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Recent developments in fire retardancy of polybutylene succinate

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Abstract

Owing to the strong public concerns about environmental protection and potential energy crisis (fossil fuels), there is a global trend of substitution of petrochemical-based polymers towards biopolymers. Polybutylene succinate (PBS), as an emerging biobased and biodegradable polymer, has drawn a great deal of interest in a number of fields. However, high flammability of PBS constitutes a major obstacle for its potential application. In this study, based on the available literature, the approaches used for the flame retardancy of PBS are systematically reviewed. Those approaches include inorganic (nano)particles, lignin, and intumescent flame retardant systems. This comprehensive review aims to outline the recent research advances in the field of flame retardancy of PBS, focusing on the preparation, properties, and mechanisms. Finally, a brief summary and perspective in flame retarding PBS is also given, which may be able to inspire the development of future research and application.

Keywords : polybutylene succinate; fire retardancy; intumescence; flame retardant

1. Introduction

The growing social and environmental concerns on the disadvantages of petrochemical-based polymers promote the rapid development of biopolymers [1, 2]. According to the report from the BCC Research (2019), the global market for bioplastics is predicted to increase from 1.6 million metric tons in 2018, to 2.7 million metric tons by 2023 [3]. Over the last decades, commercially available biopolymers have shown desirable potential as promising alternatives to partially substitute petrochemical-based plastics in a wide range of fields such as packaging, agricultural, biomedical, automotive, and electronic applications [4-8]. As an obvious evidence, it can be seen from Figure 1a that the number of published scientific papers involving biopolymer and biocomposite climbed by 271% for the period of 2009-2019.

As one of the few biopolymers (Figure 1b) that can be produced by renewable sources (biobased) and that are biodegradable, polybutylene succinate (PBS) has attracted considerable attention of researchers and engineers in various end-use applications, including bio-packaging [9, 10], tissue engineering [11-13], and medical materials [14, 15], due to the high processability [16, 17], good mechanical properties [18, 19], and thermal properties [20, 21]. The melting point of PBS is around 110 to 115 ºC, similar to that of low-density polyethylene (LDPE, 105 to 115 ºC) [22]. The tensile yield strength of unoriented PBS can achieve up to 30-35 MPa, which is comparable to that of polypropylene (PP, 19-45 MPa, average value is around 32.7 MPa) [23]. Besides, PBS is flexible and the Young's modulus of PBS can be varied in a wide range of 300-500 MPa, depending on the degree of crystallinity [23]. As a result, PBS, appeared as an appropriate candidate for replacing petrochemistry-based plastics, has displayed enormous potential in many sectors such as furnishing construction, automotive components, electrical and electronics (E&E), and transport industry [24-27], in which high flame retardancy are required.

However, it should be noted that the limiting oxygen index (LOI) of neat PBS is as low as 21-24 [28, 29], thus its high flammability restricts greatly its application.

Even though a rapidly increasing interest in PBS can be observed in Figure 1, to our knowledge, there are very few available works devoted to the flame retardancy of PBS. It can be reliably speculated that with the increasing applications of PBS, flame retardancy of PBS will play an essential role in its demand. Hence, it is timely to organize the review of the recent developments in flame retardancy of PBS. The focus of this work is primarily on the research progress of flame-retardant PBS system, it includes not only the synthesis, treatment, and formulation of flame retardants, but also the thermal properties, fire performances, and flame-retardant mechanisms of PBS composites. Besides, a brief summary and perspective in flame retarding PBS is also provided.

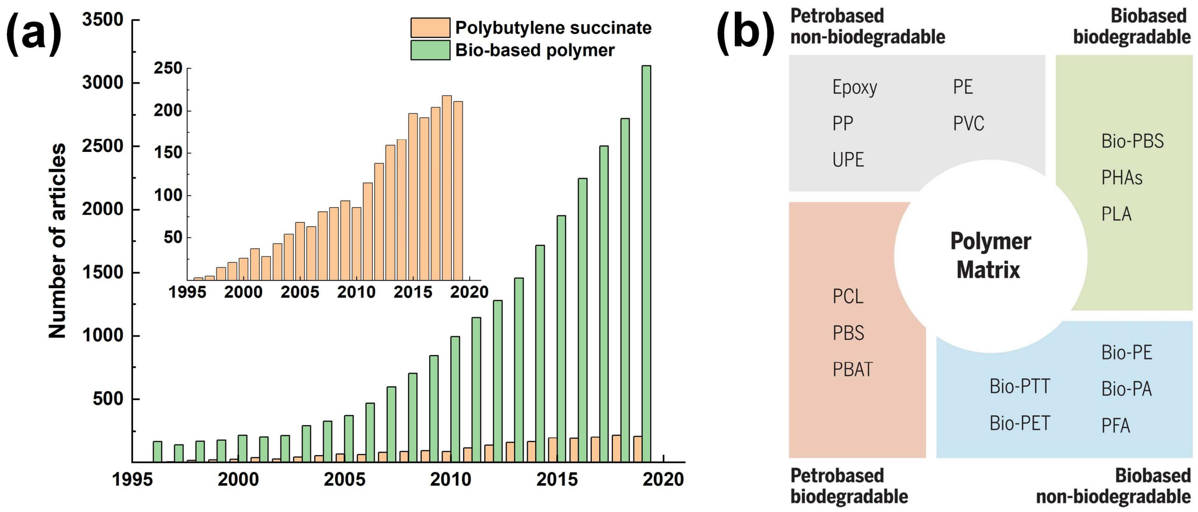

Figure 1. (a) Evolution of publications devoted to biopolymer/biocomposite and PBS from 1996 to 2019 (Web of Science database with the keywords ‘polybutylene succinate OR poly(butylene succinate)’ for PBS and ‘biopolymer OR bio-based polymer OR biocomposite OR bio-based composite’ for biopolymer/biocomposite) ; (b)Matrix polymers for composites [1].

2. Flame retardance: fire behaviors, mechanisms, and characterizations

2.1 Fire behaviors of polymer during combustion

It is well known that the combustion of polymer is highly complex coupling gas and condensed phase phenomena, and the phenomena in each phase consist of intricate physical and chemical behaviors with heat and mass transfer processes [30]. Based on the fire behaviors, several reaction zones can be identified as underneath polymer, pyrolysis zone, charring layer, and burning zone [31]. Here, a schematic model of fire behaviors of polymer combustion has been illustrated in Figure 2. In the pyrolysis zone, the radiation, conduction, and convection heat feedback from the flame lead to the surface regression and endothermal decomposition of polymer, resulting in the formation of pyrolysis volatiles [32]. The flammable pyrolysis products subsequently are released into flame zone through char layer and sustain the combustion.

For the burning zone, the combustion can be supported by the evolving combustible volatiles formed from pyrolysis zone as fuel into the fire via the radical branching reaction in the presence of air or oxygen [33]. Meanwhile, the resulting combustion products, such as nonflammable gases and solid soot (smoke), are released into the gas phase [34]. During the degradation and burning process, heavier species undergo further oxidation and crosslinked reactions and eventually may remain to form a char layer, in which the significant condensed-phase chemistry occurs [35]. The char layer, known as the most critical zone, plays a vital role in the fire behaviors of polymer, because it may be able to serve as a heat shield for underneath polymer by increasing surface radiation losses and limiting the transfer of mass and heat between pyrolysis zone and burning zone [36].

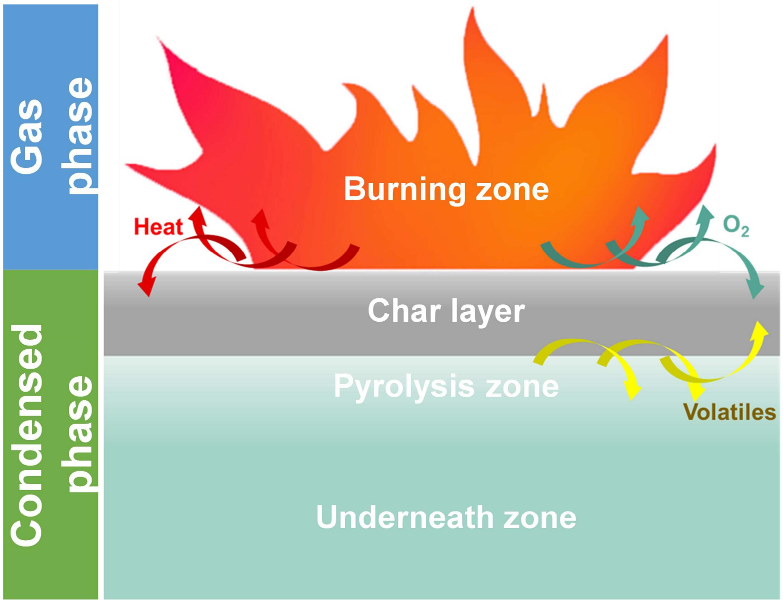

Figure 2. Chemical and physical behaviors of polymer combustion.

2.2 Flame retardant mechanisms

The fire behavior of flame-retardant polymer material is mainly governed by the interactions between polymer matrix and flame retardant (or flame-retardant group). These flame retardants can act via gas-phase mechanism and/or condensed-phase mechanism. A predominantly gas-phase mechanism of FR involves the absorption of active radicals by quenching the chain branching reactions. As a well-known example, halogen atoms, particularly Br• and Cl•, can be released as flame inhibitors into fire to inhibit the oxidation chain reaction of highly reactive species (H•, OH•) based on the scission of carbon-halogen bond [37]. However, the use of halogen-based FR may cause potential environmental risks and unavoidable public health threats due to the generation of toxic byproducts during burning process [38, 39]. An alternative approach is to introduce suitable phosphorus-containing compound as flame inhibitor into polymer, because phosphorus can promote the recombination of hydrogen and scavenge oxygen radicals [40]. On the other hand, the release of nonflammable gases can also be classified as gas-phase flame retardant mechanism because it dilutes the concentration of reactive radicals and fuel.

Benefiting from the incorporation of flame retardant, the condensed-phase mechanism can be achieved by forming a protective barrier (i.e., char layer). The homogeneous carbonaceous char acts as physical barrier to limit the transfer of heat and mass between the flame and underlying polymer and retards the decomposition of underlying polymer during combustion process. A typical example is the use of intumescent flame retardant (IFR) system, which results in the formation of highly foamed carbonaceous layer, contributing to the insulation of the substrate [41-43]. It has been pointed out that both high char yield and char quality are crucial to the condensed-phase mechanism of polymer during combustion [44]. In detail, high char yield means the forming of more nonflammable residues, accumulating on the surface of underneath polymer and acting as a physical barrier. Meanwhile, the high char quality can be obtained by improving the morphology and composition of the char. Generally, a continuous, compact, and homogeneous char exhibits higher efficiency. Besides, in terms of composition of char, the incorporation of non-flammable elements (e.g., P, Si, S, B) and/or inorganic synergists (e.g., zeolites, clay) into char structure chemically and physically reinforces the thermal stability and insulation of ceramic-like char.

2.3 Characterization methods of fire retardancy

Small scale fire tests can simulate a realistic and individual fire scenario to verify whether a certain protective goal is reached based on the applied standard or regulation [45]. Very commonly used tests to characterize the reaction to fire of polymers include the limiting oxygen index (LOI), the UL-94 vertical burning test, cone calorimetry, and microscale combustion calorimetry (MCC, also known as the pyrolysis combustion flow calorimetry (PCFC)).

The LOI test, standardized as ASTM D2863 or ISO 4589, is a frequently-used tool to assess the flammability of polymers. The LOI value determines the minimum oxygen concentration in the flowing oxygen/nitrogen mix that supports sustained burning of the specimen for 3 min or for the consumption of 5 cm of the sample length. In general, the higher the LOI value (or the higher the oxygen concentration required), the better the intrinsic flame retardancy of the material. Materials with the LOI value greater than 27% (also be identified as 28% [46, 47]) are conventionally regarded as self-extinguishing materials. Oppositely, materials with LOI lower than 21% signify highly combustible in air, and materials with a LOI value between 21% to 27% are defined as slow burning materials [48]. Interestingly, according to the work of Van Krevelen, an empirical equation (Eq. 1) has been developed to predict the LOI value of halogen-free polymeric material [49, 50]:

$$LOI \times 100 = 17.5 + 0.4CY \qquad (1)$$

where CY denotes the char yield in wt.% at 850 ℃. This equation have been extensively used to assess the thermal combustion properties of material occurred by the char formation via comparing the estimated and experimental LOI values [51].

On the basis of the standards of ASTM D3801, ISO 9773-1998, or IEC 60695-11-10, UL-94 vertical burning test evaluates the tendency of a material to extinguish or to spread the flame after removing the ignition source [52]. It measures the flame retardancy of polymers according to their vertical burning behavior as V-0, V-1, or V-2 grades. The specific combustion characteristics required for each grade have been summarized in Table 1 [31, 53]:

Table 1. Classification of materials for the UL94 Vertical burning test.

Criteria conditions	**V-0**	**V-1**	**V-2**
Afterflame time (t_1 or t_2) for each individual specimen	≤ 10 s	≤ 30s	≤ 30 s
Total afterflame time (t_1 plus t_2) for the 5 specimens	≤ 50 s	≤ 250 s	≤ 250 s

Afterflame plus afterglow time for each individual specimen after the second flame application (t_2 plus t_3)	≤ 30 s	≤ 60 s	≤ 60 s
Afterflame or afterglow of any specimen up to the holding clamp	NO	NO	NO
Cotton indicator ignited by flaming particles or drops	NO	NO	YES

Note: t_1 and t_2 represent the first and second afterflame time after removing the flame, and the time required for the fire glow to disappear is noted as the afterglow time t_3.

Cone calorimetry is one of the most powerful burning tests to characterize a developing fire scenario with a small-scale or bench-scale sample by measuring the intensity of flames (standardized as ASTM E1354 or ISO 5660) [54-56]. The fundamental of cone calorimetry is involved in the oxygen consumption in the combustion gases of a sample under a given heat flux. Noteworthy, cone calorimetry tests provide comprehensive insight into the fire properties of the material, such as heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), time to ignition (TTI, t_{ig}), total heat evolved (THE), mass loss rate, production of CO and CO_2, and total smoke released (TSR) [57]. Among the data gathered, HRR, PHRR, and TTI are regarded as the most important parameters to assess the fire performance of material [58]. Moreover, specific parameters can be calculated from cone calorimeter test results, such as the fire growth rate index (FIGRA), thermal response parameter (TRP), theoretical critical heat flux (CHF), and ignition temperature (T_{ig}).

