The Preparation of $CaCO_3$/Wood Composites Using a Chemical Precipitation Method and its Flame-Retardant and Mechanically Beneficial Properties

Lili Huang,[a] Xiaolin Yao,[b,d,]* Yongtong Huang,[d] and Qingsong Wang [c,]*

With the use of *Paulownia* wood as a substrate and a vacuum impregnation method, $CaCO_3$/wood composites were prepared. The XRD results showed that a variety of types of calcium carbonates coexisted in the composite and the elevated temperature was favorable for the aragonite type. The SEM results showed the modified wood retained the original wood structure and that $CaCO_3$ was uniformly distributed in the wood cell cavity and clung to the wood cells. The mechanical testing results showed that the mechanical properties of all the composites were obviously improved; the maximum value of strength of compression (SC) and modulus of elasticity (MOE) of the $CaCO_3$/wood composites were 32.23 MPa and 0.92 GPa, respectively, values 44.2% and 53.3% higher than those of the original wood. The maximum value of proportional limit (PL) of the composites was 29.4 MPa (38.5% increase from original wood). A cone calorimeter was used to investigate the flame retardation properties of $CaCO_3$ on the composites. The value of the heat release rate and total heat release of composites were lower than those of the original wood; the $CaCO_3$ wood composites showed good flame retarding effects.

Keywords: Wood composites; Calcium carbonate; Chemical precipitation method; Mechanical performance; Flame retardant

*Contact information: a: School of Engineering, Anhui Agricultural University, Hefei, 230036, P.R. China; b: School of Science, Anhui Agricultural University, Hefei, 230036, P.R. China; c: State Key Laboratory for Fire Science, University of Science and Technology of China, Hefei, 230026, P.R. China; d: Anhui Key Laboratory for Science and Technology of Wood, Anhui Agricultural University, Hefei, 230036, P.R. China; *Corresponding authors: yaoxiaolin@ahau.edu.cn; pinew@ustc.edu.cn*

INTRODUCTION

Woods from natural forests usually have good properties in terms of their strength and durability. However, those trees grow slowly, and their harvesting disrupts the sustainability of this high-quality wood supply. However, the gap between wood supply and demand is increasing rapidly. Fast-growing wood is a good alternative to meet the large demand for wood resources, but its inferior quality (lower density, poor mechanical properties, *etc.*) limits its applications (Kojima *et al.* 2009). Specific modifications are needed to tailor the inherent physical properties of low quality, fast growing wood (Gaff *et al.* 2015). Chemical modification is an effective approach for improving the inherent properties of polymers (Worgull *et al.* 2013). There are abundant mesopores and macropores inside the wood. Also there are active groups, such as OH groups, that associate with inorganic particles and thereby offer opportunities for modification (Merk *et al.* 2015; Fu *et al.* 2017). Eco-friendly inorganic materials can enhance the mechanical properties without compromising the beneficial properties (Devi and Maji 2013).

Wood is a macromolecular polymeric material consisting of flammable cellulose, hemicellulose, and lignin, which makes it a safety hazard (Rowell and Dietenberger 2012; Lowden and Hull 2013). The associated health and environmental concerns limit its wide utilization for residential and non-residential buildings (Fu *et al.* 2010; Ren *et al.* 2015). Therefore, flame-retardant and smoke-suppressant wood products have attracted great public attention (Marney and Russell 2008; Stark *et al.* 2010; Sharma *et al.* 2013). The development of wood modification methods that increase the flame retardance and smoke suppression performance of wood without compromising its physical properties is urgently needed (Deka and Maji 2011). In addition to their flame retarding effects, inorganic flame retardants inhibit the generation of smoke and hydrogen halide and have thus been widely used for the preparation of non-toxic and non-corrosive composite materials (Liodakis *et al.* 2010; Liodakis *et al.* 2013). Additionally, rigid inorganic materials are promising reinforcing materials for polymers (Beyer 2002); the addition of inorganic materials without changing the nature of the original wood can improve the flame retardance, smoke suppression, and mechanical properties of composites (Qu *et al.* 2005; Jiang *et al.* 2015). $CaCO_3$ is a non-toxic, environmentally friendly, and economical compound that has good compatibility with polymer substrates and endows the substrate with many excellent properties; it has been widely used in plastics and rubber packing (Gutman *et al.* 1995; Gao *et al.* 2009).

Paulownia trees, which are widely distributed in most provinces of China, could be used as short rotation woody energy crops due to its high heat value of almost 18 MJ/kg (Hidayat *et al.* 2017). The modification of *Paulownia* wood heat treatment was found to increase the weight loss and volume shrinkage, but decrease the modulus of rupture and modulus of elasticity (Chen *et al.* 2017).

In this study, *Paulownia* wood was used as the substrate to prepare $CaCO_3$/wood composites. A precursor solution was infused into the wood through vacuum impregnation, with the goal of achieving chemical precipitation, which generates $CaCO_3$ inside the wood *in situ* to develop a new wood composite. The structure and morphology of the composites were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mechanical properties of the composites were tested using a universal mechanical testing machine. Cone calorimetry was used to investigate the flame retardation properties of $CaCO_3$ on the composites.

EXPERIMENTAL

Materials

All chemicals were of analytical grade and used as received without further purification. All experiments were conducted under air atmosphere. $CaCl_2$ was purchased from the Guangdong Xilong chemical plant (Guangdong, China). Na_2CO_3 was purchased from Tianjin Bodi chemical plant (Tianjin, China). Paulownia wood was purchased from Longxi wood plant in Anqing, Anhui, China. Wood specimens were peeled and sawed until 50 mm thick, dried in a ventilated place for 1 month, then machined to the size of 20 mm (radial) by 20 mm (T) by 30 mm (R) for mechanical tests and 100 mm (L) by 100 mm (T) by 10 mm (R) for Cone tests.

