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Wood Plastic Composites: Their Properties and Applications

Kaimeng Xu, Guanben Du and Siqun Wang

Abstract

Wood plastic composites (WPCs) is one of crucial and potential engineering wood products that has been extensively employed in the fields of landscape, transportation, municipal engineering and building construction. It has gradually been used to replace the conventional wood-based composites. This chapter aims to introduce the properties and development of WPCs and illustrate how defects in their mechanical properties, biological and aging resistance, and flame retardance affect their global development. Herein, the effects on the biological durability of WPCs against algae, mold, fungi, and termites made with various wood species with different chemical extractive compositions, the natural weathering performance of WPCs and the mechanisms of protection against ultraviolet light and moisture, the effectiveness and mechanism of reinforcement of WPCs by novel alloy modification of linear and aromatic polyamides are reviewed. Additionally, the flame retardance properties, common testing methods as well as the performances of novel flame retardants for WPCs, are comparatively described. Lastly, the limitations and prospects of WPCs in future construction applications are also discussed.

Keywords: wood plastic composites, natural durability, reinforcement, flame retardance

1. Introduction

Under the global background of shortage crisis of forestry and fossil oil resources, it is estimated that there is an expectation for the application of natural fiber-reinforced composites from 12% in 2010 to 18% and 25% by 2020 and 2030, respectively [1]. With the fast-growing demands of engineering wood products for various applications, wood plastic composites (commonly abbreviated as WPC), as the most important one of natural fiber-reinforced composites, mainly produced by the thermoplastic polymers (polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS)) and the biomass particles and fibers from forestry and agricultural wastes (wood, bamboo, straw, stalk, husk and bast), which have been well considered as a crucial and novel candidate for residential and industrial constructions [2, 3]. WPC with a unique combination of advantages from wood and plastic has been extensively employed in landscaping facility, transportation, packaging, municipal engineering as well as the inner-outer decoration and structure of building [4–6], as seen in **Figures 1–3**. In recent years, WPC begins to partially replace some conventional and novel engineered wood products like wood



Figure 1.
The applications of WPC in various building construction.



Figure 2.
The applications of WPC in the indoor or outdoor ceilings and sidings.

veneer (WV), particle board (PB), medium-density fiber board (MDF), plywood (PW), oriented strand board (OSB) and laminated veneer lumber (LVL) [7].

In the initial developing period of WPC, manufacturers claim that there are many advantages for WPC including high strength and modulus, excellent dimensional stability, outstanding biological (fungi and termite) resistance and low maintenance requirement [8–10]. Hydrophilic biomass particles or fibers can be effectively encapsulated by hydrophobic thermoplastic resin to provide well protection against biological invasion. Although it had to be admitted that there was a superior weathering and biological durability for WPC than solid wood, natural aging and biological degradation of WPC by common microorganisms (mold, algae and decaying fungi) and harmful termites indeed can be observed with the damage

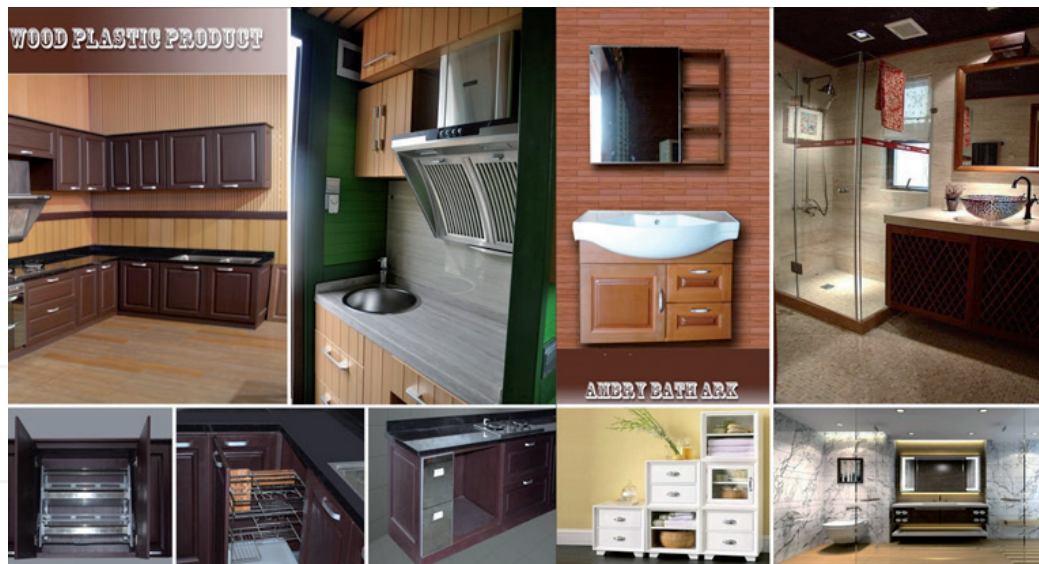


Figure 3.
The applications of WPC in the furniture, kitchen, and bathroom products.

of its external layer and interfacial bonding under the appropriate circumstance like mild ambient temperature, high humidity and oxygen content as well as strong ultraviolet (UV) radiation [11]. Meanwhile, the insufficient mechanical properties and poor flame retardance due to weak interfacial compatibility, high fire sensitivity of polyolefin resins and the strength limitation of conventional resins were gradually exposed as the service time of WPC extended, which may lead to potential failures and serious accidents in engineering construction.

Recently, a growing interest for WPC used in the field of construction becomes more popular with pervasive consciousness of environmental protection and sustainability. To further improve the mechanical properties, durability and flame retardance, selection of wood species with various extractives, alloy modification with linear and aromatic polyamides as well as the addition of flame retardants with single and synergistic effectiveness have been reported. This provides a significant technological support for WPC's future use in the construction.

2. Natural durability of WPC

2.1 Biological durability of WPC

The ever-expanding commercial market for WPC products in exterior construction engineering applications has placed more spotlights on improving the biological durability and lifetime of WPCs. The wood component of WPCs is considered as common fiber fillers with similar properties, including renewability, low density, high specific strength, and hydrophilicity. In fact, the species of wood plays a critical role in the comprehensive properties of WPCs, in addition to other factors, such as the plastic type, particle size, additives, and processing technology. Termites and other microorganisms, such as mold and fungi, can decrease the esthetic quality and mechanical strength of WPCs through discoloration and degradation by chemically altering the structures of lignin, hemicellulose, and cellulose fibers in the wood [12, 13]. However, algae colonization only affects the outer appearance of the WPC instead of the inner interfacial bonding [14]. To promote the quality and prolong the service time of the entire WPC structure, more attention needs to be paid to improving the biological durability during the engineering of the

composites in the future. The chemical composition of wood extractives, such as tannins, fatty acids, aldehydes, ketones, sugars, and starches, have been reported to have both a negative and positive effect on the susceptibility of WPC to microbial invasion [11, 15, 16].

Despite of continuing emergence of new publications in this field, there are few reports on how the identity of the wood species affects the biological durability of WPCs. Different wood species contain varying compositions of volatile chemical components. The high toxicities of some natural wood extractives have been shown to exhibit a positive effect on the resistance of WPCs to microorganisms. The susceptibility of mold in PVC-based WPCs containing maple wood was found to be higher than the analogous WPCs made with pine wood [17]. *Gloeophyllum trabeum* (brown rot) demonstrated significantly higher mass losses in PE-based WPCs compared to *Trametes versicolor* (white rot). The ranking for the white rot testing fungus for the WPCs made by five wood species was Douglas-fir > black locust > white oak > ponderosa pine > poplar, while the ranking for the brown rot testing fungus was black locust > white oak > ponderosa pine > Douglas-fir > poplar [18]. PP-based WPCs made from maple or oak were more susceptible to fungus than the PP-based WPCs made with pine [19]. PE-based WPCs containing *Parthenium argentatum*, *Parthenium incanum*, and *Parthenium tomentosum* fibers displayed better termite resistance compared to the WPCs containing pine fiber, with mass losses of 7%, 6%, and 5%, respectively. PVC-based WPCs filled with different wood species exhibited varying resistance levels to four common biological organisms, including algae, fungi, mold, and termites, as shown in **Figures 4–7**. The trend for the algal resistance was: *Liquidambar formosana* > *Cunninghamia lanceolata* and *Melaleuca leucadendra* > *Eucalyptus grandis* × *Eucalyptus urophylla* and *Pinus massoniana*. The trend for the fungal resistance to *Coriolus versicolor* was: *Cunninghamia lanceolata* > *Pinus massoniana* > *Melaleuca leucadendra* > *Liquidambar formosana* > *Eucalyptus grandis* × *Eucalyptus urophylla*; for the fungal species *Poria vaporaria*, the trend was: *Cunninghamia lanceolata* > *Eucalyptus grandis* × *Eucalyptus urophylla*, *Melaleuca leucadendra*, *Pinus massoniana* > *Liquidambar formosana*. The trend for the mold resistance was: *Cunninghamia lanceolata* and *Melaleuca leucadendra* > *Eucalyptus grandis* × *Eucalyptus urophylla* > *Pinus massoniana* > *Liquidambar formosana*. The trend for the termite resistance was: *Cunninghamia lanceolata* > *Melaleuca leucadendra* > *Eucalyptus grandis* × *Eucalyptus urophylla* > *Liquidambar formosana* > *Pinus massoniana* [11, 14, 20].

