Bio-based materials for fire retardant application in construction products: A review

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Abstract: Bio-based materials are showing great potential to be widely used in construction industry, while reducing fire risk and improving fire resistance of these alternatives also become a major concern due to their inherent flammability. Initially, this review introduces three common bio-based construction materials, including biopolymer-based materials, wood-based materials, and crop-based materials, and their fire behaviors in flaming and smoldering combustion scenarios, accompanied with some typical flame-retardant mechanisms. Sequentially, the recent achievements in improving fire resistance are mainly exhibited in detail for each kind of bio-based materials. There are numerous reports for biopolymer-based flame-retardant materials with mature flame-retardant methodology. With regard to wood-based flame-retardant materials, different criteria and methodologies are needed to evaluate the flame-retardant properties. Meanwhile, in the case of crop-based insulation materials is essential to carefully consider the fire behavior, both in flaming and smoldering combustions, and not only focus on their thermal performance. In the final section, based on the requirements of fire safety and practicality for construction materials, bio-based alternatives with excellent good fire resistance and practical performance are summarized to be a promising way to meet future challenges.

Keywords: bio-based materials; construction products; fire resistance; sustainability

Abbreviations:

Concepts for sustainability and organization names

SCM: Sustainable construction materials; **CE:** Circular Economy; **SMM:** sustainable management; **CDW:** Construction Demolition Waste; **EU:** European Union; **US:** United States; **EPA:** Environmental Protection Agency.

Polymers and other compounds

IFRs: intumescent flame retardants; **PLA:** Polylactide; **PBS:** Polybutylene succinate; **PHAs:** Polyhydroxyalkanoates; **LBL:** layer-by-layer; **APP:** Ammonium polyphosphate; **oMMT:** organically modified montmorillonite; **TAC:** triallyl cyanurate; **P-AA:** N,N'-diallyl-P-phenylphosphonicdiamide; **MOF:** metal-organic framework; **IL:** ionic liquid tetrabutylphosphonium tetrafluoroborate; **MWCNT:** multi-walled carbon nanotube; **PHB:** poly-3-Hydroxybutyrate; **PHV:** poly (3-hydroxyvalerate); **PHP:** poly(3-hydroxypropionate); **TM:** thymine; **P(3,4)HB**: Poly(3-hydroxybutyrate-co-4-hydroxybutyrate); **PHBH:** Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); **FA:** furfuryl alcohol; **ADP:** ammonium dihydrogen phosphate; **PDMA:** hydroxyl-terminated polydimethylsiloxane; **PU:** polyurethane; **WPC:** wood-plastic composite; **XPS:** extruded polystyrene foam.

Parameters and characterization

TTI: time to ignition; **T_{ig}:** ignition temperature; **HRR:** heat release rate; **PHRR:** peak to heat release rate; **MLR:** mass loss rate; **TSP:** total smoke product; **THR:** total heat release; **EHC:** effective heat of combustion; **HRC:** heat release capacity; **T_{is}:** smoldering initiation temperature; **S_p:** propagation speed of the smoldering front; **t_{ig}:** ignition times; **FGI:** fire growth index; Vac: average combustion velocity; **λ:** thermal conductivity**;** **D:** thermal diffusivity; **SEM:** scanning electron microscope; **LIFT:** lateral ignition and flame spread test; **CCT:** Cone Calorimeter test; **H-TRIS:** heat-transfer rate inducing system; **TGA:** thermogravimetric analysis; **LOI:** limit oxygen index.

1. Introduction

Construction sector, which refers to infrastructure, such as streets, bridges, railroads, and buildings etc., plays an important role in the development of urbanization and industrialization to closely affect human activities. However, with a steady rising human population in 2050 [1], the pressure from environment, economy, and society is increasing at the same time. Based on the report [2–4], the construction materials, a crucial component of construction sector, demand taking a large amount of energy due to the extraction of raw materials, manufacture processing, and disposal of demolition waste [5], as well as contribute the main emissions of greenhouse gas [6].

For the sake of relieving environmental impact and improving utilization of resources, some specific policies have been stated to promote the application of environment-friendly construction materials in various countries. For example, in China, the proportion of sustainable construction materials (SCM) should be up to 30% by 2018 in new buildings [7]. The concept of Circular Economy (CE) has been put forward in European Union's (EU) action plan to optimize the relationship between materials and environment [8]. A sustainable management (SMM) is also made by United States (US) Environmental Protection Agency (EPA) to encourage using the secondary non-hazardous materials in the built environment [9]. Japanese government issues legislation to focus on the recycling of Construction Demolition Waste (CDW) [10]. Therefore, in order to approach the strict requirements of low environmental impact, efficient utilization of resources, and economic practicality, use of bio-based materials are becoming the most effective way to achieve the approach of environmental sustainability, as shown in Fig. 1. Among them, biopolymers are intended to be used as ecofriendly construction materials to meet the requirement of disposal of construction materials [11]. Wood and natural fibers combined with other materials are developed to prepare sustainable hybrid materials [12]. Moreover, the crop by-products can also be considered as a potential alternative for construction thermal insulators [13].

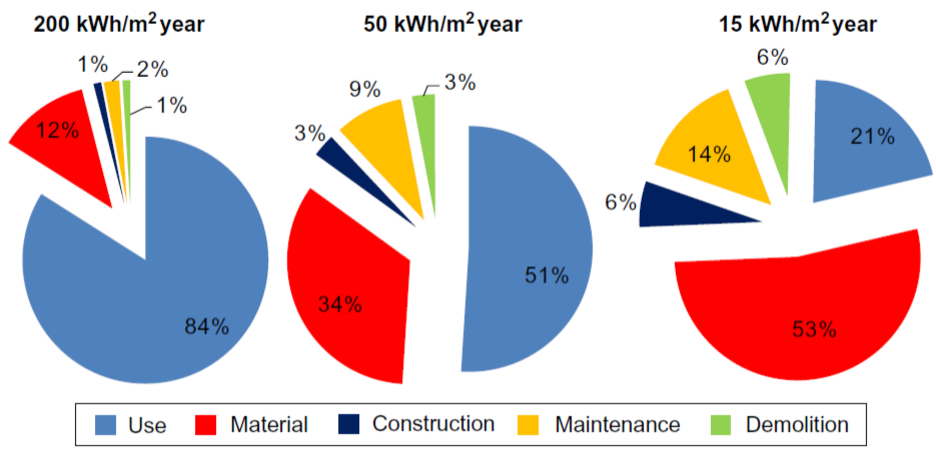

Fig. 1 Distribution of environmental impacts with improving energy performances of buildings and decreased overall consumption [14], Copyright 2017, reproduced permission from Elsevier Ltd.

As construction materials, fire risk, which is related to life safety, should be considered as a crucial performance indicator because of the inherent flammability of these bio-based materials, such as polymeric materials, wood-based hybrids, and crop-based composites. It is well known that a self-sustaining fire needs the presence of some elements named fire tetrahedron: oxidizer, heat, fuel, and chain reaction. When a fuel is exposed to a heat source, the temperature of fuel continuously increases accompanied by pyrolysis and oxidation process in the existence of oxygen, which can accelerate the further combustion. Finally, it is converted into products and heat. With regard to bio-based construction materials, the combustion of these three solid fuels is a complex reaction involving vapor and condensed phase [15]. During external heating process, volatiles from fuels' decomposition enter into the gas phase and mix with air or oxygen. When the concentration and temperature of the mixture reach a critical point, flaming combustion happens with the exothermic reaction in vapor phase, which promotes pyrolysis behaviors of the solid phase [16]. On the other hand, if a solid fuel can form a char under the condition of continuous heating, as well as following oxidation reaction and heat release are observed on the condensed phase, then smoldering combustion occurs. In comparison with flaming combustion, smoldering is a combustion with slower, lower-temperature, and flameless characteristics, which is dependent on the relationship between heat release and absorption [17]. This behavior is especially associated with the porous fuels, such as insulation materials or sawdust [18]. Generally, each fire evolution differing mainly in the heat and mass transfer can be divided into three stages of incipient stage, free-burning stage, and smoldering stage [19]. Equations 1-3 [20] illustrates simple chemical pathways for combustion of solid fuels to demonstrate the oxidation reaction on condensed and vapor phases.

$$\text{Fuel (solid)} + \text{Heat} \rightarrow \text{Pyrolyzate (gas)} + \text{Char (solid)} + \text{Ash (solid)} \quad 1$$

Heterogeneous oxidation:

$$\text{Char (solid)} + O_2 \text{ (gas)} \rightarrow \text{Heat} + CO_2 + H_2\text{O} + \text{other gases} + \text{Ash (solid)} \quad 2$$

Gas-phase oxidation:

$$\text{Pyrolyzate (gas)} + O_2 \text{ (gas)} \rightarrow \text{Heat} + CO_2 + H_2\text{O} + \text{other gases} \quad 3$$

