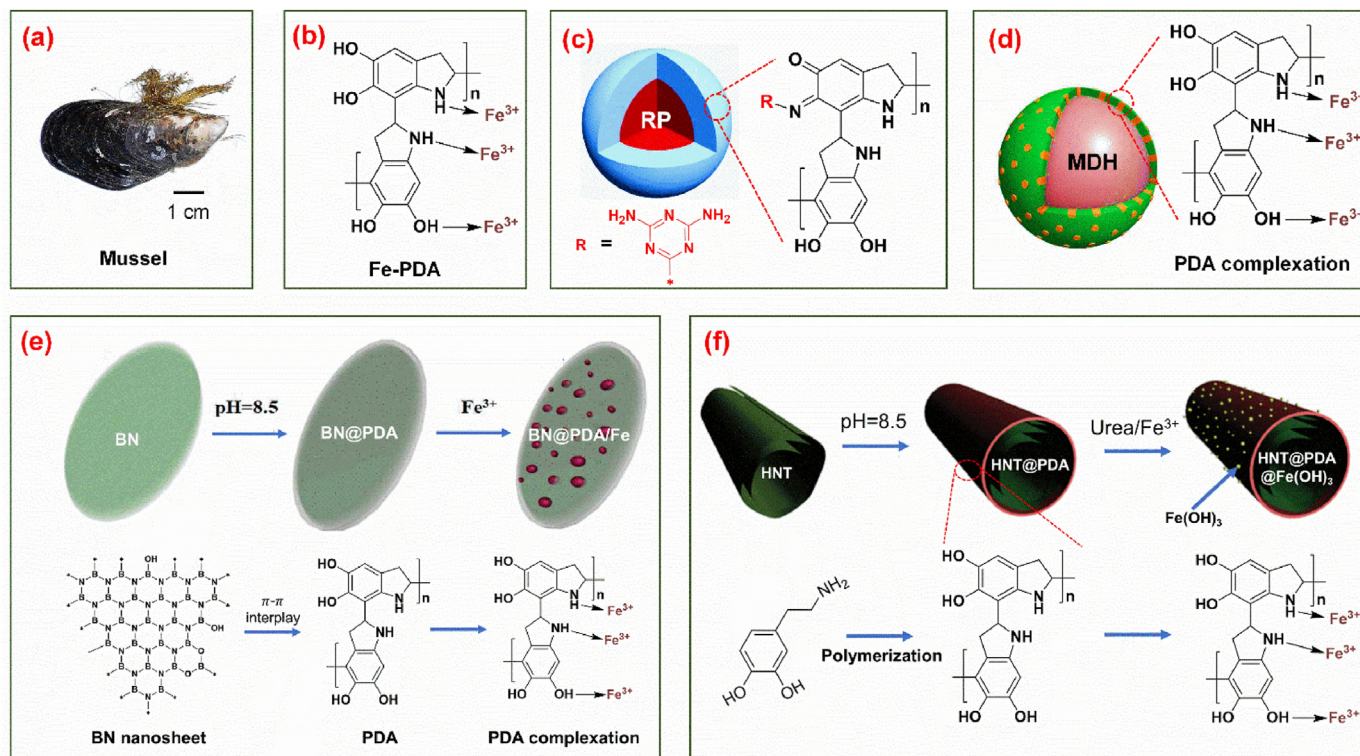
**Fig. 7.** (a) Image of mussel, (b) structure illustration of Fe-PDA based flame retardant (Redrawn from Ref. [130] Copyright (2020) Royal Society of Chemistry), (c) core-shell structure illustration of PDA coated RP (Redrawn from Ref. [132] Copyright (2021) Royal Society of Chemistry), (d) core-shell structure illustration of PDA coated MDH (Redrawn from Ref. [8] Copyright (2020) Elsevier), (e) surface functionalization of BN by Fe-PDA (Adapted permission from Ref. [131] Copyright (2018) Elsevier), and (f) surface functionalization of HNT by Fe-PDA (Adapted permission from Ref. [129] Copyright (2017) Royal Society of Chemistry).

the system decreases by 38.9%. The LOI has significantly increased from 24.2% to 34.2%, and the TSP has been reduced. PDA acts as a gas source and carbon source in the system and plays a role in gas and condensed phases. At the same time, the existence of iron ions in the system promoted more carbon residues on the polymer surface, forming a more compact barrier.

Furthermore, it is found that the catechol group in the PDA structure can capture metal ions, such as trivalent Fe, as shown in Fig. 7f. Concretely, Li et al. [129] prepared a new flame retardant HNT@PDA@Fe(OH)$_3$ by assembling Fe(OH)$_3$ and polydopamine nano coatings on halloysite nanotubes (HNT). This new flame retardant is added to EP to improve its flame retardancy. The schematic diagram of the synthesis process of HNT@PDA@Fe(OH)$_3$ nanomaterials is shown in the Figure. Compared with pure EP (LOI = 24.1%, UL-94 no grade), the LOI value of EP/HNT@PDA@Fe(OH)$_3$ is 33.9%, and the UL-94 rating is V-1. According to CCT data, the pHRR of the composite material was reduced by 41%. The composite's flame retardancy is improved due to HNT@PDA@Fe(OH)$_3$ catalytic carbonization behavior at the interface. The carbon residue in the composite material has a more continuous and dense structure.

Yun et al. [141] prepared a cellulose-based additive flame retardant, which improved the flame retardancy of PU foam and enhanced its mechanical strength. Coating PDA on the ground microcrystalline cellulose (MCC) surface while forming a phosphate coordination network on the surface of the MCC. Expandable graphite (EG) and modified MCC are mixed in PU foam. When 3 wt% modified MCC and 12% EG were added to the PU foam, the LOI of the PU composite material increased to 25.3%.