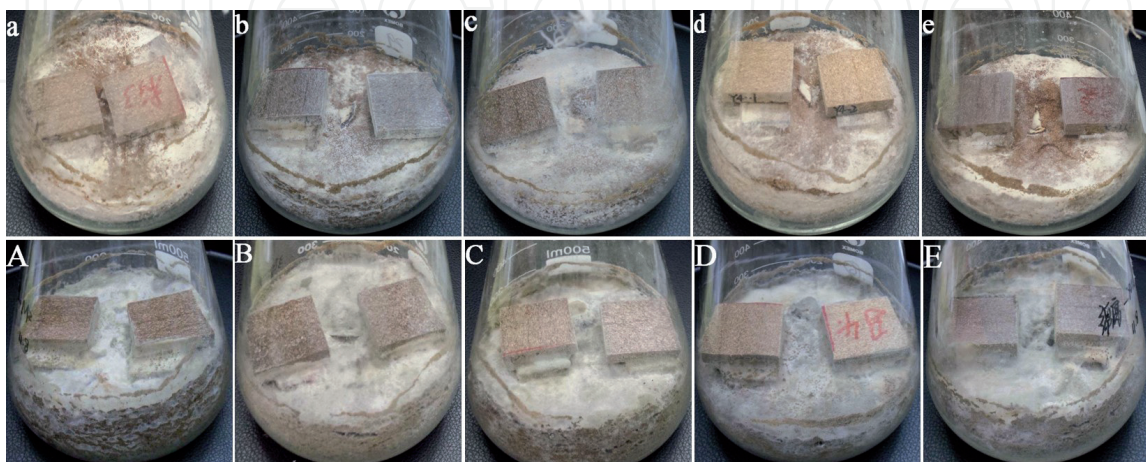


Figure 4. The decay resistance to *Coriolus versicolor* (in lowercase) and *Poria vaporaria* (in capital) testing of PVC-based WPC filled with different wood species: (a) *Cunninghamia lanceolata*, (b) *Melaleuca leucadendra*, (c) *Eucalyptus grandis* × *E. urophylla*, (d) *Pinus massoniana*, (e) *Liquidambar formosana* [20].

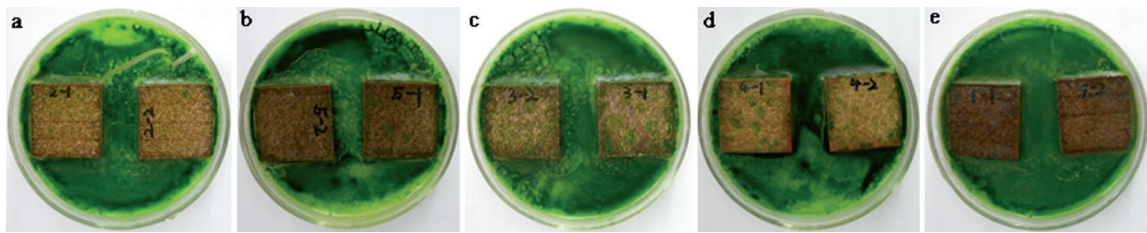


Figure 5.
The algae resistance of PVC-based WPC filled with different wood species: (a) *Cunninghamia lanceolata*, (b) *Melaleuca leucadendra*, (c) *Eucalyptus grandis* × *E. urophylla*, (d) *Pinus massoniana*, (e) *Liquidambar formosana* [14].

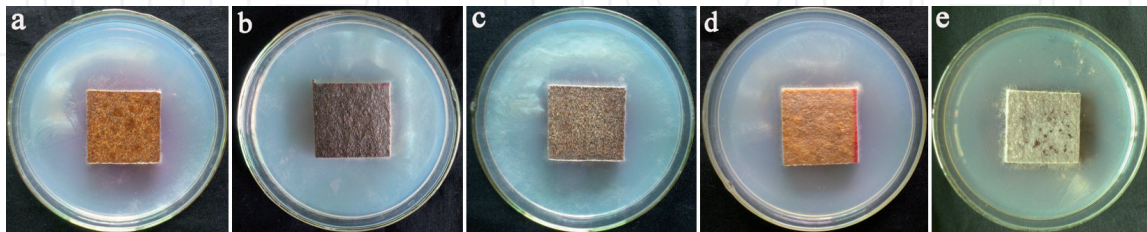


Figure 6.
The mould resistance of PVC-based WPC filled with different wood species: (a) *Cunninghamia lanceolata*, (b) *Melaleuca leucadendra*, (c) *Eucalyptus grandis* × *E. urophylla*, (d) *Pinus massoniana*, (e) *Liquidambar formosana* [11].

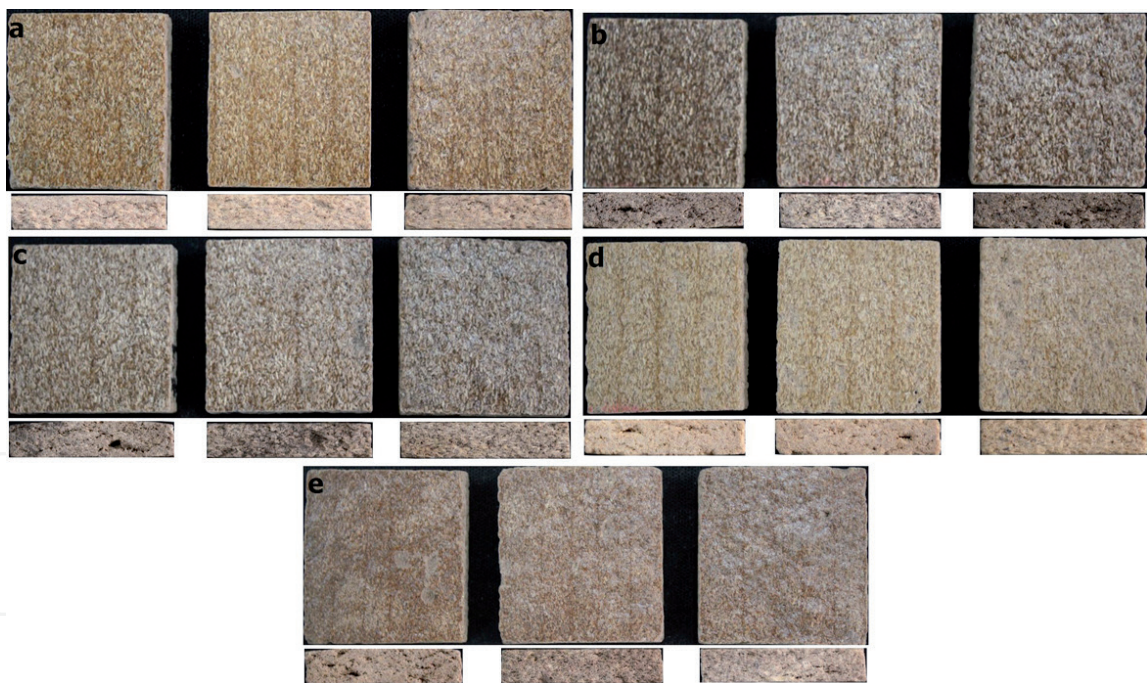


Figure 7.
The termite resistance of PVC-based WPC filled with different wood species: (a) *Cunninghamia lanceolata*, (b) *Melaleuca leucadendra*, (c) *Eucalyptus grandis* × *E. urophylla*, (d) *Pinus massoniana*, (e) *Liquidambar formosana* [11].

Several functional chemical extractives naturally present in wood varieties can either facilitate or inhibit the biodeterioration of WPCs. For example, 8-propoxycedrane, cedrol, α -cedrene, and β -cedrene in *Cunninghamia lanceolata*; 2,3-dihydro-2,2-dimethyl-3,7-benzofurandiol, 3-demethylcolchicine, and squalene in *Melaleuca leucadendra*; 2,3-dihydro-2,2-dimethyl-3,7-benzofurandiol and stigmast-4-en-3-one in *Eucalyptus grandis* × *Eucalyptus urophylla* were conducive to promoting the biological durability of WPCs. On the contrary, longifolene,

caryophyllene, and α -pinene in *Pinus massoniana*; and 4-hydroxy-3,5-dimethoxy-benzaldehyde, 3,5-dimethoxy-4-hydroxycinnamaldehyde, and cinnamyl cinnamate in *Liquidambar formosana* induced biodegradation [11]. Additionally, comparison to medium-density fiberboard, WPCs were found to demonstrate a better resistance to termites due to the presence of antifeedants, and there was a higher resistance level for PVC-based WPCs than for PE-based WPC made with the same wood particles. The biological durability of the WPC was potentially improved due to the intrinsic antimicrobial properties of PVC as well as the addition of inorganic fillers into the composites.