Preparation of $CaCO_3$/Wood Composites

Wood specimens were immersed in $CaCl_2$ solutions (concentration: 0.4, 0.8, 1.2, 1.6, and 2.0 M) for 2 h. The concentration of the precursor solution was used to control the $CaCO_3$ content in the wood. The pressure of the solutions were kept at 0.0 to 0.1 atm using a circulating water multi-purpose vacuum pump (SHB-B95, Zhengzhou Changcheng), and kept at atmospheric pressure for 6 h.

The wood specimens were removed and dried at 70 °C for 12 h in a vacuum drying oven (DZF-6020, Shanghai Jinghong). Repeating the above steps, under vacuum pressure, Na_2CO_3 solutions (the ratio of $CaCl_2$ and Na_2CO_3 concentration was 1:1) were impregnated into the wood specimens at 30, 60, and 90 °C for 3 h and then kept at 70 °C for 12 h under atmospheric pressure and, finally, dried in a vacuum oven for 48 h. The mode of action of $CaCO_3$ is described in Eq. 1.

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 \downarrow + 2\ NaCl \qquad (1)$$

Characterization of the Wood Composites

X-ray diffraction

The modified wood specimens were cooled with liquid nitrogen and ground into powder in an agate mortar, then sieved through 180 mesh filters. X-ray powder diffraction (XD-3, Puxi, Beijing, China) was performed with a scan rate of 1 °/min ranging from 10° to 80° (Cu target, tube voltage: 36 kV, tube current: 20 mA, rated power: 1.5 kW, λ = 0.15406 nm).

Particle size and morphology

Wood slice samples of 20 μm were cut through the transverse, square, and tangential sections of the wood composites, using a wheeled slicing machine. The morphology of $CaCO_3$ crystals in the composites were observed using a scanning electron microscope (Sirion 200, EFI, Holland) under an accelerating voltage of 10 kV and a working distance of 15 mm.

Mechanical Test

Sand paper was used to smooth the wood surfaces. The test specimens were put on the center of the spherical activities support of the universal mechanical testing machine (BTF-266, Bitefu, Changchun, China), pressed uniformly, and damaged in 2 min to test for the strength of compression (SC), modulus of elasticity (MOE), and proportional limit (PL) of the composites.

Cone Calorimeter Test

The combustion performance parameters of the composites were measured with a cone calorimeter (FTT, UK). The experiments of cone calorimeter were based on ISO 5660 standard. The thermal radiation power was 50 $kW\cdot m^{-2}$ and the corresponding temperature was 780 °C. The heat release rate (HRR), peak heat release rate (pk-HRR) and total heat release (THR) were measured to investigate the effects of $CaCO_3$ on the combustion behavior of the wood composites.

RESULTS AND DISCUSSION

Weight Gain Rate of $CaCO_3$/Wood Composites

Figure 1 is the diagram of the weight gain rate of the $CaCO_3$ wood composites under different $CaCl_2$ concentrations and different preparation temperatures. The weight gain rate of the composites increased with increasing precursor concentrations at different temperatures, but the pattern of increase was nonlinear. With the precursor concentration increasing, more solution infiltrated the wood to yield more $CaCO_3$. When the $CaCl_2$ concentration was 0.4 M at 30, 60, and 90 °C, the corresponding average value of weight gain rates were 4.36%, 15.5%, and 17.7%, respectively. When the $CaCl_2$ concentration increased, the weight gain rates of composites increased remarkably, but in the order of 60, 90, and 30 °C. The impregnation effect of the precursor solutions into the wood was the best when the precursor concentration was between 0.8 M and 1.2 M. When the temperature was 90 °C, more $CaCO_3$ was attached to the surface of the wood. This blocked the wood pore accessibility, which hampered Na_2CO_3 movement into the wood interior and reduced the generation of calcium carbonate, resulting in a lower calcium carbonate content in wood composites.

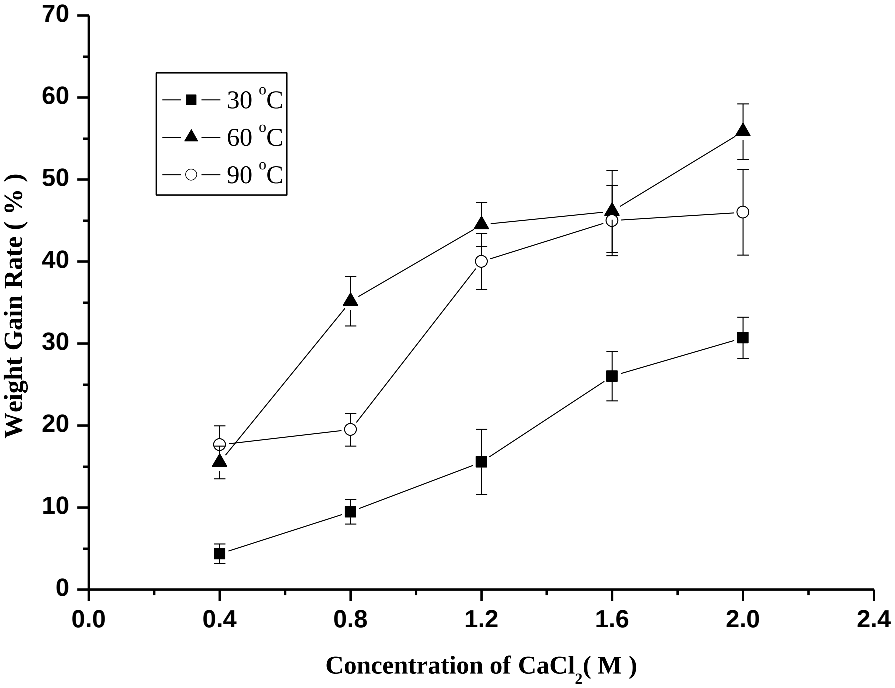

Fig. 1. Diagram of the weight gain rate of the $CaCO_3$ wood composites under different $CaCl_2$ concentrations and preparation temperature (30, 60, and 90 °C)