On the basis of combustion peculiarities of solid fuels, some typical flame-retardant mechanisms have been proposed to improve fire retardancy of these flammable materials [21]. (1) Barrier theory, which can function in both smoldering and flaming combustions. In condensed phase, flame retardants promote the formation of a good charring-layer to obstruct transfer of volatiles, oxygen, and heat. (2) Free radical quenching theory. In gas phase, free radical inhibitors released from flame retardants can scavenge flame propagating radicals (e.g., $OH^{\cdot}$ and $H^{\cdot}$, etc.) to quench the flame. (3) Other theories. For example, thermal theory, an effect to dissipate the heat from surface by increasing thermal conductivity of materials; dilution theory, a behavior to dilute the combustible gases by nonflammable volatiles generated from decomposition of flame retardant. However, in most real fire scenarios, the flame-retardant behavior is a synergistic effect by combining several fire-retardant mechanisms, as shown in Fig. 2. A typical example for this synergistic effect is intumescent flame retardants (IFRs) system, which produces the physical barrier and releases inert gases, involving CO_2 and water. Moreover, aiming to investigate the fire behavior of these bio-based materials after introducing flame retardants, corresponding important parameters are used during the research, including limiting oxygen index (LOI), ratings in UL-94 vertical test (V-

0, V-1, or V-2), time to ignition (TTI), ignition temperature (T_{ig}), heat release rate (HRR), peak to heat release rate (PHRR), mass loss rate (MLR), total smoke product (TSP), total heat release (THR), effective heat of combustion (EHC), heat release capacity (HRC), fire growth index (FGI), smoldering initiation temperature (T_{is}), propagation speed of the smoldering front (S_p), and ignition times (t_{ig}).

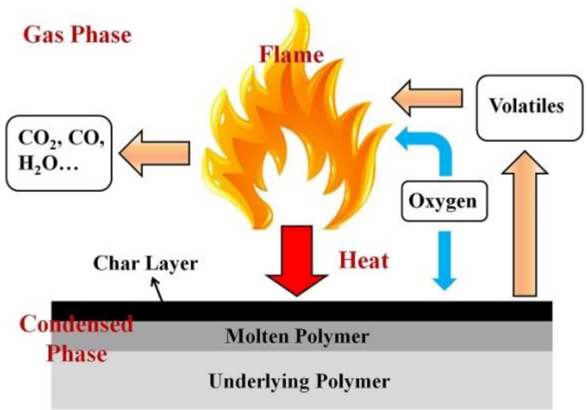

Fig. 2 Flame retardant actions during combustion [22], Copyright 2017, reproduced permission from Elsevier B. V.

This paper mainly reviews the recent progress of flame-retardant bio-based materials in construction sectors, and the dominant points involve preparation of flame retardants, development of novel methodologies, and fire behaviors of modified materials in this article. The content is described in three aspects: biopolymer-based flame-retardant materials, wood-based flame-retardant materials, and crop-based flame-retardant materials. Furthermore, some brief comments are summarized for developing bio-based flame-retardant materials to meet the future opportunities and challenges in construction sectors.

2 Toward the development of bio-based flame-retardant materials in construction sectors

2.1 Biopolymer-based flame-retardant materials

Concept of reducing carbon emissions and environment impact contributes to use of biopolymers and its composites in construction sectors, such as roofs, windows, floors, oil well, plasters, and coatings [23,24]. Biopolymers is an ambiguous term, which is defined as polymers produced by natural raw materials, microorganisms, or renewable resources. For the aim of this paper, the biopolymer is considered as a material which is converted by renewable resources into final polymer directly or the monomer is derived from renewable resource and then is obtained via chemical ways into final product [25]. Amongst them, Polylactide (PLA), Polybutylene succinate (PBS), Polyhydroxyalkanoates (PHAs), and starch are already studied to approach the requirements in construction field due to their outstanding peculiarities. However, these biopolymers possess the inherent flammability as other thermoplastics, and accordingly, there are many methods to be conducted to improve the fire performance.

Pure PLA generally shows high tensile strength, Young's modulus and good processability [26,27], but the intrinsic flammability with dripping behavior during combustion limits its further application in construction areas. Aiming to improve the flame retardancy of PLA, some flame retardants including metal oxides [28], nano compounds [29,30], cellulose fillers [31], IFRs [32], and phosphorus-containing chemicals [33,34] have been incorporated into PLA to overcome this defect by melt mixing method. Two similar types of flame retardants with core-shell structure were prepared via layer-by-layer (LbL) using these chemicals with positive or negative charges [35,36]. The core-shell structures of APP@CS@PA-Na and APP@CS@AA-nBL were observed by scanning electron microscope (SEM), as shown in Fig. 3 and Fig. 4, respectively. In this special structure, ammonium polyphosphate (APP) is utilized as core and other two chemicals as shell. After blending 10wt% content of each flame retardants with PLA, these two composites possess higher LOI value (more than 30%) and pass V-0 rating in UL-94 as compared to neat PLA. This is because the core-shell structural flame retardants offer not only efficient carbon source but also good interfacial bonding between different components, which improves the thermal stability and carbonization of PLA composites during combustion. According to the results from volatiles and residues, the dominant flame-retardant mechanism of both

APP@CS@PA-Na and APP@CS@AA-nBL focuses on the condensed phase. In most cases, incorporation of flame retardant can impart PLA adverse effect on mechanical properties, and thus PLA was mixed with 30 kGy dose of organically modified montmorillonite (oMMT) and triallyl cyanurate (TAC) to offset this defect [37]. This combination gives PLA nanocomposite with good mechanical properties, exhibiting average elongation at break of 47.8% and tensile strength of 63.6 MPa. Meanwhile, the formation of cross-linking structures during heating leads to an increased onset decomposition temperature ($T_{2wt\%}$) of 297 ℃. Some efficient phosphorus-containing flame retardants named PA-THAM and N, N′-diallyl-P-phenylphosphonicdiamide (P-AA) were synthesized and imparted PLA composites V-0 rating in UL-94 at loading of only 3 wt% and 0.5 wt%, respectively [33,38]. Owing to the low amount, the tensile properties of PLA samples almost maintain the same level. Moreover, other efficient flame-retardant systems for PLA were also developed in our group, shown in Fig. 5. As another intrinsic shortcoming of PLA, poor toughness is also getting much attention as developing fire-safety performance [39]. A synergistic system with ionic liquid tetrabutylphosphonium tetrafluoroborate (IL) and APP was added into PLA. Sample PLA/IL_1/APP_1-3wt% (containing 1.5 wt% IL and 1.5 wt% APP) simultaneously obtains good flame-retardant properties and remarkable tensile toughness, reflecting by elongation at break increased from 8.5% to 204.6%. The improved toughness is because the combination of IL and APP not only minimizes the interfacial defects between PLA and APP, but also brings a plasticization effect. In addition to physical method, chemical modification is also considered as a good way to improve the flame retardancy of PLA for solving the possible problems of affinity and durability of additives in matrix [40].

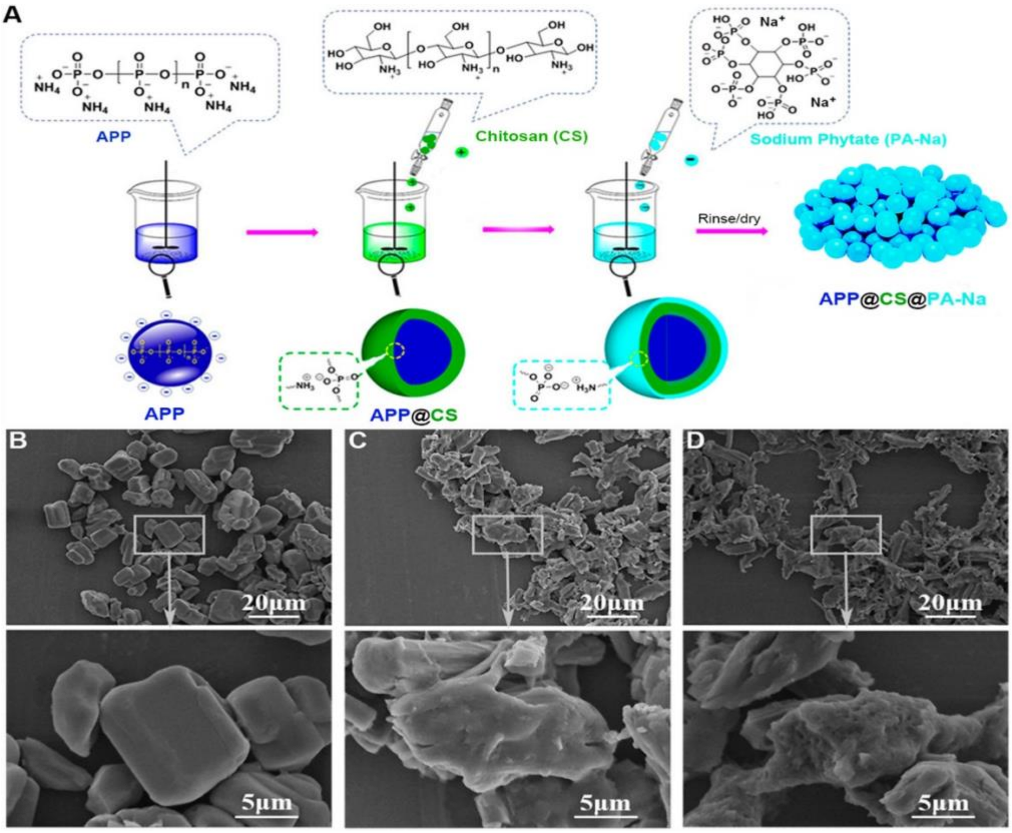

Fig. 3 (A) Schematic illustration for the fabrication of APP@CS@PA-Na via LAL assembly from water. SEM photographs of (B) APP, (C) APP@CS, and (D) APP@CS@PA-Na [35], Copyright 2019. Reproduced with permission from American Chemical Society.