Similar results for the PP-based WPCs filled with poplar, MOSO bamboo, ramin, pine, gum, cedar, and rubberwood were reported, as observed in **Figure 8**. There was a poor mold resistance of the WPC made with MOSO bamboo due to the presence of 5-hydroxymethylfurfural in the bamboo species. The WPC made with ramin wood showed high resistance to various mold species, which could be attributed to the presence of γ -sitosterol, cis-9, cis-12-octadecadienoic acid, benzyl alcohol, and 8-propoxycedrane. However, 4-hydroxy-3-methoxycinnamaldehyde and dehydroabietic acid were determined to be the crucial chemical components that mediated the high resistance of WPCs made by pine. The resistance of WPCs made with gum fillers to molds can be explained by the synergistic effect of γ -sitosterol, stigmast-4-en-3-one, and cedrol. The relatively low fungal resistance of WPCs filled with rubberwood was attributed to the relatively high content of 5-hydroxymethylfurfural. In addition, hinokitiol, cedrol, α -cedrene, thymoquinone, totarol, β -cedrene, ferruginol, hinokiol, and benzyl alcohol were found to be vital chemical compounds in WPCs filled with red cedar for manifesting a high resistance of the composite to molds. The relatively high contents of cedrol, stigmast-4-en-3-one, and 8-propoxy-cedrane in Chinese fir provided the corresponding WPC with significant resistance to mold growth. Meanwhile, the relatively low contents of α -Cedrene, β -cedrene, α -cadinol, and γ -sitosterol were beneficial for mitigating the biodegradation of WPC [21].

2.2 Natural weathering of WPC

The exposure of WPCs to ultraviolet light and moisture represents two significant natural weathering sources of WPCs in outdoor applications, which affects

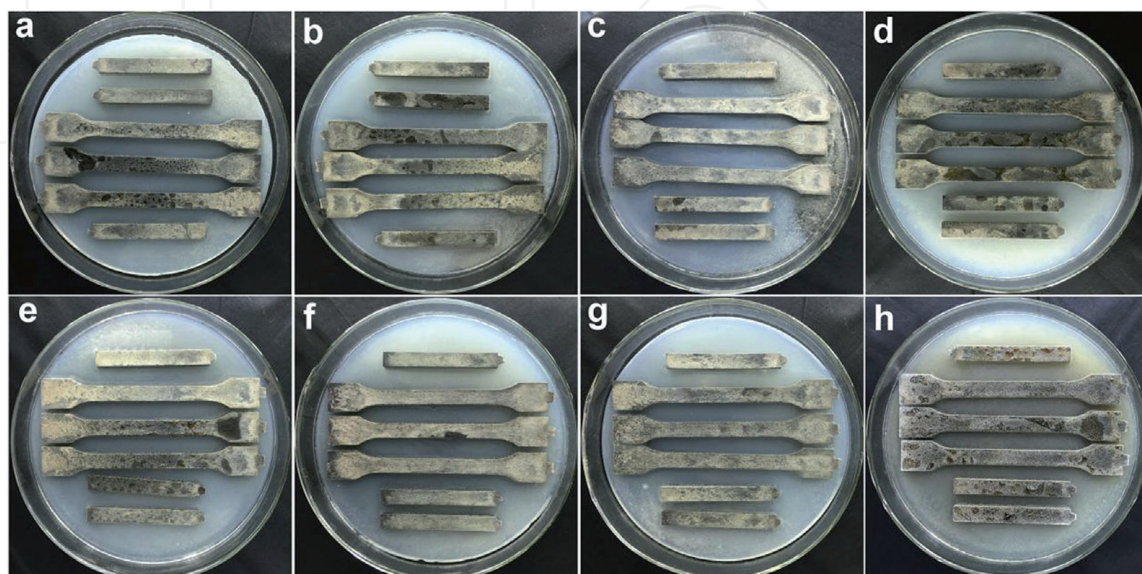


Figure 8. Mold colonization of PP-based WPC with various wood species: (a) poplar, (b) MOSO-bamboo (c) Chinese fir (d) Ramin, (e) pine, (f) gum, (g) cedar, (h) rubberwood [21].

not only the visual appearance of the WPCs but also their mechanical properties by manifesting deleterious effects such as discoloration, furrows, and separated voids [22]. The photographs of unweathered and weathered WPCs are shown in **Figure 9**.

Chromophores naturally present in polymers and biomass generally accelerate the absorption of UV light, leading to the photodegradation of WPCs. Specifically, the photo-yellowing discoloration of weathered biomass can be attributed to the breakdown of lignin into smaller chromophoric monomers, including quinones, carboxylic acids, and hydroperoxyl radicals [23]. Polymer photochemical degradation is mediated by chain scission reactions, typically through Norrish Type I and II reactions (**Figure 10**). Norrish Type I reactions lead to the formation of free radicals by the cleavage of the ketones and aldehydes. On the other hand, carbonyl and vinylic groups are generated by Norrish Type II ring-opening reactions. Consequently, these photochemical degradation reactions lead to a reduction in the degree of chain entanglements in the amorphous zone, which results in the



Figure 9.
 Photos of HDPE-based WPCs before and after natural weathering [23].

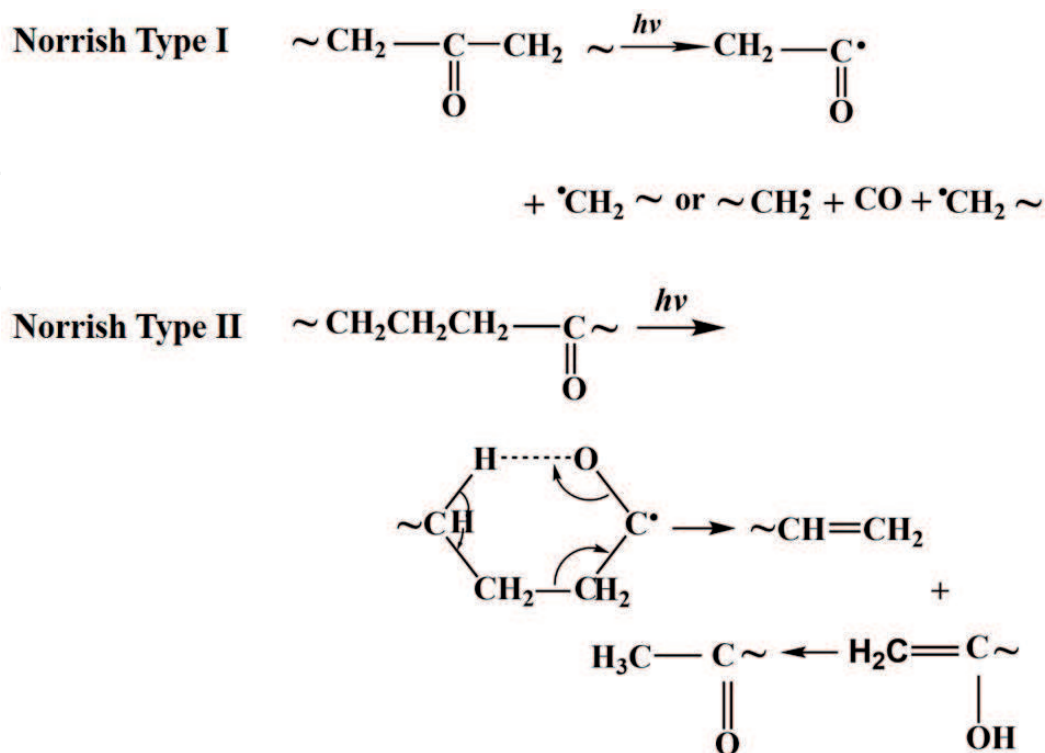


Figure 10.
 The reaction mechanism for photochemical degradation of polymer in WPC [24].

crystallization of smaller polymeric units and individual monomers, reducing the mechanical properties of the WPCs [24]. Some chemical additives, such as photostabilizers, antioxidants, and pigments have been incorporated into WPC matrices to retard the discoloration of the composites.