Figure 2 shows XRD images of $CaCO_3$/wood composite materials prepared with different $CaCl_2$ concentrations and different temperatures. Figure 2(a) shows composites prepared with solutions of $CaCl_2$ with concentrations: 0.4, 1.2, and 2.0 M at 30 °C. Figure 2(b) shows composites prepared at different temperatures (30, 60, and 90 °C) and a $CaCl_2$ concentration of 2.0 M. When 2θ was 16.5° and 22.5°, there were characteristic diffraction peaks of the wood cellulose.

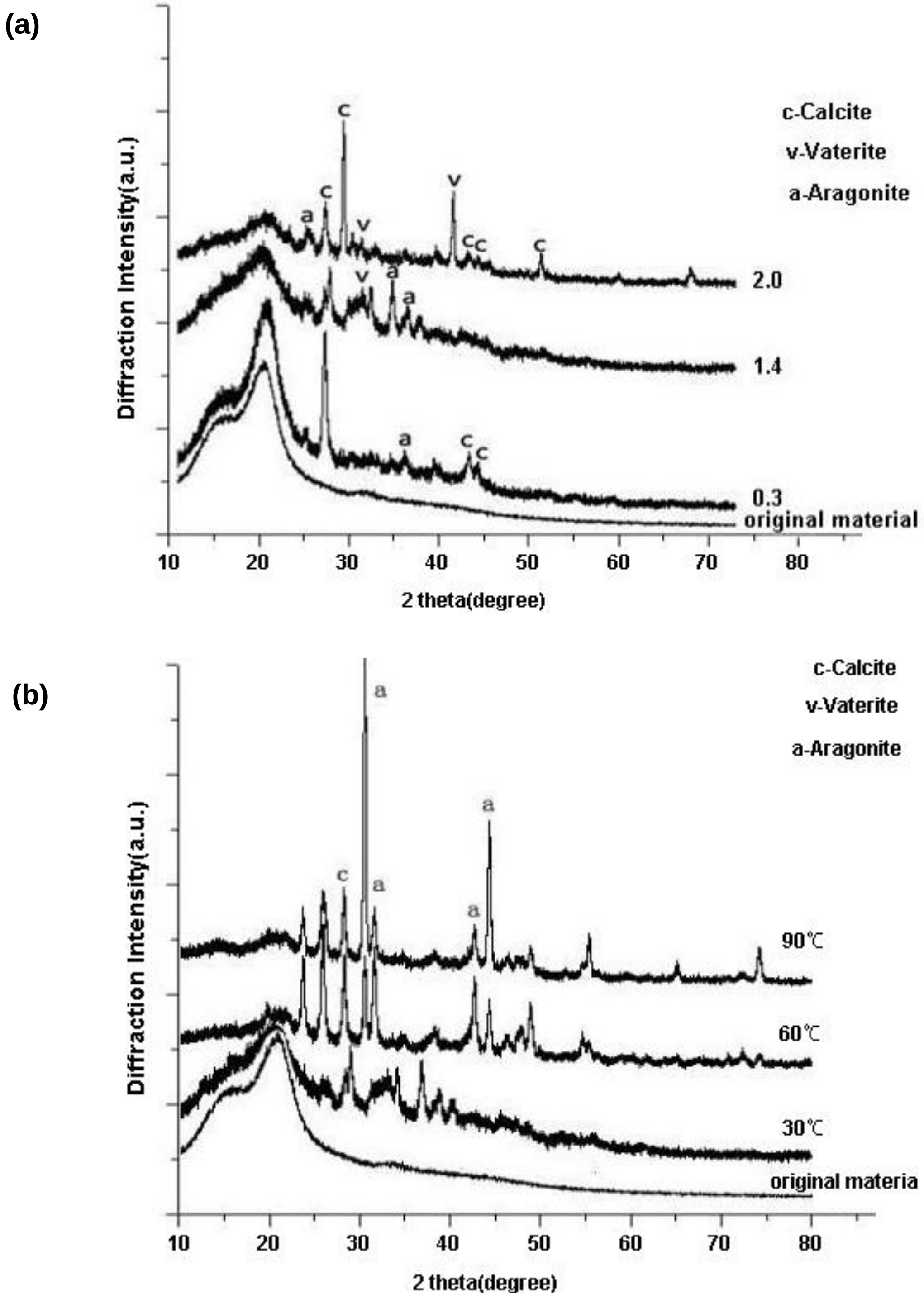

Fig. 2. Diagrams showing XRD results of $CaCO_3$/ wood composites: (a) at different $CaCl_2$ concentrations (0.4, 1.2, and 2.0 M at 30 °C) and (b) at different temperatures (2.0 M at 30, 60, and 90°C)

There were obvious characteristic diffraction peaks of calcium carbonate (2θ being 29.40°, 47.79°, and 48.50° for calcite and 26.21 and 37.27 for aragonite) (Wu *et al.* 2018; Yaseen *et al.* 2018). Thus, there were a variety of crystal types, such as calcite, aragonite, and vaterite, which coexisted in the composite.

