

Development of wood and wood ash-based hydroxyapatite composites and their fire-retarding properties

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Abstract For making efficient use of waste wood ash emitted from wood biomass plant, the wood and wood ash-based hydroxyapatite (HAp) composite was produced and their flammability characterization was studied by thermogravimetric (DTA-TG) analysis, oxygen index (OI) measurement and cone calorimeter test. The results show that the exothermic and weight loss peaks in DTA-TG combustion profiles due to their significant thermal decomposition were weakened by the HAp agent impregnation. In addition, the OI value of HAp composites was increased by the HAp combining and the OI showed a correlation with the HAp contents. Also, the cone calorimeter study revealed that the heat release rates were decreased with increasing amount of HAp injection and accordingly their total heat release has an inverse relationship to the HAp contents. These results indicate that the treatment with wood ash-based HAp agents can enhance the flame retardancy of the treated woods.

Keywords Hydroxyapatite · Fire-retardant wood · Wood ash · DTA-TG · Oxygen index · Cone calorimeter

Introduction

For economic and environmental concerns, wood biomass has attracted a great deal of attention as a substitute of fossil fuel in the past decades. In Japan, approximately 5 million tons of waste woods were produced annually from lumber sawing process [1] and also about 4.7 million tons of construction waste woods were produced in 2005 [2]. Among them, around 20–30 % was utilized as biomass fuel for energy production [1, 2]. Burning of this wood fuel generates a heat and/or electrical power at biomass-combustion plants, but at the same time enormous quantities of wood ash are excreted as waste byproducts. Since the ash content of wood is a few percent, the amount of ash emission is estimated to have reached several tens of thousands of tons each year in Japan. Moreover, given the future increased use of unallocated forest resources as wood biomass fuel, the wood ash emission is expected to increase more than ever.

At present, the wood ash is mostly treated as industrial waste and high disposal cost of them has pressed a management of biomass plants. The problem related to the disposal of wood ash is one of the most crucial factors that have been detrimental to the spread of woody biomass utilization; therefore, the beneficial reuses of the wood ash directly lead to the zero-emission use of wood biomass fuel. The ash recycling for practical applications contributes to the expanding of the wood biomass utilization, and until now, many developments have been carried out to produce salable products by reusing of them. Wood ash is reusable for horticultural fertilizer and raw material of

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concrete [3]. Also in recent study, new innovative attempts have been made to manufacture a composite board by combining the ash with wood particles and some adhesives [4]. In our study, the opportunity of another new use application method of the wood ash has been explored as a source of wood-inorganic mineral composites.

Wood ash, in other words the combustion residue of wood fuels, is mainly composed of inorganic components with unburned carbon. The first motivation of our study is to examine whether the wood ash could be put back into timbers again within the space of wood cells for the purpose of making the wood-inorganic mineral composites. In the previous studies, several wood-inorganic compound complexes have been developed with chemical agents to enhance the fire and decay resistances of the wood [5–8]. We, therefore, intend to produce a new composite material by combining the wood ash within woods. However, the ash does not fit in so easily with woods because it has high alkaline and hence causes striking discoloration of the combined woods. So in this study, the wood ash was preliminarily converted into hydroxyapatite (HAp; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) solution by a reaction with phosphoric acid, and then it was penetrated and fixed into woods to make the HAp-wood composites.

The HAp is well known as eco-friendly biomaterials and widely applied for industrial products, e.g., dental powder, bone-repairing or bone-replacing material. Since the HAp is water-insoluble material, it has a potential to be used as a fixative in wood preservative formulations. In the previous studies of wood-HAp combining, the HAp was used as fixatives of the antibacterial metal ions within woods [9], and it was also synthesized and fixed on the surface of modified bamboo with the phosphorylation methods [10]. Moreover, it is noteworthy that the HAp contains a phosphoric component like some kinds of fireproof agents; therefore, by combining with the HAp, the treated woods would improve their fire retardance. So in this study, the combustion behavior of the HAp-wood composites was examined using a thermogravimetric analyzer, an oxygen index flammability tester and a corn calorimeter to evaluate the effects of the wood ash-based HAp agent on the fire-retarding properties of the HAp-wood composites.