FIGRA is defined as the maximum slope of the function of the HRR versus elapsed time [59, 60], which can be used to assess both the fire spread rate and the fire size [61]. The larger the FIGRA value, the faster the flame growth and spread. Moreover, a comprehensive assessment of the fire behavior was proposed by Petrella by plotting THE against PHRR/TTI [62]. The fire hazard can be decreased either by decreasing the THE, benefiting from the formation of char, or by decreasing the fire growth rate (PHRR/TTI) [63]. Interestingly, as mentioned by Schartel [63], gas phase and condensed phase mechanisms of flame retardant can be indicated clearly by plotting THE against total mass loss values during the time of flame out.[64] Regarding the FR mechanism, the release ratio of CO/CO_2 obtained from cone calorimeter cannot only be utilized to assess the toxicity hazard of a material [65], but also to demonstrate the gas phase mechanism of polymeric material [66].

Based on the cone calorimetry data, flame retardancy index (FRI) criterion (see Eq. 2) has been put into practice for quantifying the flame retardant performance of different polymeric materials [67, 68]:

$$FRI = \frac{\left[THR*(\frac{PHRR}{TTI})\right]_{Neat\ Polymer}}{\left[THR*(\frac{PHRR}{TTI})\right]_{composite}} \qquad (2)$$

Generally, the higher the FRI value, the better the flame retardancy of material. Here, Vahabi and coworkers classified the flame retardancy of materials into *"poor"* (FRI < 1), *"good"* ($1 <$ FRI < 10), and *"excellent"* (FRI > 10), respectively, according to the FRI values [67].

Significantly, TRP is one of the critical parameters to evaluate the decomposition and ignition resistances of material by reflecting the thermal response rate. The higher the TRP value, the more difficult for the material to be heated and ignited under the same radiation illumination. The TRP for thermally thick materials can be generally defined in Eq. 3 [69-71]:

$$TRP = \sqrt{\kappa\rho c}\left(T_{ig} - T_O\right) \qquad (3)$$

where $\kappa\rho c$ denotes thermal inertia of material (the thermal conductivity, κ, the density, ρ, and the specific heat, c), T_{ig} is ignition temperature, and T_O represents ambient temperature.

On the other hand, the ignition time (t_{ig}) of material for the high external radiation levels (more than 20 kW/m^2) can be expressed in Eq. 4 [72]:

$$t_{ig} = \frac{\pi}{4}\kappa\rho c\left(\frac{T_{ig} - T_o}{q''_e}\right)^2 \qquad (4)$$

where q''_e is external heat flux. According to the Eq. 3, Eq. 4 can be rewritten as Eq. 5 [73]:

$$t_{ig}^{-1/2} = \frac{1}{\sqrt{\frac{\pi}{4}\kappa\rho c}}\frac{q_e''}{T_{ig} - T_O} = \frac{1}{\sqrt{\frac{\pi}{4}}TRP}q_e'' \qquad (5)$$

Clearly, $t_{ig}^{-1/2}$ is a linear function of external heat flux, and the TRP value of material can be easily obtained by calculating the slope of this function.

It is known that the larger the CHF value (q_{cr}''), the higher the heat flux required to ignite the material. CHF can be calculated from the $t_{ig}^{-1/2}$ versus external heat flux plot as Eq. 6 [72, 74]:

$$q_{cr}'' = \frac{(q'')_{intercept}}{0.76} \qquad (6)$$

Besides, ignition temperature can be found via the Janssens approach as Eq. 7 [75, 76]:

$$CHF = h_c(T_{ig} - T_o) + \varepsilon\sigma(T_{ig}^4 - T_o^4) \qquad (7)$$

where σ refers to the Stefan-Boltzmann's constant (5.67×10^{-8} W/(m^{2}K^4)), ε is the emissivity, and h_c is the convective heat transfer coefficient, which can be expressed and calculated as follows from Eqs. 8 and 9:

$$h_c = 0.01198 + 3.74 \times 10^{-4}q_e'' \qquad if\ q_e'' < 50\ kW\ m^{-2} \qquad (8)$$

$$h_c = 0.025 + 6.5 \times 10^{-4}q_e'' \qquad if\ q_e'' \geq 50\ kW\ m^{-2} \qquad (9)$$

As a rapid flammability screening tool, MCC has been extensively utilized to evaluate the fire properties of polymers by collecting the precise heat release parameters such as the HRR, PHRR, and THR (standardized as ASTM D7309-13) [77-79]. The milligram-sized sample is pyrolyzed under an inert gas atmosphere at a controlled heating program in an inner pyrolyzer, and then the decomposition products were thermally oxidized in excess oxygen at 900 ºC in a combustor [80]. It has been found that the results from the MCC correlate well with those from the other fire tests, such as LOI, UL94, and cone calorimetry [81, 82]. Meanwhile, it is also worth noting that, as an obvious disadvantage of MCC, it fails to observe the phenomenon during combustion such as swelling (intumescence), shrinking, dripping, and quenching [83].

3. Thermal and bio degradation behaviors of PBS

The thermal degradation behavior of PBS is important for their processing, application, and thermal recycling [84, 85]. The degradation parameters (e.g., the onset mass loss temperature (at 2 or 5 wt.% mass loss), maximum mass loss temperature, and maximum mass loss rate) of PBS are highly relative to the heating rate (Figure 3), and its degradation kinetic has been largely studied by comparing the activation energy of degradation in each period of mass loss based on the Ozawa, Friedman, Coats-Redfern, and Horowitz-Metzger methods [84-87].

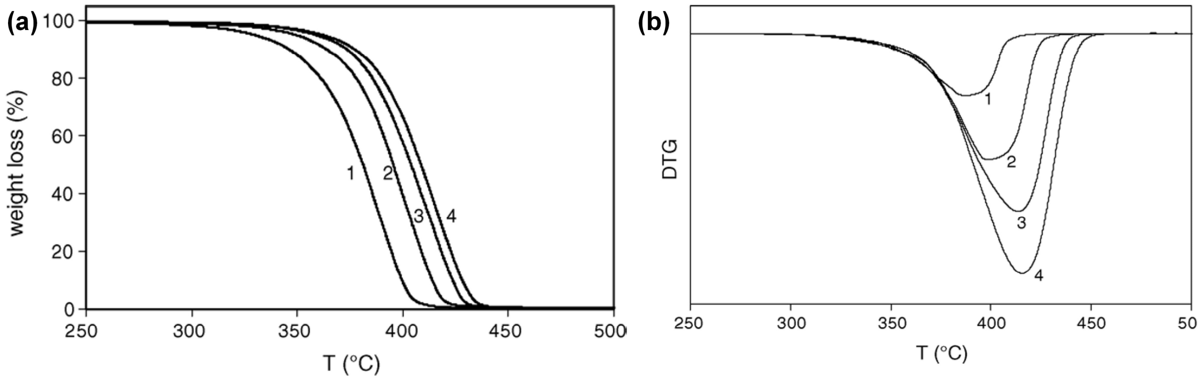

Figure 3. (a) TGA and (b) DTG curves of PBS at different heating rates: (1) 5 ºC/min; (2) 10 ºC/min; (3) 16 ºC/min; (4) 22 ºC/min [85].

Based on the previous papers [88-91], the major pyrolysis products of biodegradable polyesters are various ester compounds containing monomers and hybrid dimers. These compounds were produced mainly through the first-order reaction of random chain cleavage via *cis*-elimination. Besides, some cyclic compounds were found, which were likely yielded via intramolecular transesterification [92]. According to the work of Shih et. al. [86], it is clear that tetrahydrofuran, 1,4-butanediol, succinic anhydride, diallyl succinate, and dibutenyl succinate were found as the major pyrolysis products of PBS under lower pyrolysis temperatures (50-300 ºC). However, the major pyrolysis products of PBS became to diallyl succinate, dibutenyl succinate, 1,3-butadiene, and other cyclic succinates at higher pyrolysis temperature (550 ºC).

Figure 4 shows the detailed degradation mechanism of PBS [84, 89], the β-hydrogen next to the oxygen linkage of the ester transfers to the carbonyl oxygen of the succinate, leading to the selective cleavage of the -O-CH_2- bonds. This phenomenon results in the formation of two chains: (a) one of which has an alkenyl group, and (b) the other of which is a carboxylic acid end group. Further scission of the nearest β-hydrogen bond from the end of the chain with carboxylic acid yields succinic acid and alkenyl-terminated chain (*Path 1*). Then, the succinic anhydride is formed by the following dehydration reaction of succinic acid. Besides, after scission of the nearest β-hydrogen bond from the alkene terminated polymer chain, 1,4-butadiene and carboxylic acid terminated chains are produced (*Path 2*). Then, the carboxylic acid end of the chains may decompose to produce succinic anhydride (*Path 3 and 1*), or eliminate CO_2 to form acetate, which yield an acid molecule (*Path 4*). In addition, cyclic compounds can also be yielded through intramolecular transesterification (*Path 5*).

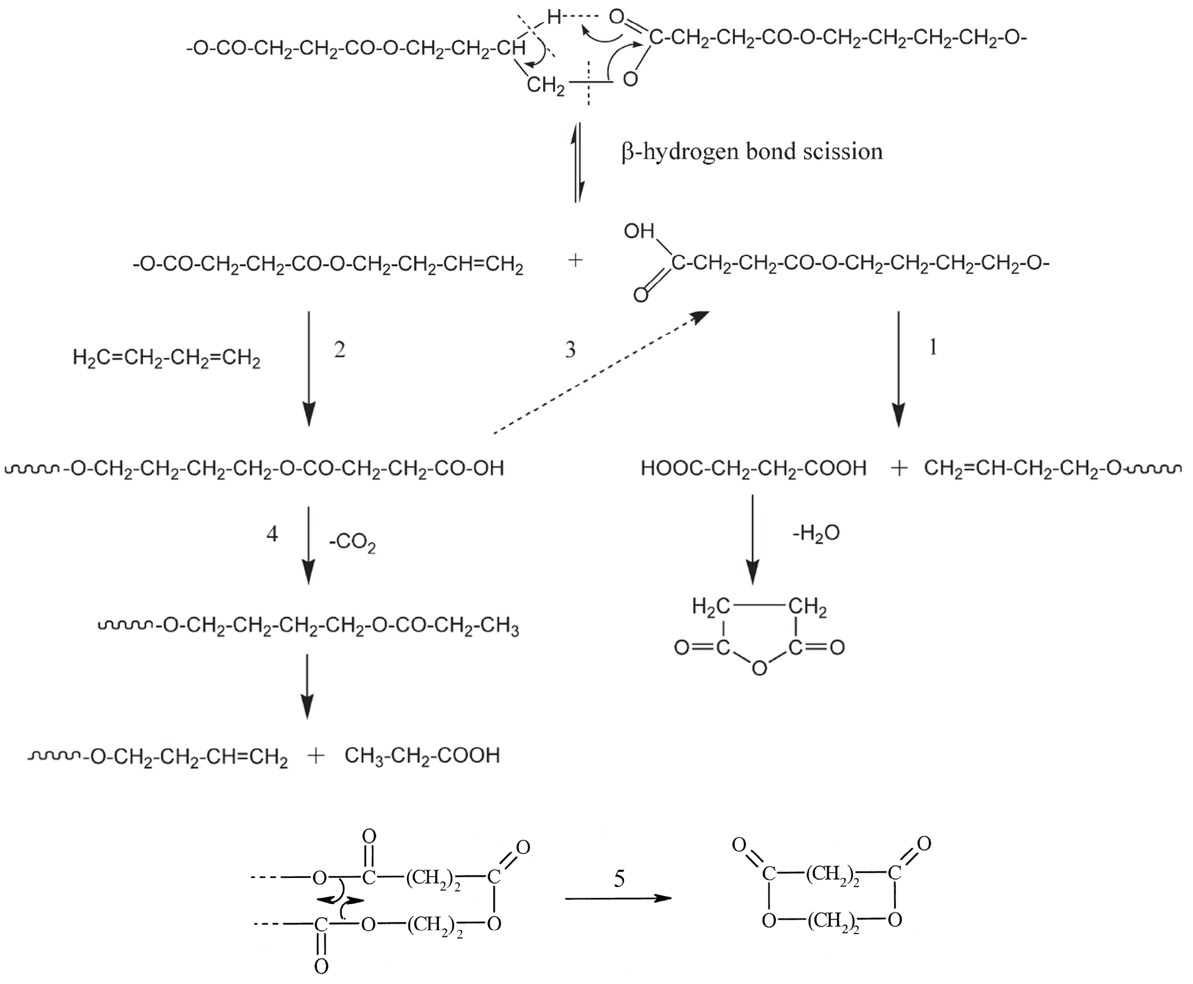

Figure 4. Thermal degradation routes of PBS [84, 89].

Compared to some common petrochemical-based polymers (e.g., PE and PP), PBS is a green and friendly environmental polymer matrix due to its well-known biodegradability [93-95]. The biodegradability of PBS has been evidenced in certain conditions (Figure 5) [96], such as in soil [97, 98], compost [99, 100], and liquid culture [101]. Indeed, some microorganisms (e.g., fusarium solani [98]) can degrade PBS by producing enzymes, which accelerate the decomposition of PBS [102].

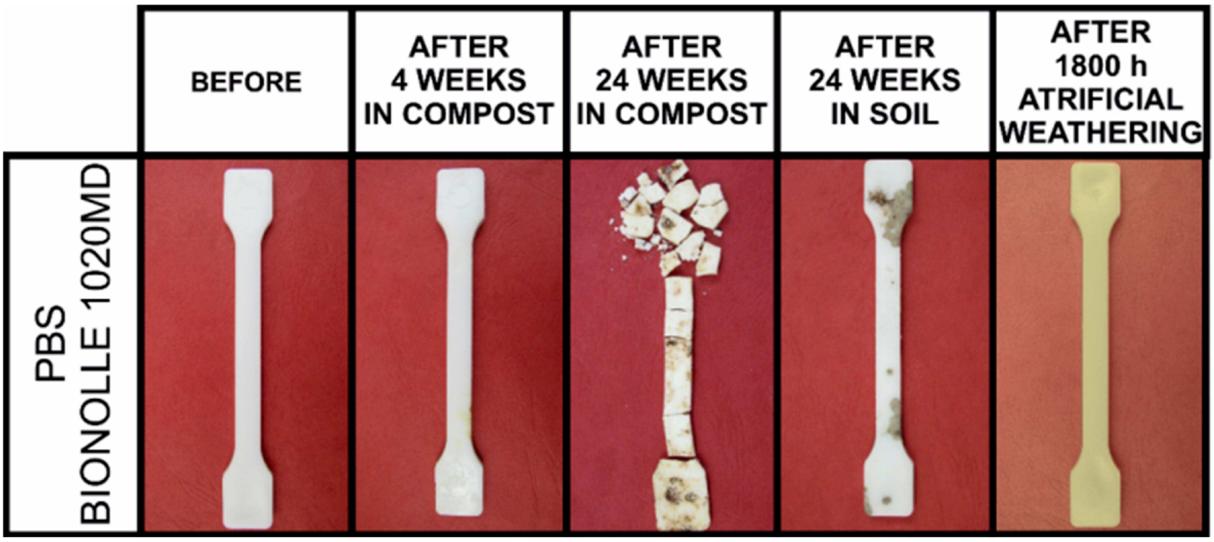

Figure 5. Photographs of the PBS before and after degradation [96].