Moisture in the air, especially during the rainy season, can be easily absorbed by the hydrophilic biomass particles in WPCs, during which the biomass particles begin to swell and create micro-voids or cracks in the polymer matrix, resulting in decreases in both the interfacial adhesion between biomass particles and plastics and the stress transfer efficiency from the matrix to the fibers (**Figure 11**). Therefore, the elastic modulus and flexural strength of the WPCs gradually decrease. In addition, the individual components of biomass (i.e., cellulose, hemicellulose, lignin, and extractives) have varying susceptibilities to photodegradation. In fact, UV light, warm temperatures, and aerial moisture typically have a synergistic effect on the natural weathering of WPCs. When the biomass particles in WPC undergo photodegradation, the surface chemical groups trend to become more hydrophilic due to the formation of water-soluble products from the breakdown of lignin. The surface wettability increases and appears more sensitive to moisture levels. It was also found that the anti-weathering discoloration of WPC was reinforced after the biomass was extracted or delignified [25]. The surface roughness of PP-based WPCs before and after weathering was measured by atomic force microscopy [26], which indicated that there was an increase in the roughness value after the photodegradation of PP, leading to the presence of some microcracks in the WPC and the loss of biomass particles, and a decrease in the interfacial bonding on the weathered surface.

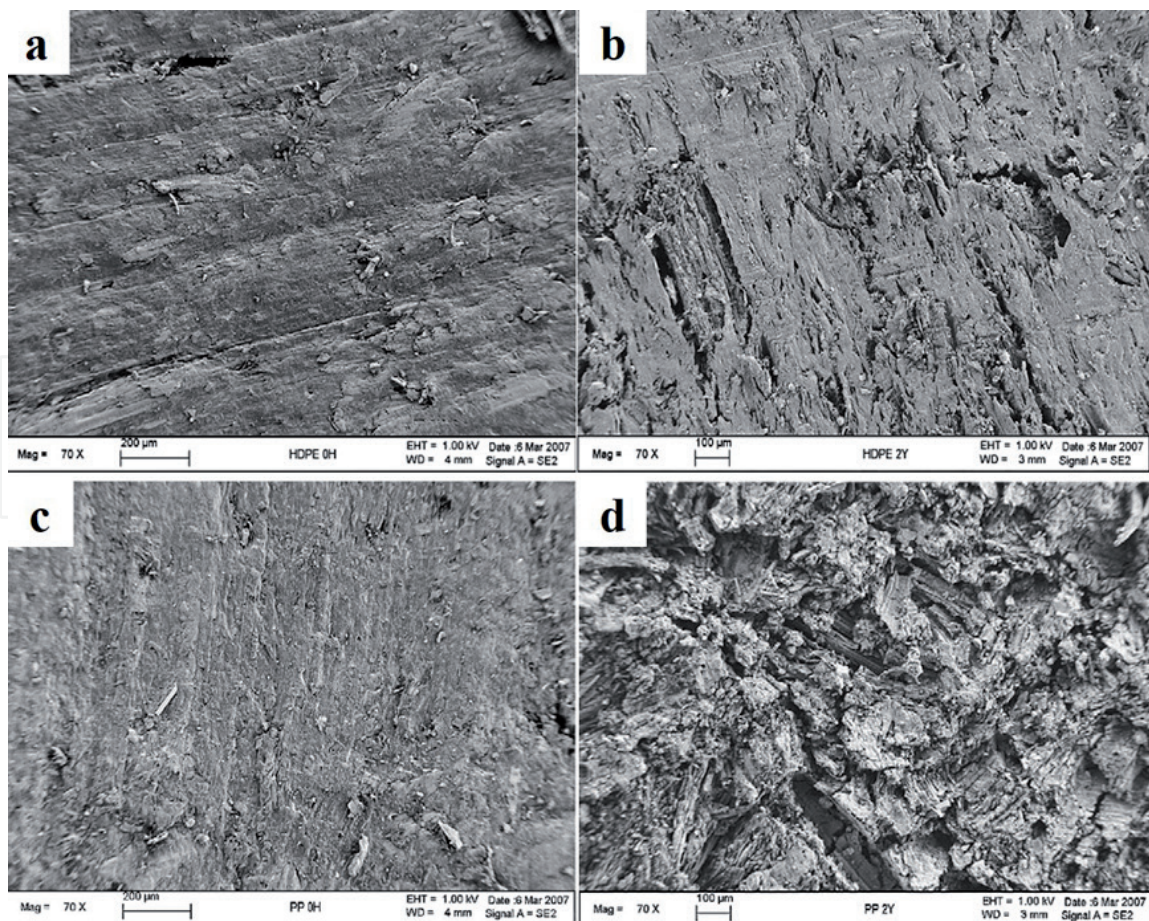


Figure 11. Scanning electron micrographs of various WPCs before and after weathering: a, c. HDPE-based and PP-based WPC that was unweathered, respectively; b, d: HDPE-based and PP-based WPC that 2-yr exterior-weathered, respectively [23].

Many studies have evaluated the natural anti-weathering properties of WPCs in various applications. WPCs containing 40 wt.% of the polymer demonstrated better resistance to natural weathering a polymer loading of 50 wt.% [27]. High humidity also was determined by various researchers to be a principal determinant of the loss of flexural strength. In WPCs prepared with rubberwood fibers and several polymeric matrices, including HDPE, LDPE, PVC, PP, and PS, PP- and PS-based WPCs had the smallest reductions in tensile and flexural strengths of the WPCs by natural weathering when the mass fraction of polymer was 60 wt.%. These results demonstrated that PP and PS were the two ideal choices for WPC engineering applications in which WPCs are required to resist high stresses and natural weathering [28].

3. Reinforcement on mechanical properties of WPC

3.1 Linear polyamide reinforcement

The unfavorable mechanical properties of WPCs made with conventional PE, PP and PVC resins led to the placement of restrictions and safety risks on engineering construction products. Polyamides 6, 66, 1010, and 11 are typical engineering polymers that exhibit high strength and stiffness, excellent chemical stability, and outstanding heat resistance, and have the potential to promote the comprehensive properties of WPCs. PA6/biomass fibers composites have been directly fabricated by hot compression, extrusion, and injection at temperatures range from 230 to 250°C. However, severe thermal decomposition and poor dispersion of biomass fillers typically occurred during these manufacturing processes [29–31].

The melting and processing temperature of polyamide polymers can be decreased by the incorporation of lithium chloride (LiCl). LiCl and either maleic anhydride-grafted polyethylene (MA-g-PE) or maleic anhydride-grafted polypropylene (MA-g-PP) exhibited a synergistic effect on the mechanical strengths of PE- or PP-based WPCs with the reinforcement of the polyamide resin. Lithium cations (Li^+) can be easily embedded into the amorphous and crystalline phases of PA6 by the coordination of amide nitrogen or oxygen atoms, thereby breaking hydrogen bonds and disrupting three-dimensional arrangements. The formation of the copolymer PA6-g-PE by the condensation of amine functionalities in the PA6 polymer with the grafted anhydrides were found to improve the interfacial bonding ability between high-density polyethylene (HDPE) and PA6. Li^+ ions could also be complexed by the oxygen atoms of the anhydrides, which, too, promoted interfacial adhesion. On the other hand, biomass particles with rich hydroxyl groups synergistically reinforced the hydrogen bonds between PA6 and the wood flour (WF), underwent esterification reactions with MA-g-PE and WF, and complexed Li^+ ions [32]. The total reaction mechanism can be depicted as **Figure 12**. The addition of 2 wt%-2.5 wt% LiCl to the MA-g-PE polymer matrix led to a maximum flexural strength, flexural modulus, and impact strength of the PE-based WPC that exceeded 100 MPa, 6000 MPa, and 12 kJ/m², respectively. Similarly, the maximum flexural strength, flexural modulus, and impact strength of the PP-based WPC with 1 wt% LiCl were 115 MPa, 6500 MPa, and 10 kJ/m², respectively [33].

