

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

1 **Abbreviations:**

2 3 **Concepts for sustainability and organization names**

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

7 8 **Polymers and other compounds**

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

20 21 **Parameters and characterization**

22 **TTI:** time to ignition; **T_{ig}:** ignition temperature; **HRR:** heat release rate; **PHRR:** peak
23 to heat release rate; **MLR:** mass loss rate; **TSP:** total smoke product; **THR:** total heat
24 release; **EHC:** effective heat of combustion; **HRC:** heat release capacity; **T_{is}:**
25 smoldering initiation temperature; **S_p:** propagation speed of the smoldering front; **t_{ig}:**
26 ignition times; **FGI:** fire growth index; **V_{ac}:** average combustion velocity; **λ:** thermal
27 conductivity; **D:** thermal diffusivity; **SEM:** scanning electron microscope; **LIFT:**
28 lateral ignition and flame spread test; **CCT:** Cone Calorimeter test; **H-TRIS:** heat-
29 transfer rate inducing system; **TGA:** thermogravimetric analysis; **LOI:** limit oxygen
30 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].

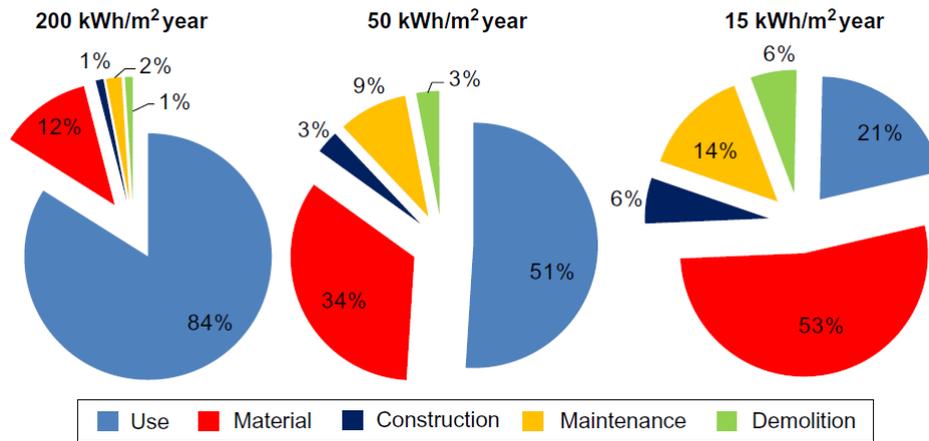
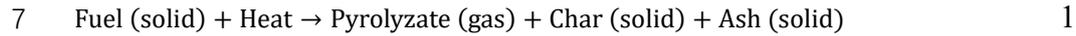


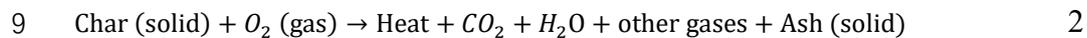
Fig. 1 Distribution of environmental impacts with improving energy performances of buildings and decreased overall consumption [14], Copyright 2017, reproduced permission from Elsevier Ltd.

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

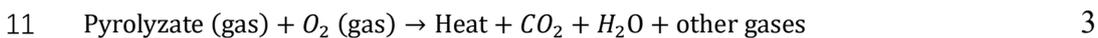
1 relationship between heat release and absorption [17]. This behavior is especially
2 associated with the porous fuels, such as insulation materials or sawdust [18]. Generally,
3 each fire evolution differing mainly in the heat and mass transfer can be divided into
4 three stages of incipient stage, free-burning stage, and smoldering stage [19]. Equations
5 1-3 [20] illustrates simple chemical pathways for combustion of solid fuels to
6 demonstrate the oxidation reaction on condensed and vapor phases.



8 Heterogeneous oxidation:

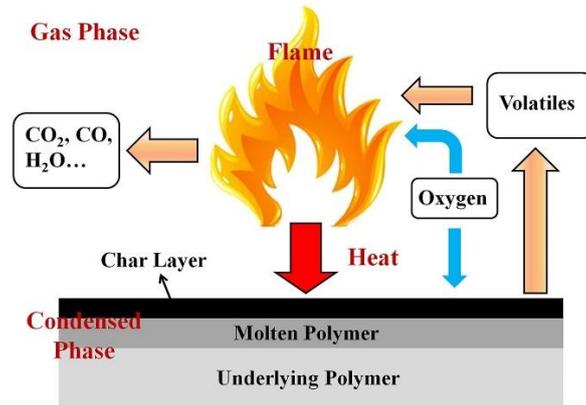


10 Gas-phase oxidation:



12 On the basis of combustion peculiarities of solid fuels, some typical flame-retardant
13 mechanisms have been proposed to improve fire retardancy of these flammable
14 materials [21]. (1) Barrier theory, which can function in both smoldering and flaming
15 combustions. In condensed phase, flame retardants promote the formation of a good
16 charring-layer to obstruct transfer of volatiles, oxygen, and heat. (2) Free radical
17 quenching theory. In gas phase, free radical inhibitors released from flame retardants
18 can scavenge flame propagating radicals (e.g., OH[·] and H[·], etc.) to quench the flame.
19 (3) Other theories. For example, thermal theory, an effect to dissipate the heat from
20 surface by increasing thermal conductivity of materials; dilution theory, a behavior to
21 dilute the combustible gases by nonflammable volatiles generated from decomposition
22 of flame retardant. However, in most real fire scenarios, the flame-retardant behavior is
23 a synergistic effect by combining several fire-retardant mechanisms, as shown in Fig.
24 2. A typical example for this synergistic effect is intumescent flame retardants (IFRs)
25 system, which produces the physical barrier and releases inert gases, involving CO₂ and
26 water. Moreover, aiming to investigate the fire behavior of these bio-based materials
27 after introducing flame retardants, corresponding important parameters are used during
28 the research, including limiting oxygen index (LOI), ratings in UL-94 vertical test (V-

1 0, V-1, or V-2), time to ignition (TTI), ignition temperature (T_{ig}), heat release rate
2 (HRR), peak to heat release rate (PHRR), mass loss rate (MLR), total smoke product
3 (TSP), total heat release (THR), effective heat of combustion (EHC), heat release
4 capacity (HRC), fire growth index (FGI), smoldering initiation temperature (T_{is}),
5 propagation speed of the smoldering front (S_p), and ignition times (t_{ig}).
6



7
8 **Fig. 2** Flame retardant actions during combustion [22], Copyright 2017, reproduced permission from Elsevier B. V.
9