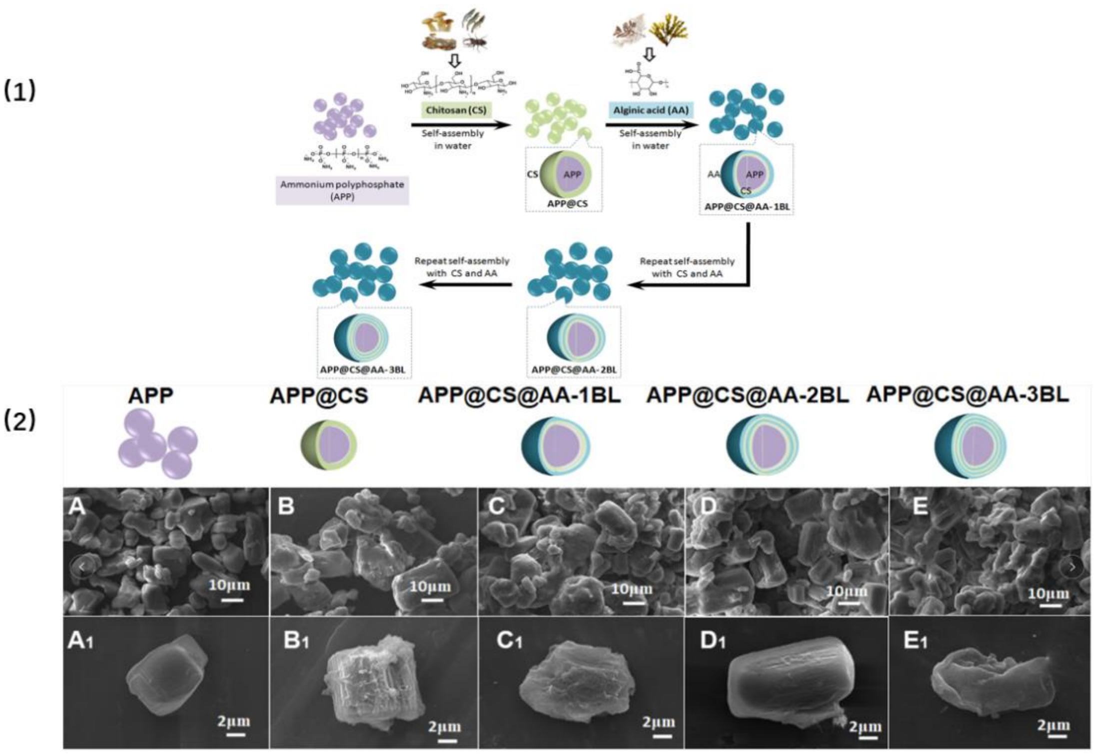

Fig. 4 (1) Synthetic diagram of APP@CS@AA-nBL, (2) SEM photos of (A, A1) APP, (B, B1) APP@CS, (C, C1)

APP@CS@AA-1BL, (D, D1) APP@CS@AA-2BL, and (E, E1) APP@CS@AA-3BL [36], Copyright 2020. Reproduced with permission from American Chemical Society.

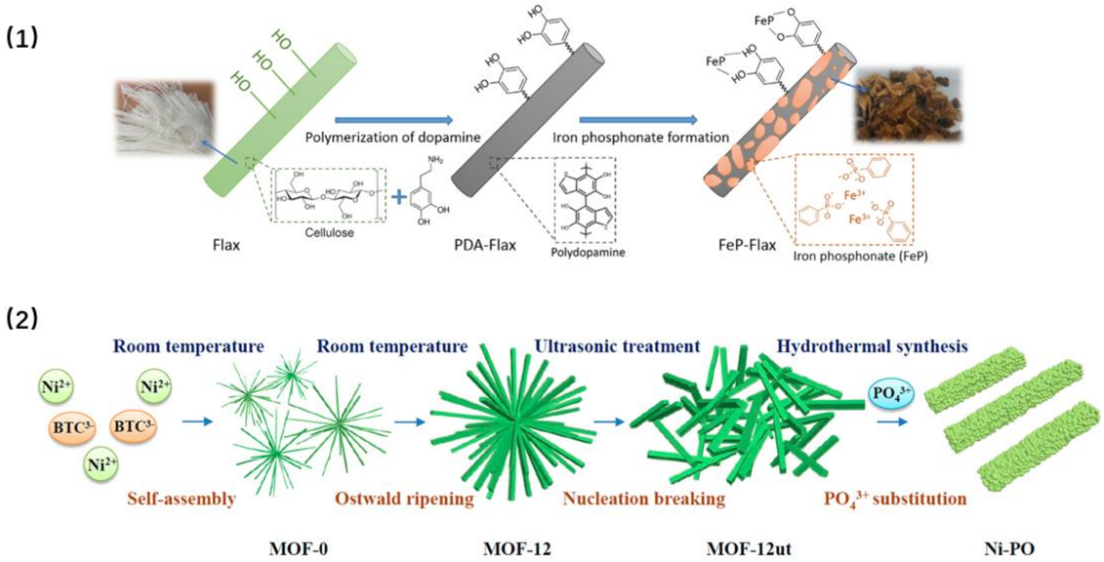

Fig. 5 (1) Scheme of reparation for flax/ Fe-phosphonate system [41], Copyright 2018. Reproduced with permission from Elsevier Ltd; (2) scheme of preparation for Ni-PO derived from metal-organic framework (MOF) [42], Copyright 2019. Reproduced with permission from American Chemical Society.

PBS has an excellent heat resistance, good mechanical properties, and easy processibility among the most biopolymers [43,44]. Thus, it is possible to meet the fire-safety requirement by combining with other materials. As mentioned in PLA-based composites, physical addition is also an efficient way to improve the flame-retardant properties of PBS. In recent years, IFRs [45], phosphorus-containing chemicals [46], and other hybrid synergistic systems [47] have been used to solve the flammability of PBS. A bio-based IFR named PA-GU was prepared and used to enhance the flame retardancy of PBS [48]. Compared with pristine PBS, composite with 10 wt% loading of PA-GU demonstrates a decrease of 59.2% and 38.6% for PHRR and THR, respectively. The improved flame retardancy can be explained as the barrier effect from IFR PA-GU, in which PA acts as acid source, and GU as charring and blowing agent. Aiming to further overcome the phenomena of fast fire growth and continuous combustion in PBS/ APP/ pentaerythritol (PBS/APP/PER) system, aminated multi-walled carbon nanotube (MWCNT) was coated onto APP and used as synergist to improve the quantity of charring layer [49]. Consequently, in comparison with control sample, a significant improvement of fire retardant is obtained in sample PBS-3 with 1wt% CNT@APP. Apart from the improvements in PHRR, THR and char mass, a decrease of fire growth index (FGI) from 3.1 to 1.6 and V-0 rating in UL-94 are also observed, shown in Fig. 6 (1). This result is attributed to a synergistic effect between fillers and IFR to promote forming a continuous char layer with high thermal stability during initial combustion stage, shown in Fig. 6 (2). Phosphorus-containing copolyesters (PPBS) were synthesized via polycondensation and used as flame retardants for PBS by melt blending method [50]. Good compatibility between components caused a good LOI value and unaffected crystalline morphology. However, the negative effects, involving high loading or limited flame-retardant efficiency, of the sole flame-retardant on matrices' properties still need to be focused, some synergistic agents have been developed to solve these problems. For example, in order to reduce addition of IFRs, Yuan Hu's [51,52] group chose fumed silica and graphene as the synergistic agents for PBS/APP/MA system based on the relationship between structure and properties. Fumed silica has large surface area, low density, and low superficial free energy in heating, which can favor being adsorbed onto the sample's surface and accelerate flame retardants to form a thermal-stable charring layer with three-dimensional interpenetrating networks. Consequently, melting dripping was suppressed and transfer of oxygen and heat was prevented during combustion of PBS, shown in Fig. 7(1). Regarding to graphene, a carbon-rich consisting nano-reinforcement with unique two-dimensional honeycomb structure, only 2wt% loading of graphene imparts PBS composite anti-dripping behavior benefitted from obstructing and heat-transferring function of graphene, listed in Fig. 7(2). In addition, PBS had also been composited with natural fibers [53,54] or nanotubes [55,56] to extend the fire retardancy and mechanical properties simultaneously, which can meet the further engineering applications.