Furthermore, Qiu and colleagues [142] prepared reduced graphene oxide (rGO) and then combined the two through the self-polymerization reaction of PDA to form a new flame-retardant nanomaterial (PDA-rGO). They are coated on flexible polyurethane foam (FPUF) by LBL. CCT results show that the pHRR and TSR of pure FPUF are 403.3 kW/m$^2$ and 174.9 m$^2$/m$^2$, respectively. The three-layer PDA-rGO polyurethane foam shows the most excellent flame retardant properties. The pHRR and TSR values of the composite material are 204.4 kW/m$^2$ and 117.0 m$^2$/m$^2$, respectively. Since PDA can produce free radical inhibitors and promote the formation of carbon residue during the combustion process, it protects the matrix to a greater extent.

In general, the flame retardant mechanism of PDA can be divided into vapor phase flame retardant and condensed phase flame retardant, which act as a carbon source and gas source in the flame retardant system. In the gas phase, PDA releases many free radical scavengers during combustion [130,142], captures H· and OH· in the matrix, and terminates the combustion reaction. In the condensed phase, PDA will promote the formation of stable carbon residue during pyrolysis and adhere to the polymer surface [131,145]. This carbon layer forms a physical barrier, which reduces heat transfer and oxygen transport, and achieves the effect of flame retardation. PDA with a few additives has excellent flame retardant efficiency, so PDA as a flame retardant has a good development prospect.

### 2.5. Tannic acid

As shown in Table 5, tannic acid (The chemical structure of TA is shown in Fig. 8a) is widely used as a flame retardant additive to modify EP, cotton, PLA, nylon, etc. For example, a new flame retardant for PLA is prepared by synthesizing TA, boric acid (BA)

**Table 5**
The formulation and core index of the functional composites with TA as a typical flame retardant filler.

| Polymer | Flame Retardant Additives | UL-94 | LOI (%) | pHRR decrease (%) | THR decrease (%) | FRI | Ref |
|---|---|---|---|---|---|---|---|
| PLA | 10 wt% LC-PA/TA | V0 | 26.9 | 24.5 | 21.1 | / | [147] |
| PLA | 5 wt%BA-TA-MEL | V0 | 27.1 | 15.3 | 6.9 | 1.08 | [148] |
| PLA | 17 wt% TA-3 wt% OMMT | / | / | 50 | 9.4 | / | [149] |
| BPC | 5 wt% chitosan/TA@5%HNT | / | 22.5 | 30.4 | 17.1 | / | [38] |
| EP | 4.0 wt% PHDT@FeCo-LDH | V0 | 29.7 | 28.3 | 52.1 | 2.22 | [150] |
| EP | APP@TA/adenine/Ni | V0 | 33.5 | 46.3 | 29.1 | 2.45 | [151] |
| PS | 20 wt% PER/APP/TGE | V0 | 35.5 | 53.8 | 43.4 | / | [152] |
| Cotton | DETA-TA-PA | / | 34 | 91.2 | 58.1 | / | [153] |
| Cotton | TA-NaOH | / | 30.2 | 81.8 | 68.75 | / | [154] |
| Cotton | TA/B@PDA | / | 28.5 | 49.1 | 31.9 | / | [155] |
| PAN | 2 wt% TA-MoS$_2$ | / | 26 | 38.1 | 29.7 | 3.92 | [156] |
| PAN | 8BL TFMCB | / | 34.8 | 68.0 | 65.2 | 15.9 | [157] |
| PU | 5 wt%TA@RGO | / | | 31.0 | 25.9 | / | [158] |
| PU | 5 wt%TA-B@CNT | / | / | 32.8 | 25.1 | / | [159] |
| Natural Rubber | 60 wt% APP/TA@GE | / | 32.1 | 39.4 | 37.3 | 3.39 | [160] |
| PVC | 10 wt% MH@PASn@TAZn | / | 30.3 | 42.2 | 1.05 | 1.09 | [161] |
| Nylon 6 | 15 wt%TC/TA | / | 25 | 52.1 | 17.4 | | [162] |

Note: *LC* means ʟ-citrulline, *BA* means boric acid, *OMMT* means organomodified montmorillonite, *BPC* means bamboo/PLA composites, *PHDT* means polyphosphazene microspheres, *DETA* means diethylenetriamine, *TFMCB* means TA/Fe$^{3+}$/A-MoS$_2$/TA-CNFs/Borate, *GE* means graphene, *TC* means terephthaloyl chloride.

and MEL in one pot [148] (Fig. 8b). When 5 wt% TA-BA-MEL was added to PLA, the LOI value of the composite was the highest and passed UL-94 V0 grade. At the same time, the flame retardant effect of these three substances on PLA was tested. It is found that the LOI value of physically blended PLA composites is only 24.6%, UL-94 reaches V2 grade.

For some other recent typical examples and core indicators are summarized in Table 5. Tannic acid is often mixed with metal compounds for modification, such as Fe$^{3+}$, Zn$^{2+}$ and Ni$^{2+}$, etc.

***Fe$^{3+}$***. In Fig. 8c, polyphosphazene microspheres (PHDTs) synthesized by condensation of tannic acid and 4,4′-dihydroxybiphenyl were modified with LDH [150], and the flame retardant named PHDT@Co-LDH. When 4 wt% of the new flame retardant

was added to EP, the LOI value of EP composites increased to 29.7%, and UL-94 reached V0. With the addition of flame retardant, the pHRR and THR of EP decreased significantly, and the FRI got 2.22. The existence of PHDTs can promote the carbonization of the EP matrix and capture free radicals to terminate the reaction.

