

Mechanical Properties and Fire Retardancy of Wood Flour/High-Density Polyethylene Composites Reinforced with Continuous Honeycomb-Like Nano-SiO₂ Network and Fire Retardant

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Abstract: The mechanical properties of wood flour/high-density polyethylene composites (WPC) were improved by adding a small amount of nano-SiO₂ to obtain a network-structured WPC with a continuous honeycomb-like nano-SiO₂ network. The wood flour was modified with a fire retardant (a mixture of sodium octabonate and amidine urea phosphate) to improve its fire retardancy. The flexural properties, creep resistance, thermal expansion, and fire retardancy of the WPC were compared to a control (WPC_{CTRL}) without nano-SiO₂ or fire retardant. The flexural strength and modulus of the WPC containing only 0.55 wt.% nano-SiO₂ were 6.6% and 9.1% higher than the control, respectively, while the creep strain and thermal expansion rate at 90°C were 33.8% and 13.6% lower, respectively. The cone calorimetry tests revealed that the nano-SiO₂ network physically shielded the WPC, giving it lower heat release and smoke production rates. The thermal expansion was further decreased by incorporating fire retardants into the WPC, which showed the lowest total heat release and total smoke production and the highest mass retention. This study demonstrates a facile procedure for producing WPC with desired performances by forming a continuous honeycomb-like network by adding a small amount of nanoparticles.

Keywords: Wood plastic composites; nano-SiO₂; mechanical properties; creep; fire retardancy

1 Introduction

Wood flour/thermoplastic composites (WPC) are environmentally-friendly materials that have been extensively used in building, decorative, and logistics packing materials [1–3]. Nonpolar polyolefins (polyethylene and polypropylene) are used as thermoplastics in WPCs due to their facile processing and forming, low cost, and similar processing temperatures to wood flour. The wood flour originates from wood processing residues, waste wood products, and agricultural and forestry residues. Weak interfaces are formed between the polar wood flour and nonpolar polyolefins due to their surface energy differences,



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which results in low mechanical strength and creep resistance of the resulting WPC, which limit their applications and shorten their service life [4–6].

Many studies have investigated methods to improve the strength and creep resistance of WPC [7], including increasing interfacial compatibility and adding inorganic nanoparticles. For example, grafting a mixture of polyethylene and polypropylene with maleic anhydride monomers improved the compatibility between grafted polymers and wood flour. The flexural strength and modulus of the resulting WPC increased by 117% and 29%, respectively, while the creep strain was lowered [8]. The incorporation of maleic anhydride-grafted polypropylene into wood fiber/polypropylene composites increased the creep modulus by nearly 28.0% at 60°C [9]. The creep resistance of wood flour/polypropylene composites increased by about 15% and 22.5% after the addition of 1 wt.% nanoclay and transition metal-modified nanoclay, respectively [10]. The flexural strength and modulus of polylactic acid composites after the wood fiber was modified with 3 wt.% organo-montmorillonite increased by 30.7% and 46.8%, respectively [11].

Nano-SiO₂ is a commercially-available inorganic filler that is easy to produce on large scales, low-cost, and easily undergoes surface modification. It has the potential to improve the creep resistance and fire retardancy of WPC [11,12]. The incorporation of 8 wt.% SiO₂ in polyethylene/polypropylene/flax ternary composites significantly reduced the creep strain and improved the relaxation modulus [12]. Adding 14 wt.% nano-SiO₂ to wood flour/polyethylene composites reduced the average heat release rate and total heat release by 30.3% and 12.8%, respectively, while it increased the smoke release [13]. To obtain satisfactory creep resistance and fire retardation, high nano-SiO₂ loadings are required when using traditional processes to directly disperse nano-SiO₂ in WPC [14,15]. This increases the cost and decreases the mechanical properties of WPC due to the agglomeration of nano-SiO₂ [15].

In order to enhance the mechanical properties and creep resistance of WPC, a continuous honeycomb-like nano-SiO₂ network was formed in a WPC using solution mixing, rotary evaporation, and mold pressing. In the network-structured WPC, SiO₂ nanoparticles were distributed only at the boundaries between the WPC pellets instead of uniformly throughout the WPC. Thus, the amount of nano-SiO₂ was significantly reduced. In order to further improve the fire retardancy of the network-structured WPC, wood flour modified with fire retardants (amidine urea phosphate and sodium octaborate tetrahydrate) was used to fabricate WPC. The flexural properties, creep resistance, thermal expansion, and fire retardancy of the resulting WPC were evaluated.

2 Experimental

2.1 Materials

HDPE pellets with a density of 0.954 g/cm³ and a melt flow index of 0.9 g/10 min were obtained from Daqing Petrochemical Co., Ltd. (Daqing, China). Wood flour (WF) with a particle size of 40–60 mesh was prepared from poplar wood (*Populus adenopoda* Maxim) in our laboratory. Maleic anhydride-grafted polyethylene (MAPE) pellets with a grafting ratio of 0.9 wt.% and a melt flow index of 1.9 g/10 min were purchased from Sunny New Technology Development Co., Ltd. (Shanghai, China). The lubricant was a mixture of stearic acid and polyethylene wax (1:1 in mass, Adisi Co., Ltd., Nanjing, China). SiO₂ nanoparticles with an average diameter of 10–15 nm (marked as nSiO₂) were obtained from Meng Tai Hu Industrial Co., Ltd. (Shanghai, China). The fire retardant (FR) was a mixture of guanlyurea phosphate (abbr: GUP; molecular formula: C₂H₉N₄O₅P; purity: 99.04%; free phosphoric acid content: 0.41%) and sodium octaborate tetrahydrate (abbr: DOT; molecular formula: Na₂B₈O₁₃·4H₂O; melting point: 741°C). The mass ratio of GUP-to-DOT was 7:3 and was made in-house. Vinyltrimethoxysilane (abbr: VTS) was purchased from Chi Ye Silicone Co., Ltd. (Shanghai, China). Ethanol solution was obtained from Tianjin Guangfu Co., Ltd. (Tianjin, China).

2.2 Experimental

2.2.1 Fire Retardant Impregnated Poplar Powder

WF was dried in a vacuum oven at 103°C for 12 h to reach 1–2% moisture content. The dried WF was impregnated in a 9 wt.% aqueous solution of fire retardant through vacuum treatment at -0.01 MPa for 6 h. Then, the impregnated WF was drained on a 100-mesh sieve, followed by vacuum drying at 80°C for 12 h to obtain the modified WF (Fig. 1). The weight gain rate of the modified WF was $11.25 \pm 1.06\%$. WF was also treated with distilled water using the same process as the unmodified WF.