The biodegradability of PBS is relative to the form and size of samples, the ambient environments, and the types of the microorganisms. As an example, Zhao and coworkers studied the biodegradability of PBS in compost (Figure 6a) [103]. After incubation for 90 days, the biodegradation percentages of PBS are 71.9%, 60.7%, and 14.1% for powder, film, and granule form samples, respectively, indicating that PBS with powder form presents the best biodegradability under compost condition.

Besides, four strains (i.e., aspergillus versicolor, penicillium, bacillus, and thermopolyspora (Figure 6 b-e)) obtained from the compost were investigated to identify the biodegradation abilities of the strains to decompose PBS. The results revealed that aspergillus versicolor was the best PBS-degrading strain in the compost.

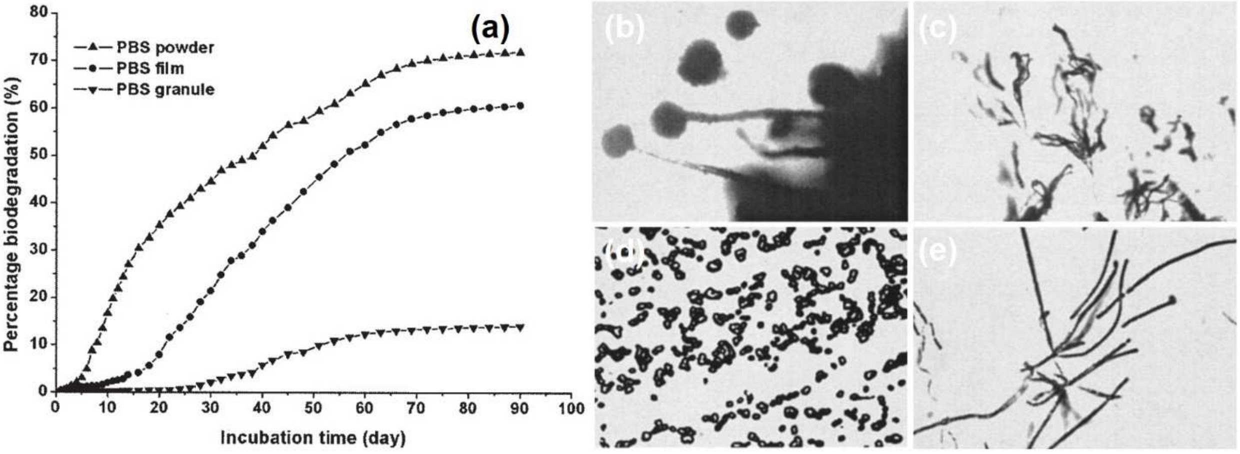

Figure 6. (a) Biodegradation of PBS samples with different forms under controlled composting conditions; and optical microscopic photographs of four strains isolated from compost : (b) aspergillus versicolor, (c) penicillium, (d) bacillus, and (e) thermopolyspora [103].

4. Flame retardancy of PBS

To tailor design the fire properties of PBS for extending its application, recent developments in different approaches used for the flame retardancy are demonstrated in this section, including inorganic (nano)particles, lignin, and intumescent flame retardant (IFR) systems.

4.1 Inorganic (nano)particles

Nowadays, inorganic nanoparticles are widely applied in the area of the flame retardancy of polymer due to the low loading, high dispersibility, good physical barrier effect, and catalytic charring performance [104-106]. The flame retardant mechanism involving nanoparticles is relative to its intrinsic properties and the interaction with the polymer matrix [36], including mainly: (a) the nanoparticles were gradually precipitated and accumulated on the surface during the gasification of the polymer and its pyrolysis products [30], (b) the nanoparticles were migrated or convected to the surface driven mainly by its lower interfacial free energy [107], and (c) nanoconfinement, the nanoparticles (e.g., nano clay) exerts spatial constraints on a polymer and its decomposition [108, 109]. A typical example is the application of nano-hydroxide (especially nano metallic hydroxides and layered double hydroxides (LDHs)), it has been reported that the presence of nanoparticles allows the improved fire performance of composite by endothermic decomposition [110, 111]. Besides, nanoparticles and/or its residues can also provide a confined and superheated site in which the trapped decomposing polymer chains obtain the possibility to undergo additional decomposition and crosslinking pathways, resulting in the formation of complex carbonaceous char network (catalytic charring effect) [53]. In addition, the migration and accumulation of nanoparticles (e.g., carbon nanotube (CNT), halloysite nanotube (HNT)) to the surface of char during combustion lead to the enhanced physical shield effect of ceramic-like carbonaceous layer [112]. Compared to halogenated flame retardant additives, nanoparticles are highly attractive because they cannot only improve the fire/smoke/toxicity performances but also simultaneously enhance the mechanical properties of polymer nanocomposite at a low addition [113].

It is worth noting that the flame-retardant properties of nanoparticles can be affected by its chemical composition, morphology, and loading. This section is a review about the flame retardancy of PBS composites using nanoparticles without any conventional flame retardant. Besides, the synergistic flame-retardant effect between nanoparticles and conventional flame retardants has been widely demonstrated based on the recent researches of fire-retardant PBS, which are illustrated in *section 4.3*.

In a detailed investigation about the flame retardancy of nanoparticles, melamine phosphate modified exfoliated molybdenum disulfide nanosheets (MP-MoS_2) were prepared and blended with PBS matrix [114]. It is obvious from Figure 7 that the presence of only 1 wt.% MP-MoS_2 nanosheets changed the thermal degradation and fire behaviors of PBS composite. The improved thermal stability and reduced flammability were probably ascribed to the physical reinforcement and catalytic charring effects of MP-MoS_2 nanosheets in PBS matrix based on the better dispersibility. Unfortunately, it can be seen from the MCC result (Figure 7b) that, with the addition of 1 wt.% MP-MoS_2, there is only a slight enhancement in flame retardancy of PBS composite in terms of PHRR value compared to that of neat PBS. Besides, other common fire tests, such as LOI and UL94 tests, are unavailable in this work.

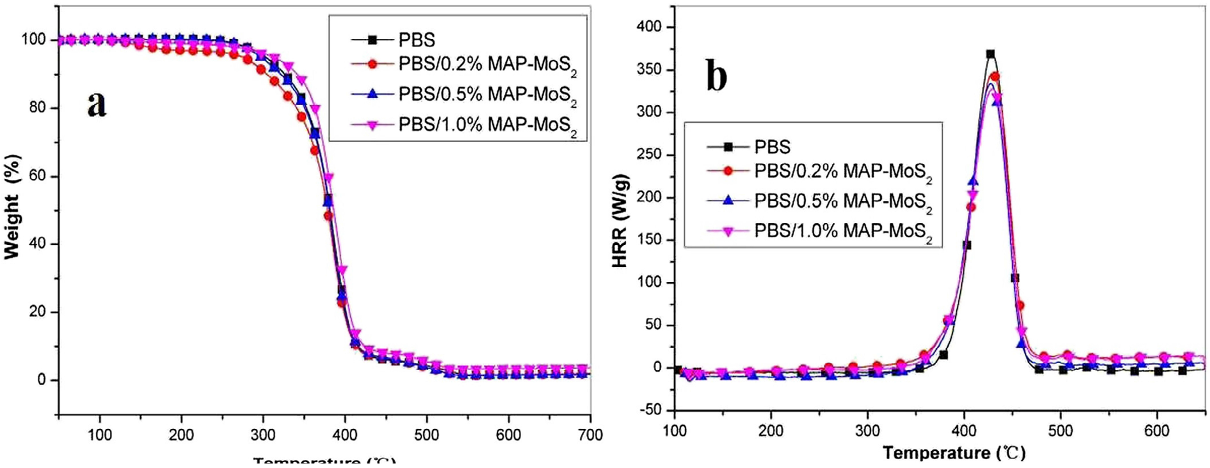

Figure 7. (a) TGA and (b) HRR curves of PBS composites based on TG and MCC tests [114].

Chen et al. studied the effect of nano carbon black (CB) on flame-retardant behaviors of PBS [115]. PBS/CB composites were prepared via melt compounding without using any additional FRs or organic surface treatment. It appears that the loading of CB affects markedly the flammability of PBS composites. Adding 10 wt.% of nano CB increased the LOI values to 28.5 % from 21.0 % for that of neat PBS. Unfortunately, the addition of CB into PBS did not bring significant improvement in the UL94 classification, indeed, all samples failed in the UL94 vertical burning test (3.2 mm) according to the burning time. However, the anti-dripping behavior can be observed in UL94 test when more than 1 wt.% CB was incorporated.

Regarding HRR curves of PBS/CB composites under the different loadings (Figure 8a), it can be found that the incorporation of 1 wt.% CB led to a slight drop in the PHRR of PBS/CB composites, while a 57% reduction was attained by the loading of 5 wt.% CB. Moreover, the

PHRR value for PBS/CB10% (10 wt.% loading) was decreased to 294 kW/m^2, which showed a reduction of 62% relative to the neat PBS (765 kW/m^2). The results suggested that a sufficient CB content is required to form a continuous and homogeneous residual char layer on the surface of sample (visual observation), which can significantly reduce the flammability of PBS composites. In addition, the THR curves showed a similar trend to that of HRR (Figure 8b).

Besides the type and loading of nanoparticle, there is evidence that the particle size of filler also plays a remarkable role on the flame retardancy of the polymer [116]. An example of enhanced fire performance was examined by studying the influence of three large-span particle sizes (20 μm, 5 μm, and 500 nm) of magnesium hydroxide (MDH) on the flammability properties of eco-friendly PBS composites (Figure 8c-d) [117]. To achieve V-0 rating (3.2 mm), the required loading for 20 μm MDH was as high as 60 wt.%, whereas for 5 μm and 500 nm particles sizes the loading was only 40 wt.%. These results demonstrated that the flame retardancy of 5 μm and 500 nm MDH on PBS was similar, and they exhibit higher efficiency than that of 20 μm MDH. Furtherly, cone calorimeter results suggested that 5 μm MDH permitted the optimal fire performance for PBS/MDH system based on the lowest PHRR and THR values (-85% and -54%, respectively). Unfortunately, the low flame-retardant efficiency and high addition of MDH cause the reduction of processability and mechanical performances of PBS. In another study, Chen et al. proposed expandable graphite (EG) as synergist to decrease the loading of MDH in PBS matrix [118]. The results presented that only co-addition of 5 wt.% EG and 20 wt.% MDH (500 nm) endowed PBS with excellent flame performances, including that the LOI value was as high as 29.4%, V-0 rating was achieved in the UL-94 test (3.2 mm), and a reduction in PHRR by 73%, which is comparable or even better than that of PBS/MDH40% composite (40 wt.% of MDH loading, LOI of 31.9%, UL94 V-0 grade, and a reduction in PHRR by 68%). More importantly, compared to PBS/MDH40% composite, PBS/MDH20%/EG5%

system displayed better thermal and mechanical properties, indicating the comprehensive improvement of PBS. Besides, it is worth noting that graphene was also studied as synergist in this work, however the flame-retardant efficiency was not good enough (for PBS/MDH20%/graphene5% composite, a LOI of 28.2%, a V-1 grade, and a reduction in PHRR by 62.5% were achieved, relative to that of neat PBS).

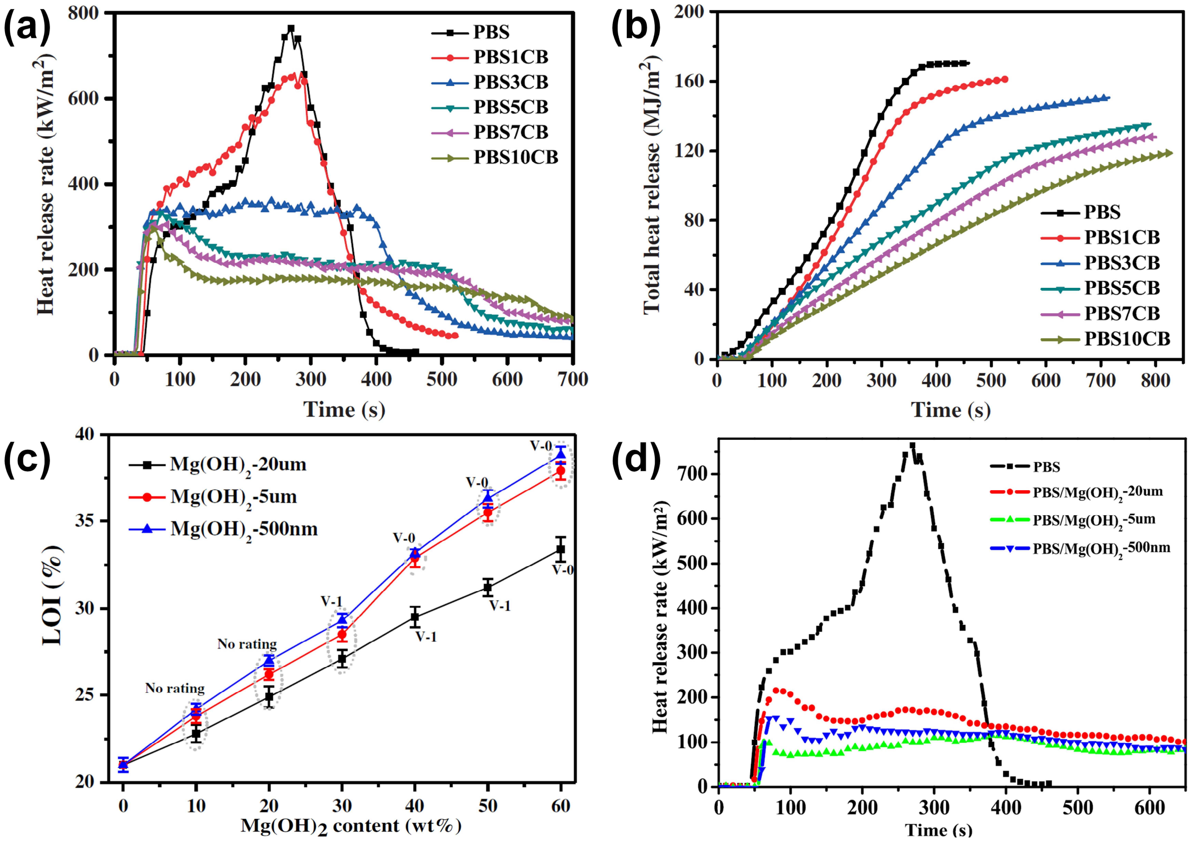

Figure 8. (a-b) HRR and THR curves of PBS/CB composites at a heat flux of 50 kW/m^2 [115]; (c) LOI, UL94 results and (d) HRR curves of PBS/MDH composites at the heat flux of 50 kW/m^2[117].