***Ni$^{2+}$***. TA, guanine and Ni$^{2+}$ are combined by electrostatic action and then assembled on the surface of the APP, which is worthy of being a green bio-based flame retardant (APP@ATNi) [151]. With 15 wt% of APP@ATNi in EP, the LOI value of the composite was 33.5%, and UL-94 reached V0. According to the results of CCT test, it can be seen that the flame retardant and smoke suppression performance of EP composites with flame retardants is significantly improved. The phenoxy produced during the combustion of TA will
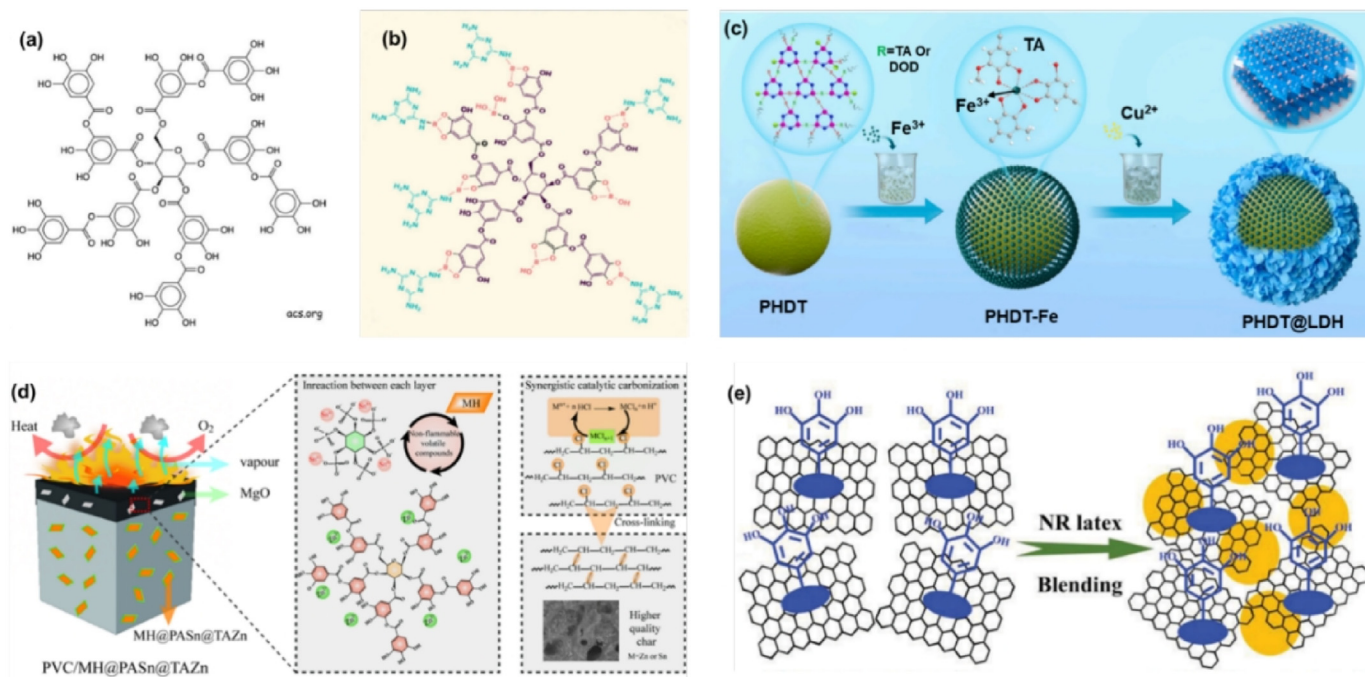


**Fig. 8.** (a) Chemical structure of TA, (b) Illustration for the fabrication of Boric Acid-TA-Melamine and PLA/BA-TA-MEL composites [148]. (c) Preparation route of PHDT@FeCo-LDH (Adapted permission from Ref. [150], Copyright (2022) Elsevier) DOD = 4,4′-Dihydroxybiphenyl. (d) Schematic diagram of PVC/MH@PASn@TAZn flame retardant mechanism (Adapted permission from Ref. [161], Copyright (2020) Elsevier). (e) TA together with other flame retardants as composite flame retardants. The preparation process for the flame retarded NR@AGT composites (Adapted permission from Ref. [160], Copyright (2020) Elsevier).

act as a free radical scavenger. At the same time, APP and guanine will produce non-combustible gas when combusted, producing a flame retardant effect in the gas phase. APP and $Ni^{2+}$ promote TA carbonization in the condensed phase to form a dense and stable carbon layer structure to protect the substrate better.

As shown in Fig. 8d, assembly of tin phytate (PASn), zinc tannate (TAZn) and magnesium hydroxide (MH) on PVC by layer-by-layer assembly method [161]. 10 wt%MH@PASn@TAZn/PVC composites were significantly improved in terms of flame retardant properties. The LOI value of their composites was 30.3%, and the residual carbon increased by 82.4%. At the same time, the smoke release of the composites was significantly reduced. The presence of TAZn and PASn in the flame retardant system can synergistically catalyze the charring and promote the production of more residual char in the matrix. MH releases non-combustible gases during combustion, diluting the concentration of oxygen in the system. Therefore MH@PASn@TAZn provides a new idea for preparing PVC flame retardant and smoke suppressing materials.

TA can be combined with other components, such as two-dimensional materials (OMMT [149], LDH [150], $MoS_2$ [156]); HNT [38], CNT [159]) and other Carbon materials [160], etc.

***OMMT***. Montmorillonite was added to tannic acid to enhance the flame retardancy of PLA [149]. Adding 17 wt%TA/3 wt%OMMT to PLA could reduce the pHRR and THR of the composites by 50% and 9.4%. The combined action of montmorillonite and tannic acid significantly increased the amount of carbon residue in the system and enhanced the flame retardancy of PLA.