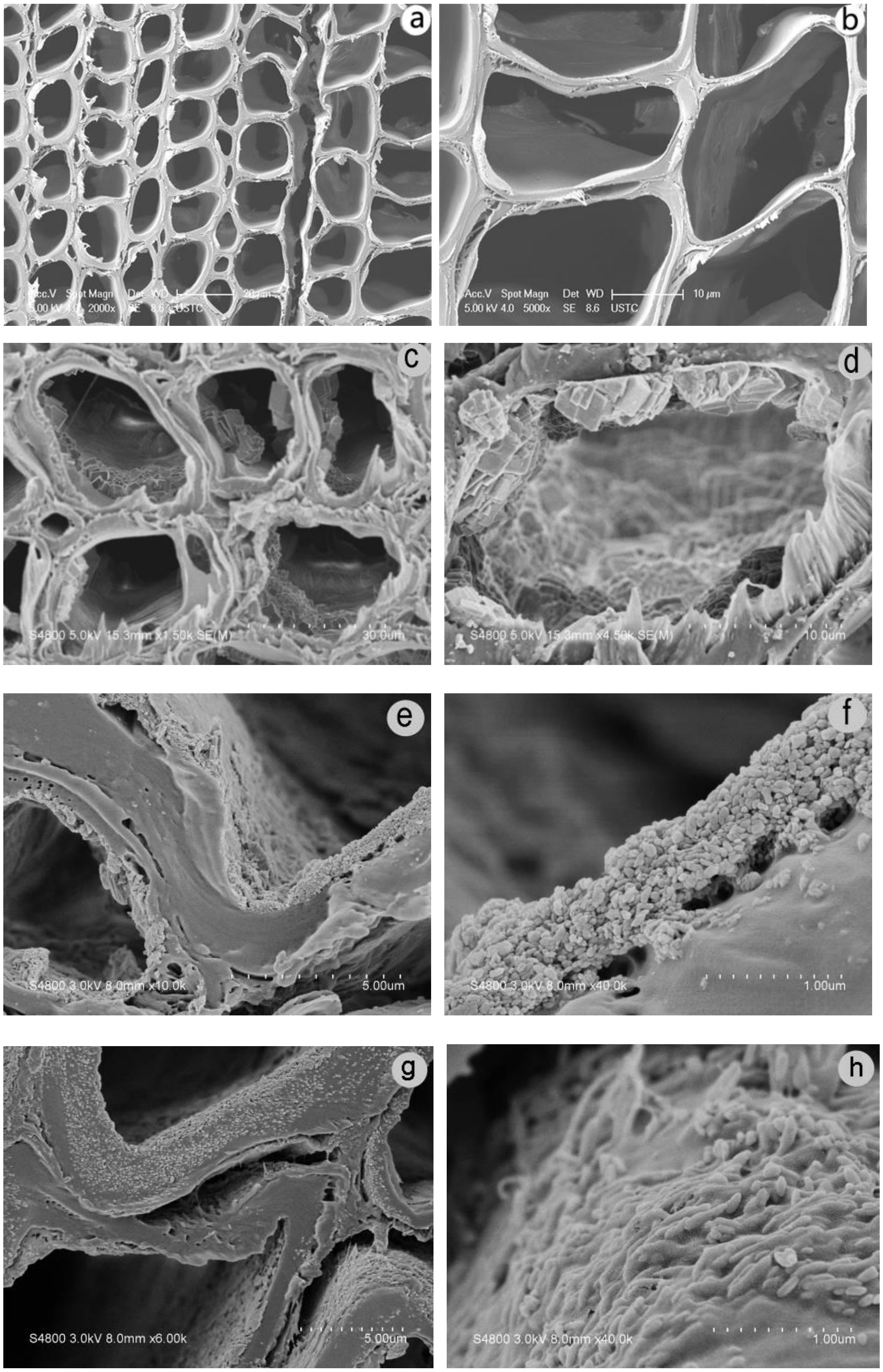

Fig. 3. Scanning electron microscope images of transverse sections of $CaCO_3$/wood composite at different preparation temperature. (a, b) original material, (c, d) composite at 30 °C, (e, f) composite at 60 °C, and (g, h) composite at 90 °C

With increases of the $CaCO_3$ content in composites, the characteristic peaks of the cellulose were weakened gradually due to the high precursor concentration reducing the crystallinity of cellulose. As shown in Fig. 2a, with the increase of $CaCl_2$ concentration, crystal types of calcium carbonate did not change obviously; they remained primarily calcite. Additionally, calcite content was high at low $CaCl_2$ concentrations. As the concentration of $CaCl_2$ was increased, the characteristics of the diffraction peaks intensity of calcium carbonate increased, especially for aragonite types. As shown in Fig. 2b, increasing the preparation temperature caused the crystal forms of calcium carbonate to change. At 30 °C, the calcium carbonate in composites was mainly composed of the calcite crystal shape. When the temperature rose, aragonite calcium carbonate content gradually increased; higher temperatures were beneficial to the formation of aragonite type of calcium carbonate. Calcite is the thermodynamically stable phase of $CaCO_3$ among of the polymorphs.

Figure 3 shows the SEM images of the transverse section of original wood and $CaCO_3$/wood composites prepared at 30, 60, and 90 °C. Figures 3a and 3b are SEM images of original wood, which show there were ample spaces in the wood fibers on the cell wall of the wood to hold particles of calcium carbonate. Figures 3c and 3d are SEM images of composites prepared at 30 °C. Calcium carbonate particles were distributed uniformly in the wooden fiber cell, were 1 to 2 μm in size, and were mainly rhombohedral shaped. $CaCO_3$ adhered to the cell wall tightly and were present in wood cell inner cavities and intercellular space. The flame retardant was distributed evenly through the entire cell wall, and numerous, minute granules were attached to the inner cell wall. The penetration of flame retardant into the cell walls could improve the dimensional stability of wood and flame retardancy.