Materials and methods

HAp treating agent formulations

Wood ash used in this experiment was obtained from a wood biomass power facility (Wood energy cooperative, Miyazaki, Japan). The sampling of the ash was performed on 25 August 2007. The ash sample was fly ash mainly produced by a burning of barks and mill ends of Japanese

cedar (*Cryptomeria japonica*) at around 600 °C and it was recovered by an electrical dust collector. Their chemical and mineralogical compositions were reported in a previous study [11]. The major element compositions were carbon (36–42 wt%), calcium (29–35 wt%), potassium (11–21 wt%) and sulfur (3.8–4.5 wt%) estimated as oxidized compounds except for carbon, and the major inorganic mineral components of the ash sample were calcium compounds, such as calcium oxide (CaO), calcium carbonate (CaCO_3), calcium hydroxide ($\text{Ca}(\text{OH})_2$) and mineral dolomite ($\text{CaMg}(\text{CO}_3)_2$), as well as the non-calcareous salt, potassium chloride (KCl).

The procedures for formulating the wood ash-based HAp agent are following the report of a preceding trial [12]. Initially, 200 g of the wood ash was dissolved in 2 L of 1 M acetic acid and then the solution was filtered to gain the Ca source solution. Also, an aqueous sodium dihydrogen phosphate NaH_2PO_4 solutions were prepared; 72 g of NaH_2PO_4 (Wako Pure Chemical Industries Co., Ltd., Tokyo, Japan) was resolved in 2 L water and then the NaH_2PO_4 solution was alkalized by adding granular NaOH reagent 30 g. After that, the Ca solution from acidizing wood ash was added to alkaline NaH_2PO_4 solution in a glass vessel with magnetic stirring under the room temperature and accordingly, the milky gel suspension of amorphous HAp with around pH 7 was gained. The obtained precipitate solutions were adjusted to have a Ca/P ratio equal to 1.67 (stoichiometric ratio of HAp) in consideration of the Ca quantity of the treated wood ash. The previous study [12] has reported that the HAp microcrystal generation was confirmed on treated woods with the above HAp suspension from a reflection electron imaging and powdered X-ray diffraction analysis, and other possible by-product salts, e.g., calcium acetate were not detected because the conceivable by-product salts were water-soluble and accordingly the water-insoluble HAp microcrystals dominated on the treated woods. Through the repeated operation of evaporation to dryness of the HAp solution, followed by a flushing with water of the evaporation residue, the HAp yield was evaluated around 50 % on the amount of wood ash in weight.

Treatment of wood specimens with HAp suspension

The wood specimens 50 × 30 × 4 mm (L, R, T) from edge-grained sliced veneers of Japanese cedar and Japanese cypress (*Chamaecyparis obtusa*) sapwoods were prepared for the fire performance evaluation with a thermogravimetric analyzer and an oxygen index flammability tester. After oven-drying at 60 °C for 72 h, the wood specimens were soaked into the HAp suspension under evacuating by rotary pump at 50 torr (6.67 Pa) for 30 min, and subsequently placed in a pressurized air at 1.1 MPa for

Table 1 Samples for combustion tests and their HAp contents

Specimens size (mm)	Treatment with HAp solution	HAp content (kg/m ³) ^A		
		Japanese cedar	Japanese cypress	Code ^B
For thermogravimetric analyze and oxygen index measurement				
50 × 30 × 4	Untreated	0	0	
	Injected under 1.1 MPa after 30 min evacuation	54.8 ± 1.4 ^a	51.2 ± 1.1 ^a	
For corn calorimeter test				
99 × 99 × 15	Untreated	0	0	HA-0
	Coating	15.8 ± 0.9 ^b	20.7 ± 1.8 ^b	HA-1
	Injected under atmospheric condition after 2 h boiling	41.8 ± 3.6 ^b	38.2 ± 1.9 ^b	HA-2
	Injected under 1.1 MPa after 30 min evacuation	75.7 ± 0.4 ^b	71.6 ± 0.8 ^b	HA-3

^A Data given as mean ± standard deviation, ^a*n* = 65, ^b*n* = 10

^B Same code used in Figs. 3, 4, 5 and Table 2

24 h. To measure the HAp uptake of the wood specimens, the treated specimens were conditioned after the HAp impregnation for 24 h and then oven-dried again at 60 °C for 72 h.