***$MoS_2$***. Peng et al. [156] used tannic acid to assist in stripping $MoS_2$ and flame retardant pan. Only 2 wt% TA-$MoS_2$ could make the LOI of the composites reach 28%, and the pHRR decreased by 38.1%. As the charring agent in the flame retardant system, TA produces many carbon layers in the combustion process. At the same time, the existence of $MoS_2$ promotes the stability of carbon formation and the tightness of carbon layers. TA will also produce free radical scavengers to inhibit combustion reactions to achieve a flame retardant effect in the gas phase.

***HNT***. TA and CS were used on the surface of halloysite (HNT) for flame retardant PLA/bamboo fiber composites (BPC) [38]. 5 wt%FR/5 wt%HNT showed good flame retardancy in the matrix. The LOI of BPC composites increased to 22.5%, and the pHRR decreased from 736.8 kW/m$^2$ to 512.8 kW/m$^2$. As a charring agent, CS/TA flame retardant system promotes the production of more carbon layers. Phenols and nonflammable gases will be produced during combustion to remove free radicals in the system. At the same time, due to the particular structure of hNT, the easily decomposed substances produced in the combustion process are easy to stay in the pipeline of HNT, which is conducive to building a denser carbon layer structure.

***CNT***. Kim et al. [159] used boron-doped carbon nanotubes (CNTs) and tannic acid to synergistically flame-retardant polyurethane composites. The addition of 5 wt% TA- B@CNTs flame retardant reduced the pHRR and THR of the composites by 32.8% and 25.1%, respectively. The flame retardant mechanism of the system is mainly condensed phase flame retardant, and TA will produce a large amount of residual carbon in the combustion process. The physical barrier formed by the carbon layer effectively insulates the heat transfer. And the existence of B@CNTs is beneficial to the formation of more stable carbon residue. Therefore, this kind of flame retardant can effectively improve the flame retardancy of polyurethane materials.

***AGT***. In Fig. 8e, a new type of intumescent flame retardant (AGT) made of TA functionalized graphene and APP to flame retardant natural rubber (NR) [160]. 60 wt% AGT significantly improves the flame retardant performance of NR. The LOI value of composites increased from 19.5% to 32.1%. According to the CCT test, the pHRR

of 60 wt% AGT/NR decreased from 731.6 kW/m$^2$ to 443.4 kW/m$^2$, and the THR decreased by 37.3%. In the flame retardant system APP and TA on the surface of graphene will catalyze the charring and form a large amount of residual char. At the same time, ATG releases $NH_3$ when it burns, which can dilute the concentration of oxygen in the system and achieve a synergistic flame retardant effect.

**Flame retardant mechanism of tannic acid**. Tannic acid often exists in plants and is easy to obtain. Because of its high carbon content and polyphenol hydroxyl structure can be used as a bio-based flame retardant. During combustion, tannic acid catalyzes carbonization to form a relatively stable carbon layer structure [148]. At the same time, the combustion will generate phenoxy radicals, and the free radicals in the capture system will terminate the combustion reaction [151,156]. At the same time, the methoxyl and phenoxy groups produced by TA in the combustion process can capture the free radicals in the system and terminate the chain reaction. This new flame retardant has achieved the flame retardant effect in both the gas and condensed phases and has a good development prospect [148]. Therefore, using tannic acid as a flame retardant has a good development prospect.

### 2.6. β-Cyclodextrin

β-Cyclodextrin is relative cheap among the three common Cyclodextrin (namely, α-Cyclodextrin, β-Cyclodextrin and γ-Cyclodextrin) and easy to be modified. It is mainly used for flame retardant EP, PP, PLA, PVC, PET etc. For example, a new type of flame retardant (β-CD@Fe@HMS) is a combination of β-CD@ferrocene (β-CD@Fe) inclusion compound and hollow mesoporous silica through self-assembly used in EP [170]. Compared with pure EP, the LOI of EP composites with 5 wt% flame retardants increased from 19.8% to 27.5%, and TSP decreased by 30.6%. In a recent study phosphorylated β-cyclodextrins (PCD) were prepared using phenyl-phosphonic acid dichloride (BPOD) modified CD [174]. The flame retardant properties of different components of APP/PCD in PLA were tested. The phosphoric acid produced during the decomposition of APP reacts with the hydroxyl group in PCD, which makes the system produce more residual carbon. The LOI of PLA/30APP-PCD reached 42.6% and the V-0 level in the vertical combustion test.

When β-CD and APP are used in a synergistic flame-retardant system, the presence of APP can make the β-CD form more carbon residue. By coating APP, hexamethylene diisocyanate (HDI) and β-CD, a new type of MCAPP can be synthesized [181]. MCAPP can be regarded as an integrated IFR system. Compared with β-CD-APP, the flame retardant efficiency of MAPP is significantly higher. By adding 3 wt% CD and 23 wt% APP, the LOI of the composite material was 29.1%, which failed the UL-94 test. The LOI of the PP composite material with 25% MAPP reached 30.9% and reached the V-0 level in the vertical combustion test. The key parameters were summarized in Table 6.

β-CD is easily functionalized. For example, monofunctional modification can be used as an intercalation modifier of LDH.

As shown in Fig. 9a, after intercalating cyclodextrin with magnesium-aluminum double hydroxide, a novel bio-based flame retardant was created by inserting ferrocene into the cyclodextrin cavity via a host–guest complexation reaction [163]. When applied to EP, 6 wt% LDH-CD-Ferrer can increase the LOI value of EP composites to 29.2%, and UL-94 can reach V1. In the CCT test, adding 6 wt% LDH-CD-Ferrer reduced the pHRR of EP Composites by 23.9%.