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

18

19 **2 Toward the development of bio-based flame-retardant materials in**

20 **construction sectors**

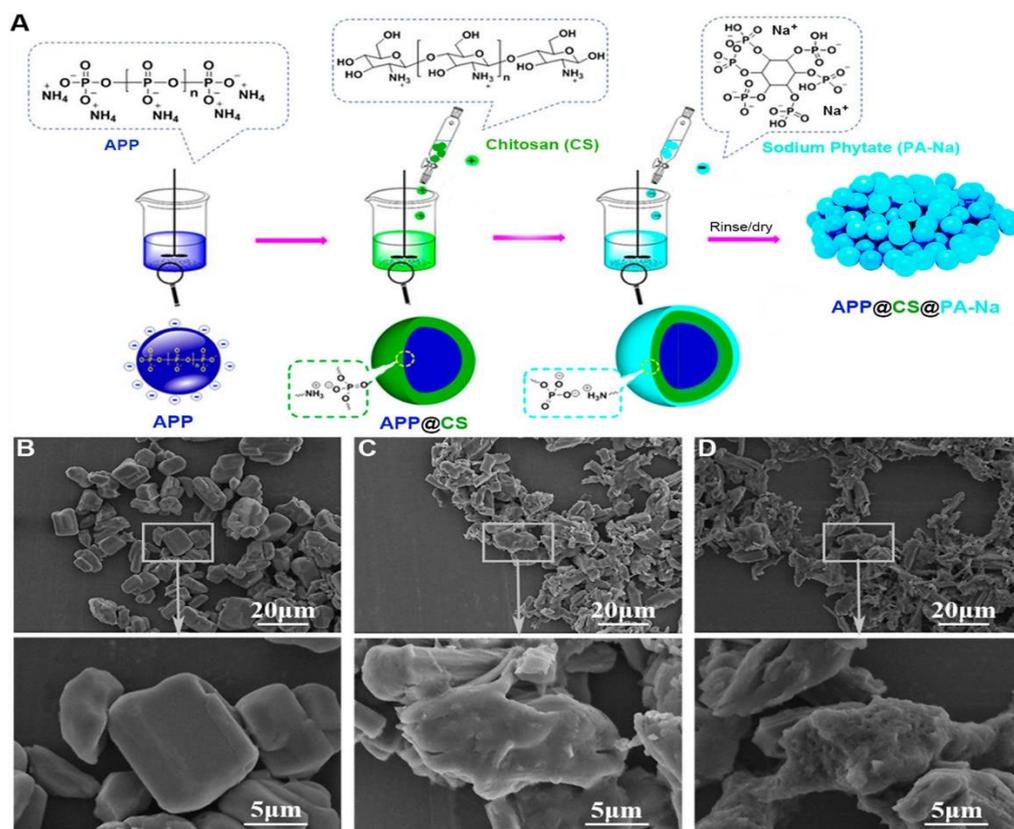
21 **2.1 Biopolymer-based flame-retardant materials**

22 Concept of reducing carbon emissions and environment impact contributes to use of
23 biopolymers and its composites in construction sectors, such as roofs, windows, floors,

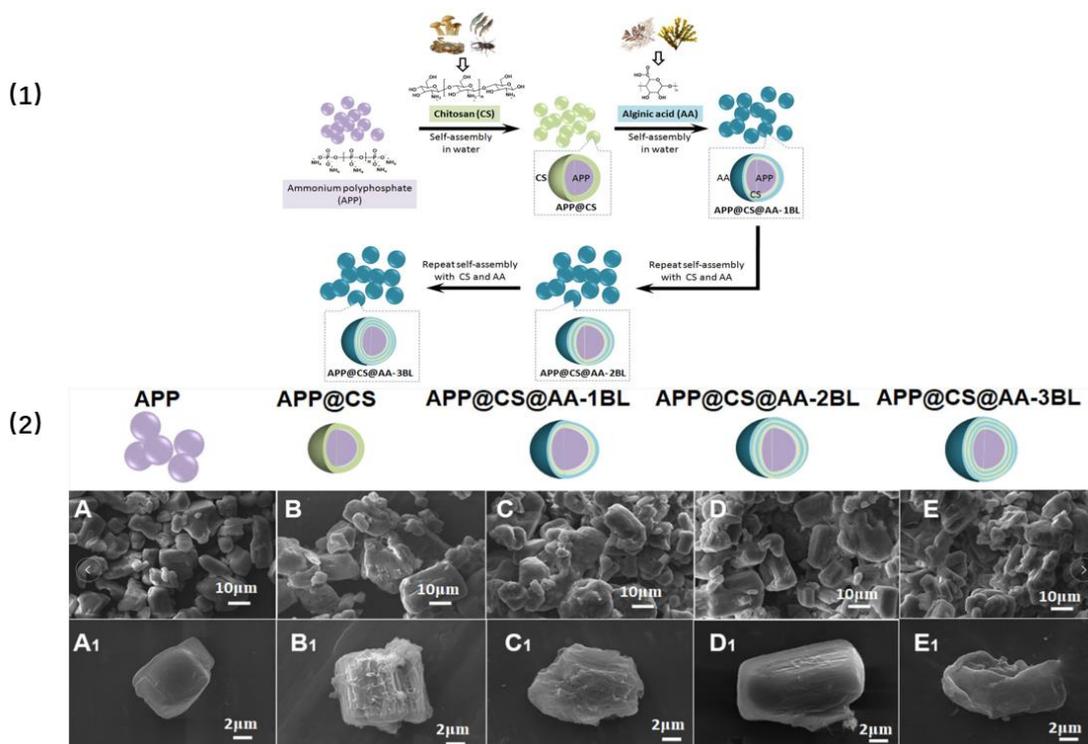
1 oil well, plasters, and coatings [23,24]. Biopolymers is an ambiguous term, which is
2 defined as polymers produced by natural raw materials, microorganisms, or renewable
3 resources. For the aim of this paper, the biopolymer is considered as a material which
4 is converted by renewable resources into final polymer directly or the monomer is
5 derived from renewable resource and then is obtained via chemical ways into final
6 product [25]. Amongst them, Polylactide (PLA), Polybutylene succinate (PBS),
7 Polyhydroxyalkanoates (PHAs), and starch are already studied to approach the
8 requirements in construction field due to their outstanding peculiarities. However, these
9 biopolymers possess the inherent flammability as other thermoplastics, and accordingly,
10 there are many methods to be conducted to improve the fire performance.