Also for evaluating the fire-retarding properties with a corn calorimeter, the test specimens 99 × 99 × 15 mm (L, R, T) were prepared from boards of Japanese cedar and Japanese cypress. After oven-drying at 60 °C for 72 h, the specimens were treated with HAp solution in three ways based on the previous cone calorimeter studies [13–15]: (1) The HAp suspension was simply spread over the surface of the specimens to coat them, and then the specimens were cured at room temperature for 4 weeks. (2) The specimens were soaked into the 100 °C boiling water for 2 h, and then soaked into the HAp suspension for 24 h under atmospheric room condition at 20 °C. (3) The specimens were soaked into the HAp suspension and placed in a vacuum at 50 torr (6.67 Pa) for 30 min, subjected to pressurized air at 1.1 MPa for 24 h. After the impregnation processes (2) and (3), the specimens were removed from the HAp solution and dried under atmospheric conditions for 4 weeks.

After these HAp-coating or impregnating processes, the specimens were oven-dried again at 60 °C for 1 week until the specimens mass stayed constant and the dry HAp retentions of all HAp-treated specimens were given in Table 1. The HAp-treated specimens and other untreated ones were stored in a temperature/humidity-controlled room at 20 °C and RH of 65 % for 4 weeks before the combustion tests.

Thermal property and fire performance evaluation

Thermogravimetric analyze

The powdered and sifted samples of the HAp composites through 0.5 mm screen were studied with a thermogravimetric analyzer (TGA-60, Shimadzu Co., Ltd., Kyoto,

Japan) and a differential thermal analyzer (DTA-60, Shimadzu Co., Ltd., Kyoto, Japan) in open atmosphere with Alumina (α -Al₂O₃) powder as a reference material. The temperature was raised from 30 to 600 °C at the heating rate of 20 °C/min, with a flow of dried air (100 mL/min).

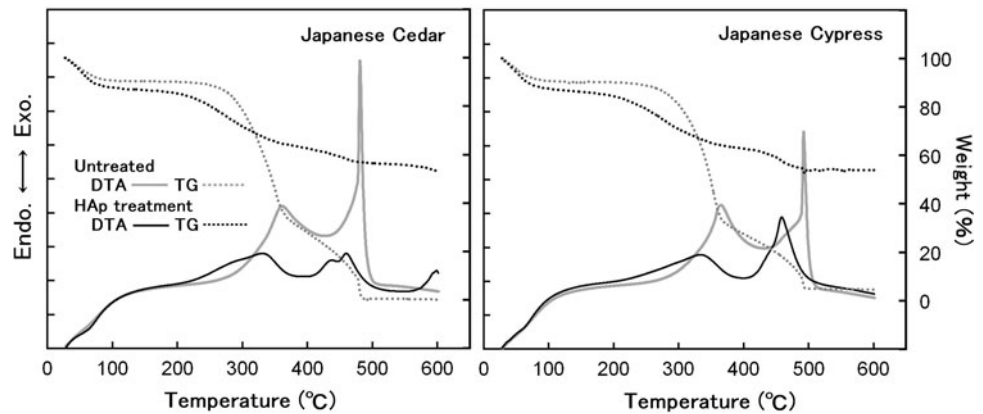
Oxygen index flammability test

The oxygen index test was conducted according to JIS K7201-2 [16] using an oxygen index flammability tester (ON-1, Suga test instruments Co., Ltd., Japan). This test measures the minimum concentration of oxygen (i.e., oxygen index, or limiting oxygen index: OI) in a flowing mixture of oxygen and nitrogen that is required to maintain flaming combustion of specimen. The specimen is ignited in the glass holder with the mixed flow of oxygen and nitrogen so the entire top tip of them is burning like a candle, and if the specimen burns for at least 3 min after the igniter is removed, or if the specimen burns down 50 mm, the oxygen concentration is judged above the oxygen index (OI). Instead, if the specimen stops flaming before those criteria, the oxygen concentration is below the OI. The procedure is repeated with upper and lower oxygen concentrations by 0.5 % until the lowest concentration of oxygen that will satisfy the criteria is determined. The trial was conducted on the 5 groups of specimens with the same amount of the HAp injection from Japanese cedar and Japanese cypress, respectively.