4.2 Lignin

As a potential sustainable green reinforcing filler and flame retardant for PBS, lignin has prompted a rapid progress over the last decades due to the impressive advantages such as high abundance, low weight, high carbon content, and rich reactive functional groups [119-122].

Noticeably, lignin is widely regarded as a waste by-product in biomass industry, and there are considerable efforts focus on the recycling and use of the lignin-containing waste materials in the field of flame retardant [123].

Eucommia residue (ER), a plantation waste containing rich lignin substances, was used directly to reinforce and flame retard PBS via melt-mixing method [124]. Compared to neat PBS, the tensile and flexural modulus of PBS/ER30% composite was improved by 87% and 72%, respectively. Meanwhile, addition of 30 wt.% ER led to 43% and 29% reduction in PHRR and THR, respectively, due to the formation of more char, exerting a fire barrier effect.

Furthermore, considerable improvement in flame retardancy of lignin can be obtained through its chemical functionalization. An effective approach in enhancing the flame-retardant effect of lignin is to introduce potential flame-retardant elements (e.g., nitrogen, silicon, and phosphorus) into the molecular structure of lignin.[125-127] The incorporation of those elements can benefit to improving the thermal stability and charring ability of lignin [121].

In our opinion, incorporation of small molecular flame retardant compound into lignin is a commonly used method to obtain lignin-based flame retardant. In the work of Chen et al. [128], a halogen-free lignin-based flame retardant (CP-lignin) was synthesized (Figure 9a), and then blended with PBS to improve the biodegradation and fire performance of PBS. The addition of CP-lignin into PBS led to an increase of the main degradation step, promoting the formation of char. As shown in Figure 9b-c, the cone calorimeter results illustrated that, when 30 wt.% of untreated lignin was added, there were only reduction of 16% and 27% of PHRR and THR, respectively, whereas for PBS/CP-lignin30% composite, the PHRR and THR value were diminished significantly by 27% and 31%, respectively, implying the improvement of fire retardancy of PBS composite. Interestingly, the residual char yield of PBS/lignin30% composite was only 2.6 wt.%, however, after incorporating 30 wt.% CP-lignin into PBS, the char yield of

PBS/CP-lignin30% obviously increased to 9.6 wt.%, which means that CP-lignin can effectively catalyze the formation of char.

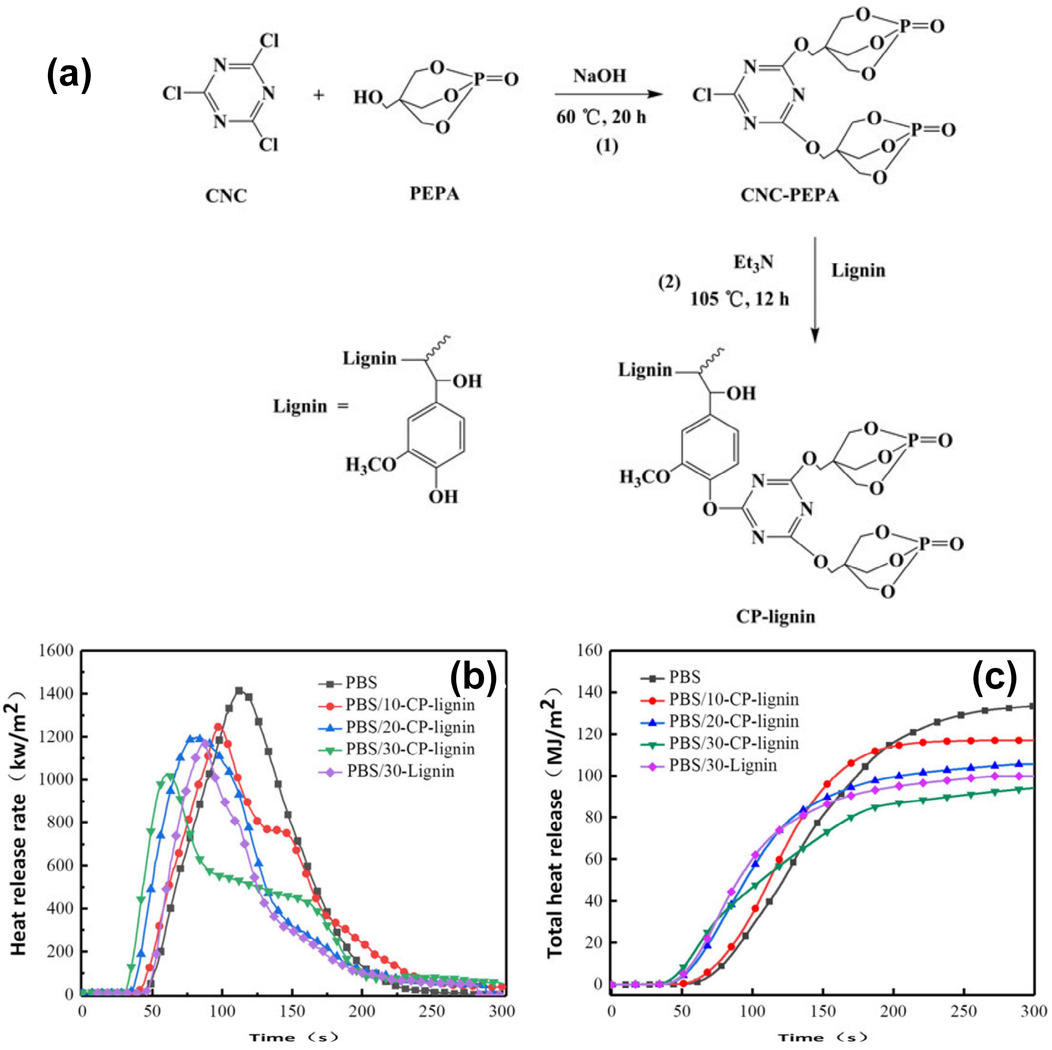

Figure 9. (a) synthesis route of CP-lignin; (b-c) HRR and THR curves of PBS/CP-lignin composites at a heat flux of 50 kW/m^2 [128].

Some articles from the literature reported the chemical modification of lignin by incorporating phosphorus-containing macromolecules into lignin structure. A macromolecule-modified lignin (PNZn-lignin, Figure 10a) was fabricated and blended with PBS via melt compounding [119]. It can be observed from cone calorimeter results (Figure 10b-c) that the addition of 10 wt.% PNZn-lignin diminished noticeably the PHRR and THR values of PBS composites by 51% and 68%, respectively, compared to that of neat PBS. The superior flame retardancy of PBS/PNZn-lignin10% composite could be ascribed to the high char yield (54.6 wt.%) and the reduced mass loss rate. Meanwhile, the total smoke production (TSP) was decreased significantly by 50%, benefitting from the strong smoke suppression effect of Zn ions. The proposed flame-retardant mechanism of PNZn-lignin can be explained as follows: the combination of the strong dehydration effect of phosphorus-containing species and high charring capability of lignin permit PBS composites to generate a compact and strong carbonaceous layer during burning ((Figure 10d), leading to the improved fire behavior.

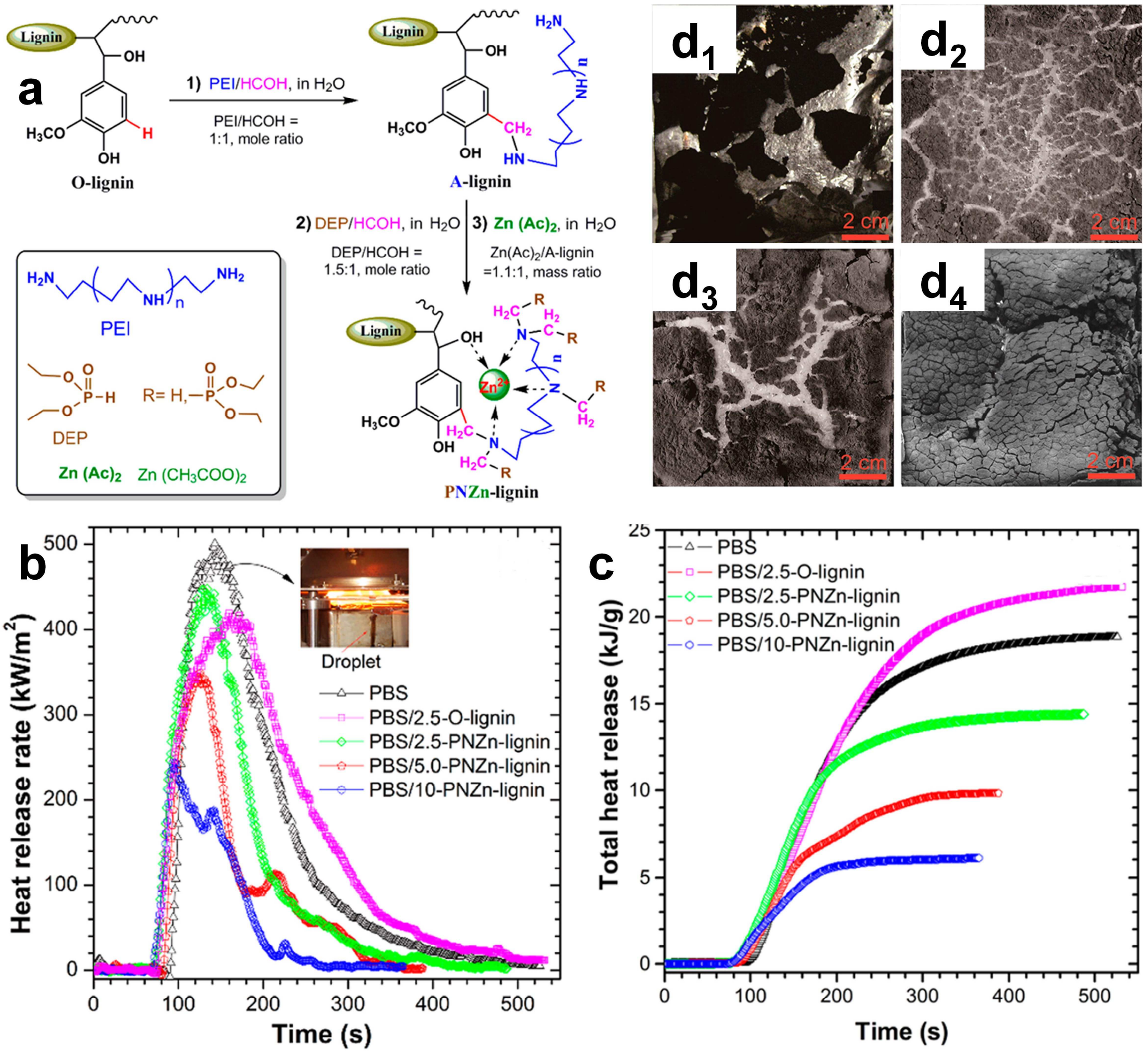

Figure 10. (a) Synthetic route of the functionalized lignin (PNZn-lignin); (b-c) HRR and THR curves of PBS composites at a heat flux of 35 kW/m^2; and residual chars of (d_1) PBS, (d_2) PBS/Olignin2.5%, (d_3) PBS/PNZn-lignin2.5%, (d_4) PBS/PNZn-lignin10% after cone calorimeter test [119].

Analogous investigation has also been carried out by Ferry et al [129]. Based on their work, two kinds of phosphonate-based macromolecules (Figure 11) were prepared and grafted onto alkali lignin. The cone calorimeter results indicated that incorporating 20 wt.% of modified lignin into PBS can significantly decrease the PHRR values of PBS composites (-51% and -52%, respectively), benefitting from the strengthened barrier effect with enhancement of char cohesion.

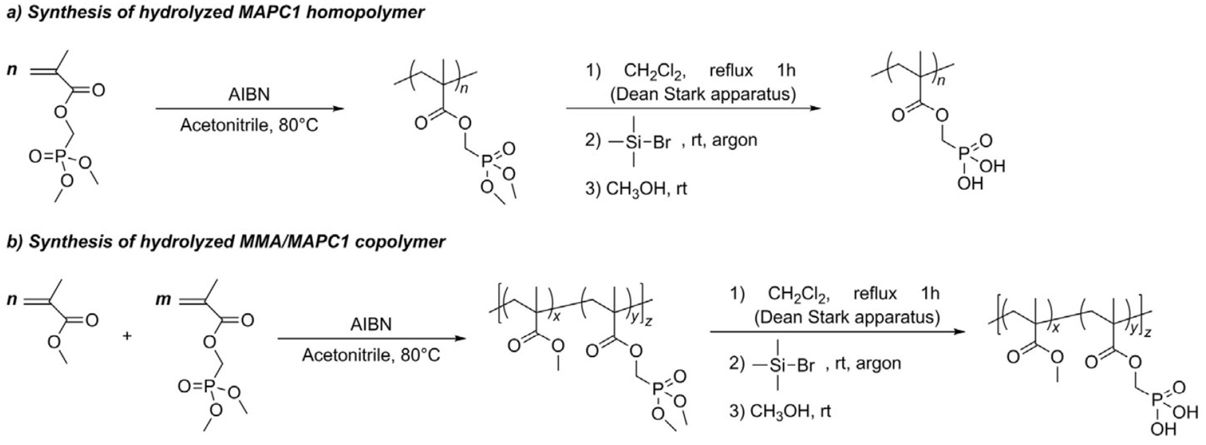

Figure 11. Synthesis routes of two kinds of phosphonate-based macromolecules [129].

Based on the observations above, it can be concluded that the flame retardant behaviors of phosphorus-containing modified lignin PBS composites mainly involve the condensed phase mechanism. A protective char layer can be formed during combustion covering the pyrolysis zone, ascribing to the conjunction of high charring capability of lignin and strong dehydration effect of phosphorus-containing species. The formed char layer appeared to act as fire barrier and thermal insulation to retard the transfer of mass (fuel) and heat.