When the temperature increased to 60 °C (Fig. 3e and 3f), granular shaped $CaCO_3$ particles, 100 nm in size, were found dispersed on the surface of the lumen of the wood fibers and closely arranged together. Interestingly, at a preparation temperature of 90 °C (Fig. 3g and 3h), calcium carbonate particles with a column-like morphology, 100 nm in diameter and 200 to 500 nm in length, appeared on the surface of the cell wall and some of them were embedded into the interior of the cell wall. As is known, the column is a typical shape of aragonite.

Mechanical Properties

Mechanical properties (SC, MOE, and PL) of $CaCO_3$/wood composite materials prepared at different precursor solution concentrations (0.4, 0.8, 1.2, 1.6, and 2.0 M) and different temperature (30, 60, and 90 °C) are listed in Table 1. The SC, MOE, and PL of the original wood were 22.4 MPa, 0.60 GPa, and 21.2 MPa, respectively.

As shown in Table 1, the values of SC, MOE, and PL of all $CaCO_3$ composites were higher than those for the original wood. The SC and PL values of the composites prepared at 30 °C increased obviously with the increase of precursor concentrations. When $CaCl_2$ concentration was 2.0 M, the SC and PL values of the composites were 31.1 MPa and 27.7 MPa, respectively. When the preparation temperature was 60 °C and 90 °C, the values of SC and PL at low precursor concentrations (0.4, 0.8, 1.2 M) were higher than the values obtained at high precursor concentrations (1.6, 2.0 M). Furthermore, the values of MOE of the composites at 30 °C and 90 °C preparation temperatures were higher than the values at a 60 °C preparation temperature. The maximum values of SC and MOE of the $CaCO_3$/wood composites were 32.2 MPa and 0.92 GPa, respectively, when the $CaCl_2$ concentration was 0.8 M at 90 °C and 30 °C. Compared with the original wood, these were increases of 44.2% and 53.3%. The maximum value of PL of the composites was 29.41 MPa when precursor concentration was 1.2 M at 90 °C, an increase of 38.5% as compared with the original wood.

Table 1. Mechanical Performance of $CaCO_3$ / Wood Composites

	30 °C			60 °C			90 °C		
$CaCl_2$ (M)	SC (MPa)	MOE (GPa)	PL (MPa)	SC (MPa)	MOE (GPa)	PL (MPa)	SC (MPa)	MOE (GPa)	PL (MPa)
0.4	25.89	0.81	21.76	27.18	0.79	22.67	29.86	0.85	27.51
0.8	26.22 ±1.42	0.90 ±0.02	21.97 ±2.34	29.05	0.67	24.35	31.05 ±1.18	0.65	27.02 ±2.01
1.2	28.71	0.87	24.52	31.84	0.65	24.79	29.73 ±1.68	0.89	27.29 ±2.12
1.6	30.29	0.88	26.18	25.71	0.77	23.84	29.16	0.81	26.17
2.0	31.12	0.91	27.73	23.41	0.73	22.57	26.87	0.79	23.25

Cone Calorimetric Analysis

The combustion phenomena of the original wood and wood composites were obviously different. The combustion process of the unmodified wood was intense, with a large flame and a large amount of black smoke generated. A layer of carbon was formed when the composites began to burn and remained until the combustion ended. Only a small flame occurred on the surface of the composites, and it burned slowly; only white smoke appeared. The $CaCO_3$ inside the wood did not take part in the reactions but changed the kinetics of the reactions that took place during the thermal degradation of wood. The formation of a char layer on the surface of the wood was observed during the combustion. Figure 4a is the picture of original wood after combustion and Fig. 4b is that of the $CaCO_3$/wood composite. The original wood was easy to combust and it can be seen from Fig. 4a the combustion residue was grey. This showed that organic substance in original wood combusted completely and the gray ash left was the product of incombustible inorganic substances.

Figure 4b shows that the combustion residue of composites was black. When the modified wood burnt, the combustion of organic substance was suppressed by $CaCO_3$, and the combustion was not complete with a layer of carbon left.