11
12 Pure PLA generally shows high tensile strength, Young's modulus and good
13 processability [26,27], but the intrinsic flammability with dripping behavior during
14 combustion limits its further application in construction areas. Aiming to improve the
15 flame retardancy of PLA, some flame retardants including metal oxides [28], nano
16 compounds [29,30], cellulose fillers [31], IFRs [32], and phosphorus-containing
17 chemicals [33,34] have been incorporated into PLA to overcome this defect by melt
18 mixing method. Two similar types of flame retardants with core-shell structure were
19 prepared via layer-by-layer (LbL) using these chemicals with positive or negative
20 charges [35,36]. The core-shell structures of APP@CS@PA-Na and APP@CS@AA-
21 nBL were observed by scanning electron microscope (SEM), as shown in Fig. 3 and
22 Fig. 4, respectively. In this special structure, ammonium polyphosphate (APP) is
23 utilized as core and other two chemicals as shell. After blending 10wt% content of each
24 flame retardants with PLA, these two composites possess higher LOI value (more than
25 30%) and pass V-0 rating in UL-94 as compared to neat PLA. **This is because the core-
26 shell structural flame retardants offer not only efficient carbon source but also good
27 interfacial bonding between different components, which improves the thermal stability
28 and carbonization of PLA composites during combustion.** According to the results from
29 volatiles and residues, the dominant flame-retardant mechanism of both

1 APP@CS@PA-Na and APP@CS@AA-nBL focuses on the condensed phase. In most
2 cases, incorporation of flame retardant can impart PLA adverse effect on mechanical
3 properties, and thus PLA was mixed with 30 kGy dose of organically modified
4 montmorillonite (oMMT) and triallyl cyanurate (TAC) to offset this defect [37]. This
5 combination gives PLA nanocomposite with good mechanical properties, exhibiting
6 average elongation at break of 47.8% and tensile strength of 63.6 MPa. Meanwhile, the
7 formation of cross-linking structures during heating leads to an increased onset
8 decomposition temperature ($T_{2wt\%}$) of 297 °C. Some efficient phosphorus-containing
9 flame retardants named PA-THAM and N, N'-diallyl-P-phenylphosphonicdiamide (P-
10 AA) were synthesized and imparted PLA composites V-0 rating in UL-94 at loading of
11 only 3 wt% and 0.5 wt%, respectively [33,38]. Owing to the low amount, the tensile
12 properties of PLA samples almost maintain the same level. Moreover, other efficient
13 flame-retardant systems for PLA were also developed in our group, shown in Fig. 5. As
14 another intrinsic shortcoming of PLA, poor toughness is also getting much attention as
15 developing fire-safety performance [39]. A synergistic system with ionic liquid
16 tetrabutylphosphonium tetrafluoroborate (IL) and APP was added into PLA. Sample
17 PLA/IL₁/APP₁-3wt% (containing 1.5 wt% IL and 1.5 wt% APP) simultaneously obtains
18 good flame-retardant properties and remarkable tensile toughness, reflecting by
19 elongation at break increased from 8.5% to 204.6%. The improved toughness is because
20 the combination of IL and APP not only minimizes the interfacial defects between PLA
21 and APP, but also brings a plasticization effect. In addition to physical method, chemical
22 modification is also considered as a good way to improve the flame retardancy of PLA
23 for solving the possible problems of affinity and durability of additives in matrix [40].

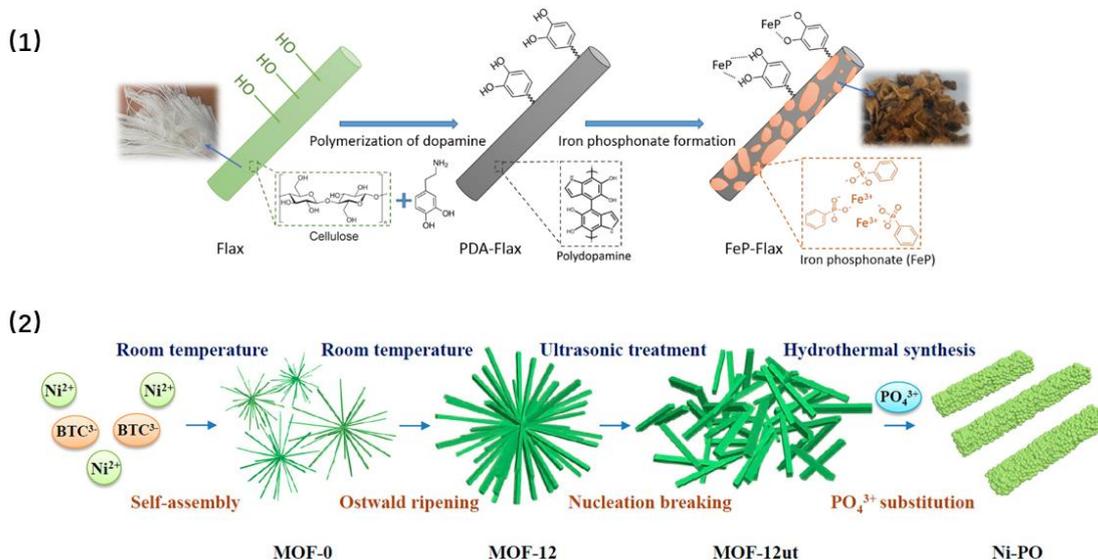


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2 **Fig. 3** (A) Schematic illustration for the fabrication of APP@CS@PA-Na via LAL assembly from water. SEM
3 photographs of (B) APP, (C) APP@CS, and (D) APP@CS@PA-Na [35], Copyright 2019. Reproduced with
4 permission from American Chemical Society.



5
6 **Fig. 4** (1) Synthetic diagram of APP@CS@AA-nBL, (2) SEM photos of (A, A1) APP, (B, B1) APP@CS, (C, C1)