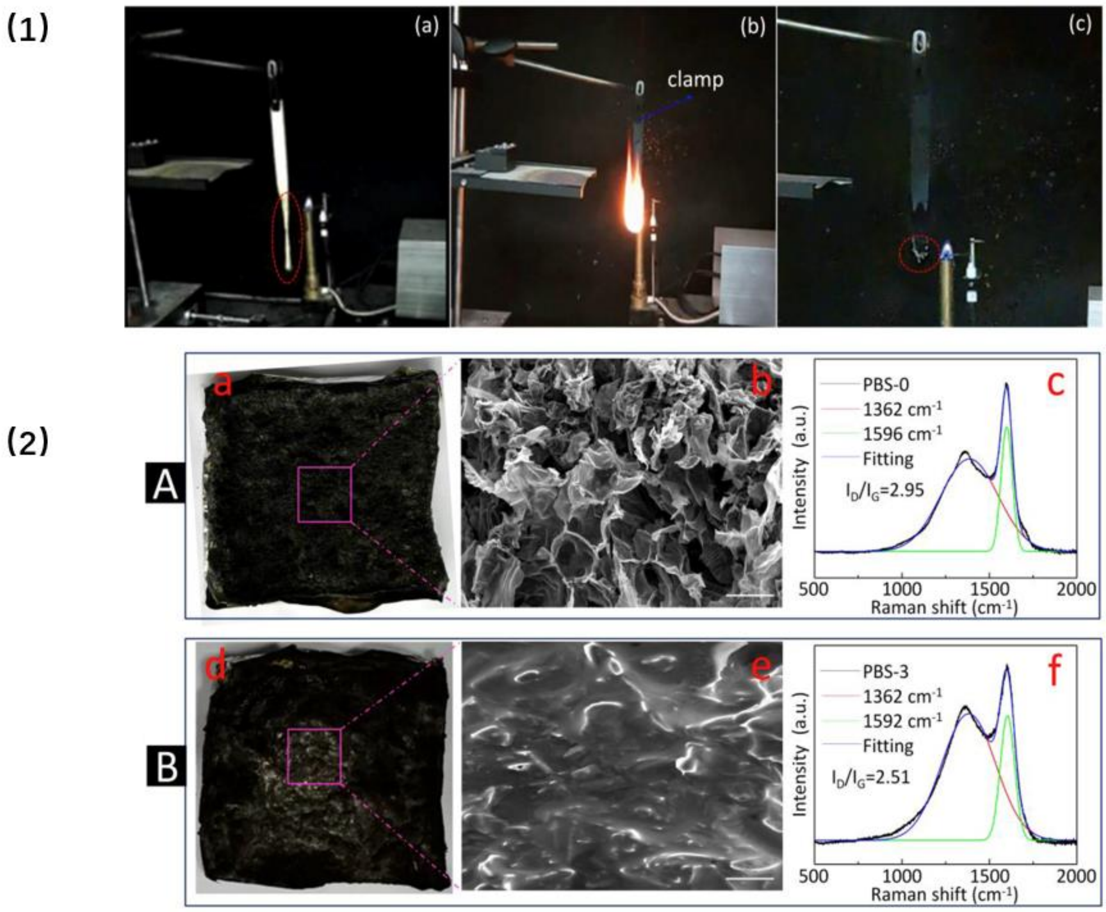

Fig. 6 (1) Photographs of UL-94 vertical tests for PBS (a), PBS-2 (b) and PBS-3 (c). (2) Digital photos (a and d), SEM (b and e, scale bar of 50 um) and Raman spectra (c and f) of char of PBS-0 (A) and PBS-3 (B) after cone calorimeter test [49] Copyright 2020. Reproduced with permission from Elsevier Ltd.

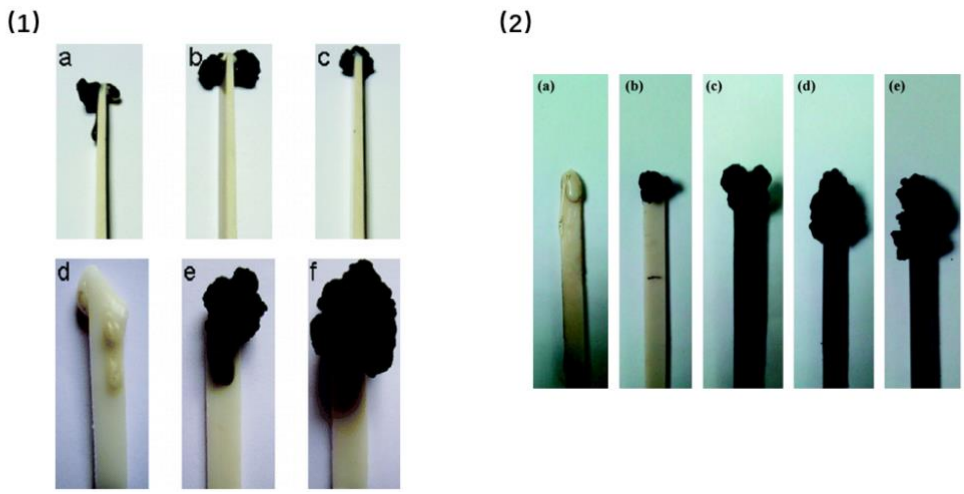

Fig. 7 Photos of char residues after combustion, (1) PBS/APP+MA/Si ratio: a) 75/25(6:1)/0, b) 75/25(5:1)/0, c) 75/25(3:1)/0, d) 100/0/0, e) 80/20(5:1)/0, f) 80/18(5:1)/2 [52], Copyright 2010. Reproduced with permission from

American Chemical Society; (2) PBS/APP+MA/GNS ratio: a) 100/0/0, b) 80/20/0, c) 80/19.5/0.5, d) 80/19.0/1.0, e) 80/18.0/2.0 [51], Copyright 2011. Reproduced with permission from American Chemical Society.

PHAs are a family of aliphatic polyesters derived mainly from microorganisms, including poly-3-Hydroxybutyrate (PHB), poly (3-hydroxyvalerate) (PHV), poly(3-hydroxypropionate) (PHP), and so on. PHAs demonstrate biodegradability, biocompatibility, thermoplasticity and versatility to offer tremendously potential opportunities in construction fields [57–59]. As thermoplastics with inherent flammability, some efforts have been made to improve the fire behaviors of these PHAs as well. As the most common type of PHAs, pure PHB was investigated by evaluating some critical parameters involving T_{ig} and HRC [60]. T_{ig} of approximate 375 ±10 ℃, as a standard to evaluate the difficulty in igniting polymers, was obtained according to the concentrations of CO, H_2, and CH_4 during decomposition. HRC, a good measure to speculate the ability of burning speed after ignition, was calculated to a lower value (765 J/g-K) for PHB than for polypropylene (1567 J/g-K) and polyethylene (1193 J/g-K), which means PHB is more difficult to flame than the other two commercial polymers. Poor thermal stability of PHB, which has strong ties with the flame-retardant performance, was also studied by adding some fillers, such as thymine (TM) and lignin [61,62]. From the results, thermal stability of modified PHB composites shows a higher thermal degradation temperature due to the presence of these stabilizers. Additionally, PHB was blended with other polymers to prepare copolymers, for example, Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) [P(3,4)HB] [63] and Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) [64]. Meanwhile, the fire retardancy of P(3,4)HB and PHBH added with IFR/ZnB and natural fillers, respectively, was investigated, illustrating a reduction of PHRR for both copolymers. Unlike PLA and PBS, which have already been addressed the flame retardancy by many researchers, there are still limited articles to report the flame-retardant properties of PHAs family. Therefore, it is essential to expand more effort to work on this field to meet more requirements of construction application.

Apart from aforementioned biopolymers, starch, a natural polymer with adhesion, adsorption, and low-cost, is getting more attention to prepare compounds with other materials for construction application, such as fillers in fresh concrete [65,66], binder for thermal insulation systems [67], viscosity modifier of asphalt [68]. Besides, starch exhibits a high content of carbon with a carbonization process under exposure to the heat source [69]. Thus, this biopolymer can be used as a synergist to improve flame-retardant properties of other biopolymers [70] besides some research progresses on fire behavior of starch itself [71].