Increasing the molecular weight of PA6 is another effective way to improve its mechanical properties. The reaction of the chain extender 2,2'-(1,4-phenylene) bis(2-oxazoline) (PBO) with the terminal groups of PA6 was found to increase the molecular weight PA6 from 33000 to 72800 after the chain extender being incorporated into the melting polycondensation systems, the mechanism of which is shown in **Figure 13**. During the initial stage of chain elongation, the two

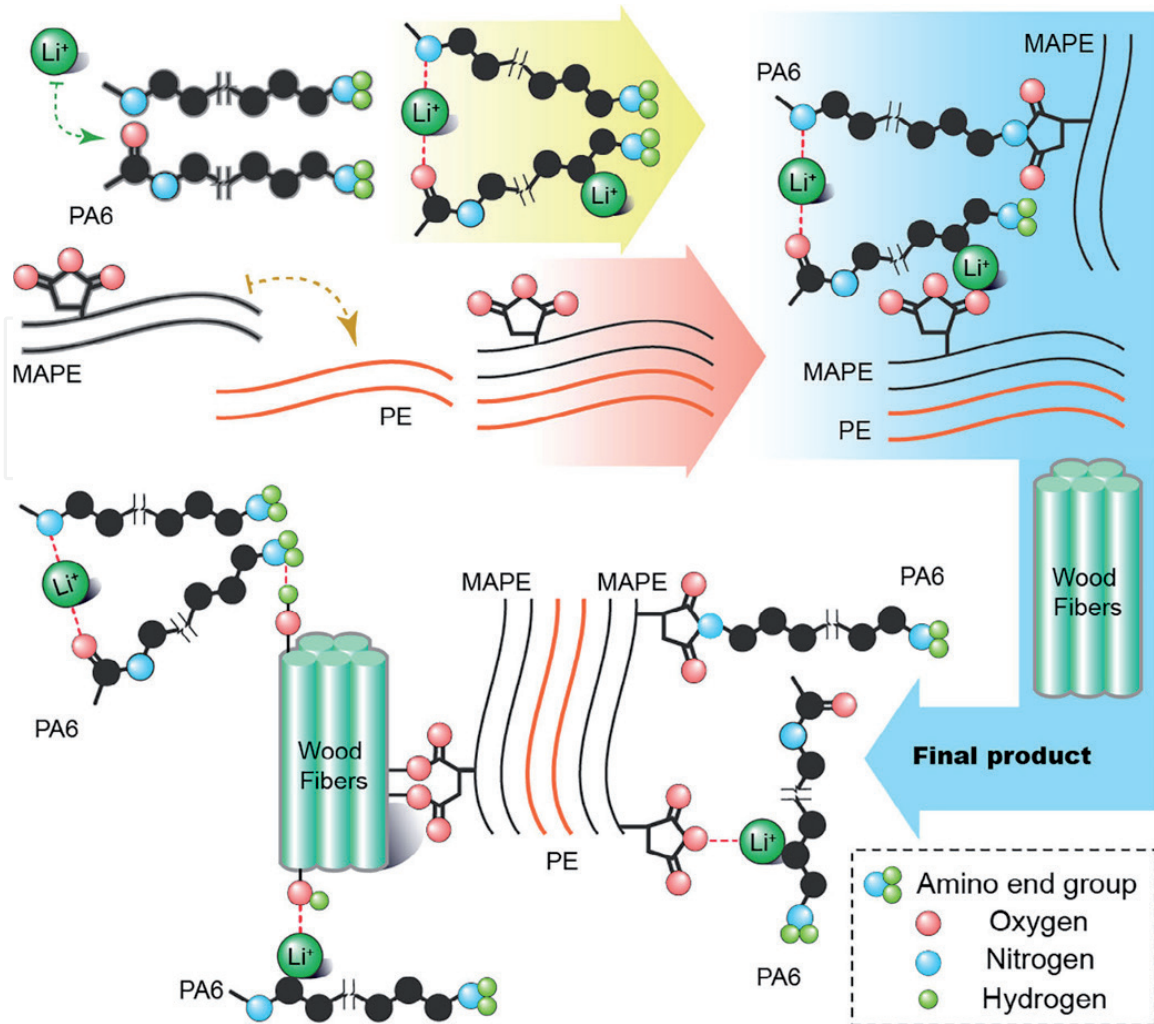


Figure 12. Reaction mechanism diagram of LiCl and MA-g-PE in PE-based WPC [32].

oxazoline rings were opened, which then reacted with the two terminal carboxylic acid groups rather than the amine functionalities of the PA6 polymer, leading to the extension of the PA6 molecular chains. In addition, hydrogen bonding between the amide groups in PA6 and the hydroxyl groups in WF, as well as the noncovalent interactions between the oxygen and nitrogen atoms in PBO and the hydroxyl groups in WF, enhanced the interfacial bonding ability of PA6 and WF. PBO and LiCl were simultaneously used to modify the PA6-reinforced WPC, after which the melting point and processing temperature of PA6 decreased from 220–190°C and 240–210°C, respectively, which effectively mitigated the discoloration and thermal decomposition of the WPC. The modification of PA6 by PBO effectively improved the mechanical properties of the WPC by increasing the tensile strength, flexural strength, and modulus by 43%, 30%, and 37%, respectively [34].

Recently, the incorporation of novel, environmentally friendly polyamide copolymers matrices PA6/11 containing ϵ -caprolactam and 11-aminoundecanoic acid into WPC products was studied. The chain extension reactions of the PA6/11 copolymer were inhibited by the generating water from condensation reactions when the ϵ -caprolactam content was high. The melting temperature of the PA6/11 copolymers with the ratio of 40 to 60 can be decreased to 120°C, which enabled the processing of the WPC below the thermal decomposition temperature of WF. In addition, when the ratio of PA6:PA11 was 70:30, the corresponding WPC exhibited outstanding ductility, with a strain at break of 15 to 20% [35].

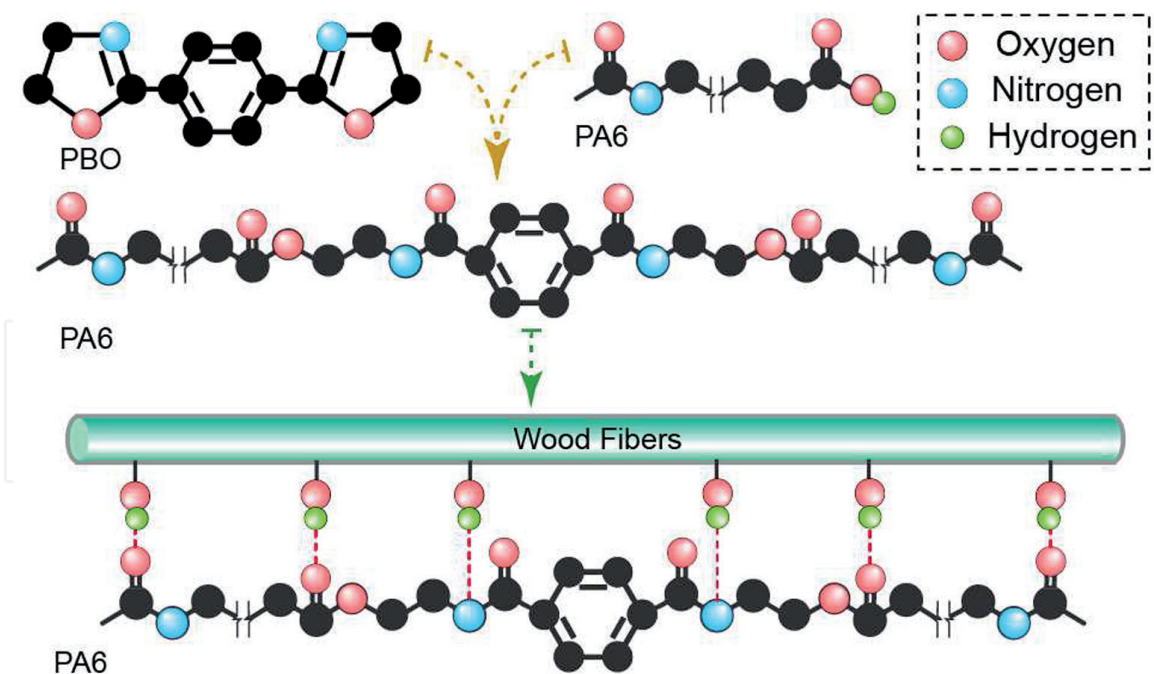


Figure 13.
Reaction mechanism diagram of the chain growth of PA6 [34].

The thermal modification of natural biomass fibers by superheated vapor has also proved to be a green, facile, and effective method for improving the mechanical and thermo-stable properties of WPCs. During this process, no chemical reactions ensue between the biomass fibers and exogenous reactants; instead, only chemical transformations within and between polymers, such as cellulose, hemicellulose and lignin, occur. Hemicelluloses are often hydrolyzed into oligomeric or monomeric structures at high temperatures. The hydroxyl groups of cellulose chains, as well as some chemical bonds that can be broken to form phenolic groups in lignin polymers, resulting in a reduction in the polarity of the biomass fibers and an improvement in their compatibility with non-polar HDPE resins [36]. The modification of rubber seed shell (RSS)-reinforced HDPE-based WPCs by superheated vapor at 200°C and 220°C is illustrated in **Figure 14**.

The superheated vapor treatment improved the mechanical strengths and thermal and dimensional stability of RSS, as well as its compatibility with HDPE. The fractured cross-section of the RSS/HDPE composites after RSS modification showed a rough morphology similar to a “thorn” due to strong interactions between the RSS and the HDPE matrix, such that the RSS fibers were pulled out during fracturing (**Figure 15**). The RSS particles modified at 200°C significantly enhanced the interfacial bonding ability of the RSS/HDPE composites and manifested outstanding mechanical properties. The flexural and tensile strengths of the RSS/HDPE composites were increased by 21.27% and 12.92% after modification of the RSS at 200°C and 220°C, respectively [37].