1 APP@CS@AA-1BL, (D, D1) APP@CS@AA-2BL, and (E, E1) APP@CS@AA-3BL [36], Copyright 2020.
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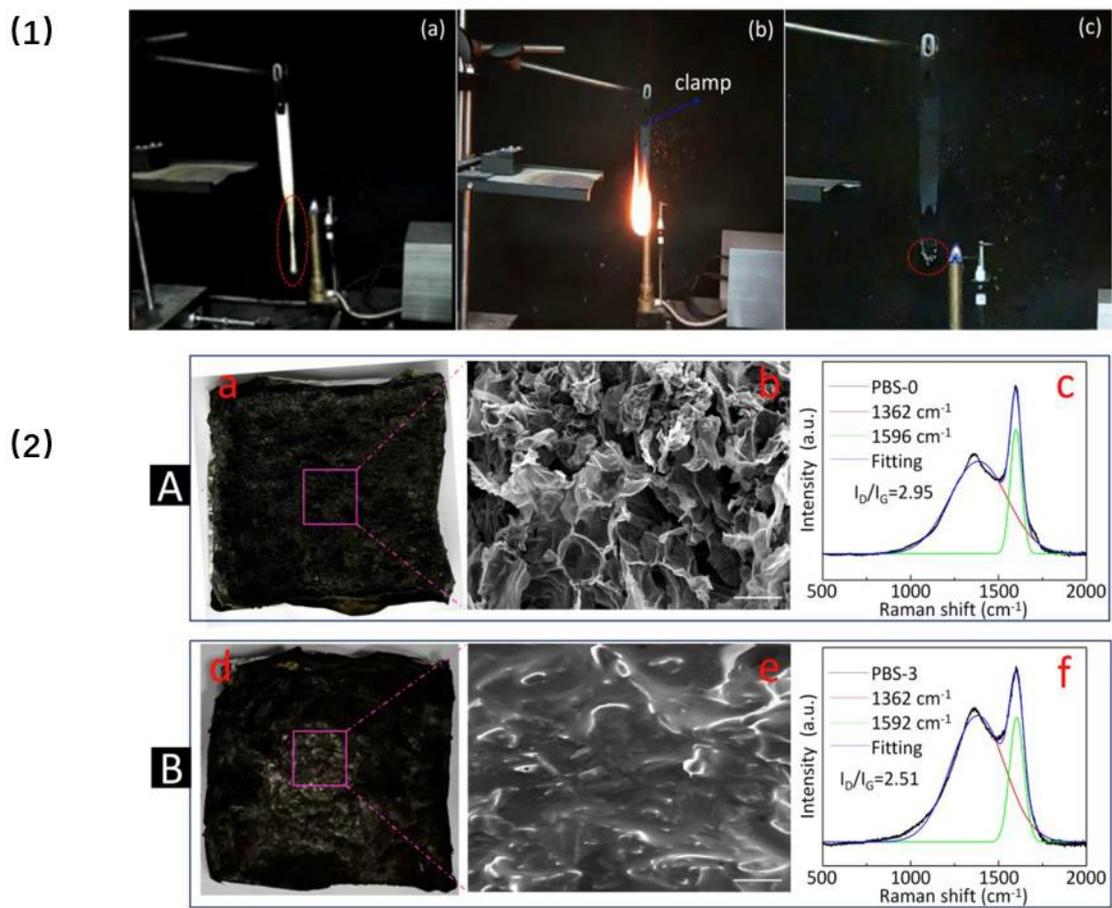
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 4 **Fig. 5** (1) Scheme of preparation for flax/ Fe-phosphonate system [41], Copyright 2018. Reproduced with permission
 5 from Elsevier Ltd; (2) scheme of preparation for Ni-PO derived from metal-organic framework (MOF) [42],
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7

8 PBS has an excellent heat resistance, good mechanical properties, and easy
 9 processibility among the most biopolymers [43,44]. Thus, it is possible to meet the fire-
 10 safety requirement by combining with other materials. As mentioned in PLA-based
 11 composites, physical addition is also an efficient way to improve the flame-retardant
 12 properties of PBS. In recent years, IFRs [45], phosphorus-containing chemicals [46],
 13 and other hybrid synergistic systems [47] have been used to solve the flammability of
 14 PBS. A bio-based IFR named PA-GU was prepared and used to enhance the flame
 15 retardancy of PBS [48]. Compared with pristine PBS, composite with 10 wt% loading
 16 of PA-GU demonstrates a decrease of 59.2% and 38.6% for PHRR and THR,
 17 respectively. The improved flame retardancy can be explained as the barrier effect from
 18 IFR PA-GU, in which PA acts as acid source, and GU as charring and blowing agent.
 19 Aiming to further overcome the phenomena of fast fire growth and continuous
 20 combustion in PBS/ APP/ pentaerythritol (PBS/APP/PER) system, aminated multi-
 21 walled carbon nanotube (MWCNT) was coated onto APP and used as synergist to

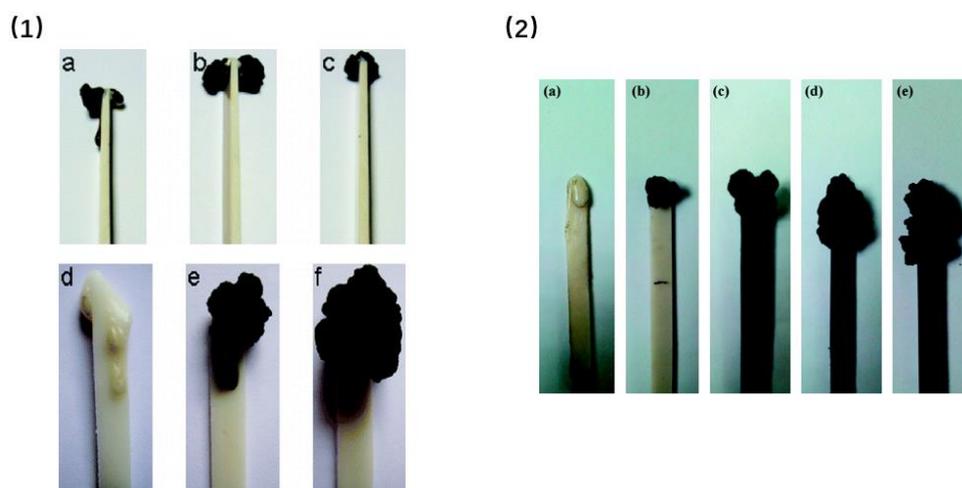
1 improve the quantity of charring layer [49]. Consequently, in comparison with control
2 sample, a significant improvement of fire retardant is obtained in sample PBS-3 with
3 1wt% CNT@APP. Apart from the improvements in PHRR, THR and char mass, a
4 decrease of fire growth index (FGI) from 3.1 to 1.6 and V-0 rating in UL-94 are also
5 observed, shown in Fig. 6 (1). This result is attributed to a synergistic effect between
6 fillers and IFR to promote forming a continuous char layer with high thermal stability
7 during initial combustion stage, shown in Fig. 6 (2). Phosphorus-containing
8 copolyesters (PPBS) were synthesized via polycondensation and used as flame
9 retardants for PBS by melt blending method [50]. Good compatibility between
10 components caused a good LOI value and unaffected crystalline morphology. However,
11 the negative effects, involving high loading or limited flame-retardant efficiency, of the
12 sole flame-retardant on matrices' properties still need to be focused, some synergistic
13 agents have been developed to solve these problems. For example, in order to reduce
14 addition of IFRs, Yuan Hu's [51,52] group chose fumed silica and graphene as the
15 synergistic agents for PBS/APP/MA system based on the relationship between structure
16 and properties. Fumed silica has large surface area, low density, and low superficial free
17 energy in heating, which can favor being adsorbed onto the sample's surface and
18 accelerate flame retardants to form a thermal-stable charring layer with three-
19 dimensional interpenetrating networks. Consequently, melting dripping was suppressed
20 and transfer of oxygen and heat was prevented during combustion of PBS, shown in
21 Fig. 7(1). Regarding to graphene, a carbon-rich consisting nano-reinforcement with
22 unique two-dimensional honeycomb structure, only 2wt% loading of graphene imparts
23 PBS composite anti-dripping behavior benefitted from obstructing and heat-
24 transferring function of graphene, listed in Fig. 7(2). In addition, PBS had also been
25 composited with natural fibers [53,54] or nanotubes [55,56] to extend the fire
26 retardancy and mechanical properties simultaneously, which can meet the further
27 engineering applications.