As shown in Fig. 9b, Hydroxypropyl sulfobutyl-β-Sodium cyclodextrin (SCD), dodecylbenzene sulfonate (DBS), and taurine (T) were used as modifiers to intercalate layered double hydroxides LDHs [166]. When 6% sCD-DBS-T-LDH was added into EP, the LOI value of the composite reached 26.8%, and UL-94 got V0. At the same time, with the addition of functional LDHs, the pHRR value of

**Table 6**
The formulation and core index of the functional composites with β-Cyclodextrin (β-CD) as a typical flame retardant filler.

| Polymer | Flame Retardant Additives | UL-94 | LOI (%) | pHRR decrease (%) | THR decrease (%) | FRI | Ref |
|---|---|---|---|---|---|---|---|
| EP | 6 wt% LDH-CD-Ferr | V1 | 29.2 | 23.9 | 5.6 | / | [163] |
| EP | β-CD@P-MOF | / | 29.5 | 53.3 | / | / | [164] |
| EP | $Fe_3O_4$@PA-CDBS-LDH | V0 | 26.8 | 55.3 | 23.3 | 2.92 | [165] |
| EP | sCD-DBS-T-LDH | V0 | 26.8 | 65.8 | / | / | [166] |
| EP | 7 wt% fCD-SDBS-PA-LDH | V0 | 26.5 | 72.3 | / | / | [167] |
| EP | 6 wt%β-CD@P-MA | / | 26.8 | 51.2 | 28.5 | 2.51 | [168] |
| EP | 3 wt% β-CD/DBPDA | / | / | 22.9 | 7.4 | / | [169] |
| EP | 5 wt%β-CD@FE@HMS | V1 | 27.5 | 11.0 | 12.3 | 3.23 | [170] |
| EP | 20 wt%β-CD@RDP | V1 | 26.5 | 94.7 | 93.4 | 380.7 | [171] |
| PLA | APP/HP-β-CD fibre | V2 | 32.5 | 39.2 | 24.2 | 2.57 | [172] |
| PLA | APP/PSil-CD powder | V0 | 32.5 | 53.7 | 21.7 | 1.53 | [173] |
| PLA | 30 wt%PCD/APP | V0 | 42.6 | 56.3 | 83.6 | 10.9 | [174] |
| PLA | 10 wt%APP/BSDH | / | / | 49.3 | 49.4 | 3.58 | [175] |
| PP | MCDPM | V1 | 26.4 | / | / | / | [176] |
| PP | 25 wt%HDI-CD@APP | V0 | 30.9 | / | / | / | [177] |
| Jute/PP | β-CD/APP/MEL | / | 27.8 | 50.4 | −6.13 | 1.71 | [178] |
| WPC | MCAPP | / | 24.8 | 57.23 | 40.0 | 5.19 | [179] |
| PET | 19 wt%APA/6 wt%CD | / | 29.5 | 42.9 | −4.5 | / | [180] |
| PVA | β-CD/HDI | V0 | 41.7 | 77.7 | 51.5 | 17.5 | [181] |
| PVC | CD@MC-cube | / | 45.2 | 20.0 | 51.3 | / | [182] |
| PU | 15 wt% CD-$H_3PO_4$ | V0 | 24.5 | 23.0 | 70.4 | 51.38 | [183] |

Note: *Ferr* means ferrocene, *CDBS* means hydroxypropyl-sulfobutyl-beta-cyclodextrin sodium, *DBS* means dodecylbenzenesulfonate, *T* means taurine, *SDBS* means sodium dodecylbenzenesulfonate, *P-MA* means N, N′-diamyl-p-phenylphosphonicdiamide, *DBPDA* means N,N′-dibutyl-phosphatediamide, *β-CD@FE@HMS* means β-cyclodextrin@ferrocene@hollow mesoporous silica microspheres, *RDP* means resorcinol bisdiphenylphosphate, *PSil* means phosphorous silane, *PCD* means phenyl phosphonic acid dichloride (BPOD) modified CD, *BSDH* means integrating β-cyclodextrin, triazin ring, and nanohydroxyapatite, *MCDPM* means the compound of melamine, β-CD and Polymethyl triethoxysilane (PMTs), *MCAPP* means that polydiphenylmethane diisocyanate (PMDI) and β-Cyclodextrin (β-CD) crosslinking and microencapsulation of APP, and *MC-cube* means $MgCO_3$ with cube-like morphology.

the composite decreased significantly, from 931 kW/m² of pure EP to 318 kW/m². As a carbon forming agent in the system, cyclodextrin increases the carbon residue produced in the combustion process of the composite and plays a role in barrier protection. The carbon layer can isolate oxygen and heat transfer entry and better protect the matrix.

As shown in Fig. 9c, Hydroxypropyl-sulfobutyl-beta-cyclodextrin was functionalized by chalcone solution to obtain f-CD. Sodium dodecylbenzene sulfonate (SDBS) was used to expand the layer spacing of LDH, then f-CD and PA were intercalated into LDH [167]. Compared with traditional LDH/EP composites, f-CD-SDBS-PA-LDH/EP composites show a better flame retardant effect. 7 wt% functional flame retardants can increase the LOI of EP from 23% to 26.5%, significantly reduce the pHRR by 72%. At the same time, the residual carbon in the system increases significantly, which shows that the flame retardant plays a crucial role in the condensed phase. It promotes the dehydration and carbonization of the matrix and isolates oxygen to stop the continuation of combustion.

As shown in Fig. 9d, $Fe_3O_4$ nanoparticles modified LDH, then functionalized with hydroxypropyl sulfobutyl-Sodium cyclodextrin (CDBS)and PA [165]. EP's flame retardant performance was improved using the obtained LDH nanohybrid material. The LDH nanohybrid material obtained was used to improve EP's flame retardant performance. The LOI of 8 wt% $Fe_3O_4$@PA-CDBS-LDH/EP composites can reach 26.8%, and UL-94 can get V-0. Compared with pure EP materials, the pHRR of composites added with flame retardant decreased from 919 kW/m² to 411 kW/m².