Superheated vapor modification mitigates the severe thermal degradation of biomass fibers during the heating processing, while the interfacial bonding can be promoted at the ideal ratio. The fractured surfaces of the PA6/HDPE/WF composite with HDPE:PA6 ratios of 8:2 and 7:3 both exhibited a rough appearance with many voids and separated structures, corresponding to the poor compatibility among WF, PA6, and HDPE [38]. These results were consistent with the weak interfacial bonding of PA6/HDPE/clay composites with when the weight ratio of HDPE:PA6 was 80:20 [39]. However, the HDPE:PA6 compatibility was markedly improved when the HDPE:PA6 ratio was 6:4, as the composite exhibited a coarse cross-section

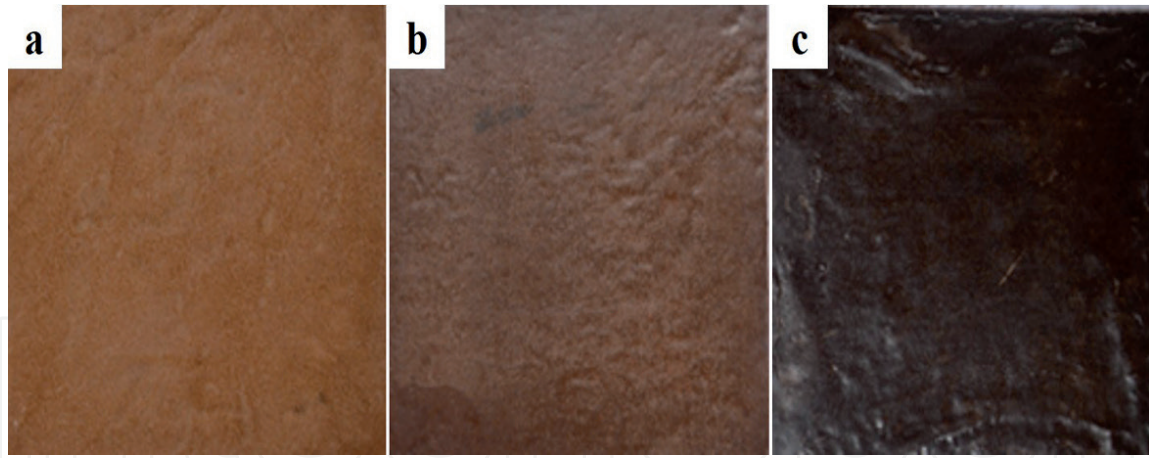


Figure 14. The HEPE-based WPC with RSS modified by various superheated vapor temperatures: a. control, b. 200°C, c. 220°C [37].

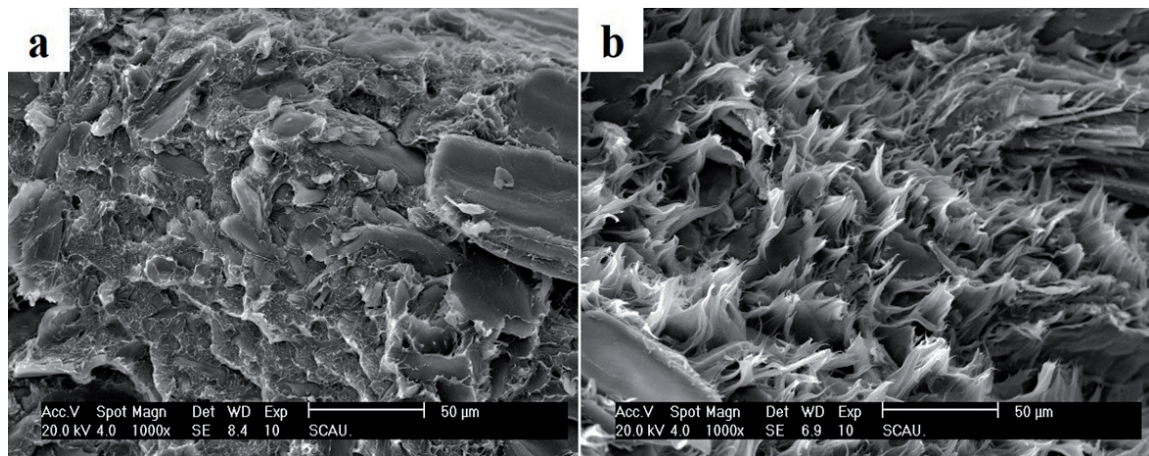


Figure 15. Micro-morphology of the HDPE/RSS composites with unmodified and modified RSS by superheated vapor: a. unmodified, b. modified [37].

consistent with “thorns” similarly with **Figure 15**. The effect could be attributed to WF pulling out during fracturing with a strong interfacial bonding as mentioned above. The PA6 and modified wood fibers synergistically reinforced the interfacial adhesion only at a 6:4 ratio of HDPE:PA6, which was determined to be the optimal ratio. The flexural strength and flexural modulus of the PA6/HDPE/WF composite increased by 82.05% and 64.08%, respectively, compared to the control HDPE-based WPC. In addition, the tensile and impact strengths increased by 93.47% and 120.45%, respectively, and the maximum thermal degradation temperatures corresponding to the first and second decomposition stages increased by 7.17°C and 8.99°C, respectively. Moreover, the water absorption ratio of the PA6/HDPE/WF composite was controlled within 1.50%. Overall, these results demonstrated that the HDPE/PA6-modified WF composites have great potential in construction and building engineering applications as WPC products (**Figure 16**).

3.2 Aromatic polyamide reinforcement

Poly(p-phenylene terephthalamide), manufactured under the name Kevlar® by the Dupont corporation, is a linear polyamide featuring additional benzene rings in the polymer chain. Kevlar fibers (KFs) can be used as another novel reinforcement for WPC because they are resistant to combustion and have a high specific strength and modulus, superior toughness, and excellent chemical and thermal stability.

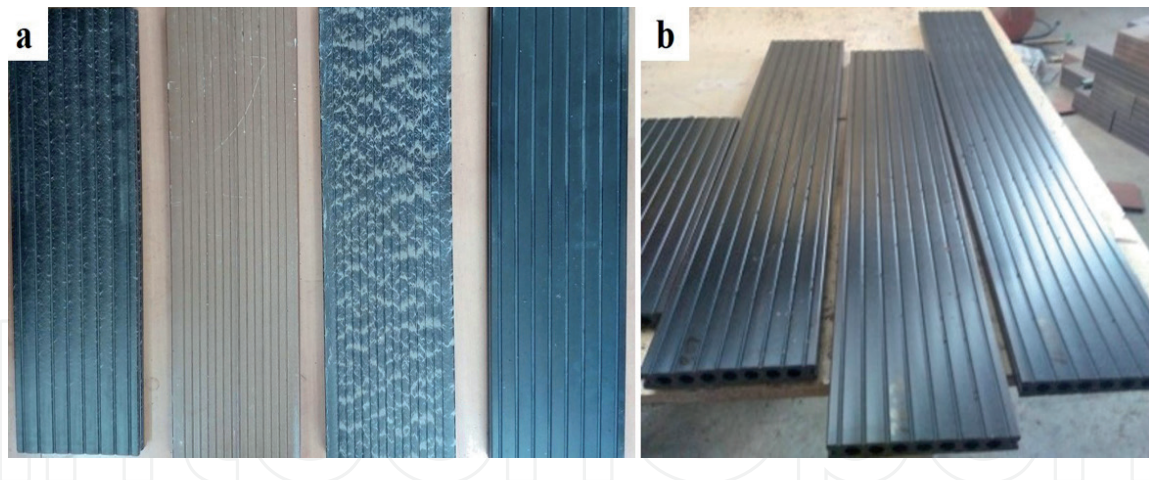


Figure 16.
The PA6/HDPE/modified WF composites: a. the samples with different ratios in the lab, b. the products in the factory.