2.2 Wood-based flame-retardant materials

As a kind of conventional natural material, wood have been applied to both structure parts and interior finish in outdoor and indoor places for many centuries owing to its suitably aesthetic, acoustic, durable, thermal, and mechanical properties. Wood generally goes through thermal decomposition stages involving oxidation, ignition, combustion, and carbonization at the condition of elevating temperature, and meanwhile, a permanent loss of mass and strength will take place resulted from the thermal decomposition of major components consisted of hemicellulose (225-325 °C), cellulose (325-375 °C), lignin (250-500 °C). The inherent flammability of this fibrous substance is a great contribution to property losses in construction industry. Therefore, in order to improve fire-safety performance of wood products, some potential treatments can also be used for fire retarding wood, including addition of inorganic minerals, formulation containing boron, phosphorus, and nitrogen, or nanocomposites [72]. Laia Haurie et al. [73] found that the fire reaction of several tropical wood species was correlated to morphology, mineral composition, and density. Moreover, boron salt and sulphate salt were incorporated into wood via impregnation method, and consequent enhancements were observed in fire resistance [74,75]. Based on the environmental concern and energy consumption, this section will be limited to the flame-retardant modification of wood-based composites focusing on laminates, plywood, fiberboard and wood-plastic composite by pressure impregnation [76], coating [77], adhesive modification [78] and other technologies.

Laminates are usually found in indoors' elements, particularly in flooring, to keep from wetting, and some significant achievements on fire resistance of laminates can be found in many publications. Pressure impregnation, a widely useful method for introducing additives into wood-based materials, was used to infiltrate an efficient flame retardant consisted of furfuryl alcohol (FA) and ammonium dihydrogen phosphate (ADP) into wood substrate. Resultantly, a hydrophobic FA/ADP network produced via in-situ polymerization during curing [79]. This Wood/PFA/ADP composite exhibits prominent improvement in flame retardancy, displayed in Fig. 8, which was reflected in reduction of PHRR, THR, obvious smoke suppression, and ignition resistance due to char formation and incombustible gases release during combustion. Besides, an increase in mechanical properties is also obtained attribute to enhanced dimensional stability after the additives was filled into the cell cavities of wood. In order to preserve a well dispersion of flame retardant in wood, a wood laminate with 16.2 wt% of bentonite nanosheets were prepared via delignification and densification processes, which simultaneously displays good flame retardancy and mechanical strength [80]. At a condition of an open flame, self-extinguishing behavior and postponed ignition time were observed in the modified wood laminate. In contrast, control sample ignited within 19 s, as well as a strong flame started at 30 s, listed in Fig. 9. These phenomena can be clarified that the delignification and densification processes sequentially favor forming porous structure and 3D protective layer with impervious and dense structure in bentonite-infiltrated wood laminate. The special structure leads to the preservation of bentonites in wood cells to form a heat shielding to obstruct the transfer of heat and mass during burning. Moreover, the existence of bentonite nanosheets enhances interfacial affinity between nanosheets and nanocellulose due to hydrogen bonding networks, which contributes to a significant increase of mechanical properties.

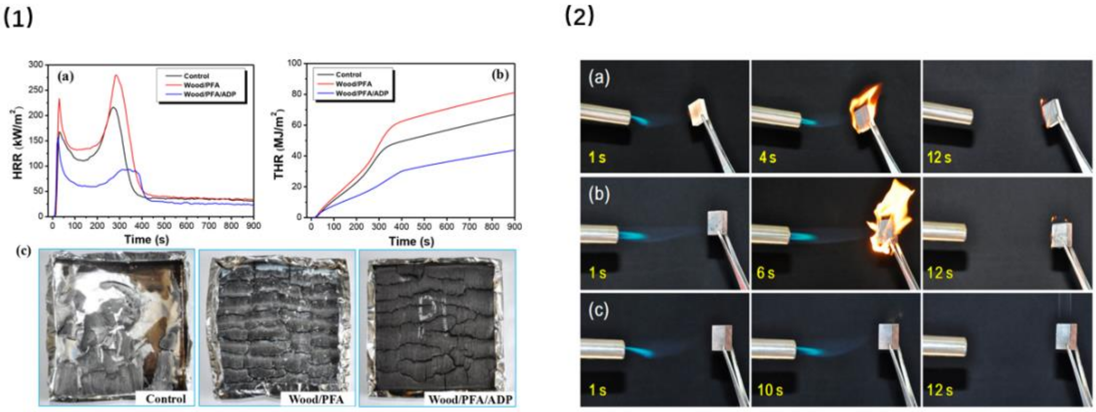

Fig. 8 Wood/PFA/ADP laminate. (1) results from cone calorimeter test: (a) HRR curves, (b) THR curves, and (c) digital photos of char residues after combustion of control Wood, Wood/PFA, and Wood/PFA/ADP. (2) the flammability test: (a) control Wood, (b) Wood/PFA, and (c) Wood/PFA/ADP [79], Copyright 2018. Reproduced with permission from American Chemical Society.

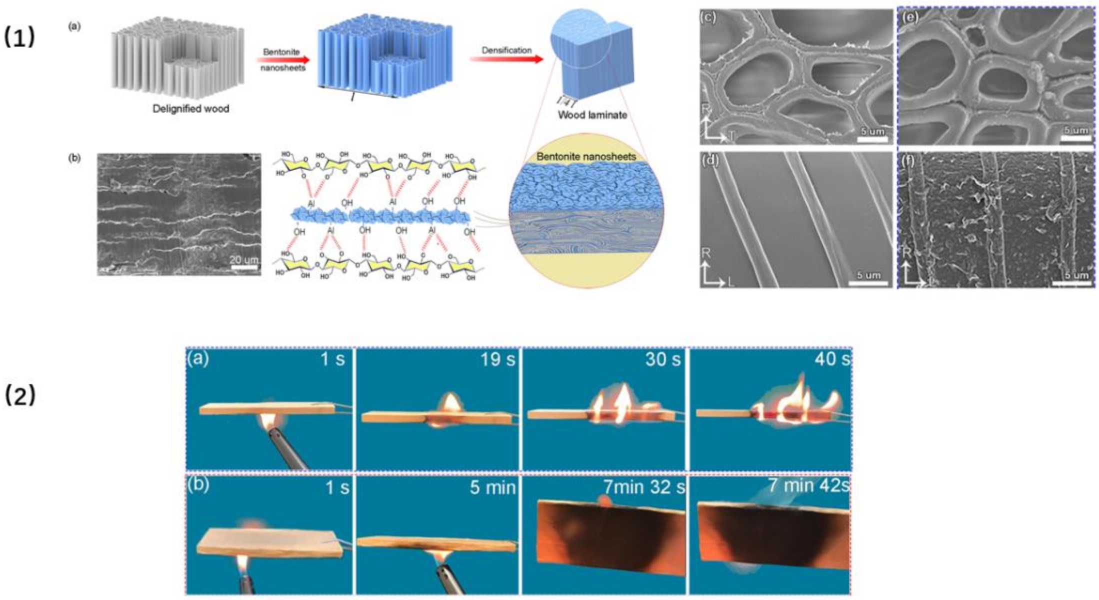

Fig. 9 A bentonite-infiltrated wood laminate. (1) scheme illustration of the structure and scanning electron microscopy (SEM): (a) delignified wood structure with aligned channel and porosity for bentonite penetration; densified process for impervious and dense structure with good compatibility between cellulose nano fibers and nanosheets, (b) SEM image of the modified wood laminate and the formation of hydrogen bonding networks, (c and d) cross-sectional and side view SEM images of natural wood cell walls, (e and f) cross-sectional and longitudinal view SEM images of bentonite-infiltrated delignified wood. (2) the flammability test: (a) natural wood laminate, (b) bentonite-infiltrated wood laminate [80], Copyright 2019. Reproduced with permission from Elsevier B.V.

Plywood, which is made from wood veneers by bonding process, is a widely engineered wood product available in residential construction areas, such as floors, furniture, roofs, and other structural applications thanks to its shrinkage resistance, high strength, flexible performance, et al [81]. In terms of fire safety, plywood is also getting much concern to improve the flame resistance [82]. Silicon-containing chemicals were used successfully as flame retardants due to their excellent thermal stability, low toxic gas, and low HRR [83]. A silica fume-based hybrid modified with hydroxyl-terminated polydimethylsiloxane (PDMS) was explored and introduced into plywood as a fireproof coating [84]. When the kinematic viscosity of PDMS was fixed with 350 cps, a good flame-retarding plywood was obtained with a decreased value of FGI (by 50%), average combustion velocity (Vac: 6.74×10^{-2} %/s), as well as smoke suppression (TSP: by 78.8%) compared with control sample. This enhancement is because PDMS can fill into clearance from the amorphous silicate and facilitate forming a network structure due to coexistence of hydrogen bonding from Si-OH and PDMS-OH. Consequently, an intact and smooth siliceous physical-layer forms to prevent the transfer of heat and mass during combustion. Coating, as a convenient and effective approach to improve the flammability, also causes some adverse effects of aging and appearance problems on wood-based composites. Hence, differing from coating on the surface of wood substrate directly, an adhesive modification technology has been developed to enhance delamination resistance and flame retardancy of glued plywood, which refers to a silicone-based adhesive with vinyl-silane treated aluminum hydroxide [85]. This multifunctional adhesive system (SI/plywood) and conventional polyurethane-based adhesive system (PU/plywood) were prepared. Meanwhile, Mydrin test and lateral ignition and flame spread test (LIFT) were carried out to investigate the effect of adhesive on fire-resistance, auto-ignition and flame propagation of plywood, respectively, listed in Fig. 10. As expected, PU/plywood burned out after 25 min in Mydrin test and demonstrated auto-ignited behavior with obvious charring and delamination in LIFT. In contrast, a superior fire resistance with no ignition phenomena was observed for SI/plywood at the same conditions in both combustion tests, which is attributed to a thermally stable residue generated by SI adhesive system.