4.3 Intumescence

Intumescence, defined as a process of enlarging or swelling, is widely used to make flame retarded materials [42]. During intumescence, the intumescent material swells when exposed to heat or flame, forming a porous carbonaceous foam which can serve as a barrier to prevent heat and mass (oxygen and pyrolysis product) from directly reaching the surface of the material [130]. Intumescent flame retardant (IFR) systems, emerged as one of the most promising trends, provide remarkable advantages over traditional flame retardants (e.g., halogenated flame retardants, and metallic hydroxides) due to the low toxicity and high flame retardant efficiency [131-133]. A typical intumescent system consists of three active components: an acid source, a char forming agent (also called carbonization agent), and a blowing agent [134]. It is worth noting that the specific ingredients of intumescence should be composed based on the polymer matrix. Besides, in order to further improve the flame retardancy of PBS, IFR systems would be used commonly in conjunction with synergistic agents, which are also discussed in this section.

In short, this section focuses on the recent progress in the field of intumescent PBS. It can be divided into three parts: the first part discusses the synergistic flame-retardant effect between IFR and synergistic agents in PBS composites, here we especially investigate the application of ammonium polyphosphate (APP)-based IFR system. The second part is devoted to microencapsulated ammonium polyphosphate (MAPP)-based intumescent PBS composites because microencapsulating is an effective strategy to improve the compatibility and hydrophobicity of PBS/APP composites. The last part of this section is involved to other IFR systems of PBS.

4.3.1 Ammonium polyphosphate-based IFR systems

As a commercially available flame retardant, APP has drawn a great deal of interest in the development of fire retardant polymers due to its low cost, high efficiency, and easy process [42].

For instance, a water-crosslinking technique was used to improve the fire retardant and anti-dripping properties of PBS composites using tetraethoxysilane (TEOS) as coupling agent and APP as flame retardant [135]. In this work, TEOS-treated APP was mixed with PBS to prepare flame retardant composites, then the obtained composites were treated with deionized water at 70 ℃ for 0.5 to 4 h to crosslink PBS chains via the reaction between PBS and TEOS (the mechanism was shown in Figure 12). After 4 h hot water treatment, the LOI values of composite with 15 wt.% TEOS-treated APP ranged from 24% to 28%, and V-0 rating was achieved in UL-94 test (1.27 mm); whereas the composite with 15 wt.% untreated APP (without TEOS) was only classified as V-2 rating, implying the enhanced fire performance of composite after water-crosslinking between PBS and TEOS.

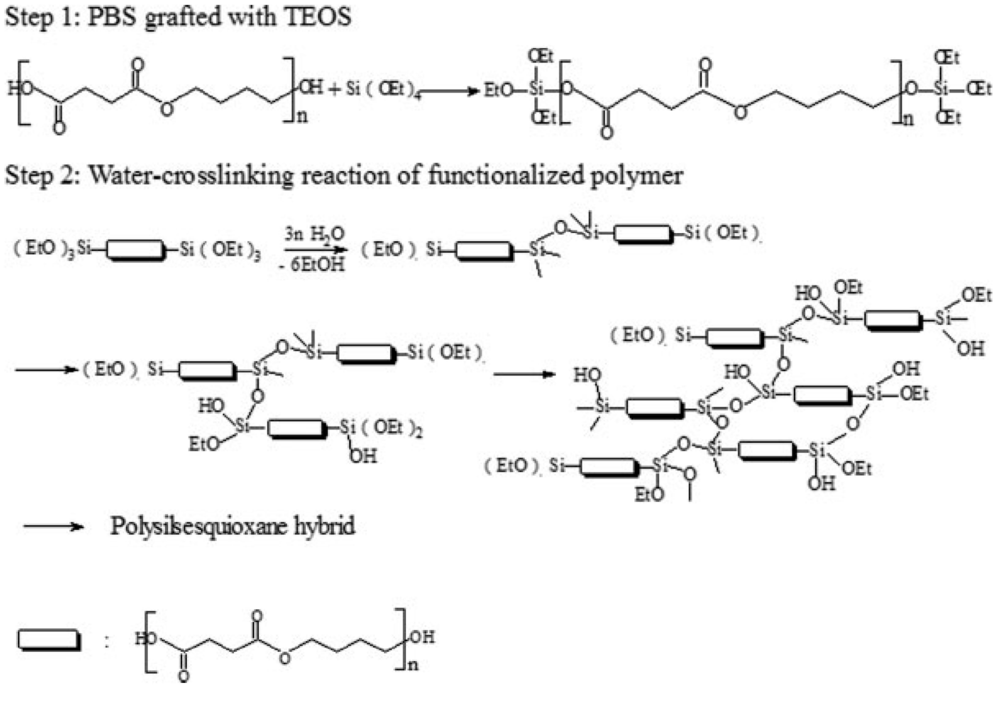

Figure 12. Water-crosslinking reaction mechanism of PBS/APP composites [135].

Based on previous work (see Table 2), it is known that APP shows low intumescent flame retardant efficiency for PBS when used alone [136]. Accordingly, in order to develop highly efficient intumescent system, it is quite crucial to introduce appropriate components to improve fire performance of PBS. Here, several promising approaches are proposed by incorporating: (a) char-forming agents; (b) synergistic agents; (c) char-forming agents and synergistic agents; (d) blowing agents and synergistic agents; (e) char-forming agents and blowing agents as well synergistic agents into PBS/APP systems.

As mentioned earlier, the natural fibers are widely used in the field of biocomposite due to its low cost, low density, improved mechanical properties, and availability from renewable resources [60, 137]. In the investigation of Dorez et al. [138], natural fibers, including cellulose, hemp, flax, sugar cane, and bamboo, were incorporated into PBS as reinforcement and char forming agents to improve the mechanical and fire performances. In most cases, a char layer was observed for PBS/fiber composites at 30% loading after cone calorimeter test (Figure 13). It is noteworthy that a minimum fiber loading was required to form a protective carbonaceous barrier for heat and mass transfer, and the resulting multicellular char suppressed the growth of HRR and leaded to the reduction of PHRR. Furthermore, with the incorporation of 5wt.% APP, PBS/flax/APP (mass ratio of 65:30:5) composite showed a significant decrease in the PHRR by 57%. It can be concluded that the addition of APP caused the phosphorylation of the flax fibers and accelerated the charring of composite, benefiting to the formation of a continuous and strong char layer.

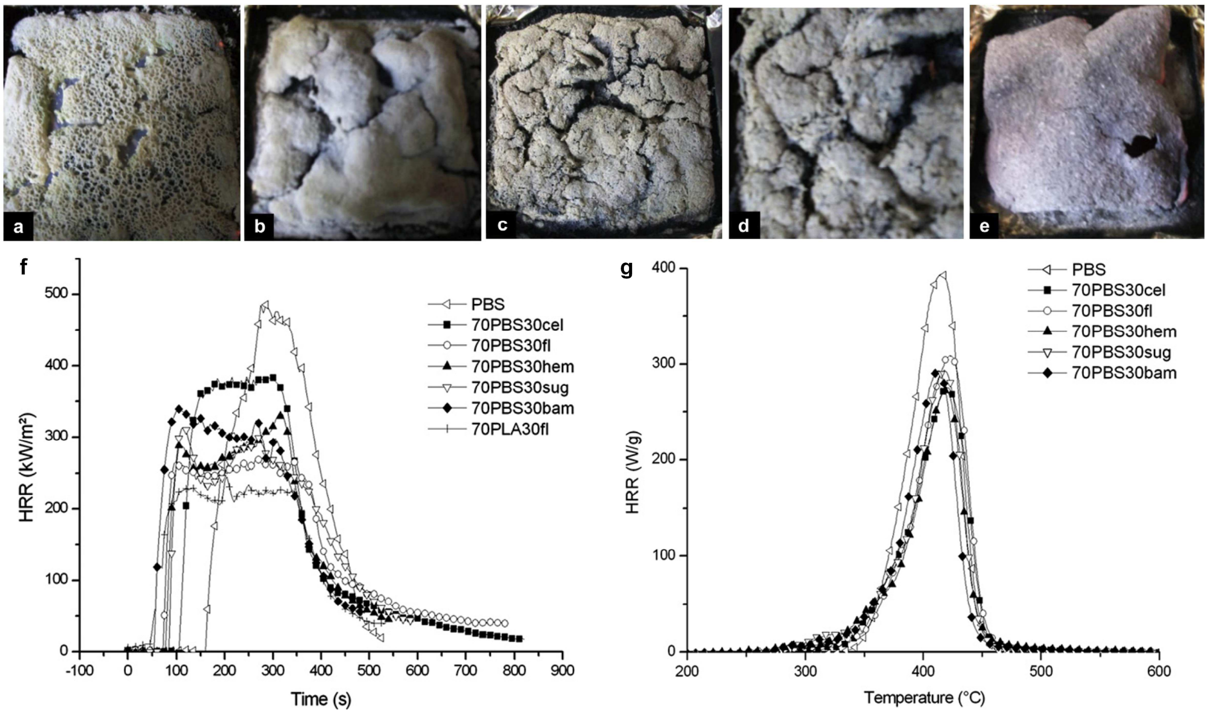

Figure 13. Char residues of (a) PBS/cellulose30%, (b) PBS/hemp30%, (c) 70PBS/flax30%, (d) PBS/sugar cane30%, (e) PBS/bamboo30% composites after cone calorimeter test; (f) the HRR curves of PBS/fiber composites based on cone calorimeter test at a heat flux of 35 kW/m^2, and (g) HRR curves of PBS/fiber composites based on MMC test [138].

Meanwhile, the same authors further studied the influence of three phosphorous compounds (APP, dihydrogen ammonium phosphate (DAP), and phosphoric acid (PA)) on the fire retardancy of PBS/flax biocomposites [139]. The results showed that the combination of the 3 wt.% of phosphorous compounds with PBS and flax fibers (mass ratio of 70:30) promoted the formation of strong char barrier, resulting in remarkable reductions in the PHRR values (-37%, -24%, and -25%, respectively, relative to PBS/flax composite). Similarly, Jiang et al. demonstrated the mechanical and fire properties of PBS/decayed wood (masson pine) biocomposites using APP, aluminum hypophosphite (AHP), and calcium hypophosphite (CaHP) as flame retardants and $CaCO_3$ as a reinforcing component [140]. Compared to PBS/decayed wood composite (mass ratio of 60:40), the co-addition of 2.9 wt.% $CaCO_3$ and 2.9 wt.% APP, AHP, and CaHP significantly enhanced the tensile strength (19.8%, 22%, and 18.2%, respectively) and decreased the PHRR values (-15%, -21%, and -10%, respectively) of composites. Indeed, the incorporation of APP, AHP, and CaHP promoted the formation of reinforced char layer, which limited the transfer of heat and fuel during combustion.

Charring polymers can act as char forming agent in intumescent systems, such as polyamide 6 [141, 142] and polyurethane [143, 144]. Thus, biobased poly(isosorbide carbonate) (PIC) was synthesized and incorporated as char former to develop green intumescent flame retardant PBS composites based on APP as acid source [136]. Hu et al. found that, compared to neat PBS, the addition of 30 wt.% of APP/PIC at a mass ratio of 3:1 reduced significantly the PHRR and THR values of PBS composites by 24% and 48%, respectively; meanwhile, for PBS/APP30% (with 30 wt.% APP content) composite, PHRR and THR were only decreased by 19% and 25%, respectively. Interestingly, the mass loss calorimeter (MLC) results indicated that the residual char yield of PBS/APP was 23%, whereas the char yield of PBS/PIC/APP composite was increased to 44%, implying that PIC appeared to act as carbonization agent and enhance remarkably char forming effect in intumescent FR system. In another work of Hu and co-workers [145], analogous results were demonstrated by developing a series of isosorbide-based compounds modified by silicon, sulfur, or phosphorus-containing functional groups for PBS/APP system.

As mentioned in *Section 3.1*, nanoparticles play irreplaceable roles in the flame retardancy of polymer based on the excellent fire behaviors [113]. During the last decades, new developments in the use of nanoparticles as synergists to improve fire performance of polymers attract great research interest owing to the improved mechanical, barrier, and anti-dripping properties at low contents [146]. The effect of nanoparticles on flame retardancy of PBS composites depends not only on its properties (including physical and chemical behaviors), but also on the interactions with IFR and PBS. It has been found that the IFR system combined with suitable nanoparticle is capable of yielding a continuous, crack-free, and ceramic-like protective char, leading to the improved FR effectiveness [113].

As displayed in Table 2, HNT and sepiolite combined with APP were respectively incorporated into PBS matrix via melt blending [147]. The results showed that addition of both HNT and sepiolite reduced the flammability for PBS composites. Obviously, compared to halloysite, sepiolite showed better fire behaviors in PBS/APP system, which can be attributed to the better dispersibility of sepiolite and the formation of homogeneous protective char layer. The catalytic charring effect of HNT and sepiolite mainly derives from the promoted crosslinking/charring reactions between acid sites formed from APP and decomposing PBS chains due to the nano-confinement environment provided by HNT and sepiolite. Furthermore, with the co-addition of alkali lignin, a 67% reduction in PHRR was obtained for PBS/APP/sepiolite/lignin composites, indicating the significant improvement in flame retardancy.

Wang et al. investigated the effects of APP, HNT, and renewable soy protein (SP) on fire behavior of PBS composites [148]. It is well known that SP can play simultaneously the roles of char forming and blowing agents due to the abundant hydroxyl and carbonyl groups and the high amount of nitrogen (~16 wt.%). The authors reported that the best char-forming capability for PBS can be obtained when the mass ratio of APP/SP is 2:1 (called EIFR). As also shown in Table 2 and Figure 14a-b, the addition of EIFR significantly diminished the PHRR and THR values of PBS by 42% and 16%, respectively. Besides, the LOI value of PBS/EIFR20% (with 20 wt.% content) was increased to 30.2%, relatives to 28.5% for PBS/APP20% system. However, it only reached V-1 rating in UL94 test (3 mm). A synergistic effect was observed between HNT and EIFR in PBS composite based on the LOI and UL94 as well cone calorimeter tests. The results demonstrated that, with the co-addition of 1 wt.% HNT and 20 wt.% EIFR, the

PBS/EIFR20%/HNT1% showed lower flammability (the LOI value is as high as 34.8%) than that of PBS/EIFR20%, meanwhile UL-94 V-0 rating has been achieved. A mechanism was proposed to describe the enhanced fire performance where HNTs tends to migrate and accumulate on the surface of carbonaceous layer during degradation and burning process, and acts as physical or chemical cross-linking barrier to reinforce the char (Figure 14c-g). The glassy protective carbonaceous layer reduces the transfer of both heat and mass effectively, resulting in better fire-resistant properties.