Corn calorimeter test

The cone calorimeter (Toyoseiki, Japan) was also used for the fire-retardant experiment of the HAp composites at Kumamoto University, Japan. The specimen was wrapped in aluminum foil and exposed horizontally to an external heat flux of 50 kW/m². A spark igniter was applied to ignite the specimens. During the test, oxygen concentration of the

Fig. 1 DTA (solid) and TG (dot) curves of untreated woods (gray) and HAp composites (black) from Japanese cedar (left) and Japanese cypress (right)



exhaust gas and sample weight was measured every 2 s, and the heat release rate (HRR) and total heat release (THR) were obtained. The cone calorimeter tests were conducted on two samples from each group of HAp-treated specimens (HA-0 to HA-3, Table 1).

Results and discussion

Thermogravimetric analysis

The results of the DTA and TG measurements are shown in Fig. 1. The untreated wood samples of Japanese cedar and Japanese cypress undergo two degradation steps, the first exothermic peak appeared at around 360 °C and the subsequent peak occurred at 480–490 °C due to their glowing. Their weight loss started gradually at around 270 °C and rapidly occurs at the exothermic peak temperatures. The similar thermal characteristics of Japanese cedar and Japanese cypress were reported in the previous study [17]. Meanwhile, in the case of HAp composites, it can be found that the HAp composite shows higher decomposition rate in TG curve up to around 300 °C with their exotherm starting, but subsequent exothermic peaks were weakened compared with the untreated samples and as a whole, exothermal and weight loss profiles of the HAp composites became smoother than those of the untreated samples. Also, the weakened exothermic peak temperatures of the HAp composites were shifted to the 20–30 °C lower in relation to those from the untreated ones. The similar changes in DTA-TG thermal profiles were reported in the previous studies especially intended for the wood treatment with phosphoric agents: e.g., fire-retardant-treated woods with several phosphoric agents [18] and cellulose crystals treated with phosphoric acid [19]; therefore, it implied that the injected HAp solution contributed to the thermogravimetric change of the treated woods as a phosphoric component carrier.

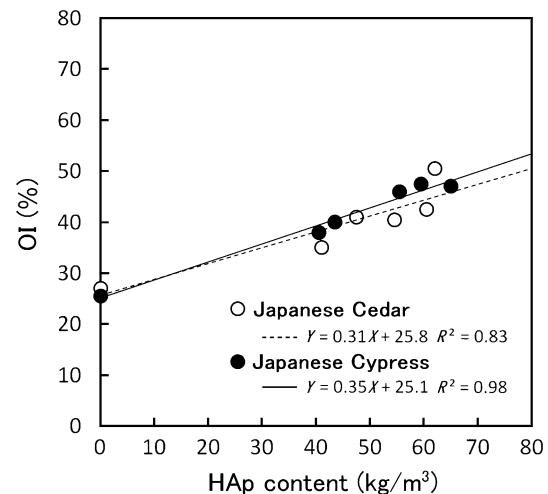


Fig. 2 Oxygen index increased linearly with increasing HAp contents from Japanese cedar (open circles, dot-line) and Japanese cypress (filled circles, solid-line)

OI measurement

The results of the OI measurements are shown in Fig. 2. The OI values of untreated woods from Japanese cedar and Japanese cypress were 27.0 and 25.5, respectively, and the similar values were reported in previous study [20]. Once the untreated samples ignited at OI condition, they burned with a red flame and smoke. In contrast, the HAp-injected specimens were difficult to keep burning without raising the oxygen concentration and the HAp composites burned at around higher OI values with a small flame and less smoke. It can be observed from Fig. 2 that the OI values of the HAp composites with 40–60 kg/m³ HAp contents were raised to around 40–50 %. These OI values trended to be raised with increasing amount of the HAp injections, and there was a high correlation between the two. These results indicate that the injection of HAp solution can increase the flame retardancy of the treated woods.