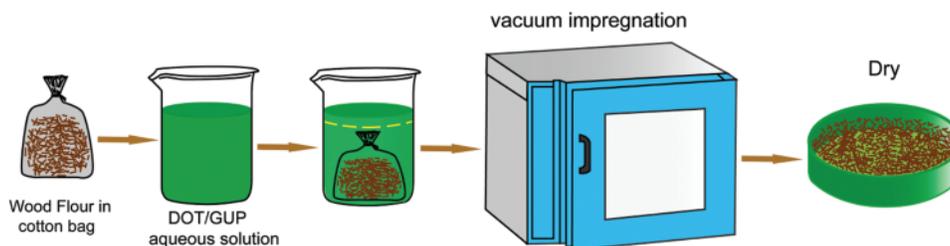


Figure 1: Schematic diagram of wood flour impregnated with fire retardant

2.2.2 Preparation of WPC

The unmodified WF or modified WF and HDPE, MAPE, and lubricant were compounded for 8 min at ambient temperature using a high-speed mixer (SHR-10A; Tongsha Plastic Machinery Company, Zhangjiagang, China). The mixture was melt-blended through a co-rotating twin-screw extruder (diameter = 40 mm, L/D = 30, SJSH-30, Nanjing Rubber Machinery Corp., Nanjing, China) at a temperature range of 145–165°C. The resulting extrudates were pelletized.

Preparation of control WPC and fire retardant (FR)-modified WPC: The obtained pellets were molded into panels (160 mm × 160 mm × 3 mm) using a flat vulcanizing machine (XH-406B; Zhuosheng Machinery Equipment Co., Ltd., Dongguan, China) at 180°C with a pressure of 12 MPa for 3 min after pre-pressing for 15 min. The obtained WPC panels with unmodified WF or modified WF were referred to as WPC_{CTRL} and WPC_F, respectively. The weight ratio of each component in the panels is shown in Tab. 1.

Table 1: Weight ratio of each component in WPC panels (wt.%) (WPC_{CTRL} = control; WPC_S = WPC panel with nSiO₂ network; WPC_F = WPC panel with fire retardant modified wood flour; WPC_{SF} = WPC panel with nSiO₂ network and fire retardant modified wood flour)

Sample	nSiO ₂	Fire retardant	Wood flour	HDPE	MAPE	lubricant
WPC _{CTRL}	0	0	50	45	3	2
WPC _S	0.55	0	49.45	45	3	2
WPC _F	0	5.63	44.37	45	3	2
WPC _{SF}	0.75	5.63	43.62	45	3	2

Preparation of network-structured WPC based on nSiO₂: The pellets obtained in Section 2.2.2 were uniformly mixed with nSiO₂ (3 wt.% based on the WPC pellets) using an electric mixer in an ethanol solution. Subsequently, nSiO₂-coated WPC pellets were obtained after evaporating ethanol. The nSiO₂-coated pellets were screened through a 30-mesh sieve to remove self-agglomerated nSiO₂. The WPC panels prepared using the nSiO₂-coated pellets with unmodified WF and modified WF were marked as

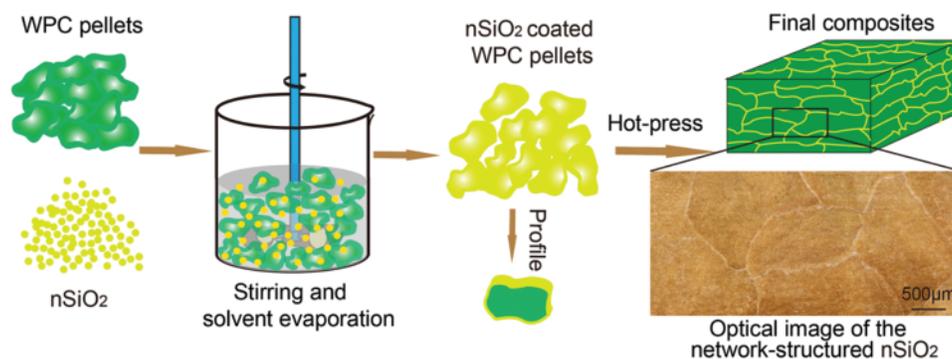


Figure 2: Schematic diagram of processing process of the network-structured WPC

WPC_S and WPC_{SF}, respectively. The amounts of nSiO₂ coated on the pellets were calculated and are shown in Tab. 1. In the network-structured WPC panels, nSiO₂ was distributed at the boundary between the WPC pellets (Fig. 2). The optical microscopic image in Fig. 2 shows that nSiO₂ formed a continuous honeycomb-like network in the WPC.

2.3 Characterization

The micro-morphologies of the WPC pellets and the cross-sections of the WPC panels were observed using a scanning electron microscope (SEM, FEI QuanTa200, FEI Co., Hillsboro, OR, USA) at an accelerating voltage of 12.5 kV. The WPC pellets and panels were sputter-coated with gold. In addition, the elemental distribution of the surfaces of the WPC pellets was analyzed using energy-dispersive spectrometry (EDS).

The flexural properties of the WPC panel samples (80 mm × 13 mm × 4 mm) were analyzed by a universal mechanical testing machine (CMT5504, MTS Systems Co., Ltd, China) according to ASTM D790-10. Eight replicates were tested for each group.

Creep and relaxation tests of samples (35 mm × 12 mm × 3.5 mm) were performed on a dynamic mechanical analyzer (Q800, TA Instruments Inc., SA). Isothermal (50°C) creep was tested for 50 min under a load of 2 MPa within the elastic deformation regime. Relaxation was tested under a constant strain of 0.1%, and the change in the relaxation modulus was recorded.

Thermal expansion of the specimens measuring 10 mm × 10 mm × 3.5 mm (length × width × thickness) was analyzed along the thickness direction using a thermomechanical analyzer (Q400, TA Instruments Inc., USA). Specimens were heated from room temperature to 100°C at a heating rate of 20 °C/min and then held at 100°C for 3 min to eliminate the thermal history and moisture. A quartz probe was in contact with the specimens under a loaded of 0.05 N. The tests were conducted from −40°C to 90°C at a heating rate of 3°C/min under a nitrogen atmosphere.

The fire retardancy tests of WPC specimens measuring 100 mm × 100 mm × 3.5 mm were conducted using a cone calorimeter (Fire Testing Technology Ltd., East Grinstead, UK) according to ISO 5660-1 at a heat flux of 50 kW/m². The heat release rate (HRR), total heat release (THR), smoke production rate (SPR), total smoke production (TSP), and residual mass were recorded. Two replicates were tested for each group. The residuals after combustion were analyzed by a digital camera and SEM.