As shown in Fig. 9e, green and environmental friendly intumescent flame retardant (MCDPM) was prepared by phosphorylation of cyclodextrin and reaction with MEL [176]. Adding 30 wt% MCDPM to PP can increase the LOI of the composite from 17% to 26.4%. Phosphorylated cyclodextrin was esterified to form a protective matrix with cross-linked carbon residue groups. Therefore, MCDPM has a good flame retardant effect and can better protect the EP matrix.

Cyclodextrin has a particular hollow structure, which can be used as a flame retardant loading and slow-release agent. In the above, we also found that cyclodextrins can form complexes through host-guest recognition when intercalating LDH. Similarly, cyclodextrins can also be directly prepared by complex to obtain new flame retardants. In addition to the above-mentioned ferrocene [163] and Chalcone [167], common guest molecules also include N,N′-diacyl-p-phenylphosphonamide, N, N′-dibutyl phosphate diamine and $C_{60}$.

As shown in Fig. 9f, cyclodextrins are often used as crosslinking components because of their polyhydroxy nature. It acts as a carbon source in the intumescent flame retardant system. For example, Wang et al. [179] coated β-CD on the surface of APP. Then polydiphenylmethane diisocyanate (PMDI) is crosslinked with β-CD, which is worthy of a new microencapsulated APP flame retardant (MCAPP). Flame retardant PP composites were prepared by mixing MCAPP with wood flour and PP (WPC). The LOI value of WPC/30 wt% MCAPP was 24.8%, and the pHRR value of the composite decreased significantly. At 700 °C, the residual carbon content of WPC/MCAPP composites increased significantly from 9.8% of WPC to 34.8%. In MCAPP, β-CD as a carbon source decomposes at high temperatures, and the catalytic system generates a stable carbon layer. The carbon layer insulates oxygen and heat to achieve the purpose of flame retardant. At the same time, APP produces non-combustible gases such as $NH_3$ and $H_2O$ during pyrolysis to prevent combustion.

As shown in Fig. 9g, Wang's team [168] prepared a β-CD inclusion complex (IC) with N,N′-diacyl-p-phenylphosphonamide (P-MA). It was proved, by characterization experiments, that the molar ratio of β-CD/P-MA in the inclusion complex was 2:1. It was found that the carbonization ability of IC is significantly superior to the simple blending of PM. The combustion performance of epoxy resin of IC and PM was compared. When the addition amount of flame retardant was 6%, the LOI value of EP/PM was 25.5%, and EP/IC was 26.8%. Compared with EP, the pHRR of 6 wt% EP/IC is 51% lower than EP.
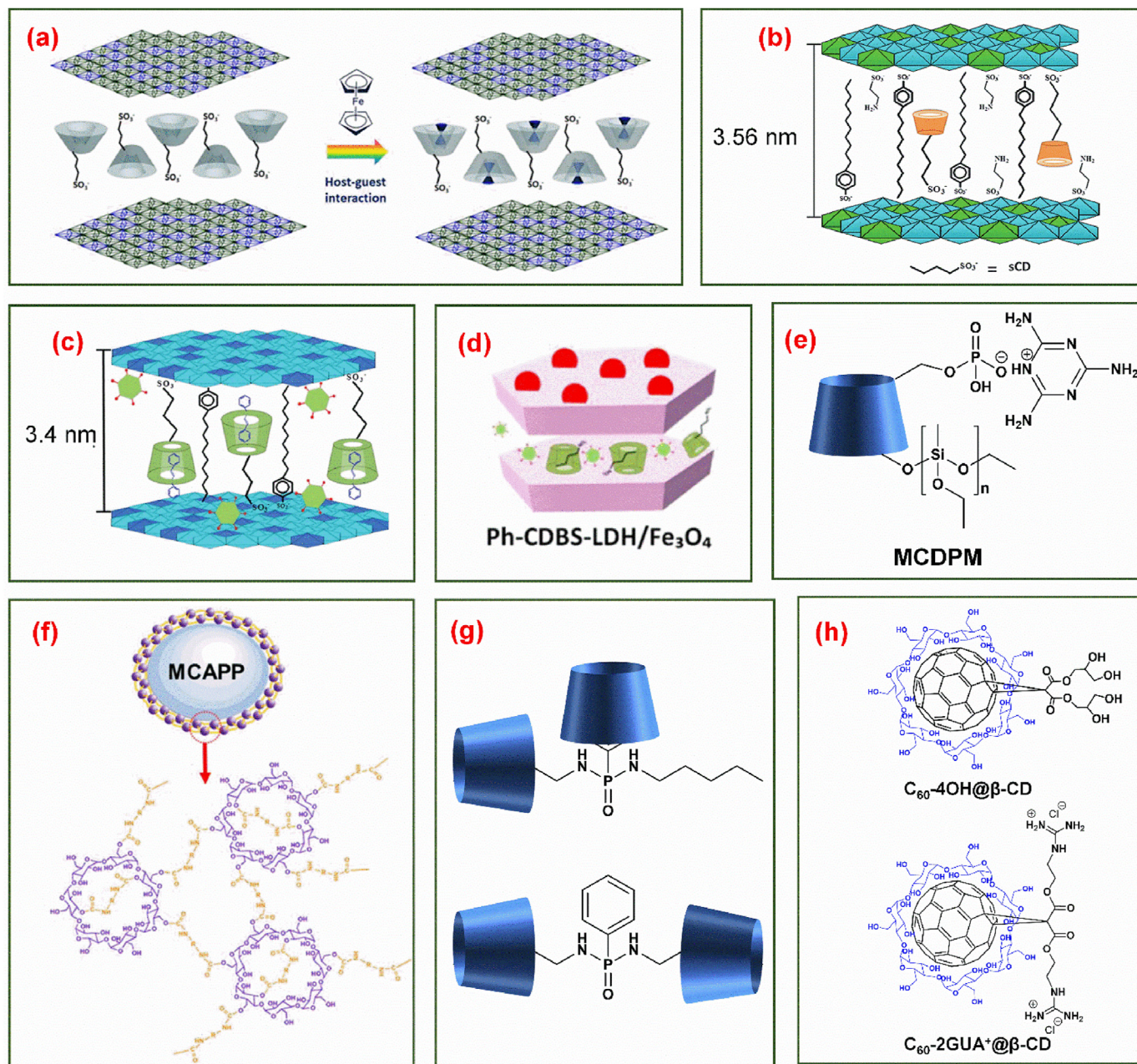
**Fig. 9.** (a) Schematic illustration of precipitation and host-guest interaction (Adapted permission from Ref. [163], Copyright (2019) Elsevier). (b) Schematic diagram of anions structure intercalated in the functionalized LDH by one-step synthesis method (Adapted permission from Ref. [166], Copyright (2015) Royal Society of Chemistry). (c) Schematic diagram of the anion structure and intercalated functionalized LDHs (f-CD-Ph-DBS-LDH) by the one-step synthesis method (Adapted permission from Ref. [167], Copyright (2016) Royal Society of Chemistry). (d) Preparation process of Fe3O4@Ph-CDBS-LDH hybrid (Adapted permission from Ref. [165], Copyright (2016) ACS Publications). (e) Preparation and modification process of MCDPM (Redrawn from reference Copyright [176] (2020) Springer). (f) Formation process of MCAPP (Adapted permission from Ref. [179], Copyright (2015) Wiley). (g) *N, N′*-diamyl-p-phenylphosphonicdiamide/CD complex [168], and (h) The complex structure of $C_{60}$-2GUA$^+$-β-CD and $C_{60}$−4OH-β-CD [184].