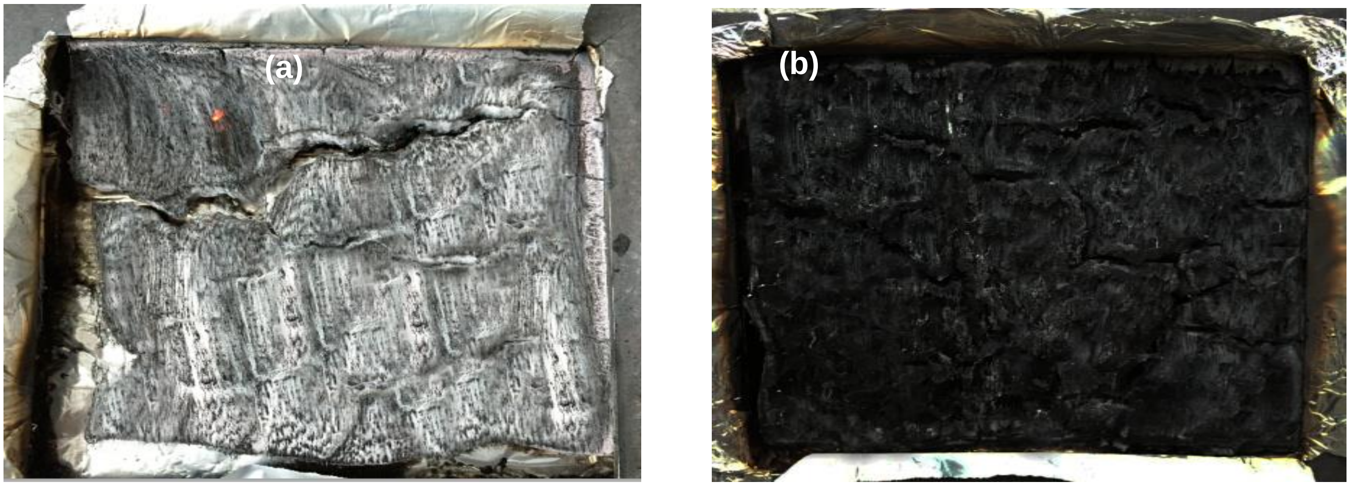

Fig. 4. Pictures of the combustion residues of original wood (a) and $CaCO_3$/wood composite (b)

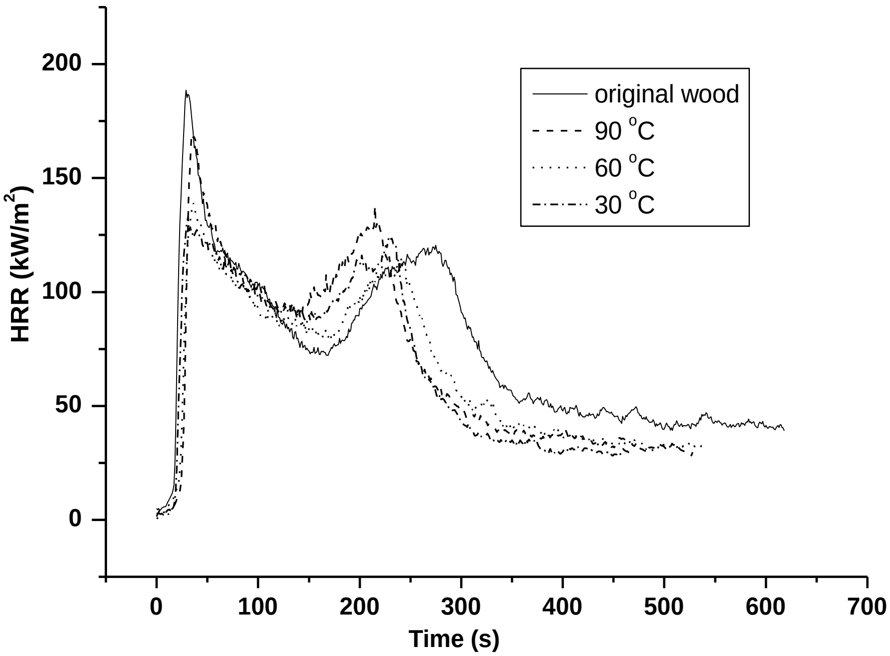

Fig. 5. HRR curves of original wood and $CaCO_3$/wood composites at different temperatures

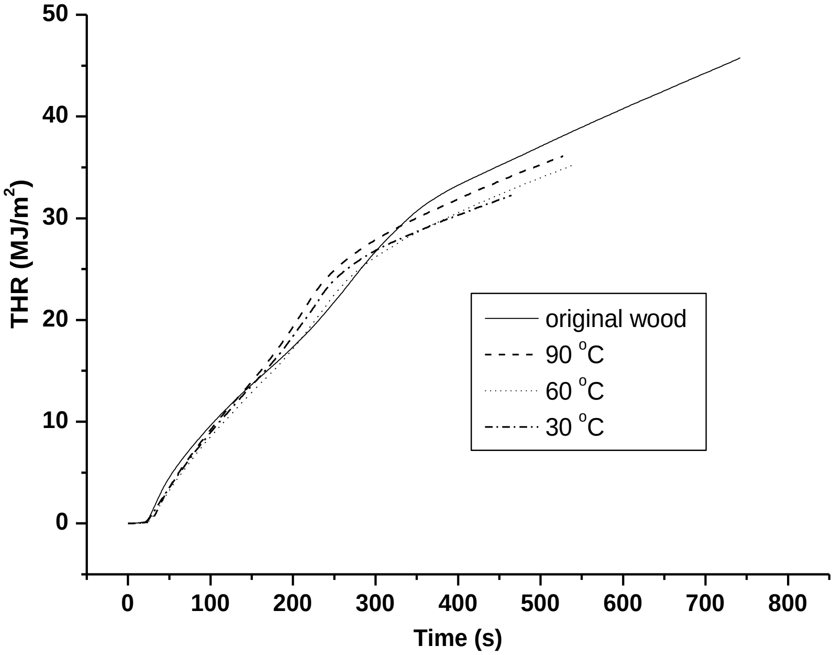

Fig. 6. THR curves of original wood and $CaCO_3$/wood composites at different temperatures.

Table 2. Cone Calorimeter Results for Original Wood and Composites

sample	mean HRR (kW/m2)	first pk-HRR (kW/m2)	second pk-HRR (kW/m2)	THR (MJ/m2)
Original wood	74	189	121	45
30 °C, 2.0M	70	133	124	32
60 °C, 2.0M	66	139	115	35
90 °C, 2.0M	69	168	138	36

Heat release rate (HRR) and total heat release (THR) are important parameters that reflect the heat release during wood combustion and play important roles in determining fire disasters. The characteristic curves of HRR and THR of original wood and wood composites prepared at different temperatures versus time are shown in Figs. 5 and 6 (at 30, 60, and 90 °C and a $CaCl_2$ concentration of 2.0 M).