3 Results and Discussion

3.1 Morphological Analysis

The WPC_{CTRL} pellets had a rough and uneven surface on which the WF was imbedded in an HDPE matrix (Fig. 3a). The surface morphology of the WPC_F pellets was similar to that of the WPC_{CTRL} pellets

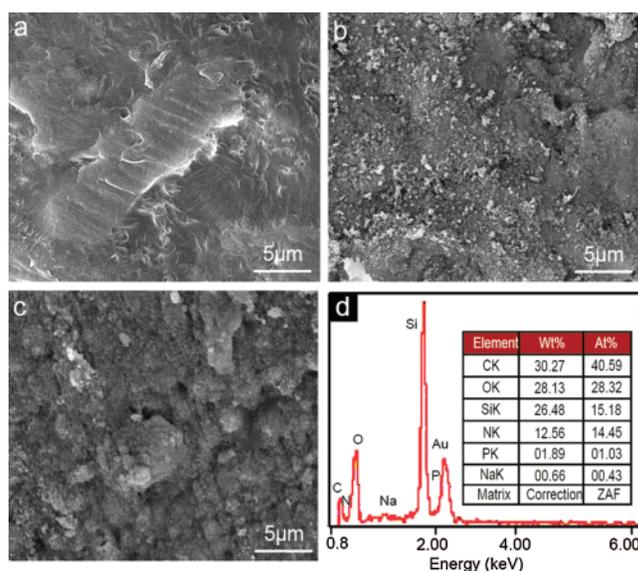


Figure 3: SEM micrographs of the surface of the WPC control pellets (a), the WPC pellets coated with nano-SiO₂ (b), and the fire retardant modified WPC pellets coated with nano-SiO₂ (c); EDS corresponding to Fig. 3c (d)

(not shown). The nSiO₂ particle aggregates were visible on the WPC_S pellets (Fig. 3b). For the WPC_{SF} pellets, the nSiO₂ particles and WF were enveloped by a viscous substance (Fig. 3c). The EDS result showed that the viscous substance contained a small amount of N and P (Fig. 3d), indicating that it may be the product of dissolving GUP in ethanol. The viscous substance could facilitate the adhesion of more nSiO₂ particles, as demonstrated by the higher nSiO₂ content on the WPC_{SF} pellet surface than on the WPC_S pellet surface (Tab. 1).

The SEM micrographs of the cross-sections of the flexural-fractured WPC panels are shown in Fig. 4. The HDPE matrix underwent plastic deformation, as shown in the fracture cross-sections of the WPC_{CTRL} and WPC_F (Figs. 4a and 4b). This was a result of the flexural failure loading mode [16]. A continuous nSiO₂-rich region was observed on the fractured cross-section of WPC_S (Fig. 4c). This region exhibited brittle fracture compared with the WPC region due to the high nSiO₂ content, and there was no obvious boundary between the WPC pellets after hot-pressing. Furthermore, the high-magnification images of the nSiO₂-rich region showed a mixture of nSiO₂ and HDPE (Fig. 4d) due to the diffusion of molten HDPE into the nSiO₂ lamella during hot-pressing. Compared with the WPC_S, the WPC_{SF} showed a wider nSiO₂-rich region on the fractured cross-section (Fig. 4e) due to the higher nSiO₂ content. The nSiO₂-rich region of WPC_{SF} (Fig. 4f) exhibited more ductile fracture behavior compared with WPC_S (Fig. 4d), possibly because the viscous substance enveloping the nSiO₂ surface reduced the interfacial compatibility between nSiO₂ and HDPE in the nSiO₂-rich region of WPC_{SF}.

3.2 Flexural Properties

The flexural strength of WPC_S (37.3 MPa) was higher than that of WPC_{CTRL} (35.0 MPa) due to the formation of a rigid nSiO₂ network (Fig. 5a) which could transfer stress due to its compatibility with the HDPE matrix [17]. Compared with the WPC_{CTRL}, the flexural strength of WPC_F (33.5 MPa) was slightly lower due to the weak interfacial bonding between the fire retardant-impregnated WF and HDPE matrix [18,19]. The flexural strength of WPC_{SF} (33.0 MPa) was further decreased compared with that of WPC_F because the viscous substance weakened the nSiO₂ network.

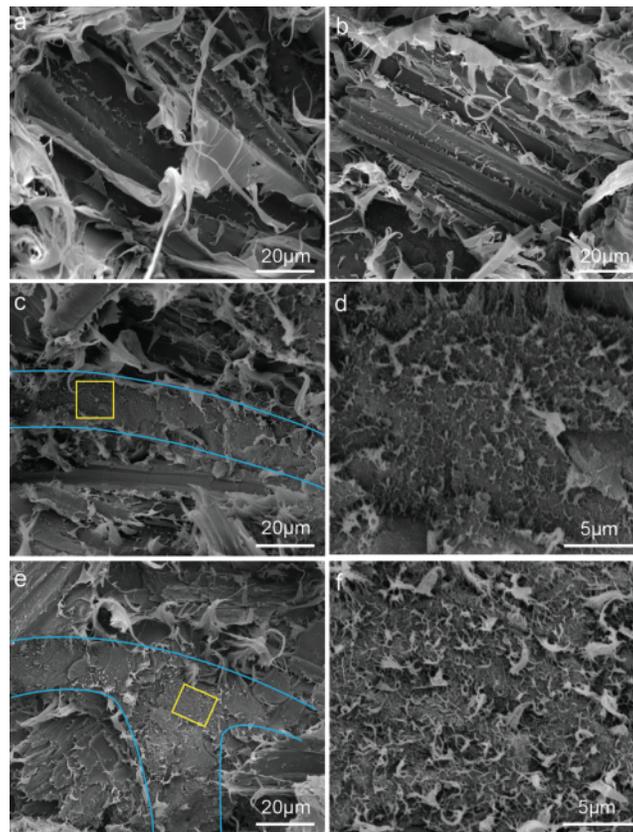


Figure 4: SEM micrographs of the flexural-fractured section of the WPC control panel (a, $\times 1000$), WPC panel with fire retardant modified wood flour (b, $\times 1000$), WPC panel with nSiO₂ network (c, $\times 1000$; d $\times 5000$), and WPC panel with nSiO₂ network and fire retardant modified wood flour (e, $\times 1000$; f, $\times 5000$). Yellow rectangles in (c) and (e) demonstrate the region shown in (d) and (f), respectively