The β-CD and *N, N′*-dibutyl phosphate diamide (DBPDA) are mixed at a molar ratio of 1:1, and the obtained inclusion compound is used to increase the flame retardant properties of EP [169]. When only 3 wt% IC is added to EP, the carbon residue rate reaches 38.5%. Compared with pure EP, the residual carbon increased by 23.1%, and the pHRR value of the composite material decreased by 22.9%. The amount of smoke emitted while burning the material is also significantly reduced. The flame retardant performance of EP composites with inclusion compound is significantly better than that of DBPDDA, β-CD and EP composite materials.

As well reported and shown in Fig. 9h, CD has the function of catalytic carbonization. $C_{60}$ is reported to be a free radical sponge, and it is widely used as flame retardant. Therefore, we believe that the complexes obtained by combining the $C_{60}$ and CD will also be a kind of effective flame-retardant additive [184].

The flame retardant mechanism of cyclodextrin is mainly due to its polyhydroxy structure. Cyclodextrin will be dehydrated and carbonized during combustion to produce a large amount of carbon residue. The more stable and compact the carbon layer, the better the matrix protection. As a physical barrier, the carbon layer

effectively insulates the transmission of oxygen and heat and plays an essential role in the flame retardance of the condensed phase.

### 2.7. Other bio-based flame retardants

In addition to the above-mentioned several mainstream biomass flame retardants, other bio-based flame retardants, including starch, sodium alginate, protein, etc., also attract the researchers' attention. Here, we briefly show some typical research progress and applications by taking starch, sodium alginate and its derivatives, DNA, etc., as examples.

Starch is a common biopolymer material with low cost, easy degradation and renewable advantages. It is widely used in food, clothing and other fields, and its application in the field of flame retardants has also received great attention [185]. For example, Yue et al. [186] used esterified starch as an interface modifier for surface treatment of cassava residue. The flame-retardant polybutylene succinate (PBS)/cassava residue fibre composite material uses flame-retardant treated fibres to prepare IFR. When the flame retardant content is 30 wt% m (cassava residue): m (IFR) = 1:5, the composite material's tensile strength and impact strength are increased by 40% and 62%, respectively. In addition, the LOI of composite materials is 37.3%, and UL-94 reaches the V0 level. During combustion, the three-dimensional carbonized layer formed by the flame retardant and the combustion product of PBS plays a supporting role.

Oxidized starch (OS) and APP are added to PLA to prepare PLA/OS/APP composites [187]. The addition amount of APP in the flame retardant system is 10 wt%, and the addition amount of OS is changed to test the flame retardant performance of the composite material. Compared with pure PLA, the pHRR of PLA composites with 7 wt% OS was reduced by 51.88%. The PLA matrix is protected by the carbon layer produced by combustion.

Qu et al. [188] synthesized hydrolyzed starch phosphonic acid melamine (HSPM) and found a good flame retardant effect on PU. After adding 30 wt% HSPM, the LOI value of PU increases to 29.0%, and the flame retardant grade reaches V-0. HSPM will produce a large amount of carbon residue during the combustion process to form a protective layer to avoid the combustion of the substrate. At the same time, combustion will produce a certain amount of incombustible gas, and diluted oxygen prevents the combustion from proceeding. It is found that the thermal degradation performance of starch phosphate carbamate (SPC) is affected by the degree of substitution (DS) [189]. As the DS of SPC increases, SPC forms more phosphates in the condensed phase during combustion, which increases the degree of carbonization of the matrix.

As an edible product, sodium alginate has been widely used due to its green environmental protection and flame retardant performance. Liu [190] constructed a polysaccharide-based flame retardant coating (WSC-SA-Cu) composed of water-soluble chitosan (WSC) sodium alginate (SA) and copper ion on polyester fabric by LBL. Using microscale combustion calorimetry, the unmodified sample's HRR value and THR can be measured at 343.31 w/g and 46.11 kJ/g, respectively. The samples containing 16 WSC-SA-Cu (II) layers were 214.29 w/g and 38.49 kJ/g. The limiting oxygen index WSC-SA-Cu (II) of the sample is better than that of the unmodified sample. The vertical combustion reflects the self-extinguishing phenomenon of the sample containing WSC-SA-Cu (II) in 35 s. The self-extinguishing time is inversely proportional to the number of sample layers. The addition of flame retardant significantly improves the flame retardancy of polyester fabric.