According to Fig. 5, there were two exothermic peaks in the combustion process of the original wood and composites. The first maximum peak represents the typical combustion characteristic of wood and the second peak corresponds to the charcoal burning. The mean HRR, first pk-HRR, second pk-HRR and THR of original wood and composites are described in Table 2. The mean HRR of the original wood was 74 $kW{\cdot}m^{-2}$ for the samples prepared at 30, 60, and 90 °C; the mean HRRs were 70, 66, and 69 $kW{\cdot}m^{-2}$. The first pk-HRR of the original wood was 189 $kW{\cdot}m^{-2}$ and this appeared at 29 s. The second pk-HRR was 121 $kW{\cdot}m^{-2}$ at 275 s. For the sample prepared at 30, 60, and 90 °C, the first pk-HRR was 133, 139, and 168 $kW{\cdot}m^{-2}$, compared with the original wood. These results represent decreases of 30%, 26%, and 11%, respectively, and the times of the pk-HRR were 31, 36, and 37s. For the sample at 30, 60 and 90 °C, the second pk-HRRs were 124, 115 and 138 $kW{\cdot}m^{-2}$, and the time of the second pk-HRR were 229, 241 and 215 s. The second peak of the composites appeared earlier than the original wood. The HRRs and the first pk-HRRs of the composites were lower than those of the original wood. The heat release rate of the modified wood, to some extent, decreased. Additionally, the heat release rate curves became relatively flat, especially at 60 °C, and HRR and pk-HRR fell the most.

Figure 6 shows THR (total heat release) curves of original wood and $CaCO_3$/wood composites at different temperatures *versus* time. It is apparent that the THR of the original wood was 45$MJ{\cdot}m^{-2}$. For the samples at 30, 60, and 90 °C, the THR were 32, 35, and 36 $MJ{\cdot}m^{2}$. Compared with the original wood, the decreases were 29%, 22%, and 20%, respectively. The combustion time of the original wood was 742 s, and the combustion time of the samples prepared at 30, 60, and 90 °C were 465, 542, and 528 s. Compared with the original wood, the decreases were 37%, 27%, and 29%, respectively.

According to Figs. 4, 5, 6, and Table 2, the $CaCO_3$ layer became a barrier on the heating surface and lowered the pk-HRR. The barrier decreased the diffusion of oxygen into the specimen and the flammable pyrolysis products, which ultimately decreased the fire's spread ability. The $CaCO_3$/wood composites showed good flame retardance activity.

CONCLUSIONS

1. $CaCO_3$/wood composites were successfully prepared using chemical precipitation methods *in situ*. The XRD results showed that a variety of types of calcium carbonates coexisted in the composite and that elevated temperature was favorable for the aragonite type. The SEM images showed that the structure of the modified wood remained untouched and that $CaCO_3$ was uniformly distributed in wood cell cavities and closely clung to the wood.
2. The mechanical testing results showed that the mechanical properties of all the composites were obviously improved. The maximum value of SC's and MOE's of the $CaCO_3$/wood composites were 32.2 MPa and 0.92 GPa, respectively, which represent increases of 44.2% and 53.3% as compared with the original wood. The maximum value of PL of the composites was 29.41 MPa or an increase of 38.5%.

3. Cone calorimeter tests showed that the addition of $CaCO_3$ apparently reduced the HRR and THR of wood.
4. In summary, the incorporation of flame retardant $CaCO_3$ significantly improved the mechanical properties and flame retardant performance of the fast-growing wood.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Open Fund of State Key Laboratory of Fire Science (KF2014007) and the Leading Talent Team project of Universities in Anhui Province, as well as the project of Introducing and Stabilizing Talents in Anhui Agriculture University (wd2017-1).

REFERENCES CITED

Beyer, G. (2002). “Nanocomposites: A new class of flame retardants for polymers,” *Plast. Addit. Compound.* 4(10), 22-28. DOI: 10.1016/S1464-391X(02)80151-9

Chen, L., Wang, S., Meng, H., Wu, Z., and Zhao, J. (2017). "Synergistic effect on thermal behavior and char morphology analysis during co-pyrolysis of paulownia wood blended with different plastics waste," *Appl. Therm. Eng.* 111, 834-846. DOI: 10.1016/j.applthermaleng.2016.09.155

Deka, B. K., and Maji, T. K. (2011). “Effect of TiO_2 and nanoclay on the properties of wood polymer nanocomposite,” *Compos. Part A Appl. Sci. Manuf.* 42(12), 2117-2125. DOI: 10.1016/j.compositesa.2011.09.023

Devi, R. R., and Maji, T. K. (2013). “Interfacial effect of surface modified TiO_2 and SiO_2 nanoparticles reinforcement in the properties of wood polymer clay nanocomposites,” *J. Taiwan Inst. Chem. Eng.* 44(3), 505-514. DOI: 10.1016/j.jtice.2012.11.018

Fu, Q., Medina, L., Li, Y., Carosio, F., Hajian, A., and Berglund, L. A. (2017). "Nanostructured wood hybrids for fire retardancy prepared by clay impregnation into the cell wall," *ACS Appl. Mater. Inter.* 9(41), DOI: 10.1021/acsami.7b10008

Fu, S. Y., Song, P. G., Yang, H. T., Jin, Y. M., Lu, F. Z., Ye, J. W., and Wu, Q. (2010), "Effects of carbon nanotubes and its functionalization on the thermal and flammability properties of polypropylene/wood flour composites," *J. Mater. Sci.* 45(13), 3520-3528. DOI: 10.1007/s10853-010-4394-7

Gao, Y., Liu, L., and Zhang, Z. (2009), "Mechanical performance of Nano-CaCO3 filled polystyrene composites," *Acta Mech Solida Sin.* 22(6), 555-562.