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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 μm) 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.



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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

1 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)
2 80/18.0/2.0 [51], Copyright 2011. Reproduced with permission from American Chemical Society.

3

4 PHAs are a family of aliphatic polyesters derived mainly from microorganisms,
5 including poly-3-Hydroxybutyrate (PHB), poly (3-hydroxyvalerate) (PHV), poly(3-
6 hydroxypropionate) (PHP), and so on. PHAs demonstrate biodegradability,
7 biocompatibility, thermoplasticity and versatility to offer tremendously potential
8 opportunities in construction fields [57–59]. As thermoplastics with inherent
9 flammability, some efforts have been made to improve the fire behaviors of these PHAs
10 as well. As the most common type of PHAs, pure PHB was investigated by evaluating
11 some critical parameters involving T_{ig} and HRC [60]. T_{ig} of approximate 375 ± 10 °C,
12 as a standard to evaluate the difficulty in igniting polymers, was obtained according to
13 the concentrations of CO, H₂, and CH₄ during decomposition. HRC, a good measure to
14 speculate the ability of burning speed after ignition, was calculated to a lower value
15 (765 J/g-K) for PHB than for polypropylene (1567 J/g-K) and polyethylene (1193 J/g-
16 K), which means PHB is more difficult to flame than the other two commercial
17 polymers. Poor thermal stability of PHB, which has strong ties with the flame-retardant
18 performance, was also studied by adding some fillers, such as thymine (TM) and lignin
19 [61,62]. From the results, thermal stability of modified PHB composites shows a higher
20 thermal degradation temperature due to the presence of these stabilizers. Additionally,
21 PHB was blended with other polymers to prepare copolymers, for example, Poly(3-
22 hydroxybutyrate-co-4-hydroxybutyrate) [P(3,4)HB] [63] and Poly(3-hydroxybutyrate-
23 co-3-hydroxyhexanoate) (PHBH) [64]. Meanwhile, the fire retardancy of P(3,4)HB and
24 PHBH added with IFR/ZnB and natural fillers, respectively, was investigated,
25 illustrating a reduction of PHRR for both copolymers. Unlike PLA and PBS, which
26 have already been addressed the flame retardancy by many researchers, there are still
27 limited articles to report the flame-retardant properties of PHAs family. Therefore, it is
28 essential to expand more effort to work on this field to meet more requirements of
29 construction application.

30

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

9

10 **2.2 Wood-based flame-retardant materials**

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

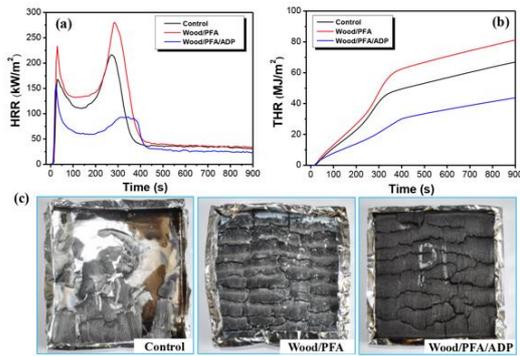
1 coating [77], adhesive modification [78] and other technologies.

2

3 Laminates are usually found in indoors' elements, particularly in flooring, to keep from
4 wetting, and some significant achievements on fire resistance of laminates can be found
5 in many publications. Pressure impregnation, a widely useful method for introducing
6 additives into wood-based materials, was used to infiltrate an efficient flame retardant
7 consisted of furfuryl alcohol (FA) and ammonium dihydrogen phosphate (ADP) into
8 wood substrate. Resultantly, a hydrophobic FA/ADP network produced via in-situ
9 polymerization during curing [79]. This Wood/PFA/ADP composite exhibits prominent
10 improvement in flame retardancy, displayed in Fig. 8, which was reflected in reduction
11 of PHRR, THR, obvious smoke suppression, and ignition resistance due to char
12 formation and incombustible gases release during combustion. Besides, an increase in
13 mechanical properties is also obtained attribute to enhanced dimensional stability after
14 the additives was filled into the cell cavities of wood. In order to preserve a well
15 dispersion of flame retardant in wood, a wood laminate with 16.2 wt% of bentonite
16 nanosheets were prepared via delignification and densification processes, which
17 simultaneously displays good flame retardancy and mechanical strength [80]. At a
18 condition of an open flame, self-extinguishing behavior and postponed ignition time
19 were observed in the modified wood laminate. In contrast, control sample ignited within
20 19 s, as well as a strong flame started at 30 s, listed in Fig. 9. These phenomena can be
21 clarified that the delignification and densification processes sequentially favor forming
22 porous structure and 3D protective layer with impervious and dense structure in
23 bentonite-infiltrated wood laminate. The special structure leads to the preservation of
24 bentonites in wood cells to form a heat shielding to obstruct the transfer of heat and
25 mass during burning. Moreover, the existence of bentonite nanosheets enhances
26 interfacial affinity between nanosheets and nanocellulose due to hydrogen bonding
27 networks, which contributes to a significant increase of mechanical properties.