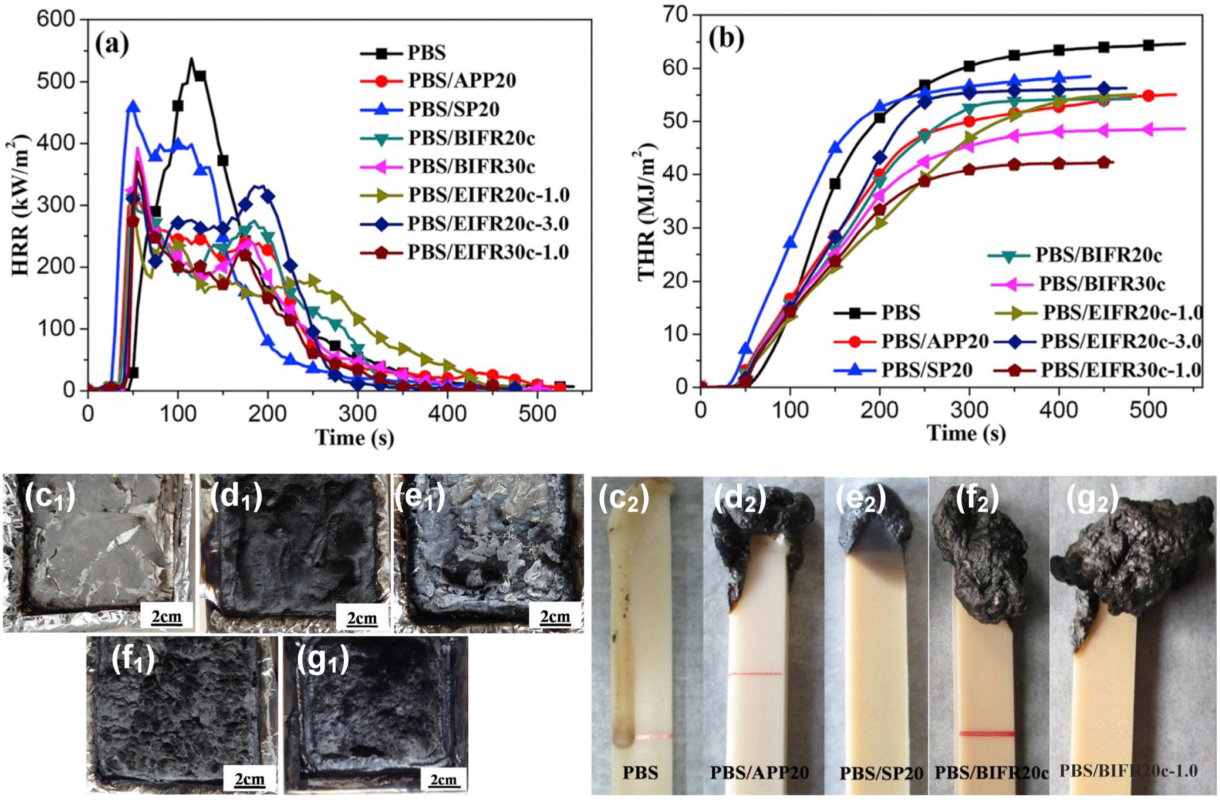

Figure 14. (a-b) HRR and THR curves of PBS composites at a heat flux of 35 kW/m^2; residual chars of (c) PBS, (d) PBS/APP20%, (e) PBS/SP20%, (f) PBS/EIFR20%, (g) PBS/EIFR20%/HNT1% composites after cone calorimeter and LOI tests [148].

In addition, as shown in Figure 15a-d, one-dimensional aminated multi-walled carbon nanotube (MWCNT-NH_2) electrostatically wrapped with APP (CNT@APP) has been employed in combination with IFR (fabricated by APP and PER with a mass ratio of 2:1) to impart carbonization and intumescent flame retardant properties to PBS composite system [149]. It was obvious from UL94 and cone calorimeter tests (Table 2, Figure 15e-g) that the presence of CNT@APP permitted excellent anti-dripping and char-forming properties (65.7% char yield), high UL94 grade (V-0, 3.2 mm), and lower PHRR and THR values to PBS/IFR20% composite. Furthermore, the mechanism of flame-retardant enhancement was attributed to the formation of compact homogeneous carbonaceous char with high thermal stability during combustion.

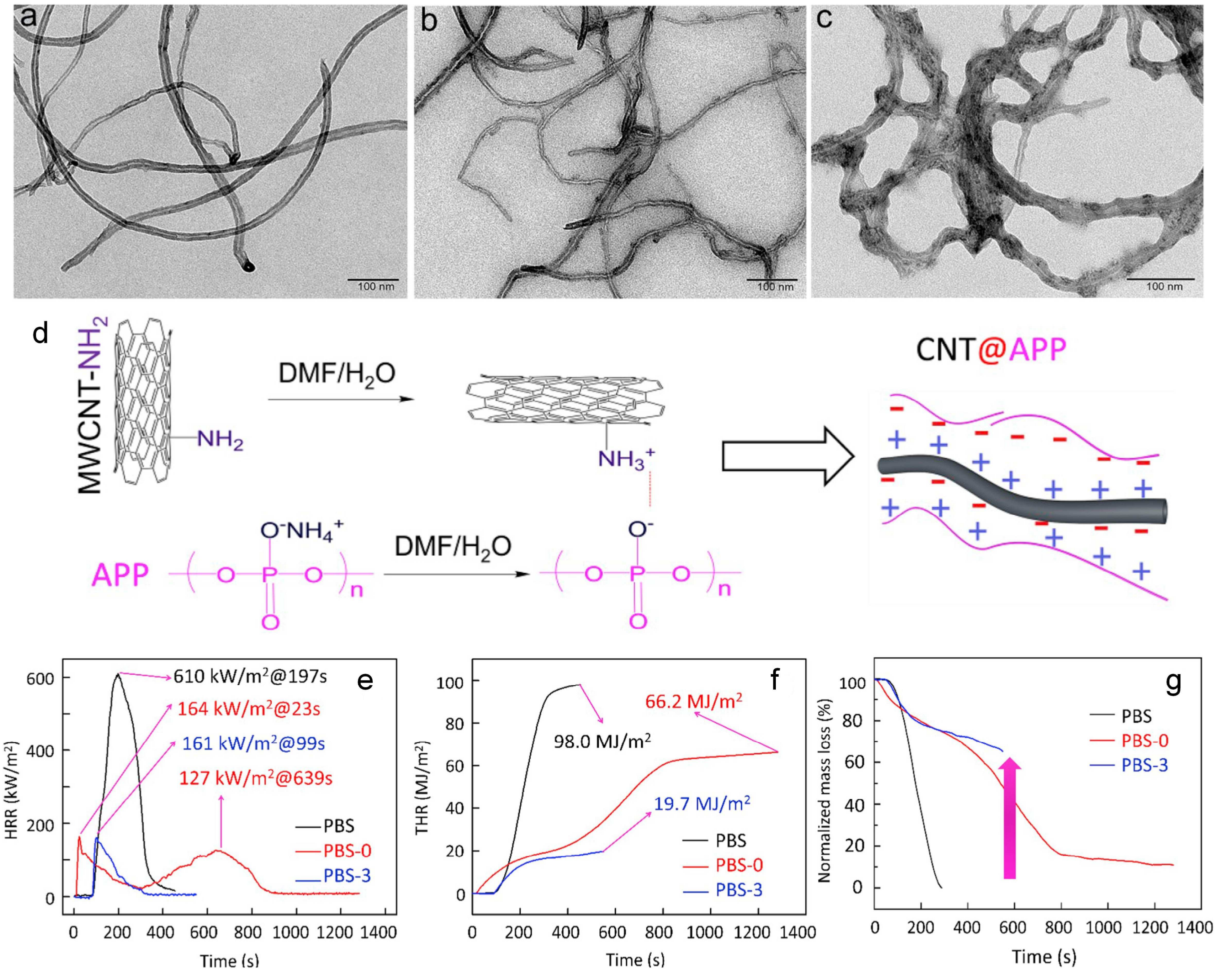

Figure 15. TEM images of (a) aminated multi-walled carbon nanotube (MWCNT-NH$_2$), (b-c) CNT@APP; and (d) scheme of electrostatically APP-coated MWCNT-NH$_2$; (e-g) HRR, THR, and mass loss curves of PBS composites at a radiant heat flux of 35 kW/m^2 (PBS-0: PBS/IFR20%, PBS-3: PBS/IFR19%/CNT@APP1%) [149].

Table 2. Fire performance of APP-based intumescent PBS systems in combination with synergistic agent and char forming agent.

APP content (%)	**Char forming agent and content (%)**	**Synergistic agent and content (%)**	**LOI (%)**	**UL-94 rating**	**Cone calorimeter**				**Ref.**
					Heat flux (kW/m^2)	**Δ PHRR (%)**	**Δ THR (%)**	**Char (%)**	
20	/	/	/	/	50	-55	-17	20.4	[147]
/	/	HNT, 5	/	/		-16	4	2.6	
/	/	Sepiolite, 5	/	/		-26	2	5.6	
15	/	HNT, 5	/	/		-56	-6	14.6	
15	/	Sepiolite, 5	/	/		-57	-11	16.5	
6.67	Alkali lignin, 6.67	Sepiolite, 6.67	/	/		-67	-8	13.0	
20	/	/	28.5	V-2	35	-41	-15	12.7	[148]
30	/	/	33.3	V-0		/	/	/	
13.3	SP, 6.7		30.2	V-1		-42	-16	16.1	
13.3	SP, 6.7	HNT, 1	34.8	V-0		-43	-15	15.3	
/	/	/	/	NR	35	/	/	/	[149]
13.33	PER, 6.67	/	/	V-2		-73	-32	11.6	
12.67	PER, 6.33	CNT@APP, 1	/	V-0		-74	-80	65.7	

Note: (1) HNT: halloysite nanotube, SP: Soy protein, PER: pentaerythritol; (2) ΔPHRR: the reduction of PHRR compared with neat PBS, ΔTHR: the reduction of THR compared with neat PBS.

A conventional blowing agent, melamine (MA) is widely applied in the intumescent systems for various polymers such as polypropylene [150, 151], polyethylene [152, 153], polyurethane [154, 155], polylactide [156-158], and ethylene vinyl acetate [159, 160]. In previous work, it has been proposed that the combination of MA with APP in a suitable ratio can significantly improve fire performance of polymer composite [157]. The decomposition routes of PBS/APP/MA upon heating or combustion include mainly: (a) the decomposition of APP forms a large amount of ammonia and phosphorus-containing species, such as HPO_3, H_3PO_4, $H_4P_2O_7$; (b) PBS chains decompose and react with phosphorus-containing acids to form P-O-C structure-containing units, accompanied by the generation of conjugated polyenes. (c) melamine releases ammonia and gradually forms melam, melem, and melon with the increase of temperature, which tend to migrate upward [161]. Besides, in order to further improve the flame-retardant efficiency of composite, APP/MA-based IFR system is generally used in conjunction with synergists. Table 3 summarizes the fire performance of PBS composites based on APP/MA intumescent flame retardants and synergists.

Multicomponent tetrametallic MgAlZnFe layered double hydroxides (MgAlZnFe LDHs) was synthesized by the coprecipitation method, and then added into PBS with APP/MA (mass ratio of 5:1) via melt blending [162]. With the incorporation of 1 wt.% MgAlZnFe LDHs and 19 wt.% APP/MA (IFR), the LOI value of sample was increased to 35% and V-0 rating was achieved in UL94 test (Table 3). In addition, the cone calorimeter results demonstrated that the PHRR and THR values were remarkably decreased by 30% and 19%, respectively, relative to that of neat PBS. As shown above, it is recommended to use MgAlZnFe as a synergist to promote the formation of a compact char layer during combustion. In particular, compared to PBS/IFR20%, tensile strength and flexural strength of composites were simultaneously improved by 9% and 8% when the IFR was partially substituted with 1 wt.% MgAlZnFe LDHs.

Similar conclusions reported that magnesium hydroxide sulfate whisker (MHSH) can play both synergistic flame retardant and reinforcement effects in PBS/APP/MA composites [163]. In this regard, incorporating 25 wt.% APP/MA, at a mass ratio of 5:1, into PBS permits to obtain a LOI value of 37.5% and UL94 V-0 rating (3 mm). The substitution of 2 wt.% APP/MA by MHSH not only permitted excellent fire retardant (LOI value of 39.8% and V-0 rating) and anti-dripping properties to PBS composites, but also increased its tensile strength by 33.3% in comparison with that of PBS/APP/MA composite (Table 3). A possible mechanism was proposed where MHSH and APP/MA provided a ceramic-like intumescent shield to the underlying matrix.

A number of synergistic agents, such as esterified starch-modified cassava dregs (ES-CD) [164, 165], urea-kaolinite [166], hexakis (4-aldehyde phenoxy)cyclotriphosphazene grafted kaolinite (K-HAPCP) [161], fumed silica [167], organically acetyl quaternary ammonium-modified Ca-montmorillonite (OMMT) [168], and graphene [29], have also been conducted on APP/MA-based intumescent PBS systems. The fire performance of those PBS composites based on the combination of different synergists and APP/MA (mass ratio of 5:1 or 2:1) are also been given in Table 3. The presence of APP/MA and synergists promote the generation of an intumescent and ceramic-like protective char layer, resulting in the enhancement of fire retardancy.

Table 3. Fire performance of APP/MA based intumescent PBS formulations in combination with different synergistic agents.

Mass ratio of APP: MA and its content (%)	**Synergistic agent and content (%)**	**LOI (%)**	**UL-94 rating**	**Cone calorimeter**				**Ref.**
				Heat flux (kW/m^2)	**Δ PHRR (%)**	**Δ THR (%)**	**Char (%)**	
5:1, 20	/	30	V-1	25	-15	-22	/	[162]
5:1, 19	MgAlZnFe LDHs, 1	35	V-0	25	-30	-19	/	
5:1, 25	/	37.5	V-0	35	-48	-16	30.7	[163]
5:1, 23	MHSH, 2	39.8	V-0	35	-50	-11	27.3	
5:1, 25	ES-CD, 5	37.3	V-0	/	/	/	/	[164]
5:1, 23	MHSH, 2 ES-CD, 5	39.6	V-0	35	-36	-9	/	[165]
5:1, 25	/	31.7	NR	50	-23	-11	20.8	[166]
5:1, 20	Urea-kaolinite, 5	40.1	V-0	50	-49	-27	27.7	
5:1, 20	K-HAPCP, 5	36.6	V-0	50	-49	-18	29.3	[161]
5:1, 18	Fumed silica, 2	36	V-0	/	/	/	/	[167]
2:1, 20	/	32.6	V-2	35	-37	-24	14.1	[168]
2:1, 20	OMMT, 1	36.3	V-0	35	-67	-49	29	

2:1, 18	Graphene, 2	33.0	V-0	/	/	/	/	[29]

Note: (1) MgAlZnFe-LDHs: MgAlZnFe-CO_3 layered double hydroxide; MHSH: magnesium hydroxide sulfate whisker; ES-CD: esterified starch-modified cassava dregs; Urea-kaolinite : urea and kaolinite hybrid with the weight ratio of 1:1; K-HAPCP: hexakis (4-aldehyde phenoxy) cyclotriphosphazene grafted kaolinite; OMMT: organically (acetyl quaternary ammonium) modified Ca-montmorillonite; (2) ΔPHRR: the reduction of PHRR compared with neat PBS, ΔTHR: the reduction of THR compared with neat PBS.