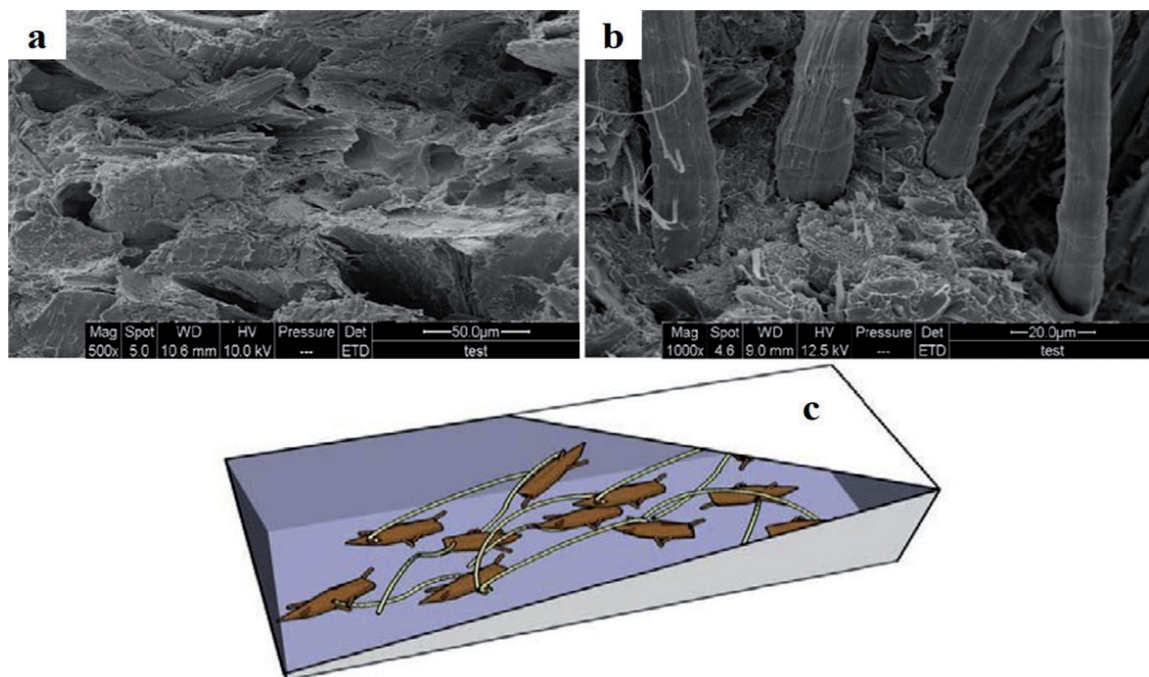


Figure 17.
The Kevlar reinforced HDPE-based WPC: a. HDPE/WF, b. HDPE/WF/KF, c. the assumed configuration of KF [40].

While KFs have been incorporated into WF/HDPE composites, their chemical inertness and low surface energy were found to be deleterious to the interfacial adhesion of the polymers within the composites. Prior to the addition of KFs, many voids and holes between the WF and the HDPE matrix on the fractured surface with the pullout of WF were attributed to poor interfacial adhesion (**Figure 17a**). The modification of KFs with allyl and 3-trimethoxysilylpropyl groups improved the compatibility between the WF and HDPE matrices, resulting in an increase in the mechanical properties of the composites (**Figure 17b**). The tensile strength and modulus of the KFs-reinforced WPC increased to 23.1% and 31.4%, respectively, while the notched and unnotched impact strengths of the reinforced WPC increased to 42.8% and 52.3%, respectively, when the KF loaded was below 3% compared to the unmodified WPC. In addition, the alkoxy groups on the KFs can be hydrolyzed to generate silanol groups or siloxane networks, which can engage in hydrogen bonding with the hydroxyl groups in WF. There was a physical anchor bonding among the melting of HDPE, KF, and WF. Meanwhile, free-radical

reactions between HDPE chains and allyl groups may have occurred during the extrusion process. The flexible KFs with diverse S, J, C, and I configurations is shown in **Figure 17c**. The major structural failures included matrix, fiber, and interface fractures as well as fiber fibrillation and buckling. The various configurations of the KFs contributed to the mechanical interlocking among KF, WF, and HDPE components, which promoted an efficient stress transfer from the resin matrix to the KFs. Therefore, the reinforcement of WPCs with KFs can bestow the WFCs with the strength and toughness required for engineering applications [40]. However, until now, there has been very limited research conducted in the field of Kevlar and natural biomass fiber-reinforced composites. Nonetheless, the incorporation of KFs into WFCs can be considered a promising modification for the improvement of the mechanical properties of WPCs in various engineering applications in the future.

4. Flame retardance properties of WPC

The continued development of WPCs for a variety of different engineering applications, as well as the increased demand for more safety-consciousness products, has necessitated the development of flame-resistant materials as a substitute for some of the conventional engineering materials used in WPCs. Currently, PE- and PP-based WPCs are most often utilized in building exterior and outdoor products because PP and PE both have a high sensitivity to flame, which means they can quickly burn when ignited, leading to hazardous scenarios. Meanwhile, PVC-based WPCs are most often used in indoor products; although PVC has a relatively low flammability and inherent self-inhibited flame properties compared to PE and PP, PVC often does not comply with the safety requirements and regulations of governments because it releases a significant amount of toxic smoke while burning. Thus, it is necessary to improve the flame resistance of WPCs to expand their potential engineering applications. Many strategies that have been developed to enhance the flame resistance of WPCs can be divided into two general categories. The first is the incorporation of fire retardants into biomass particles and polymers during the compression, injection, and/or extrusion processes. The other strategy entails the pretreatment of the biomass particles with liquid flame retardants by impregnation, after which the particles can be combined with the polymers using the conventional processes.

The major flame retardants used in WPCs include halogenated and nonhalogenated chemicals. The halogenated flame retardants mainly include brominated and chlorinated molecules that function to reduce the heat release and inhibit combustion by quenching the burning of the materials. Nevertheless, they emit toxic or corrosive gases that harmful to the environment while burning. Hence, they have been gradually withdrawn from use because of added pressure from many governments around the world. In recent years, though, some novel halogen-free flame retardants like phosphorus-based flame retardants, boron-based flame retardants, metal hydroxide flame retardants and intumescent flame retardants have been developed.

4.1 The testing methods of flame retardancy for WPC

Many different evaluation methods of flame retardancy are available for various materials, among which the limited oxygen index (LOI), UL-94 V, and cone calorimeter burning testing are most frequently used for WPC products.

4.1.1 Limiting oxygen index

The LOI, which is also referred to as the critical oxygen index (COI) or oxygen index (OI), was first introduced by Fenimore and Martin in 1966. It is defined as the minimum concentration of oxygen in an atmosphere composed of a mixture of oxygen (O₂) and nitrogen (N₂) at 25°C required for supporting the continuous flaming combustion of a material sample. LOI has been included in several international and national standards, such as ISO 4589 and ASTM D2863 [41]. Specifically, the testing involves placing a WPC sample with a candle-like shape vertically in a glass column while feeding the sample an atmosphere of O₂ and N₂. After the WPC sample is ignited from the top, the oxygen concentration is decreased (i.e. the nitrogen concentration is increased) until the minimum oxygen concentration that allows for the sustained burning of the sample is determined. Prior to observation and evaluation, the sample should be at a stable burning stage. The testing can be considered as an effective result if one of two situations occurs: either the sample continues burning 3 min after the removal of the fire source or the consumed length of the sample is within 5 cm [42]; otherwise, a new sample should be retested at an adjustable O₂ concentration. The LOI test has been considered one of the most useful testing methods for determining the flame retardance of PE-based and PP-based WPCs since it can provide a precise rating on a numerical basis.

4.1.2 UL-94 V

The UL-94 V method was initially designed to evaluate the flammability of plastic materials for parts in devices and appliances and is also accepted throughout the world as a standardized method. Similar to the LOI, it also is used to assess the flame retardancy of PE-, PP- or PS-based WPCs. In this method, a bar-shaped sample is placed vertically and held from the top. The sample is ignited twice by a Bunsen burner, and the total sustained combustion time is recorded after each burning. A second burning will be conducted if the sample is self-extinguished after the first burning. Based on the results, the WPCs can typically be classified into V-0, V-1, and V-2 levels. The V-0 level means that the specimen is extinguished less than 10 s after it is ignited. The V-1 level corresponds to a maximum combustion time of a sample of less than 50 s without any combustible drips, or the combustion time for five samples is less than 25 s [43]. Often, standard cotton is positioned under the sample to determine whether the combustible drips will ignite the cotton. The sample is classified as V-2 when the combustion times comply with the requirements of V-1 level, but some of the flammable drips ignite the cotton.

4.1.3 Cone calorimeter

The LOI and UL-94 V methods generally are facile, fast, and reproducible. However, these methods typically only provide a single test parameter. The test results cannot be well-quantified and are difficult to correlate with the burning behavior of the material in a real fire scenario. In addition, the evaluation of identical materials using different experimental methods can generate conflicting results. Instead, cone calorimetry is the most effective way to measure and simulate the flammability behavior of a medium-sized WPC sample, as it provides abundant test parameters, including the time to ignition (TTI), heat release rate (HRR), mass loss rate (MLR), total heat release (THR), total smoke release (TSR), and effective heat of combustion (EHC) [42]. It also can be used to predict the large-scale testing results in fire-protection engineering, and it is incorporated into various

international standards like ISO 5660 and ASTM E1354 because of its availability. The basic principle of cone calorimetry relies on the measurement of decreasing oxygen concentration in a mixture of gases during the combustion of a sample exposed to a constant heat flux.