The gel method prepared a new type of flame retardant material of zinc alginate (ZA) and nano cuprous oxide ($Cu_2O$) [191]. The flame retardancy of ZA-$Cu_2O$ is significantly enhanced than that of ZA. The LOI value ZA increased from 49% to 58%. The pHRR of the composite flame retardant material is reduced by 48.8%. $Cu_2O$ will promote the carbon formation of the matrix during the combustion process, forming a denser carbon protective layer, so the flame retardant performance is better. Add alginate to cotton fibre [192]. The addition of seaweed salt fibre significantly improves the flame retardancy and high-temperature thermal degradation properties of cotton fibre. The THR, pHRR, TSP and combustible volatiles release of cotton/alginate fibre is significantly reduced.

Zhang [193] proposed a simple and environmentally friendly synthesis method to prepare calcium alginate/silver chloride (CA/AgCl) nanocomposites with excellent flame retardant properties. The results show that the LOI of CA/AgCl (60%) nanocomposites is higher than CA (48%), reaching the V-0 level in the UL-94 test. Compared with CA, the TSR of CA/AgCl is reduced by 91%. It shows particularly effective smoke suppression properties. IFR is prepared from phosphorylated sodium alginate, APP and pentaerythritol [194]. IFR-PP composite material is formed by melt blending. The pHRR of the pure PP sample is 782 kW/m$^2$, and the pHRR of the IFR-PP composite is 335 kW/m$^2$.

DNA is a biomacromolecule consisting of phosphoric acid, pentacarbonyl, and nitrogen-containing bases [195]. Suryaprabha et al. [196] used DNA, silver nitrate ($AgNO_3$) and octadecyltriethoxysilane (ODTS) as raw materials to enhance the flame retardant superhydrophobic coating on cotton fabric that was successfully prepared by the solution impregnation method. Fabrics not coated with flame retardant will burn rapidly within 5 s. The flame retardant superhydrophobic cotton fabric began to burn slowly after removing the fire source and gradually extinguished itself. The deposition of DNA on cotton fabric increases the thermal stability of cotton fabric and reduces the propagation speed of flame. Carosio et al. [197] painted DNA on the PET foam. Compared with APP coated PET composites, DNA/PET materials can effectively inhibit the generation of droplets. Compared with pure PET samples, the pHRR value of DNA/PET composites decreased by 25%. Wang [198] prepared flame retardant microspheres with excellent thermal stability by reacting DNA monomer nucleotide with melamine-formaldehyde resin and used them in PP/IFR system. It was found that the addition of IFR can be reduced by more than 30% by adding 1 wt% microsphere.

Moreover, a new type of environmentally friendly bio-based flame retardant was prepared using the wheat straw (WS), and silica microencapsulated APP (OS-MCAPP) as raw materials [199]. This bio-based flame retardant is added to PP to prepare a flame-retardant composite material. When the content of OS-MCAPP is 20 wt% and WS: PP = 3:1, the oxygen index of the composite material reaches 28.5%. Compared with pure PP, the pHRR of PP composite material is reduced by 81%, and the THR value is reduced by 61.2%. The flame retardant will produce incombustible gas to dilute the oxygen during the combustion process and prevent the combustion from achieving the flame retardant effect.

### 3. Summary and perspective

With the objective of developing green and environmentally friendly bio-based flame retardants, researchers have invested significant efforts as described along this work. Obviously, plenty of achievements with high academic insights and industrial potential have been obtained. Since most bio-based materials have a low flame retardant effect, they need to be combined with other substances leading to further modifications. At present, the basic modification method of bio-based flame retardant materials is to introduce flame retardant elements, such as nitrogen, phosphorus, silicon, etc., into bio-based molecules. Nevertheless, the development of bio-based flame retardants still faces many challenges:

(1) Due to the low flame retardant efficiency of bio-based flame retardants, high amount of them usually is needed in order to reach satisfied flame retardancy. However, high loading of the additives may greatly affect the mechanical properties. What's more, the thermal stability of bio-based flame retardant is relatively low and the char residual in the combustion is not stable enough.

(2) There are still some barriers to the industrialization of bio-based flame retardants due to some still not matured techniques.

(3) The high cost and complex fabrication process. Various components increase uncertainty and direct or potential costs for industrial applications.

Therefore, these challenges above have to be considered in some investigations on bio-based flame retardants in the future. Although the development of bio-based flame retardants still faces many challenges, this is still a promising and sustainable approach in real industrial applications. Besides, some research lines relevant to bio-based flame retardants should be further developed, as exposed:

(1) Open source. With the in-depth research of bio-based materials and the continuous progress of extraction technology, more novel and diverse bio-based materials that can be used as flame retardants should be explored. At the same time, it can also focus on the comprehensive utilization of biomass waste resources, broaden the raw material sources of bio-based flame retardants, and prepare high-efficiency, green and low-cost bio-based flame retardants.

(2) Deep development. Further functionalization of bio-based flame retardants, such as the introduction of multifunctionally chemical groups to molecules. A modification of this kind may improve the flame retardancy of the bio-based flame retardants, enhancing their compatibility with polymer matrix and bring new functions to the polymers.

(3) Low-cost sustainable flame retardants exploration. Seek green processes (such as green solvent, solvent-free, simplified procedures) for production attempts and actively seek cost-effective research. At the same time, it can be combined with new energy and other fields to create a comprehensive, sustainable, safe, high-tech field.

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## 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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