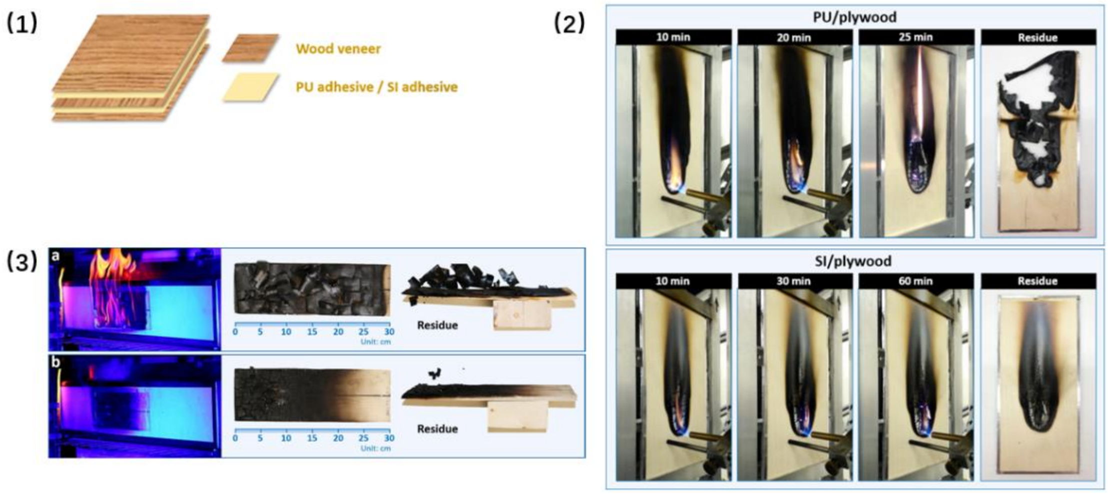

Fig. 10 (1) Preparation scheme of plywood samples. (2) images from Mydrin test for PU/plywood and SI/plywood. (3) images from LIFT for 5 min: (a) PU/plywood, (b) SI/plywood [85], Copyright 2018. Reproduced with permission from Elsevier Ltd.

Moreover, other wood-based products, such as fiberboard and wood-plastic composite (WPC), are also considered as good materials for residential and industrial sectors because of their favorable performance, ecofriendly, and low cost. Take a typical natural material for example, bamboo can be utilized in entire houses, bridges, scaffoldings and other structural elements due to its special interior structure, high strength-to-weight ratio, and water-resistance [86–88]. Therefore, many efforts are making to develop novel bamboo composites [89], or improve the poor fire resistance for further application [90]. Aiming to know the burning behavior when bamboo is exposed to fire, three thermally thick bamboo samples with different adhesive, density, and thickness were tested to investigate the basic flammability parameters based on data from Cone Calorimeter test (CCT) [91]. For all testing samples, the critical heat flux for ignition was 15 kW/m^2, and critical mass loss rate, which increased with the external radiant flux, was between 2 and 4.5 g/ $m^2 \cdot s$ within the flux range of 15-80 kW/m^2. These experiments elucidate that bamboo probably consumed more energy to ignite than other timber species and went through a following smoldering combustion after flaming stage, which needed further work to quantify. A fiberboard made from bamboo biomass exhibits fire safety and high internal bonding strength to offer an economically potential alternative for structural and furniture applications [92]. However, to date there are still limited papers on the fire resistance of this material itself except some bamboo-based hybrids. For example, bamboo/epoxy [93], bamboo/PLA [94], and bamboo/PBS [95] have been obtained by modification with some FRs, which demonstrates better flame-retardant properties compared with control samples. Besides, other WPCs with enhanced flame retardancy are also developed to meet the requirements of construction industry [96,97].

2.3 Crop-based flame-retardant materials

The variety of agriculture plant ranging from wheat, rice, corn, barley, sugarcane, sunflower and others produces abundant by-products, which are identified as potential substitutes to develop external envelope of construction materials by offering good thermal properties and energy consumption [98–100]. In comparison with conventional thermal insulators, such as wools, rigid boards, and foams, these novel crop-based materials possess sustainable, ecofriendly, renewable, local available, and affordable advantages [101,102]. On the flip side, recycling crop byproducts is also an efficient solution to tackle some environmental problems generated by common disposals involving dumping, incineration, land filling, composting, etc. As thermal insulation materials in construction sectors, some important requirements should be fulfilled in thermal performance, involving thermal conductivity (λ: W/m·K) and thermal diffusivity (D: m^2/s), technical properties including processing and durability, as well as fire behaviors in both flaming and smoldering combustion. Therefore, for the purpose of resource recycling and fire safety, this section will emphasize the fire behaviors for crop-based thermal insulation materials, which is derived from byproducts from wheat, rice, corn, barley, and other crops.

Wheat is one of the most widely cultivated cereal over the world. The wheat straw, as one considerable byproduct among others, remains after harvesting to be utilized as thermal insulator [103–105]. Generally, a material can be considered as a thermal insulator with attributes of lower thermal conductivity, as described by the quantity of heat transmitted passing through a unit area of a homogeneous material, and high value of specific heat capacity, which expresses the ability to store energy and can provide low thermal diffusivity values [106]. Wheat straw without any additives was chosen as raw material to compress into samples with different densities (75, 125, and 175 kg/m^3), while some commercial thermal insulation samples, such as XPS and mineral wool, were also prepared as references [107]. The bench-scale (CCT) and medium-scale (H-TRIS: heat-transfer rate inducing system) experiments were performed to investigate fire behavior of these samples. From the results, wheat straw sample with lowest density demonstrates the best reactions to both fire and insulation tests, listed in Table 1. Meanwhile, the board with lowest density showed less HRR (81.05 kW/m^2) than that of XPS (141.48 kW/m^2), which indicates that the wheat straw board appears less fire risk in the early stages as compared to XPS. Additionally, a similar temperature history was observed between compressed straw and mineral wool in early heating stages in the H-TRIS test, listed in Fig. 11. In the light of these results, the wheat straw appears potential to be used as thermal insulation material in building sectors. Yang Gao [108] et al. fabricated a fiberboard consisted of wheat straw and bio-based binder, into which nano-zirconia powder was incorporated to improve the flammability. Samples with the presence of ZrO_2 withstand more time to ignite under exposure to an open fire and illustrate a heat resistance via favoring forming charring layer. On the contrary, reference sample without ZrO_2 is very prone to combust. Other wheat straw boards treated with different additives were also prepared to study the effect of different modifications on the flame-retardant properties [109]. In comparison to untreated sample, the introduction of flame retardant imparts wheat straw board a downward trend for HRR, THR, and EHC, which is because that the FR accelerates the carbonization process of straw. Besides, another flammability trial was conducted to study the fire reaction of wheat straw particleboard, demonstrating a retarded flame spread in the sample treated with linseed oil [110].

Table 1 Results from CCT and thermal conductivity of compressed straw samples with heat flux of 50 kW/m^2 [107]

Density (kg/m^3)	Performance in Combustion: t_{ig}+300s burning duration					λ(W/m·K)
	TTI (s)	HRR (kW/m^2)	PHRR (kW/m^2)	EHC (MJ/kg)	MLR(g/s)	
75	6 (-)	60.74 (-)	171.42 (-)	11.61 (-)	0.046 (-)	0.049 (-)
125	6 (0%)	73.21 (+21%)	178.88 (+4%)	10.42 (-10%)	0.062 (+34%)	0.052 (+5%)
175	8 (+33%)	70.06 (+15%)	177.41 (+3%)	10.14 (-13%)	0.061 (+31%)	0.059 (+20%)

Note: The percentages in brackets refer to the relative difference between the specimen and the 75 kg/m^3 sample's values.