Gaff, M., Gašparíka M., Borůvkaa V., and Haviarovváb E. (2015), "Stress simulation in layered wood-based materials under mechanical loading," *Mater Des.* 87, 1065-1071. DOI: 10.1016/j.matdes.2015.08.128

Gutman, E., Bobovitch, A., Rubinchik, I., Shefter, S., Lach, S., Utevski, L., and Muskatel, M. (1995). “Thermal degradation of flame-retardant components in filled and unfilled ABS plastics,” *Polym Degrad Stabil.* 49(3), 399-402. DOI: 10.1016/0141-3910(95)00122-3

Hidayat, W., Qi, Y., Jiang, H. J., Febrianto, F., Kim, and H. N. (2017). "Effect of mechanical restraint on the properties of heat-treated *Pinus koraiensis* and *Paulownia tomentosa* woods," *BioResources.* 12(4), 7539-7551. DOI: 10.15376/biores.12.4.7539-

7551
Jiang, J., Li J., and Gao, Q. (2015), "Effect of flame retardant treatment on dimensional stability and thermal degradation of wood," *Constr Build Mater.* 75, 74-81. DOI: 10.1016/j.conbuildmat.2014.10.037

Kojima, M., Yamamoto, H., Okumura, K., Ojio, Y., Yoshida, M., Okuyama, T., Ona, T., Matsune, K., Nakamura, K., Ide, Y., Marsoem, S. N., Sahri, M. H., and Hadi Y. S. (2009). "Effect of the lateral growth rate on wood properties in fast-growing hard wood species," *J. Wood Sci.* 55(6), 417-424. DOI: 10.1007/s10086-009-1057-x

Liodakis, S., Antonopoulos, I., and Kakardakis, T. (2010). "Evaluating the use of minerals as forest fire retardants," *Fire Safety J.* 45(2), 98-105. DOI: 10.1016/j.firesaf.2009.11.002

Liodakis, S., Tsapara, V., Agiovlasitis, I. P., and Vorisis, D. (2013). "Thermal analysis of Pinus sylvestris L. wood samples treated with a new gel-mineral mixture of short- and long-term fire retardants," *Thermochimica Acta*. 568, 156-160. DOI:10.1016/j.tca.2013.06.011

Lowden, L., and Hull, T. (2013). "Flammability behaviour of wood and a review of the methods for its reduction," *Fire Sci. Rev.* 2(1), 4. DOI: 10.1186/2193-0414-2-4

Marney, D. C. O., and Russell, L. J. (2008). "Combined fire retardant and wood preservative treatments for outdoor wood applications–A review of the literature," *Fire Technol.* 44(1), 1-14. DOI: 10.1007/s10694-007-0016-6

Merk, V., Chanana, M., Keplinger, T., Gaan, S., and Burgert, I. (2015). "Hybrid wood materials with improved fire retardance by bio-inspired mineralisation on the nano-and submicron level," *Green Chem.* 17(3), 1423-1428. DOI: 10.1039/c4gc01862a

Qu, H., Wu, W., Jiao, Y., and Xu, J. (2005). "Thermal behavior and flame retardancy of flexible poly(vinyl chloride) treated with $Al(OH)_3$ and ZnO," *Polym Int.* 54(11), 1469-1473. DOI: 10.1002/pi.1870

Ren, Y., Wang, Y., Wang, L., and Liu, T. (2015). "Evaluation of intumescent fire retardants and synergistic agents for use in wood flour/recycled polypropylene composites," *Constr Build Mater.* 76, 273-278. DOI: 10.1016/j.conbuildmat.2014.12.004

Rowell, R., and Dietenberger, M. A. (2012). "Thermal properties, combustion, and fire retardancy of wood," in: *Handbook of Wood Chemistry and Wood* Composites (2nd Ed.), R. M. Rowell (ed.), CRC Press, Boca Raton, FL, USA.

Sharma, N. K., Verma, C., Chariar, V. M., and Prasad R. (2013). "Eco-friendly flame-retardant treatments for cellulosic green building materials," *Indoor Built. Environ.* 24(3), 422-432. DOI: 10.1177/1420326X13516655

Stark, N. M., White, R. H., Mueller, S. A., and Osswald, T. A. (2010). "Evaluation of various fire retardants for use in wood flour-polyethylene composites," *Polym. Degrad. Stab.* 95(9), 1903-1910. DOI: 10.1016/j.polymdegradstab.2010.04.014

Worgull, M., Schneider, M., Röhrig, M., Meier, T., Heilig, M., Kolew, A., Feit, K., Hölscher, H., and Leuthold, J. (2013). "Hot embossing and thermoforming of biodegradable three-dimensional wood structures," *RSC Adv.* 3(43), 20060-20064. DOI: 10.1039/c3ra42642d

Wu, Z. G., Wang, J., Guo, Y., and Jia, Y. R. (2018). "Exploring the influence of reaction parameters on the preparation of calcium carbonate by spontaneous precipitation," *Cryst. Res. Technol.* 53(4), 1700120. DOI: 10.1002/crat.201700120

Yaseen, S. A., Yiseen, G. A., and Li, Z. (2018). "Synthesis of calcium carbonate in alkali solution based on graphene oxide and reduced graphene oxide," *J. Solid State Chem.* 262, 127-134. DOI: 10.1016/j.jssc.2018.03.005

Article submitted: March 30, 2018; Peer review completed: May 13, 2018; Revised version received and accepted: June 29, 2018; Published: July 17, 2018.
DOI: 10.15376/biores.13.3.6694-6706