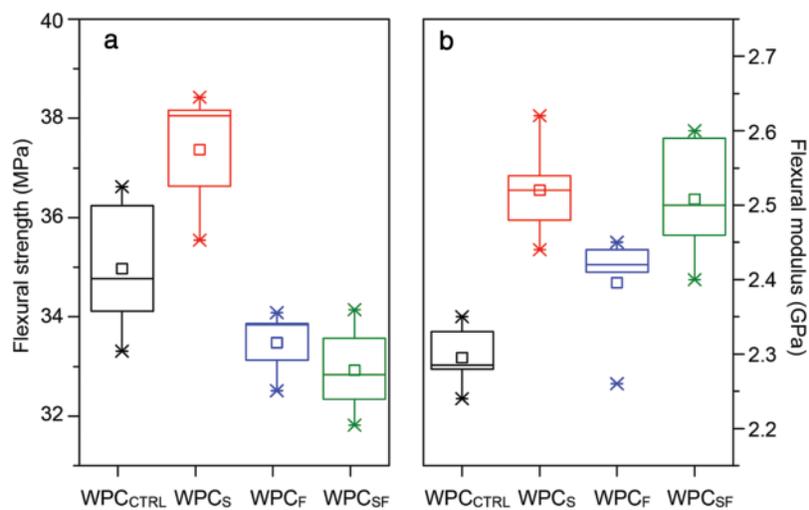


Figure 5: Flexural strength (a) and flexural modulus (b) of the WPC. (The abbreviations in the figure are the same with Tab. 1)

The flexural modulus of WPC_S was 9.1% higher than that of the WPC_{CTRL} due to the formation of a rigid nSiO₂ network (Fig. 5b). Unlike flexural strength, the flexural modulus of WPC_F was higher than that of WPC_{CTRL}. This was attributed to the positive effect of the rigid fire-retardant particles (DOT and GUP) on the modulus, which compensated for the negative effect of the weak interfacial effect between the modified-WF and HDPE [20]. The flexural modulus of WPC_{SF} was higher than that of WPC_F, which may have resulted from the combined action of rigid fire retardant particles and nSiO₂ network.

3.3 Creep and Relaxation Analysis

The creep resistances of the four WPC panels followed the order: WPC_{CTRL} < WPC_F < WPC_{SF} < WPC_S (Fig. 6a). The creep strain of WPC_S (0.047%) was significantly lower than that of WPC_{CTRL} (0.071%) after applying an external force for 45 min. This was attributed to the formation of a rigid nSiO₂ network in WPC_S, which served as a rigid support that transmitted stress and provided deformation resistance. Compared with WPC_{CTRL}, the lower creep strain of WPC_F arose due to the introduction of the rigid fire retardant [1]. The creep strain of WPC_{SF} was slightly higher than that of WPC_S, possibly because the viscous substance wrapping the nSiO₂ reduced the rigidity of the nSiO₂ network in WPC_{SF}. Similar to the improved creep resistance, the relaxation moduli of WPC_S, WPC_F, and WPC_{SF} were higher than that of WPC_{CTRL} (Fig. 6b). The relaxation modulus of WPC_S was 21.3% higher than that of WPC_{CTRL}, indicating that the introduction of a rigid nSiO₂ network effectively resisted the deformation of WPC caused by the constant external force.

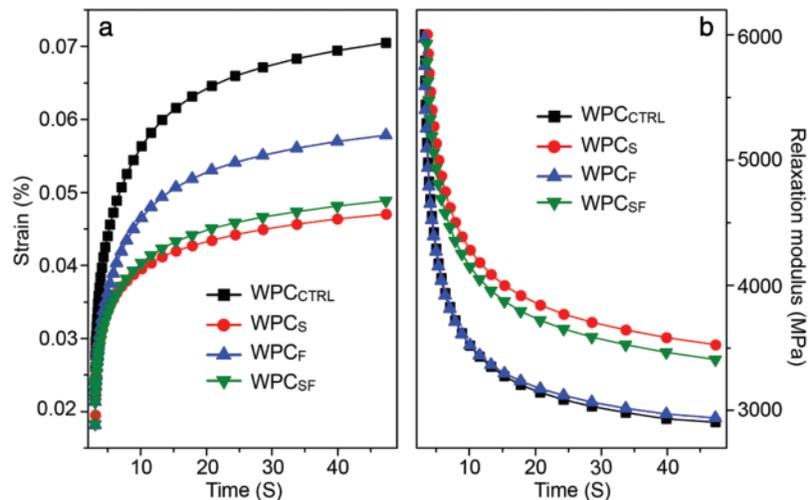


Figure 6: Creep strain (a) and relaxation modulus (b) of the WPC. (The abbreviations in the figure are the same with Tab. 1)

3.4 Thermal Expansion Behavior

The thermal expansion rates of WPC_S, WPC_F, and WPC_{SF} were lower than that of WPC_{CTRL} and ranged from -40 to 90°C (Fig. 7a). This was due to the presence of a rigid nSiO₂ network and fire retardant which were inherently not prone to thermal expansion [21]. The WPC_{SF} showed the lowest thermal expansion rate over the test temperature range compared with the other WPC panels due to its higher nSiO₂ content. The thermal expansion rates of WPC_{SF}, WPC_F, WPC_S, and WPC_{CTRL} at 90°C were 19.9%, 24.3%, 24.2%, and 28.0%, respectively. The linear coefficient of thermal expansion (LCTE) increased with temperature, and a higher increment was observed after 50°C (Fig. 7b). This was because the thermal motion of HDPE increased with the temperature, causing an increase in the macroscopic volume of WPC [22]. It

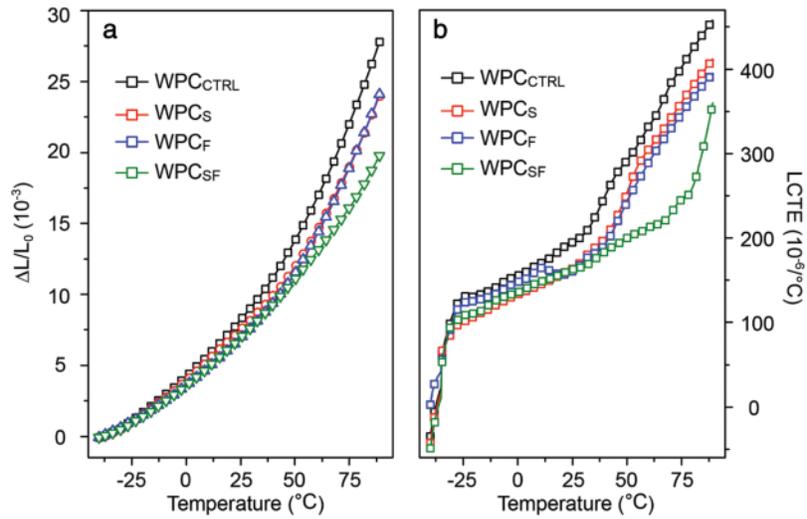


Figure 7: Thermal expansion rate (a) and linear coefficient of thermal expansion (b) of the WPC. (The abbreviations in the figure are the same with Tab. 1)

was found that the LCTE of WPC_{SF} was significantly lower than that of WPC_{CTRL}, suggesting that the wider rigid nSiO₂ network region effectively reduced the thermal expansion.