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(1)



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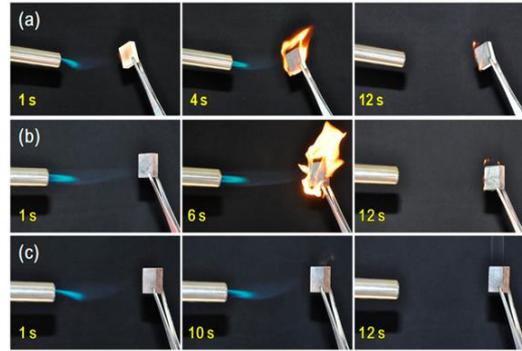
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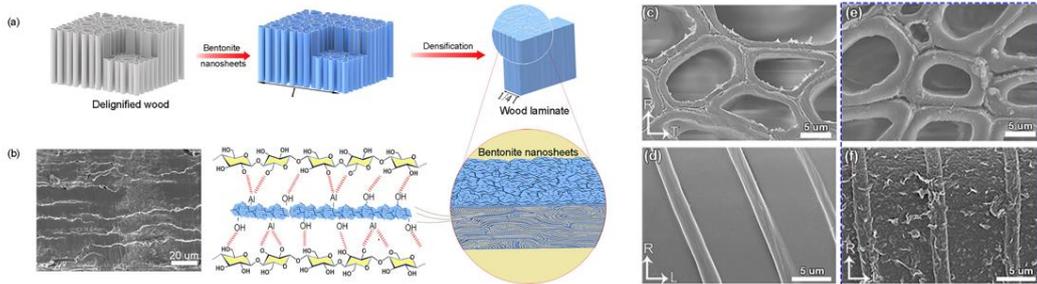
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Fig. 8 Wood/PFA/ADP laminate. (1) results from cone calorimeter test: (a) HRR curves, (b) THR curves, and (c) digital photos of char residues after combustion of control Wood, Wood/PFA, and Wood/PFA/ADP. (2) the flammability test: (a) control Wood,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

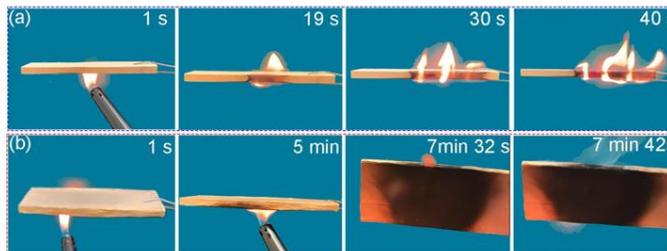
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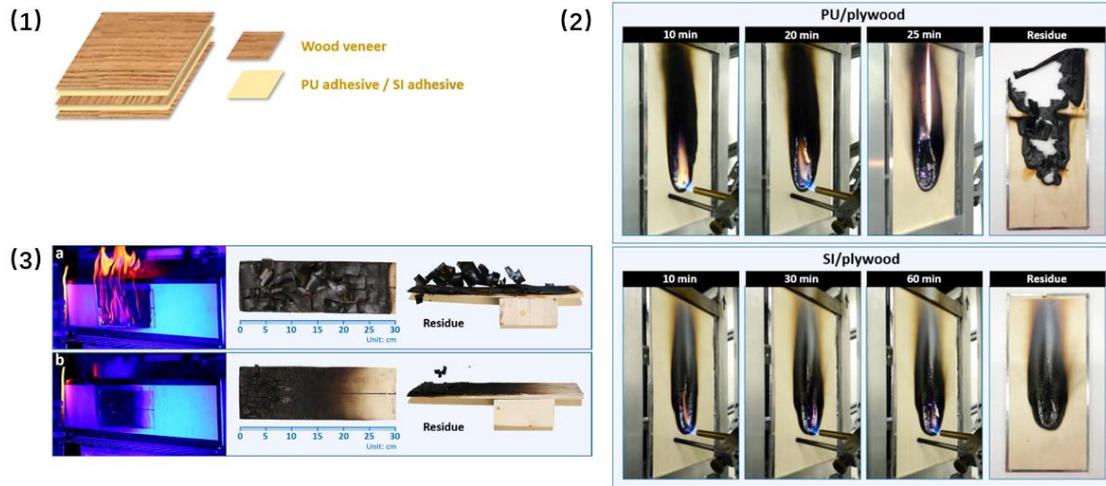
Fig. 9 A bentonite-infiltrated wood laminate. (1) scheme illustration of the structure and scanning electron microscopy (SEM): (a) delignified wood structure with aligned channel and porosity for bentonite penetration; densified process for impervious and dense structure with good compatibility between 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.

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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 (V_{ac} : 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

1 was observed for SI/plywood at the same conditions in both combustion tests, which is
2 attributed to a thermally stable residue generated by SI adhesive system.

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6 **Fig. 10** (1) Preparation scheme of plywood samples. (2) images from Mydrin test for PU/plywood and SI/plywood.

7 (3) images from LIFT for 5 min: (a) PU/plywood, (b) SI/plywood [85], Copyright 2018. Reproduced with permission

8 from Elsevier Ltd.

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10 Moreover, other wood-based products, such as fiberboard and wood-plastic composite
11 (WPC), are also considered as good materials for residential and industrial sectors
12 because of their favorable performance, ecofriendly, and low cost. Take a typical natural
13 material for example, bamboo can be utilized in entire houses, bridges, scaffoldings and
14 other structural elements due to its special interior structure, high strength-to-weight
15 ratio, and water-resistance [86–88]. Therefore, many efforts are making to develop
16 novel bamboo composites [89], or improve the poor fire resistance for further
17 application [90]. Aiming to know the burning behavior when bamboo is exposed to fire,
18 three thermally thick bamboo samples with different adhesive, density, and thickness
19 were tested to investigate the basic flammability parameters based on data from Cone
20 Calorimeter test (CCT) [91]. For all testing samples, the critical heat flux for ignition
21 was 15 kW/m^2 , and critical mass loss rate, which increased with the external radiant
22 flux, was between 2 and $4.5 \text{ g/ m}^2\cdot\text{s}$ within the flux range of $15\text{-}80 \text{ kW/m}^2$. These

1 experiments elucidate that bamboo probably consumed more energy to ignite than other
2 timber species and went through a following smoldering combustion after flaming stage,
3 which needed further work to quantify. A fiberboard made from bamboo biomass
4 exhibits fire safety and high internal bonding strength to offer an economically potential
5 alternative for structural and furniture applications [92]. However, to date there are still
6 limited papers on the fire resistance of this material itself except some bamboo-based
7 hybrids. For example, bamboo/epoxy [93], bamboo/PLA [94], and bamboo/PBS [95]
8 have been obtained by modification with some FRs, which demonstrates better flame-
9 retardant properties compared with control samples. Besides, other WPCs with
10 enhanced flame retardancy are also developed to meet the requirements of construction
11 industry [96,97].