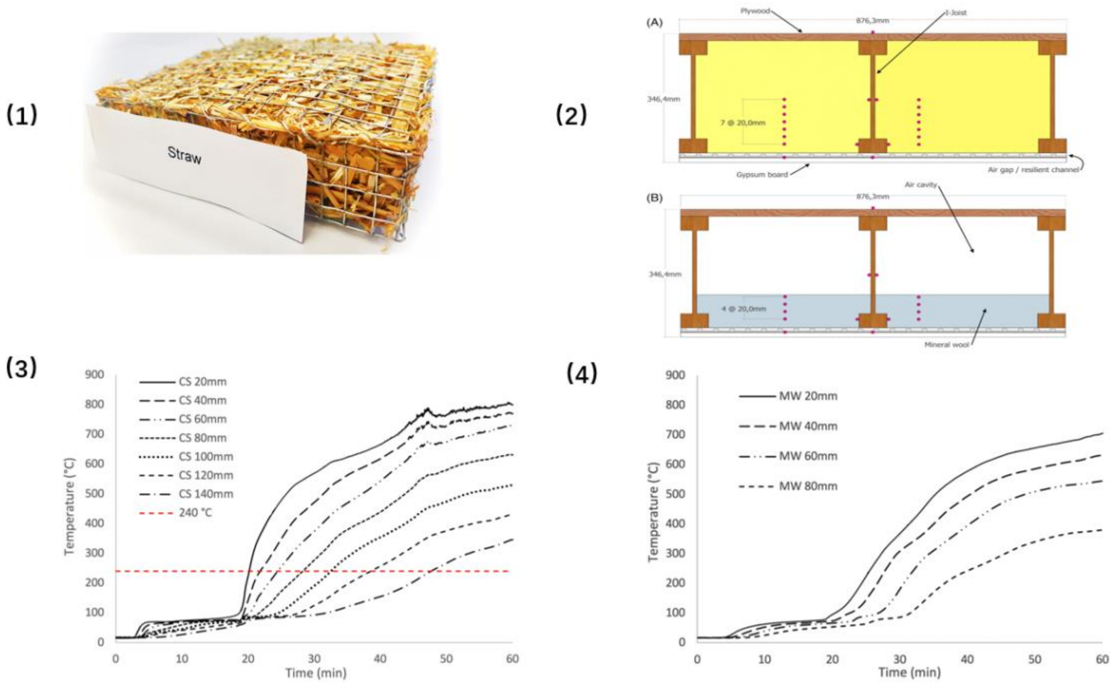

Fig. 11 (1) Compressed wheat straw specimen. (2) Thermocouple locations in H-TRIS test: A, compressed wheat straw, B, mineral wool. (3) Average temperature evolution for compressed wheat straw (CS) in H-TRIS test. (4) Average temperature evolution for mineral wool (MW) in H-TRIS test [107], Copyright 2020. Reproduced with permission from John Wiley & Sons Ltd.

Husk and straw residues derived from rice, one of the most widely consumed crop commodities, have been utilized as biomass thermal insulators in construction sectors

[111,112]. Rice husk, hard coating on the rice grain, yields extensive char and silica during heating [113,114], which can contribute to improving the fire performance. In order to clarify the thermal decomposition mechanism of rice husk, Saad [115] investigated the pyrolysis kinetic and combustion characteristic parameters via analyzing samples with different sizes ranged from 38-200 µm to 200-1000 µm. As a lignocellulose, rice husk exhibits predominant stages of thermal degradation caused by moisture and volatile removal, degradation of hemicellulose, decomposition of cellulose and lignin degradation. Meanwhile, these pyrolysis processes vary with heating rate and particle size. With the increase of heating rate, the curves from thermogravimetric analysis (TGA) shifted to higher temperature, which is because poor heat transfer performance leads to incremental temperature gradient within biomass and results in insufficient time for reaching final temperature of each degradation zone. Moreover, particles with larger size (200-1000 µm) showed higher activation energy (E) and less combustible characteristic with lower T_{ig} and t_{ig} than another sample with smaller size (38-200 µm). The differences between different samples are attributed to not only mineral content or thermal conductivity, but also separation or change of structure and composition during physical treatment [116]. Mitchell et al. [117] made a comparison between XPS and rice husk/ mycelium bio-board, and an anticipated superiority of flame retardancy was found in biomass system due to the existence of carbonaceous char and imbedded silica during combustion [118]. Resultantly, rice husk particleboard demonstrated significant reduced values for PHRR, TSP by 73.5% and 96.6%, respectively, as well as longer estimated time to flashover in room fire test. Moreover, some parameters on smoldering behavior of rice husk containing initiation temperature, particle size, and gas products were also studied by Saad group [119,120]. The transition from smoldering to flaming combustion was exhibited by investigating fire spread of rice fuel-bed under convective heating process, shown in Fig. 12 [121]. Rice straw, another bio-based isolation material, was also studied by Yingfeng et al. [122] by manufacturing straw-magnesium cement (SMC). Additionally, it was proved that rice straw had more tendency towards self-heating, which could trigger the

occurrence of biofuel self-ignition, than rice husk did [123]. This difference is caused by chemical component, physical properties, bulk density, and surrounding environment.

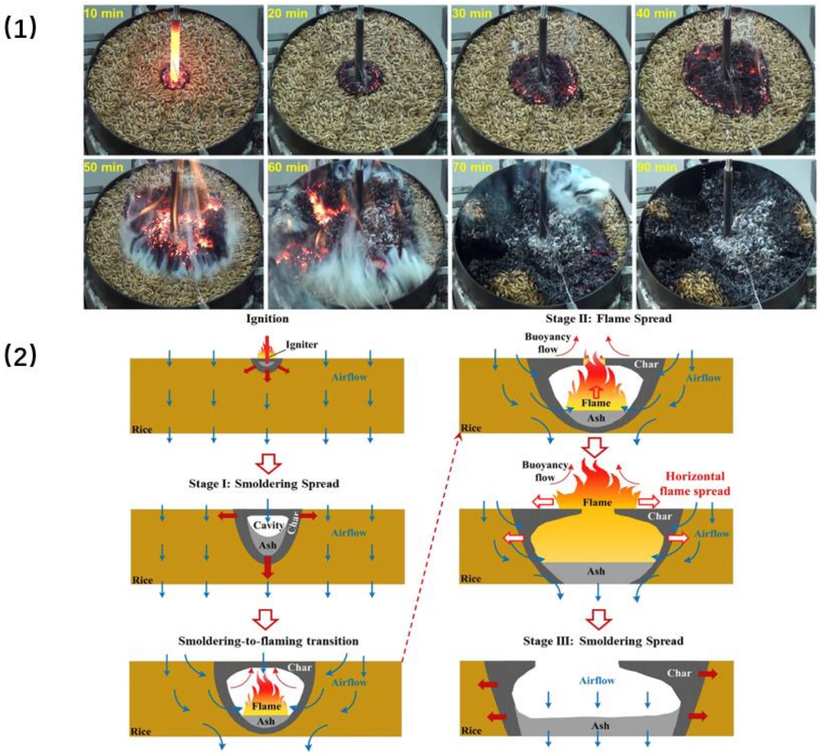

Fig. 12 Investigation of ignition and fire spread of rice fuel-bed: (1) digital photos of rice bed combustion process with airflow of 0.6 m/s; (2) scheme of ignition and fire spread of rice bed during convective heating process [121], Copyright 2020, Reproduced with permission from Elsevier Ltd.

Corn, another common cereal crop in the world, can produce extensive byproducts every year, such as stalk, leave, husk, tassel, and cobs, which can be found in construction thermal materials with acceptable thermal conductivity [124,125]. Fig. 13 lists some thermal panels made from corn byproducts. Corn pith extracted from the interior part of corn stalk possesses a porous spongy tissue and was selected as raw material to prepare thermal insulation board [126]. Compared with control sample, the crop-based board mixed with corn pith and alginate, shown in Fig. 14 (1), demonstrates better fire behavior in both microscale combustion calorimetry and lager scale flammability test, which was used to investigate the ignition and extinguish abilities.

The mixture of corn pith and alginate exhibited reduction of PHRR and THR by 33.6% and 31.8%, respectively, and there was only one ignition with duration of 7 s within 5 min. However, a smoldering process was observed simultaneously. Aiming to improve this phenomenon, boron-containing chemicals, which are generally used as flame retardants due to not only good fire retardancy but also little impact on other properties, were incorporated into corn pith/ alginate system by the same group [127]. Besides some improvements in flaming combustion, the presence of 9 wt% boric additive in crop-based particleboard delayed the occurrence of smoldering and reduced propagation speed by approximately 40%, shown in Fig. 14 (2 and 3)). Furthermore, a mixture of 3 wt% of boric acid and 6 wt% APP postponed the initial temperature of smoldering from 280 °C to 310 °C, which even reached the same level of wood fiberboard. In addition, as demonstrated in Fig. 15, corn grain [128] and corn stalk [129] were taken as the subjects to study the effect of particle size and moisture content on the downward smoldering combustion of fuel bed, which takes place in natural smoldering of biomass fuels. The results indicate that samples with small granular diameter and low moisture are prone to smoldering due to a higher contact area of oxygen and less required heat for vaporization. Other factors including airflow rate, air permeability, chemical properties, and density of fuel bed on combustion of corn byproducts boards were analyzed by other researchers as well [130,131].