3.5 Combustion Characteristics

The WPC_{CTRL} was burned to ashes (Fig. 8a). The white residual material on the surface of WPC_S was nSiO₂, and the bottom was mainly carbonized wood flour (Fig. 8b). The cracks produced on the WPC_S

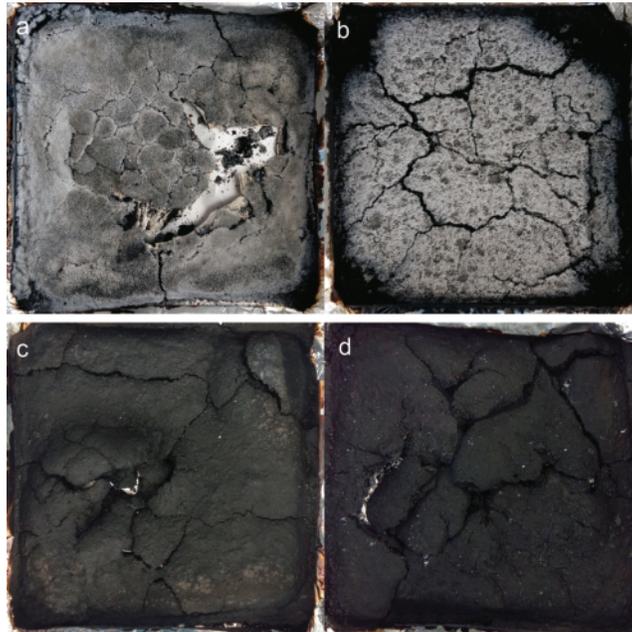


Figure 8: Digital photographs of the residues of four kinds of WPC after cone test: WPC control panel (a), WPC panel with nSiO₂ network (b), WPC panel with fire retardant modified wood flour (c), and WPC panel with nSiO₂ network and fire retardant modified wood flour (d)

residuals were caused by the gas impact, which was responsible for the higher smoke release of WPC_S after 300 s. The residuals of WPC_F also exhibited cracks (Fig. 8c). The combustion residuals of WPC_{SF} were thicker than those of WPC_F because the wider nSiO₂ network region hindered the gas release and the gas impulse caused the expansion of the residuals [4] (Fig. 8d). The physical integrity of the WPC_F and WPC_{SF} residues were poor, indicating a weak strength, which did not help reduce the heat and smoke release of WPC_F and WPC_{SF}. In contrast to WPC_S, no nSiO₂ was deposited on the surface of the WPC_{SF} residues, possibly because the APP and PPA produced by the decomposition of GUP reacted with nSiO₂ to form pyrophosphate silicon [13].

The WPC_{CTRL} was burnt into short carbon fragments (Fig. 9a). Compared with WPC_{CTRL}, the EDS results indicated the formation of an nSiO₂ crust on the residuals surface of WPC_S (Fig. 9b) and a complete carbon skeleton of WF on the bottom of the residuals (not shown). The residuals of WPC_F were dense (Fig. 9c), and their surfaces were coated by lamellar sodium octabonate (Fig. 9d). P and N were detected on the WPC_F residuals by EDS (Fig. 9d), indicating that the degradation products of GUP, such as PPA, also remained on the surface of the residuals. Similar to WPC_F, compact residuals were observed for WPC_{SF} (Fig. 9e). Its surface was coated by a layer of a glassy substance containing Na, P, N, and Si (Fig. 9f), which indicated that this film may be composed of sodium octabonate, polyphosphoric acid, pyrophosphate silicon, and unreacted nSiO₂.

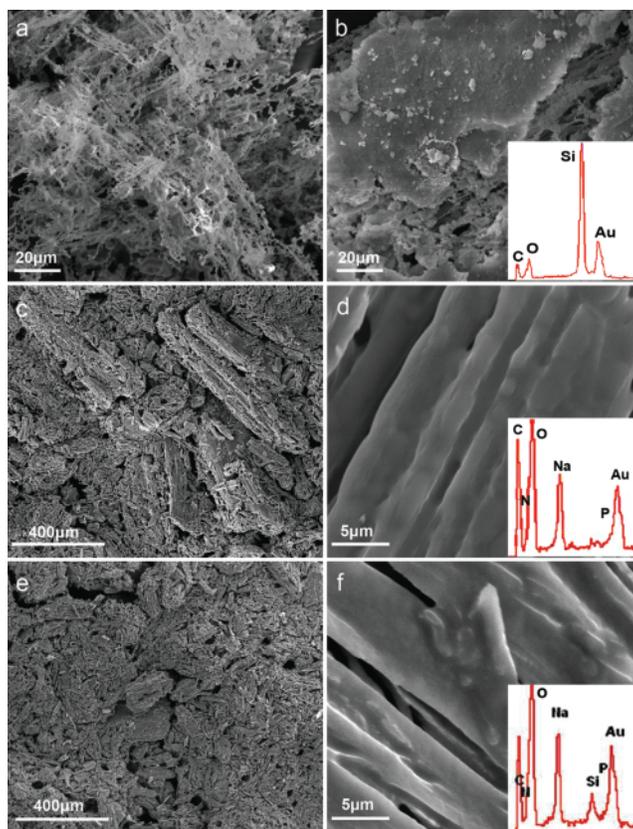


Figure 9: SEM of the WPC residual: the WPC_{CTRL} (a, $\times 1000$), the surface of WPC_S (b, $\times 1000$), the surface of WPC_F (c, $\times 100$; d, $\times 5000$), the surface of WPC_{SF} (e, $\times 100$; f, $\times 5000$), the line drawings in the lower right corner of figure (b), (d), and (f) are from EDS. (The abbreviations are the same with Tab. 1)