In addition, a similar IFR system, fabricated by APP/MA/PER at a mass ratio of 4:1:1, was adopted for improving the fire retardancy of PBS in conjunction with HNT [169]. Compared to PBS/IFR30% composite, the substitution of 1.5 wt.% IFR by HNT make the LOI to jump from 42% to 58% and concurrently reducing PHRR, THR, and TSP values by 42%, 19%, and 69%, respectively (Figure 16a-c). Besides, for PBS/IFR28.5%/HNT1.5% composite, a continuous and crack-free char layer can be observed after cone calorimeter test (Figure 16d-h), indicating that the addition of HNT changed the degradation and fire behaviors of intumescent PBS composite and resulted in the enhanced fire retardancy by limiting heat and mass transfer.

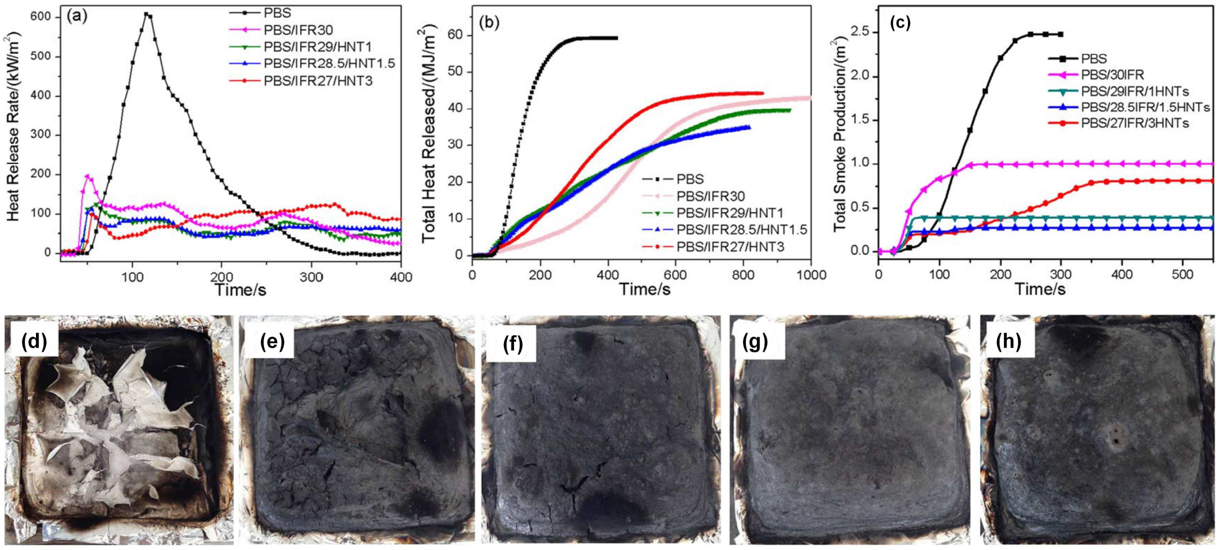

Figure 16. (a-c) HRR, THR, and TSP curves of PBS composites at a heat flux of 30 kW/m^2; char residues of (d) PBS, (e) PBS/IFR30%, (f) PBS/IFR29%/HNT1%, (g) PBS/IFR28.5%/HNT1.5%, and (h) PBS/IFR27%/HNT3% composites after cone calorimeter test [169].

4.3.2 Microencapsulated ammonium polyphosphate-based IFR systems

It is noted that the poor water resistance and inferior compatibility of APP lead to the possible deterioration in mechanical properties as well as fire retardant efficiency of materials during long-time use [134]. Currently, microencapsulation technology was widely applied for the surface modification of APP to meet the demand of fire retardancy of polymers through varying the surface materials [170, 171].

In a study by Hu and co-workers [172], ethyl cellulose was selected as the shell to microencapsulate APP (Figure 17a-b), and the resulting MAPP showed excellent thermal stability and hydrophobicity. The maximum mass loss temperature (T_{max}) value of MAPP was improved by 53 ºC in air condition after the microencapsulation of APP. Moreover, the MAPP and char forming agent (CFA, prepared by the reaction of cyanuric chloride and ethylenediamine) were melt blended with PBS to prepare flame retardant PBS composites. For the PBS/MAPP15%/CFA5% (mass ratio of 80:15:5) system, the LOI value was raised to 35.5% from 22.0% for that of neat PBS, and V-0 rating was reached in UL-94 test (3 mm). Besides, a significant decrease in PHRR by 46.6% was obtained (Figure 17c). Obviously, it showed better fire performance than that of PBS/APP15%/CFA5% composite (34.5% of LOI, UL94 V-1 rating, a 17% reduction in PHRR). Moreover, the thermal stability and mechanical properties of the composite was also improved after the microencapsulation.

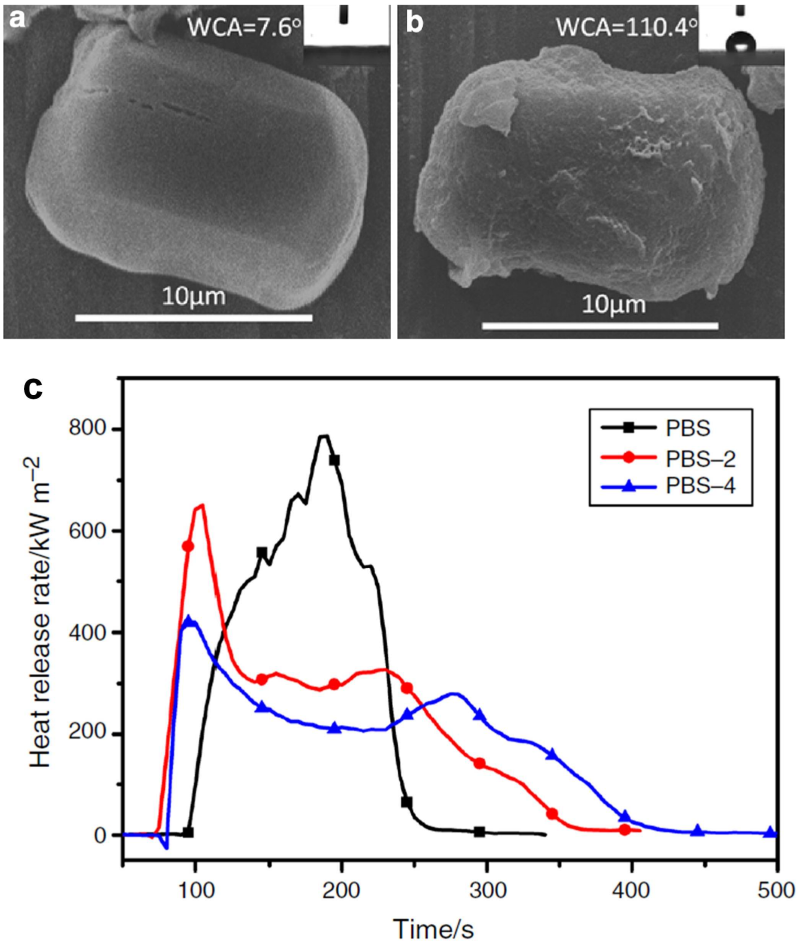

Figure 17. SEM images of (a) APP and (b) MAPP particles (the insets are the picture of water contact angle); and (c) HRR curves of PBS composites at a radiant heat flux of 35 kW/m^2 (PBS-2: PBS/APP15%/CFA5% composite, PBS-4: PBS/MAPP15%/CFA5% composite) [172].

Similarly, melamine-formaldehyde resin, another common shell material, was also been used to microencapsulate APP (MFAPP), and it has been demonstrated to be an effective approach in flame retarding PBS/BF(bamboo fiber) composites [173]. Indeed, compared to PBS/BF composite (mass ratio of 30:50), PBS/BF30%/MFAPP20% composite (containing 30 wt.% of BF and 20 wt.% of MFAPP) turned out to give a remarkable improvement in UL94 test (3 mm, from no rating to V-0 rating). Meanwhile, a reduction by 47% of PHRR was reached by cone calorimetry.

In other study, CNT-modified APP hybrids (CAPP, Figure 18) were prepared via the reaction between APP and CNTs in the medium of (3-aminopropyl)triethoxysilane (APTS), and then adopted to PBS matrix [174]. The total loading of filler was kept at 20 wt.% for all samples. In the case of PBS/CAPP20% (with 0.2 wt.% content of CNTs in APP), incorporating 20 wt.% of CAPP into PBS not only improved the LOI value (from 22.0% for neat PBS to 29.5%), but also enhanced greatly the anti-dripping property of PBS composite. As shown in Figure 19, PBS/CAPP20% (0.2 wt.% of CNTs) reached V-0 rating in UL94 test (3 mm). Beside this, a reasonable mechanism was proposed by the authors. They suggested that the presence of CNTs in APP contributes to the formation of reinforced ceramic-like intumescent char layer, which significantly slows down the release of heat and pyrolyzed gas.

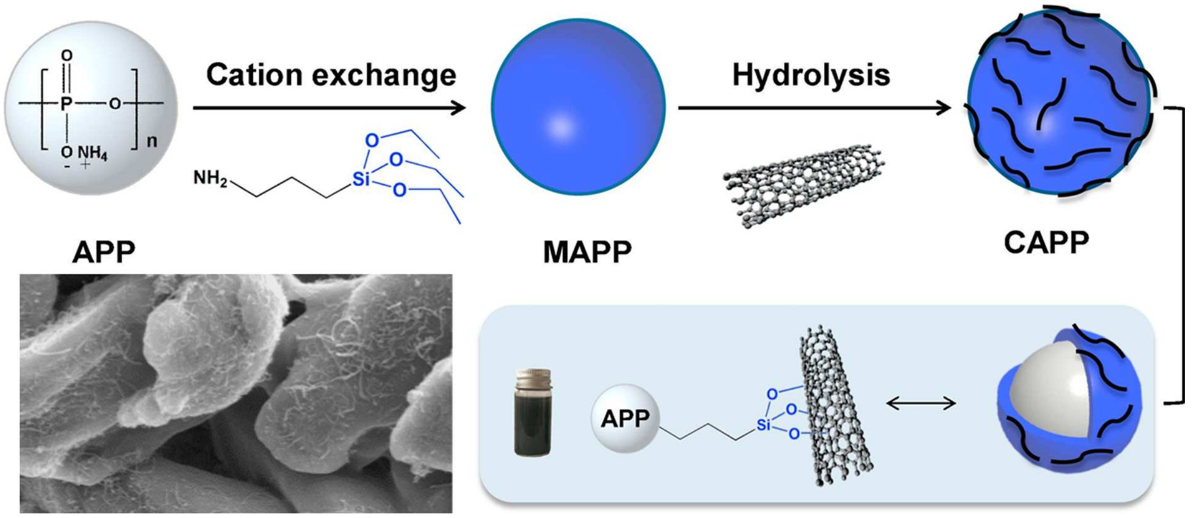

Figure 18. Schematic diagram and SEM image of CAPP [174].

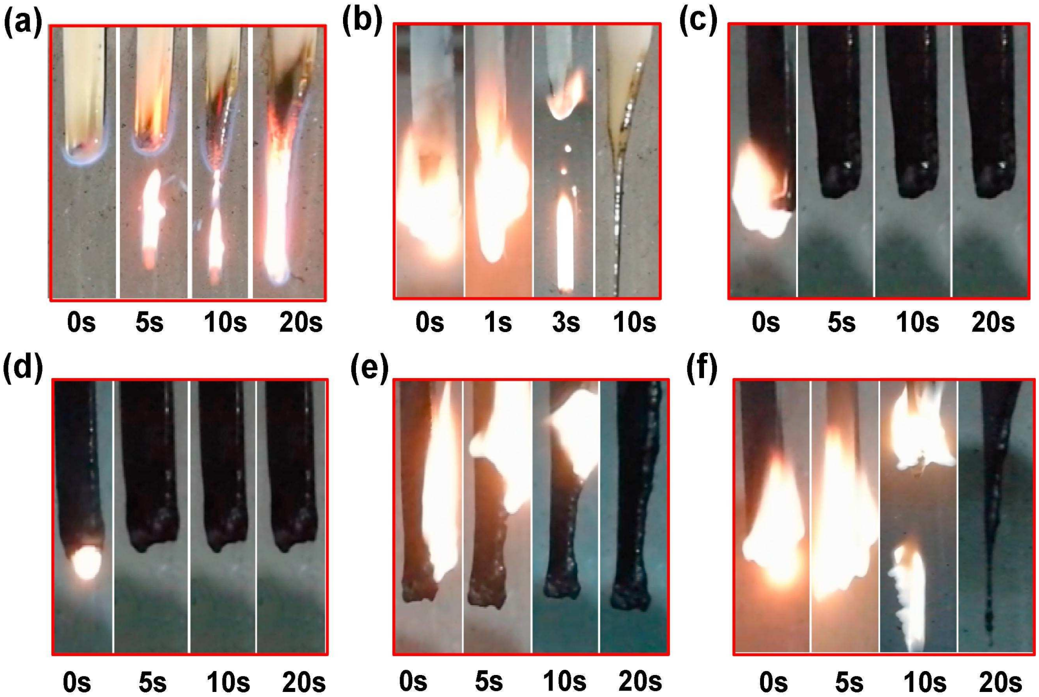

Figure 19. Digital photos of (a) neat PBS, (b) PBS/APP20%, (c) PBS/CAPP20% (0.1 wt.% of CNTs), (d) PBS/CAPP20% (0.2 wt.% of CNTs), (e) PBS/CAPP20% (0.4 wt.% of CNTs), and (f) PBS/APP19.8%/CNT0.2% composites during the UL-94 tests (different time after first (a) or second (b–f) ignition) [174].