Fig. 13 Thermal insulation panels made from corn byproducts: (1) corn tassel/ polyester system [132], Copyright 2020. Reproduced with permission from Elsevier Ltd. (2) corn stalk/ Magnesium Phosphate Cement [133], Copyright 2018. Reproduced with permission from Elsevier B.V. (3) a) corn cob/ bio-binders [134], Copyright 2019. Reproduced with permission from Elsevier Ltd. b) corn cob/ wood glue [135], Copyright 2011. Reproduced with permission from Elsevier B.V. (4) corn pith/ epoxy system [136], Copyright 2016. Reproduced with permission from Elsevier Ltd.

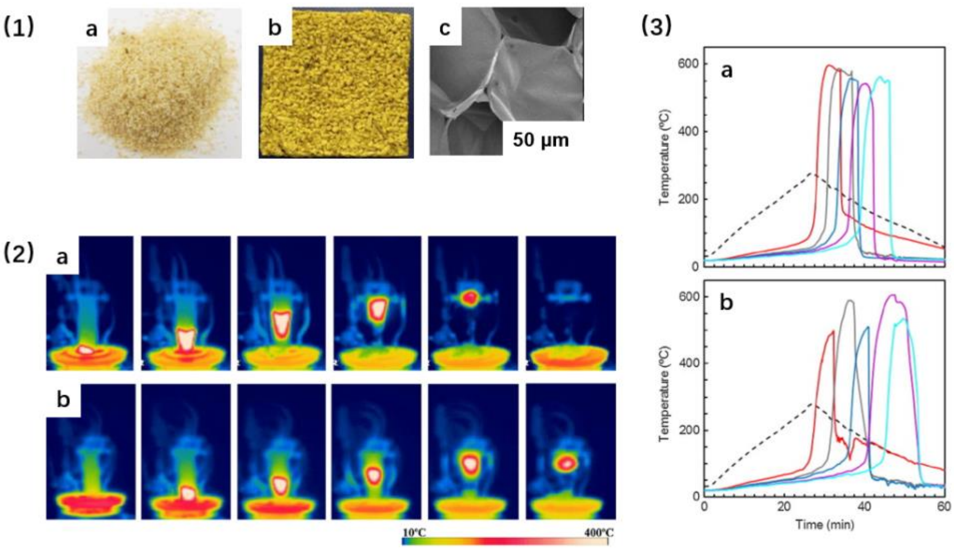

Fig. 14 (1) Corn pith/ alginate thermal insulation: a) sieved particles with size of about 2 mm; b) corn pith/ alginate board; c) micromorphology of corn pith [126], Copyright 2015. Reproduced with permission from Elsevier Ltd. (2) infrared images for a) corn pith/ alginate and b) corn pith/ alginate/ boric acid in smoldering test, (3) temperature evolutions of thermocouples for a) corn pith/ alginate and b) corn pith/ alginate/ boric acid in smoldering test [127], Copyright 2017. Reproduced with permission from Elsevier Ltd.

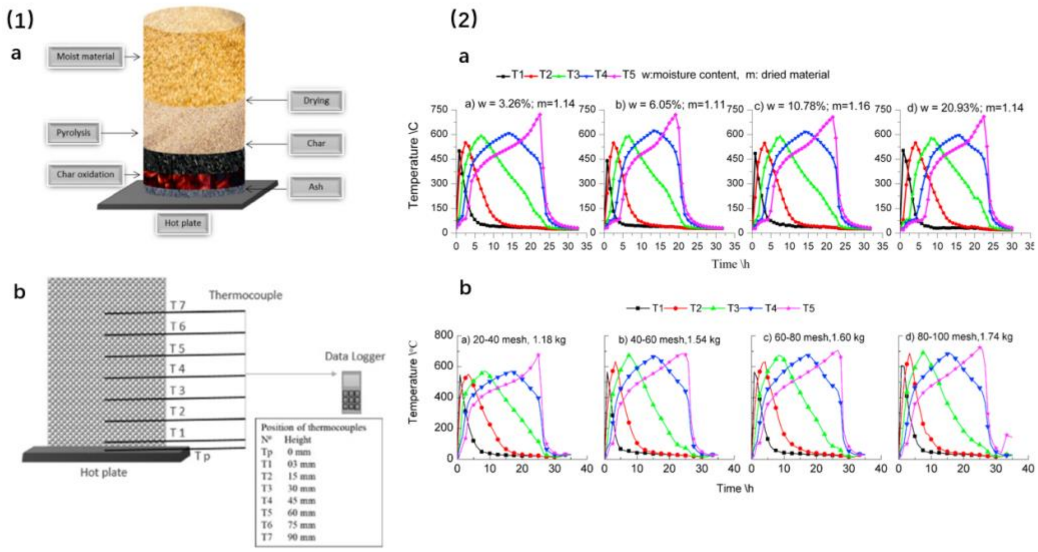

Fig. 15 (1) a) Experimental mode for smoldering propagation in a downward mode; b) experimental set-up for thermocouples' locations [128], Copyright 2020. Reproduced with permission from Elsevier B. V. (2) a) effects of moisture content on smoldering temperature; b) effects of particle size on smoldering temperature [129], Copyright 2014. Reproduced with permission from Elsevier Ltd. Note: the thermocouples' locations were set in different way for these two papers.

As mentioned in previous part, these crop byproducts are also composed of cellulose, hemicellulose, lignin and other substance, as well as undergo a similar thermal degradation process accompanied by volatiles generation and oxidation reaction. Because the chemical composition of crops varies with growth environment, species, and location of plant, the combustion behavior is also affected by complex factors, such as the relationship between lignin content and ignition behavior, effect of chemical content and graphitic structure on thermal decomposition process, or more extra elements. However, improving flame retardancy still constitutes a critical problem for crop-based thermal insulators applied to construction industry. Especially for smoldering [137,138], which can convert into flaming combustion under certain conditions, more achievements are needed to approach the requirement of fire safety for these novel thermal insulation materials.

3 Conclusion and Perspectives

Environmental impact from materials is becoming a greater investment in construction industry, and use of bio-based materials is considered as an efficient solution for the issues of energy consumption, effective utilization of resources, health and environment concerns. With respect to construction materials, fire safety represents the principal concern for employing bio-based alternatives. This review presents the progresses of flame-retardant research for three kinds of bio-based materials applied to construction sectors over the past decade, involving biopolymer-based flame-retardant materials, wood-based flame-retardant materials, and crop-based flame-retardant materials. Plenty of attention is already paid to developing more available standards and methodologies for minimizing fire risk. Especially for biopolymer-based materials, various flame retardants are incorporated into matrices via chemical or physical ways to increase flame retardancy based on barrier theory or free radical capture effect or a combination of both. Fire resistance of wood-based materials are mainly achieved by impregnation, coating, or adhesive modification, which can introduce additives into substrate. Concerning crop-based materials, both flaming and smoldering combustion behaviors are investigated due to the solid fuel with porous structure and chemical composition. Moreover, further work is still demanded to overcome current disadvantages of these novel bio-based alternatives:

i In order to completely achieve the target of bio-based material, the development of bio-based flame retardants with affordable and high-efficient performances is also a critical step to suppress the hazard reproduced from flame retardant. As far as bio-inspired compounds, such as phytic acid, polydopamine, cyclodextrin, and vegetable extracted products, an increasing achievement is done to improve the fire resistance of various substrates due to their excellent char-forming ability. Nevertheless, further investigation would be on exploring processing technique of these biobased additives, and/ or combining different flame-retardant actions to produce a mature bio-based system as widely available as commercial products.

ii The comprehensive properties of bio-based materials must be considered simultaneously when deal with improving fire behaviors. This is related to a good match between FRs and substrate. The use of current flame-retardant compounds dominantly benefits the fire retardancy, and then a major focus is essential on solving the compatibility and dispersion of the components to maintain or improve the original mechanical properties, thermal conductivity, thermal stability, processing performance, durability, water resistance and so on. For example, lignocellulose, a promoting agent for more char yield, would significantly decrease mechanical properties of biopolymers at large loading due to the poor affinity, which restricts the industrial application of these biomass-originated additives.

iii There is still limitation between laboratory stage and commercial application in some cases, even though great progresses have been done for bio-based flame-retardant materials. As concerns crop-based thermal insulation materials, the most research proposed to enhance thermal conductivity rather than fire behavior to meet the engineering requirements. The same flame-retardant system might demonstrate different fire reactions in various fire scenarios like flaming and smoldering combustions. Therefore, it is not a simple duplication from current standards including LOI, UL-94, CCT, MCC, etc. for industry application. In parallel, establishing more appropriate criteria is necessary to keep the balance between fire performance, health, economic, and environment for these biomass-derived materials, because an efficient flame-retardant system might be high-cost or cause health issues.

To summarize, future challenge involves developing novel bio-originated construction materials with outstanding superiority in fire retardancy, mechanical properties, thermal performance, and other availabilities.

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