Compared with WPC_{CTRL} , the HRR of WPC_S decreased slightly before 300 s during combustion (Fig. 10a) because the $nSiO_2$ network exerted physical shielding and catalytic charring effects [23]. However, the $nSiO_2$ loading (0.55%) was insufficient to significantly decrease the HRR of WPC_S . After 300 s of combustion, the HRR of WPC_S was higher than that of WPC_{CTRL} (Fig. 10a) due to the formation of a large number of cracks on the surface of the residuals (Fig. 8b). These cracks provided channels for heat and combustible gases to penetrate, increasing the HRR [24]. The HRR and THR of WPC_F were lower than those of WPC_{CTRL} (Figs. 10a and 10b). The reasons for the reduction may be as follows: (1) the thermal decomposition reactions of the fire retardant (GUP and DOT) could absorb heat from the fire source. The small molecular gasses (H_2O , NH_3 , and CO_2) produced by the decomposition of GUP and DOT could reduce the O_2 concentration, which decreased oxidative pyrolysis [25]; (2) the glassy sodium borate that was produced from the degradation of DOT coated the residuals and provided physical protection [26]; (3) the decomposition products of GUP may have catalyzed the charring of WF [20]. Compared with WPC_F , WPC_{SF} showed a slightly lower HRR and THR, which may have been due to the synergistic effect of the $nSiO_2$ network and fire retardants (DOT and GUP).

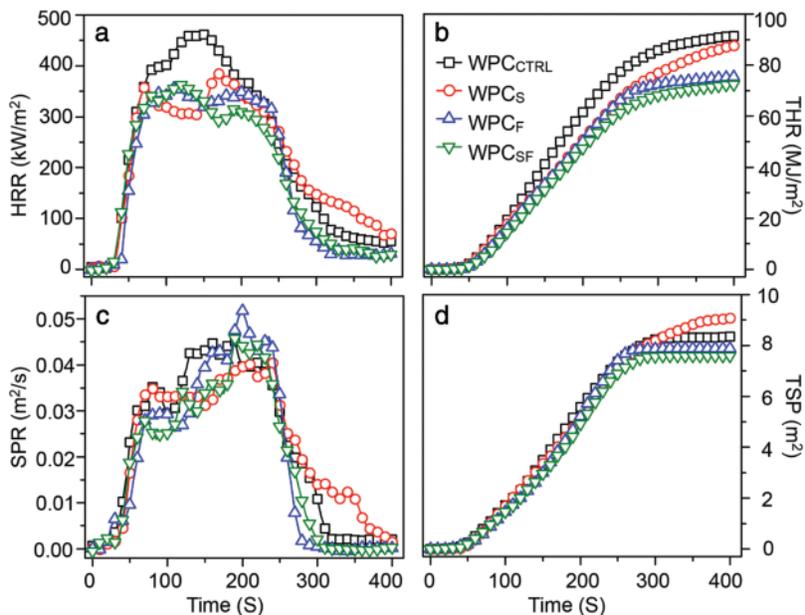


Figure 10: Heat release rate (HRR) (a), total heat release (THR) (b), smoke production rate (SPR) (c), and total smoke production (TSP) (d) of the WPC. (The abbreviations in the figure are the same with Tab. 1)

The SPR and TSP of WPC_S were higher after 300 s compared with those of WPC_{CTRL} (Figs. 10c and 10d). These increased values were due to the production of cracks in the residues during the later stage of combustion, which resulted in the combustion of the bottom substances and an increased smoke release [24]. As for WPC_F , an instantaneous increase in SPR was observed at 200 s. This may be due to the release of the bottom substances due to the local collapse of the residuals (Fig. 8c). The SPR and TSP of WPC_{SF} were lower than those of WPC_{CTRL} , although cracking occurred in the WPC_{SF} residuals (Fig. 8d). The shielding effect of the glassy sodium borate on the bottom substances and the release of H_2O , NH_3 , and CO_2 during combustion reduced the combustion power, which decreased the smoke release of WPC_{SF} .

The combustion reactions are shown in Fig. 11. The silanol groups on the $nSiO_2$ surface acted as active catalytic sites for Brønsted acids that catalyzed the carbonization of WF in WPC_S and WPC_{SF} by removing H