4.2 Flame retardants for WPC

4.2.1 Phosphorus-based flame retardants

Phosphorus-based flame retardants can be traced back to the nineteenth century when ammonium phosphate was used to prevent the burning of theater curtains in France. The surface of wood materials has been coated with a mixture of phosphoric acid and other curable resins to modify the flammability of various materials in early Canada. Nowadays, it has become an important flame retardant for improving the flame resistance of WPCs. Phosphoric acid can facilitate the formation of char in the condensed phase and reduce the presence of flammable radicals in the gas phase, which leads to an enhancement of the flame retardance of WPCs [44]. Several kinds of phosphorus-based flame retardants, including ammonium polyphosphate (APP), aluminum hypophosphite (AHP), monoammonium phosphate (MAP), melamine phosphate (MP), melamine polyphosphate (MPP), and red phosphorus (RP), have been introduced into the formulations of polyolefin-based WPCs. **Table 1** lists the cone calorimetry testing results for WPCs containing several phosphorus-based flame retardants. It was concluded that there APP demonstrated a better flame resistance of WPC compared to DAP and MPP, while the effectiveness of DAP was lower than MPP.

4.2.2 Boron-based flame retardants

Boron-based flame retardants, which often contain additional functionalities, such as smoke suppressants, afterglow suppressants, and antitracking agents, are early used for cellulose-containing products [50]. However, the use of zinc borates (ZB) and a mixture of boric acid (BA) and borax (BX) as flame retardant in WPCs

| WPC samples | Weight ratio | TTI (s) | pHHR (kW/m ²) | THR (MJ/m ²) | Reference |
|-------------|--------------|---------|---------------------------|--------------------------|-----------|
| WF/PP | 60/40 | 21 | 359 | 87 | [45] |
| WF/PP/APP | 60/40/20 | 22 | 208 | 68 | [45] |
| WF/PP | 40/60 | 19 | 535 | 319 | [46] |
| WF/PP/MPP | 36/56/8 | 20 | 470 | 300 | [47] |
| WF/PP | 40/60 | 19 | 535 | 319 | [46] |
| WF/PP/DAP | 36/56/8 | 19 | 495 | 299 | [46] |
| WF/HDPE | 30/70 | 28 | 194 | 71 | [48] |
| WF/HDPE/APP | 30/70/10 | 19 | 113 | 62 | [48] |
| WF/HDPE | 40/60 | 35 | 422 | 102 | [49] |
| WF/HDPE/MPP | 40/60/35 | 36 | 202 | 45 | [49] |
| WF/HDPE | 40/60 | 23 | 523 | 335 | [46] |
| WF/HDPE/DAP | 37/57/4 | 22 | 466 | 311 | [46] |

Table 1.

Results of cone calorimeter for polyolefin-based WPC with various phosphorus-based flame retardants.

has gained more attention. **Table 2** lists the cone calorimetry testing results for WPCs with two typical boron-based flame retardants. PP-based and PE-based WPCs demonstrated improved fire retardance due to increased TTI and decreased pHRR and THR values after incorporating ZB and BA-BX. The polyolefin WPC containing ZB demonstrated a superior effectiveness over BA-BX, but ZB has been determined to not be an ideal flame retardant for PVC-based WPCs because PVC has an intrinsic flame resistance given the presence of chlorine atoms in the polymer [54].

4.2.3 Metal hydroxide flame retardants

Metal hydroxides can consume a significant amount of heat energy from the surroundings as well as release water during thermal decomposition [55]. Magnesium hydroxide (MH) and aluminum trihydroxide (ATH) are two commonly used flame retardants in PP-based WPCs. **Table 3** lists the cone calorimetry testing results for WPC containing these metal hydroxides. The flame retardance of the WFC samples with varying weight ratios of WF, PP, and MH were different. Compared to the control samples, both WFC samples containing MH and AHH demonstrated a noticeable improvement in their flame resistance due to higher TTI and lower pHRR and THR values compared to the WFC samples without MH and AHH.

4.2.4 Expandable graphite (EG) flame retardants

Expandable graphite (EG) is a layered crystal consisting of sheets of carbon atoms tightly bound to each other. Some chemicals, such as sulfuric acid and potassium permanganate, can be inserted into the carbon layers of graphite. When subjected to heat, EG can expand up to 300 times compared to its original volume, which produces an insulating layer that can provide excellent flame resistance for WPCs [58]. EG appeared to be more effective for the polymer component of WPCs than the WF component when the weight ratios of the two varied from 60:40 to 40:60 (**Table 4**). Furthermore, EG exhibited the best flame retardance for PP-based WPC, with the lowest pHRR and THR values, compared to all the flame retardants mentioned above.

| WPC samples | Weight ratio | TTI (s) | pHRR (kW/m ²) | THR (MJ/m ²) | Reference |
|---------------|--------------|---------|---------------------------|--------------------------|-----------|
| WF/PP | 40/58 | 19 | 505 | 253 | [51] |
| WF/PP/ZB | 40/58/10 | 22 | 402 | 237 | [51] |
| WF/PP | 40/60 | 19 | 535 | 319 | [47] |
| WF/PP/BA-BX | 37/57/4 | 20 | 465 | 318 | [47] |
| WF/PE | 50/45 | 25 | 505 | 373 | [52] |
| WF/PE/ZB | 50/35/10 | 26 | 320 | 255 | [52] |
| WF/HDPE | 40/60 | 26 | 516 | 319 | [46] |
| WF/HDPE/BA-BX | 37/57/4 | 25 | 510 | 320 | [46] |
| WF/PVC | 35/58 | 26 | 160 | 49 | [53] |
| WF/PVC/ZB | 35/58/6 | 27 | 209 | 43 | [53] |

Table 2.
 Results of cone calorimeter for polyolefin-based WPC with various boron-based flame retardants.

| WPC samples | Weight ratio | TTI (s) | pHRR (kW/m ²) | THR (MJ/m ²) | Reference |
|-------------|--------------|---------|---------------------------|--------------------------|-----------|
| WF/PP | 40/58 | 19 | 505 | 253 | [51] |
| WF/PP/MH | 40/48/10 | 25 | 407 | 249 | [51] |
| WF/PP | 50/46.7 | 21 | 563 | 93 | [56] |
| WF/PP/ATH | 50/36.7/10 | 25 | 467 | 99 | [56] |
| WF/PP | 50/43 | 28 | 395 | 162 | [57] |
| WF/PP/ATH | 40/43/10 | 30 | 336 | 152 | [57] |

Table 3.
Results of cone calorimeter for polyolefin-based WPC with various metal hydroxide flame retardants.

| WPC samples | Weight ratio | TTI (s) | pHRR (kW/m ²) | THR (MJ/m ²) | Reference |
|-------------|--------------|---------|---------------------------|--------------------------|-----------|
| WF/PP | 60/40 | 21 | 358 | 87 | [45] |
| WF/PP/EG | 60/40/20 | 32 | 181 | 64 | [45] |
| WF/PP | 40/60 | 20 | 390 | 90 | [59] |
| WF/PP/EG | 40/60/25 | 24 | 99 | 39 | [59] |
| WF/PP | 60/40 | 28 | 358 | 102 | [60] |
| WF/PP/EG | 60/40/25 | 23 | 84 | 48 | [60] |

Table 4.
Results of cone calorimeter for PP-based WPC with expandable graphite flame retardants.

4.2.5 Prospect of flame retardants in WPC

While all WPC samples containing individual flame retardants displayed decreased pHRR and THR values, they still demonstrated limited effectiveness under the mandatory flame condition. In the future, the development of flame retardants for WPCs will be more focused on the synergism between multiple components to further improve the flame retardance and the interfacial compatibility in the compound system. Intumescent flame retardants (IRFs), which consist of a char-forming agent, dehydrating agent, and blowing agent, have attracted significant attention because of their environmental friendliness and high efficiency [61]. However, moisture absorption and incompatibility with polymers are potential drawbacks for blowing agents and carbonic sources. Therefore, novel flame retardants that are nontoxic, have excellent flame resistance, and are highly compatible with polymers should be developed in the future.

5. Conclusions

Wood plastic composites has a significant potential and brilliant prospect in the application of building construction. WPC products like sidings, ceilings, windows, and floorings with the special advantages in environmental protection and sustainable development can effectively promote the coordinated development of wood-based engineering products in the “next-generation” green construction. However, the main defects on low mechanical properties, weak biological and aging resistance and poor flame retardance limit its further development. The novel modification ways including the selection of wood species, alloy reinforcement and synergistic improvement on flame resistance can be used to effectively facilitate the promotion of comprehensive properties of WPC, which achieves to the related requirements in

the field of building construction. Future works also should focus on these necessary problems. In addition, the coextrusion technology with solid woods, functional polymers or metals is also a promising modification method for engineered WPC for construction in the future.

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Conflict of interest

There is no conflict of interest in this field.

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