4.3.3 Others

A comparative study of melamine phosphate (MP), melamine phosphite (MPi), and melamine hypophosphite (MHP) was investigated on the fire-retardant efficiency of PBS composites [175]. The LOI and cone calorimeter results demonstrated that the additions of MP, MPi, and MHP significantly reduced the flammability of PBS composites (Figure 20). In detail, under the same content of fillers (from 0 to 30 wt.%), the LOI values of PBS composites followed the sequence of $LOI_{MP} < LOI_{MHP} < LOI_{MPi}$. Meanwhile, dramatic reductions of PHRR (-33%, -49%, and -54%, respectively) were observed for PBS composites containing 30 wt.% of MP, MPi, and MHP. Among them, PBS/MPi composite showed the longest TTI (105 s), followed by PBS/MP (86 s) and PBS/MHP (81 s). Besides, V-0 classification were reached for all of samples with 30 wt.% loadings in UL94 tests (3 mm).

Based on the TG-FTIR and in-situ FTIR results, it can be found that, except for the diluting effect in gas phase by the release of nonflammable gases from the decomposition of melamine structure in MP, MPi, and MHP, only condensed phase mechanism occurred in MP, while combined condensed and gas phase mechanisms have been demonstrated in both MHP and MPi due to the existence of PH_3, which was released from MHP and MPi during decomposition and acted as a radical scavenger. The flame-retardant behavior of PBS/MP composite was ascribed to the intumescent flame retardant properties of MP, which promoted the formation of intumescent carbonaceous layer on the surface of sample during burning. Based on the similar structure, MPi and MHP acted in a similar way as MP in condensed phase. However, for PBS/MPi and PBS/MHP composites, the release of PH_3 captured radicals in gas phase and got oxidized rapidly into orthophosphoric acid and further form polyphosphoric acid, which covers the surface of PBS matrix and catalyzes the formation of fire-resistant char layer.

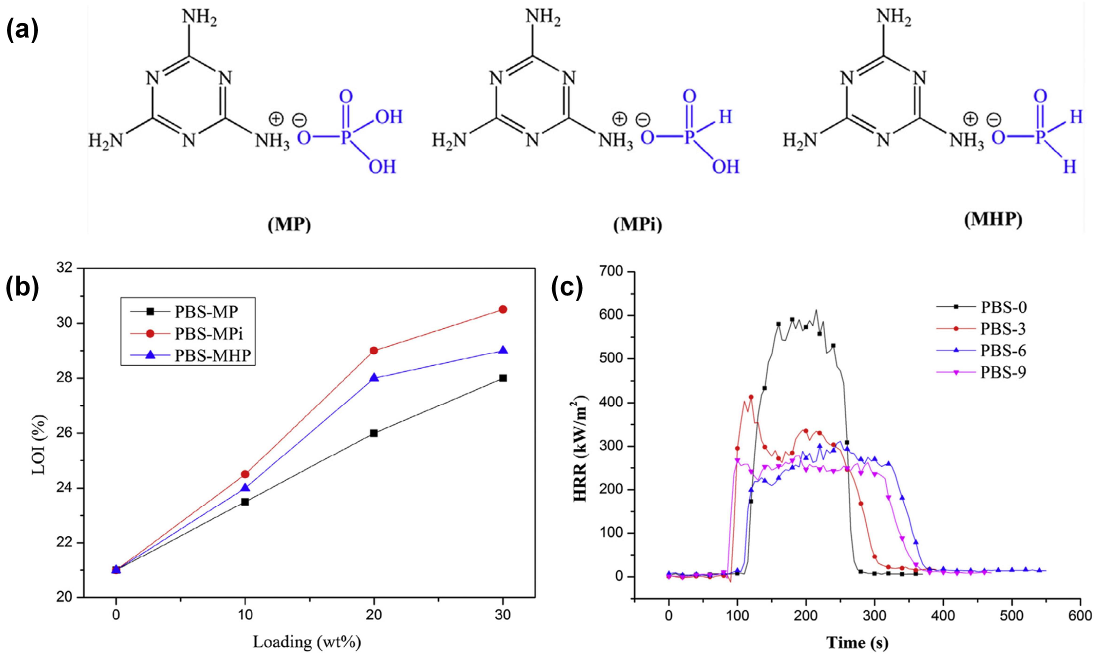

Figure 20. (a) The chemical structures of MP, MPi, and MHP; (b) the effect of MP, MPi, and MHP loadings on the LOI value of the PBS composites; (c) HRR curves of PBS composites at an external heat flux of 35 kW/m^2 (PBS-0: neat PBS, PBS-3: PBS/MP30%, PBS-6: PBS/MPi30%, and PBS-9: PBS/MHP30%) [175].

The same group has also conducted a research to find out the effects of MP and two nanoparticles (graphene and polyhedral oligomeric silsesquioxanes (POSS)) on the mechanical, thermal, and flame retardant properties of PBS [176]. The total loading of filler in PBS was 20 wt.%, and the content of synergists changes from 0 to 2 wt.%. The UL94 test showed that all POSS-containing composites were just classified as V-1 rating (3 mm), whereas the co-addition of 2 wt.% graphene and 18 wt.% MP into PBS brought the vertical burning classification to V-0 rating. The cone calorimeter test results (Figure 21a-d) indicated that, with the addition of 18 wt.% of MP and 2 wt.% of POSS, PBS/MP18%/POSS2% composite achieved a decrease in PHRR by 40%, similar to the reduction of PBS/MP20% composite (-40%); meanwhile the PHRR values was diminished by 63% with respect to the incorporation of 18 wt.% of MP and 2 wt.% of graphene. Even though the presence of POSS (from 0.5 to 2 wt.%) improved the residual char yield of PBS/MP composites (Figure 21e), they failed to form a continuous char layer during combustion, leading to poor fire property of composites. For PBS/MP18%/graphene2% composite, the significant improvement in the fire performance of composite can be ascribed to the superior fire barrier effect of complete and thermal-oxidative stable char layer.

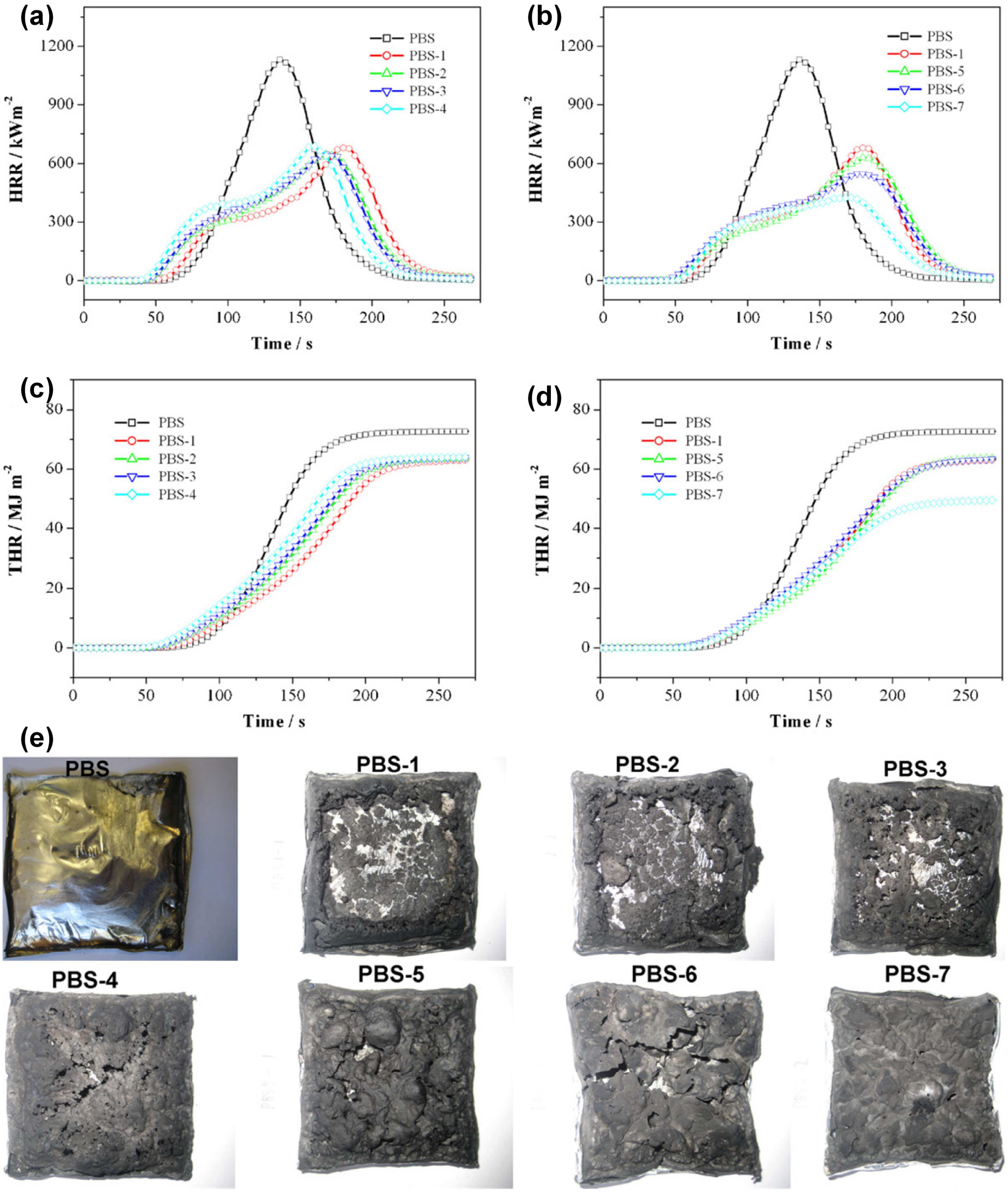

Figure 21. (a-d) HRR and THR curves of PBS composites at a heat flux of 50 kW/m^2; (e) char residues after cone calorimeter test (PBS-1: PBS/MP20%, PBS-2: PBS/MP19.5%/POSS0.5%, PBS-3: PBS/MP19%/POSS1%, PBS-4: PBS/MP18%/POSS2%, PBS-5: PBS/MP19.5%/Graphene0.5%, PBS-6: PBS/MP19%/Graphene1%, PBS-7: PBS/MP18%/Graphene2%) [176].

Besides, a fully biobased intumescent flame retardant (PA-GU) was developed by Chen and coworkers based on the ionic reaction of phytic acid and guanosine [177]. It was found that the addition of 10 wt.% PA-GU significantly decreased the PHRR and THR values of PBS (59.2% and 38.6%, respectively). Unfortunately, all PBS composites (containing PA-GU from 10 wt.% to 30 wt.%) just achieved V-2 rating in UL94 test (3 mm).

5. Summary and perspectives

PBS is showing great potential for substituting petrochemical-based polymers in many fields, where flame retardancy is claimed as an indispensable requirement. This review attempts to give comprehensive insight into the development of the flame retardancy of PBS based on the articles published in the last decades.

Among the flame retardants, conventional inorganic (nano)particles (e.g., magnesium hydroxide, expanded graphite, carbon black) still play significant roles in flame retarding PBS due to the advantages of abundant, low-cost, non-toxic, and eco-friendly. However, as the main disadvantage, high loading is typically required to meet the demand of fire safety standards, which may deteriorate the mechanical properties of composites. It is worth mentioning that in terms of enhancing the mechanical and char formation as well as fire-resistant properties of PBS, chemically modified natural materials (especially lignin) can be used for substituting traditional flame retardants to some extent, thus resulting in fully biobased PBS composites.

Throughout this review, it can be concluded that the formation of a continuous and insulating char plays an important role in protecting PBS during combustion. In this regard, one of the most promising approaches for forming expanded char layer is to fabricate highly effective IFR system. So far, much attentions have been devoted to design intumescent formulations for PBS, for instance the combination of ammonium polyphosphate and melamine in a mass ratio of

5:1 or 2:1. Beside this, synergist (e.g., nanoparticles) can be considered as determining factor for intumescent formulations because the fire properties of PBS composite may be enhanced intensely by a small amount of a synergist in the intumescent formulation. Indeed, in most instances, the results point out that synergists serve to optimize the fireproofing performances of IFR PBS composites by forming a ceramic-like intumescent carbonaceous char with improved coherency and insulation.

Even though many strategies have been surveyed in this work, new formulations should be created to enhance fire retardant efficiency of PBS. From a perspective point of view, subsequent development can more focus on new intumescent flame retardant systems (not limited to traditional components) and bio-sourced flame retardants. In summary, this work outlines almost all the current flame-retardant researches of PBS, which should help developing new high performance systems.

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Nomenclature

AHP, aluminum hypophosphite; APP, ammonium polyphosphate; APTS, (3-aminopropyl)triethoxysilane; CaHP, calcium hypophosphite; CAPP, carbon nanotube-modified ammonium polyphosphate; CB, carbon black; CFA, char forming agent; CHF, critical heat flux; CNT, carbon nanotube; CY, char yield; DAP, dihydrogen ammonium phosphate; E&E, electrical and electronics; EG, expandable graphite; EIFR, ammonium polyphosphate and soy protein mixture with the weight ratio of 2:1; ER, Eucommia residue; ES-CD, esterified starch-modified cassava dregs; FIGRA, fire growth rate index;FR, flame retardant; FRI, flame retardancy index; HNT, halloysite nanotube; HRR, heat release rate; IFR, intumescent flame retardant; K-HAPCP, hexakis (4-aldehyde phenoxy) cyclotriphosphazene grafted kaolinite; LDH, layered double hydroxide; LDPE, low-density polyethylene; LOI, limiting oxygen index; MA, melamine; MAPP, microencapsulated ammonium polyphosphate; MCC, microscale combustion calorimetry; MDH, magnesium hydroxide; MFAPP, melamine-formaldehyde resin microencapsulated ammonium polyphosphate; MgAlZnFe-LDHs, MgAlZnFe-CO3 layered double hydroxide; MHP, melamine hypophosphite; MHSH, magnesium hydroxide sulfate whisker; MLC, mass loss calorimeter; MMT, montmorillonite; MP, melamine phosphate; MPi, melamine phosphite; OMMT, organically (acetyl quaternary ammonium) modified Ca-montmorillonite; PA, phosphoric acid; PA-GU, compound obtained by the reaction between phytic acid and guanosine; PBS, polybutylene succinate; PCFC, pyrolysis combustion flow calorimetry; PE, polyethylene; PER, pentaerythritol; PHRR,peak heat release rate; PIC, poly(isosorbide carbonate); POSS, polyhedral oligomeric silsesquioxanes; PP, polypropylene; SP, soy protein; TEOS, tetraethoxysilane; THE, total heat evolved; THR, total heat release; T_{ig}, ignition temperature; TRP, thermal response parameter; TSR, total smoke released; TTI, time to ignition; Urea-kaolinite, urea and kaolinite hybrid with the weight ratio of 1:1; ΔPHRR, the reduction of PHRR compared with neat PBS; ΔTHR, the reduction of THR compared with neat PBS.

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