12

13 **2.3 Crop-based flame-retardant materials**

14 The variety of agriculture plant ranging from wheat, rice, corn, barley, sugarcane,
15 sunflower and others produces abundant by-products, which are identified as potential
16 substitutes to develop external envelope of construction materials by offering good
17 thermal properties and energy consumption [98–100]. In comparison with conventional
18 thermal insulators, such as wools, rigid boards, and foams, these novel crop-based
19 materials possess sustainable, ecofriendly, renewable, local available, and affordable
20 advantages [101,102]. On the flip side, recycling crop byproducts is also an efficient
21 solution to tackle some environmental problems generated by common disposals
22 involving dumping, incineration, land filling, composting, etc. As thermal insulation
23 materials in construction sectors, some important requirements should be fulfilled in
24 thermal performance, involving thermal conductivity (λ : W/m·K) and thermal
25 diffusivity (D : m²/s), technical properties including processing and durability, as well
26 as fire behaviors in both flaming and smoldering combustion. Therefore, for the
27 purpose of resource recycling and fire safety, this section will emphasize the fire
28 behaviors for crop-based thermal insulation materials, which is derived from
29 byproducts from wheat, rice, corn, barley, and other crops.

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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/m³), 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/m²) than that of XPS (141.48 kW/m²), 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 ZrO₂ 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 ZrO₂ 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

1 carbonization process of straw. Besides, another flammability trial was conducted to
 2 study the fire reaction of wheat straw particleboard, demonstrating a retarded flame
 3 spread in the sample treated with linseed oil [110].

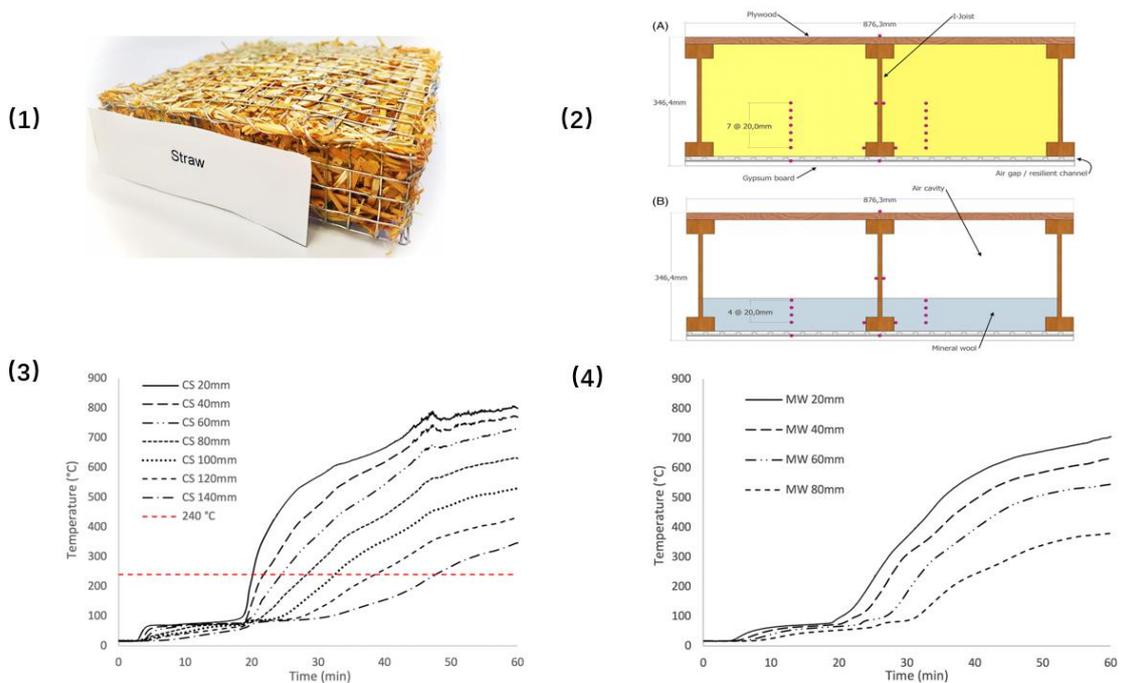
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5 **Table 1** Results from CCT and thermal conductivity of compressed straw samples with heat flux of 50 kW/m² [107]

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%)

6 Note: The percentages in brackets refer to the relative difference between the specimen and the 75 kg/m³ sample's values.

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

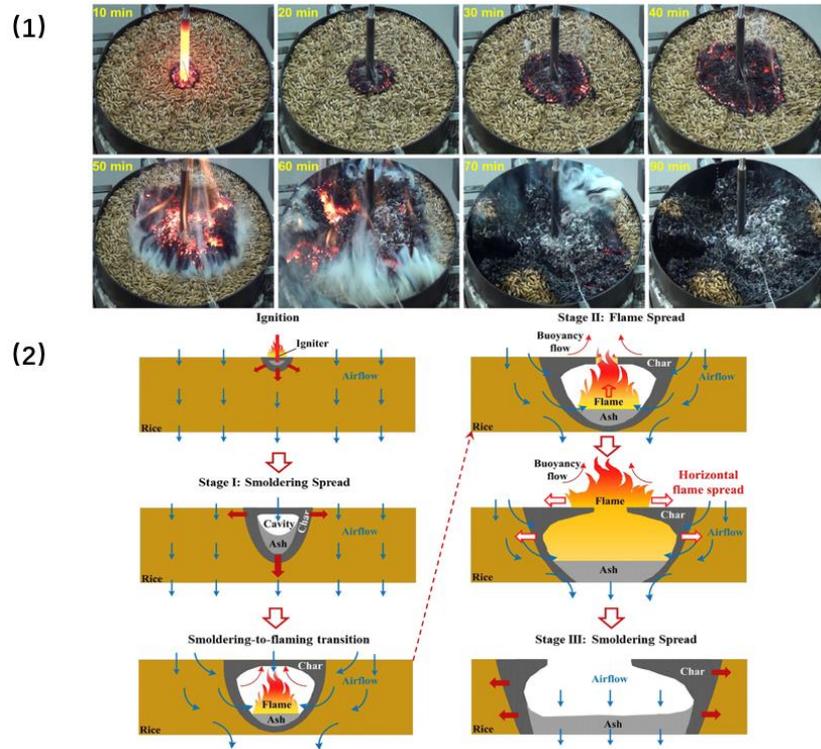
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14 Husk and straw residues derived from rice, one of the most widely consumed crop
 15 commodities, have been utilized as biomass thermal insulators in construction sectors