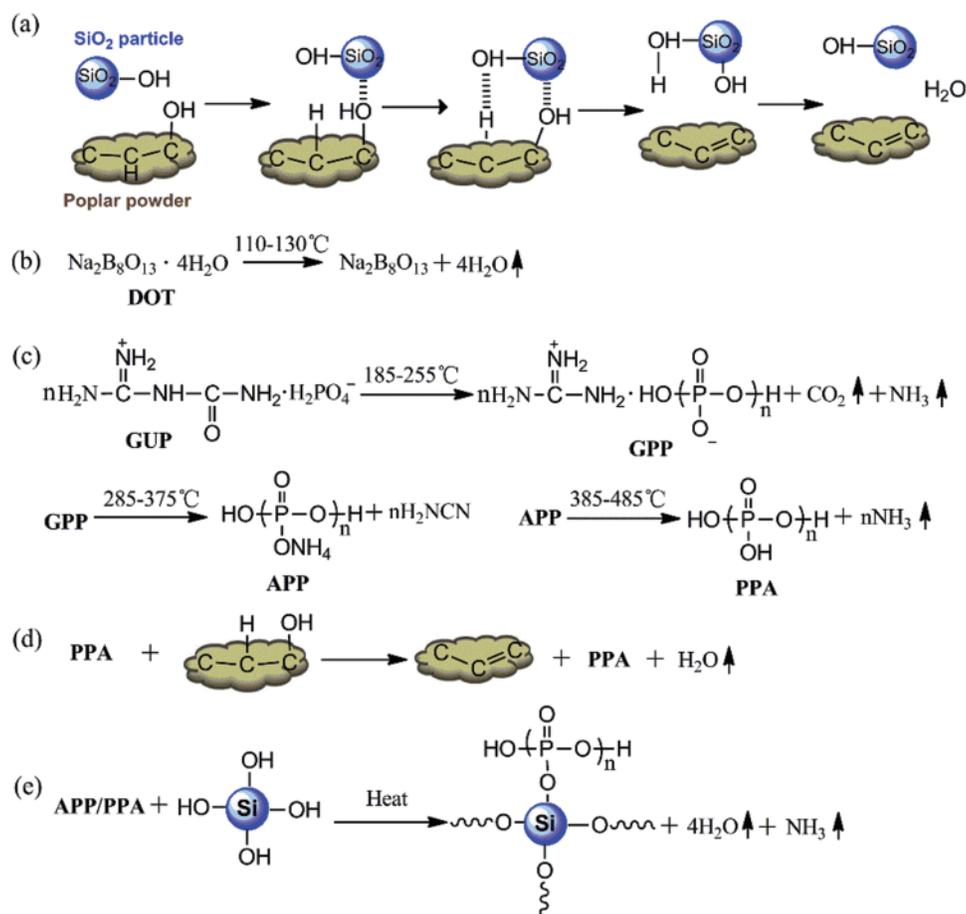


Figure 11: Possible reactions during combustion

and O (Fig. 11a). The formation of a carbonized layer protected the substrate from fire and heat, which decreased the heat release [27]. The DOT in WPC_F and WPC_{SF} decomposed into non-combustible sodium borate and water at 130°C. The sodium borate acted as a barrier, and the water could absorb heat as it evaporated, which both helped reduce the burning rate [28] (Fig. 11b). The GUP decomposed into CO₂, NH₃, and condensed guanidine phosphate (GPP) at temperatures higher than 185°C. The produced GPP further decomposed into ammonium polyphosphate (APP) above 285°C, and the APP decomposed into polyphosphate acid (PPA) and NH₃ above 380°C [29]. The APP and PPA then catalyzed the carbonization of WF by removing H and O [30] (Figs. 11c and 11d), and the formation of a stable carbon layer played a shielding effect to isolate the heat and O₂. The APP or PPA generated during combustion reacted with the nSiO₂ in WPC_{SF} to produce pyrophosphate silicon, H₂O, and NH₃, which could absorb heat and dilute O₂ (Fig. 11e) [13].

The mass retention of WPC_S was similar to that of WPC_{CTRL} (7.2%) after burning for 400 s due to the extremely low nSiO₂ loading in WPC_S (Fig. 12). The mass retention of WPC_F and WPC_{SF} was obviously higher than that of WPC_{CTRL} due to the formation of stable carbon layers. The mass-loss rates (the slope of the curve) of WPC_S, WPC_F, and WPC_{SF} were lower than WPC_{CTRL}, which indicated that the introduction of an nSiO₂ network and fire retardant reduced the burning rate of WPC.

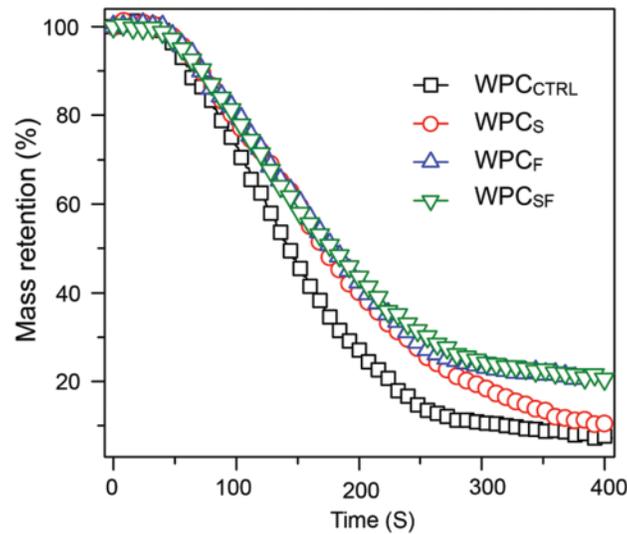


Figure 12: The mass retention of the WPC during combustion. (The abbreviations in the figure are the same with Tab. 1)

4 Conclusions

In this study, a facile approach was used to fabricate WPC with a continuous honeycomb-like nano-SiO₂ network (WPC_S). The rigid nano-SiO₂ network improved the strength and dimensional stability of WPCs at a considerably low nano-SiO₂ content (0.55 wt.%) compared with WPC_{CTRL}. When the WF was modified with fire retardants (DOT and GUP), the flexural modulus and creep resistance of the network-structured WPC (WPC_{SF}) also increased compared with WPC_{CTRL}. WPC_{SF} showed the lowest thermal expansion rate and LCTE, and its flexural strength only decreased by 5.5% compared with that of WPC_{CTRL}. Additionally, WPC_{SF} showed an improved fire retardancy compared with WPC_{CTRL}. The results presented here demonstrated that an efficient and facile procedure could be used to produce WPC with desired functions through the formation of continuous honeycomb-like nanoparticle networks.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

References

1. Hao, X., Yi, X., Sun, L., Tu, D., Wang, Q. et al. (2019). Mechanical properties, creep resistance, and dimensional stability of core/shell structured wood flour/polyethylene composites with highly filled core layer. *Construction and Building Materials*, 226, 879–887. DOI 10.1016/j.conbuildmat.2019.07.329.
2. Meenakshi, C. M., Krishnamoorthy, A. (2019). Study on the effect of surface modification on the mechanical and thermal behaviour of flax, sisal and glass fiber-reinforced epoxy hybrid composites. *Journal of Renewable Materials*, 7(2), 153–169. DOI 10.32604/jrm.2019.00046.