1 [111,112]. Rice husk, hard coating on the rice grain, yields extensive char and silica
2 during heating [113,114], which can contribute to improving the fire performance. In
3 order to clarify the thermal decomposition mechanism of rice husk, Saad [115]
4 investigated the pyrolysis kinetic and combustion characteristic parameters via
5 analyzing samples with different sizes ranged from 38-200 μm to 200-1000 μm . As a
6 lignocellulose, rice husk exhibits predominant stages of thermal degradation caused by
7 moisture and volatile removal, degradation of hemicellulose, decomposition of
8 cellulose and lignin degradation. Meanwhile, these pyrolysis processes vary with
9 heating rate and particle size. With the increase of heating rate, the curves from
10 thermogravimetric analysis (TGA) shifted to higher temperature, which is because poor
11 heat transfer performance leads to incremental temperature gradient within biomass and
12 results in insufficient time for reaching final temperature of each degradation zone.
13 Moreover, particles with larger size (200-1000 μm) showed higher activation energy
14 (E) and less combustible characteristic with lower T_{ig} and t_{ig} than another sample with
15 smaller size (38-200 μm). The differences between different samples are attributed to
16 not only mineral content or thermal conductivity, but also separation or change of
17 structure and composition during physical treatment [116]. Mitchell et al. [117] made
18 a comparison between XPS and rice husk/ mycelium bio-board, and an anticipated
19 superiority of flame retardancy was found in biomass system due to the existence of
20 carbonaceous char and imbedded silica during combustion [118]. Resultantly, rice husk
21 particleboard demonstrated significant reduced values for PHRR, TSP by 73.5% and
22 96.6%, respectively, as well as longer estimated time to flashover in room fire test.
23 Moreover, some parameters on smoldering behavior of rice husk containing initiation
24 temperature, particle size, and gas products were also studied by Saad group [119,120].
25 The transition from smoldering to flaming combustion was exhibited by investigating
26 fire spread of rice fuel-bed under convective heating process, shown in Fig. 12 [121].
27 Rice straw, another bio-based isolation material, was also studied by Yingfeng et al.
28 [122] by manufacturing straw-magnesium cement (SMC). Additionally, it was proved
29 that rice straw had more tendency towards self-heating, which could trigger the

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

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

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

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

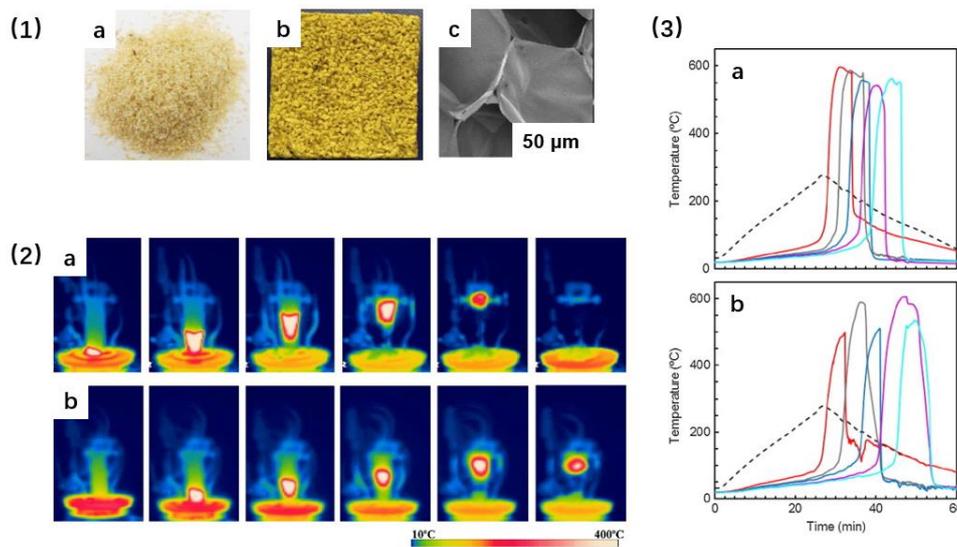
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1 **Fig. 13** Thermal insulation panels made from corn byproducts: (1) corn tassel/ polyester system [132], Copyright
 2 2020. Reproduced with permission from Elsevier Ltd. (2) corn stalk/ Magnesium Phosphate Cement [133],
 3 Copyright 2018. Reproduced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

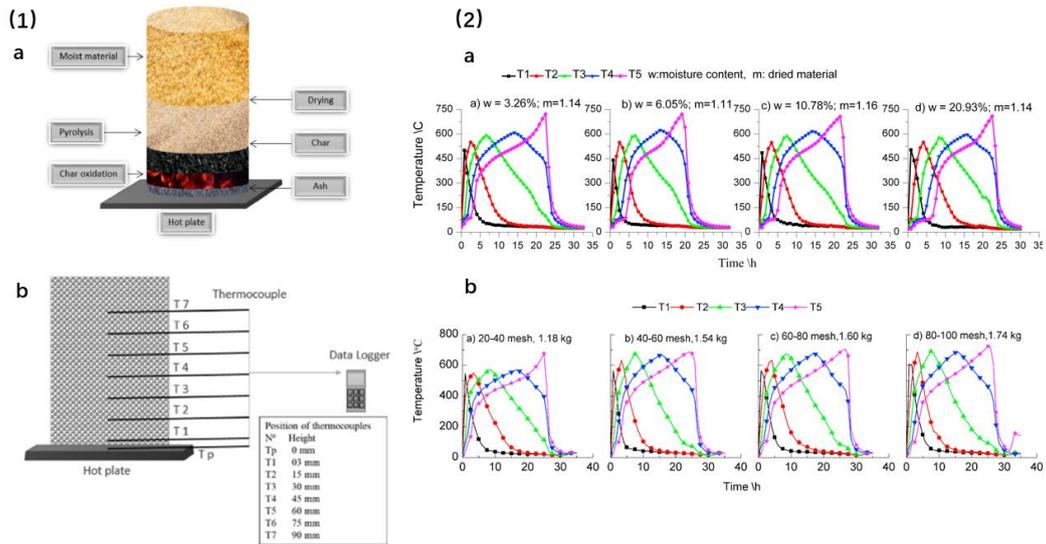
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9 **Fig. 14** (1) Corn pith/ alginate thermal insulation: a) sieved particles with size of about 2 mm; b) corn pith/ alginate
 10 board; c) micromorphology of corn pith [126], Copyright 2015. Reproduced with permission from Elsevier Ltd. (2)
 11 infrared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

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2 **Fig. 15** (1) a) Experimental mode for smoldering propagation in a downward mode; b) experimental set-up for
 3 thermocouples' locations [128], Copyright 2020. Reproduced with permission from Elsevier B. V. (2) a) effects of
 4 moisture content on smoldering temperature; b) effects of particle size on smoldering temperature [129], Copyright
 5 2014. Reproduced with permission from Elsevier Ltd. Note: the thermocouples' locations were set in different way
 6 for these two papers.

7

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

20

21

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.

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

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

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

25

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