3. Tazi, M., Erchiqui, F., Godard, F., Kaddami, H. (2014). Evaluation of mechanical properties and durability performance of HDPE-wood composites. *Journal of Renewable Materials*, 2(4), 258–263. DOI 10.7569/JRM.2014.634120.
4. Zhou, H., Xiao, Z., Wang, Y., Hao, X., Xie, Y. et al. (2020). Conductive and fire-retardant wood/polyethylene composites based on a continuous honeycomb-like nanoscale carbon black network. *Construction and Building Materials*, 233, 117369–117377. DOI 10.1016/j.conbuildmat.2019.117369.
5. Guan, Y. H., Huang, J. Q., Yang, J. C., Shao, Z. B., Wang, Y. Z. (2015). An effective way to fire-retard biocomposite with ethanolamine modified ammonium polyphosphate and its fire retardant mechanisms. *Industrial & Engineering Chemistry Research*, 54(13), 3524–3531. DOI 10.1021/acs.iecr.5b00123.
6. Hao, X., Zhou, H., Wang, Q., Wang, H., Song, Y. et al. (2018). Reinforcement of wood flour/HDPE composite with a copolyester of p-hydroxy benzoic acid and 2-hydroxy-6-naphthoic acid. *Journal of Applied Polymer Science*, 47338(15), 1–8. DOI 10.1002/app.47338.
7. Subrahmanian, V., Albert, N. E. M. (2019). Studies on physical chemistry of rubber-rice husk ash composites. *Journal of Renewable Materials*, 7(2), 171–192. DOI 10.32604/jrm.2019.00090.
8. Gao, H., Xie, Y., Ou, R., Wang, Q. (2012). Grafting effects of polypropylene/polyethylene blends with maleic anhydride on the properties of the resulting wood-plastic composites. *Composites Part A: Applied Science and Manufacturing*, 43(1), 150–157. DOI 10.1016/j.compositesa.2011.10.001.
9. Lee, S. Y., Yang, H. S., Kim, H. J., Jeong, C. S., Lim, B. S. et al. (2004). Creep behavior and manufacturing parameters of wood flour filled polypropylene composites. *Composite Structures*, 65(3–4), 459–469. DOI 10.1016/j.compstruct.2003.12.007.
10. Yadav, S. M., Yusoh, K. B. (2018). Subsurface mechanical properties and subsurface creep behaviour of modified nanoclay-based wood-plastic composites studied by nanoindentation. *Polymer Bulletin*, 76(5), 2179–2196. DOI 10.1007/s00289-018-2497-5.
11. Liu, R., Luo, S., Cao, J., Peng, Y. (2013). Characterization of organo-montmorillonite (OMMT) modified wood flour and properties of its composites with poly(lactic acid). *Composites Part A: Applied Science and Manufacturing*, 51, 33–42. DOI 10.1016/j.compositesa.2013.03.019.
12. Siengchin, S., Dangtungee, R. (2014). Polyethylene and polypropylene hybrid composites based on nano silicon dioxide and different flax structures. *Journal of Thermoplastic Composite Materials*, 27(10), 1428–1447. DOI 10.1177/0892705714526916.
13. Pan, M., Mei, C., Du, J., Li, G. (2014). Synergistic effect of nano silicon dioxide and ammonium polyphosphate on flame retardancy of wood fiber-polyethylene composites. *Composites Part A: Applied Science and Manufacturing*, 66, 128–134. DOI 10.1016/j.compositesa.2014.07.016.
14. Zhou, H., Hao, X., Wang, H., Wang, X. Y., Liu, T. et al. (2018). The reinforcement efficacy of nano- and microscale silica for extruded wood flour/HDPE composites: the effects of dispersion patterns and interfacial modification. *Journal of Materials Science*, 53(3), 1899–1910. DOI 10.1007/s10853-017-1650-0.
15. Pan, M. Z., Lian, H. L., Mei, C. T. (2012). Flammability of nano silicon dioxide-wood fiber-polyethylene composites. *Journal of Composite Materials*, 47(12), 1471–1478. DOI 10.1177/0021998312448499.
16. Jiang, L., Wolcott, M. P., Zhang, J., Englund, K. (2007). Flexural Properties of surface reinforced wood/plastic deck board. *Polymer Engineering & Science*, 47(3), 281–288. DOI 10.1002/pen.20705.
17. Potts, J. R., Shankar, O., Du, L., Ruoff, R. S. (2012). Processing-morphology-property relationships and composite theory analysis of reduced graphene oxide/natural rubber nanocomposites. *Macromolecules*, 45(15), 6045–6055. DOI 10.1021/ma300706k.
18. Donmez, C. A., Mengeloğlu, F., Karakus, K. (2015). Effect of boric acid and borax on mechanical, fire and thermal properties of wood flour filled high density polyethylene composites. *Measurement*, 60, 6–12. DOI 10.1016/j.measurement.2014.09.078.
19. Baysal, E., Yalinkilic, M. K., Altinok, M., Sonmez, A., Peker, H. et al. (2007). Some physical, biological, mechanical, and fire properties of wood polymer composite (WPC) pretreated with boric acid and borax mixture. *Construction and Building Materials*, 21(9), 1879–1885. DOI 10.1016/j.conbuildmat.2006.05.026.

20. Ayrlimis, N., Akbulut, T., Dundar, T., Mengelolu, F., Buyuksari, U. et al. (2012). Effect of boron and phosphate compounds on physical, mechanical, and fire properties of wood-polypropylene composites. *Construction and Building Materials*, 33, 63–69. DOI 10.1016/j.conbuildmat.2012.01.013.
21. Suzuki, N., Kiba, S., Yamauchi, Y. (2011). Bimodal filler system consisting of mesoporous silica particles and silica nanoparticles toward efficient suppression of thermal expansion in silica/epoxy composites. *Journal of Materials Chemistry*, 21(38), 14941–14947. DOI 10.1039/c1jm12405f.
22. Rao, Y. Q., Blanton, T. N. (2008). Polymer nanocomposites with a low thermal expansion coefficient. *Macromolecules*, 41(3), 935–941. DOI 10.1021/ma7020216.
23. Kashiwagi, T., Gilman, J. W., Butler, K. M., Harris, R. H., Asano, A. (2000). Fire retardant mechanism of silica gel/silica. *Fire & Materials*, 24, 277–289. DOI 10.1002/1099-1018(200011/12)24:63.O.CO;2-A.
24. Zhao, Q., Zhang, B., Quan, H., Yam, R. C. M., Yuen, R. K. K. et al. (2009). Fire retardancy of rice husk-filled high-density polyethylene ecocomposites. *Composites Science and Technology*, 69(15–16), 2675–2681. DOI 10.1016/j.compscitech.2009.08.009.
25. Winandy, J. E., Wang, Q., White, R. H. (2008). Fire-retardant-treated strandboard: properties and fire performance. *Wood and Fiber Science*, 40(1), 62–71. DOI 10.1177/0040517507082635.
26. Wu, G. F., Xu, M. (2014). Effects of boron compounds on the mechanical and fire properties of wood-chitosan and high-density polyethylene composites. *BioResources*, 9, 4173–4193.
27. Tsutsumi, K., Kurata, N., Takata, E., Furuichi, K., Nagano, M. et al. (2014). Silicon semiconductor-assisted Brønsted acid-catalyzed dehydration: highly selective synthesis of 5-hydroxymethylfurfural from fructose under visible light irradiation. *Applied Catalysis B: Environmental*, 147, 1009–1014. DOI 10.1016/j.apcatb.2013.10.032.
28. Wang, Q., Li, J., Winandy, J. (2004). Chemical mechanism of fire retardance of boric acid on wood. *Wood Science and Technology*, 38(5), 375–389. DOI 10.1007/s00226-004-0246-4.
29. Li, B., Zhang, X., Su, R. (2002). An investigation of thermal degradation and charring of larch lignin in the condensed phase: the effects of boric acid, guanyl urea phosphate, ammonium dihydrogen phosphate and ammonium polyphosphate. *Polymer Degradation and Stability*, 75(1), 35–44. DOI 10.1016/S0141-3910(01)00202-6.
30. Samyn, F., Bourbigot, S., Duquesne, S., Delobel, R. (2007). Effect of zinc borate on the thermal degradation of ammonium polyphosphate. *Thermochimica Acta*, 456(2), 134–144. DOI 10.1016/j.tca.2007.02.006.