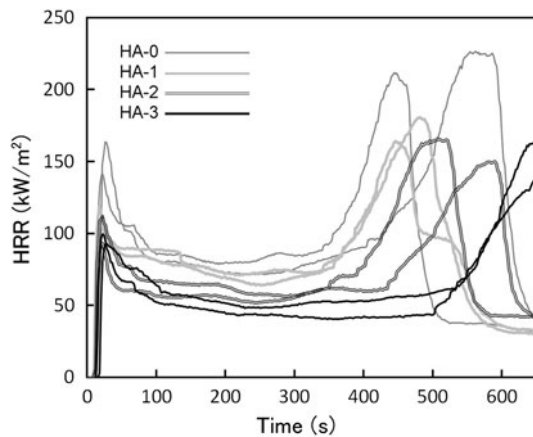


Fig. 3 Heat release rate (*HRR*) curves of HAp composites with Japanese cedar. See Table 1 for symbols HA-0 to HA-3

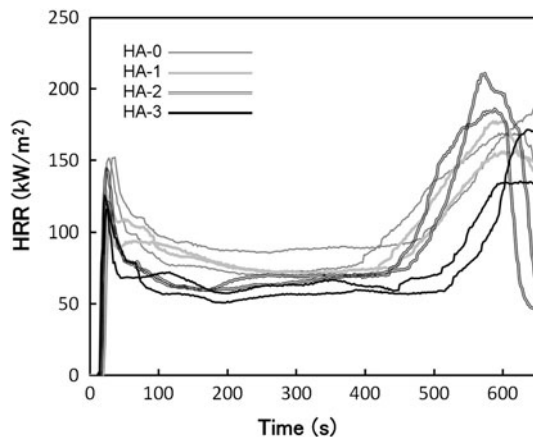


Fig. 4 Heat release rate (*HRR*) curves of HAp composites with Japanese cypress. See Table 1 for symbols HA-0 to HA-3

Cone calorimeter study

Figures 3 and 4 show the heat release rate (*HRR*) curves of the HAp composites with Japanese cedar and Japanese cypress, respectively. The *HRRs* of all analyzed samples (HA-0 to HA-3) show two separate peaks during their combustion which indicate the gradual burning after the initial charred layers were formed. Although the second *HRR* peak risings were basically dependent on the experimental condition, e.g., thickness of test specimens and their adiabatic condition, the second *HRR* peaks were detected in this measurement as with the previous reports on the cone calorimeter studies of chemically treated woods [13–15].

In view of the *HRR* curves according to heating time, a first sharp *HRR* peaks appeared at the range up until 60 s,

Table 2 Heat release rates of HAp composites from cone calorimeter test

Sample code	HAp content (kg/m ³)	Heat release rate (<i>HRR</i>)		
		Maximal value of <i>HRR</i> (kW/m ²)	Average <i>HRR</i>	
			<i>HRR</i> ₆₀ (kW/m ²) ^a	<i>HRR</i> ₃₀₀ (kW/m ²) ^b
Japanese cedar				
HA-0	0.0	211.7	110.3	89.2
	0.0	226.4	117.8	84.4
HA-1	16.5	164.0	95.8	81.4
	16.8	180.7	90.6	76.0
HA-2	43.2	165.5	85.8	66.7
	48.4	149.9	66.5	57.5
HA-3	77.1	109.8	81.0	59.2
	78.1	118.8	74.1	52.2
Japanese cypress				
HA-0	0.0	169.2	111.7	82.3
	0.0	166.1	116.2	95.5
HA-1	20.7	177.4	98.7	83.2
	23.8	156.9	104.3	84.0
HA-2	40.6	186.2	92.6	71.4
	43.6	210.8	88.9	68.5
HA-3	74.0	134.1	79.7	67.0
	74.4	124.7	87.7	61.9

^a The averaged heat release rate from the starting ignition to ending 60 s later

^b The averaged heat release rate from the starting ignition to ending 300 s later

and at this time range, the peak *HRR* values of the HAp composites (HA-1 to HA-3) were slightly declined compared with those of the control (HA-0). Also over the following period from 60 to 300 s between two heat release peaks, the *HRRs* tend to be decreased with increasing amounts of the HAp contents and the subsequent rising of second *HRR* peaks tends to be delayed with the HAp increasing. These results reflected a parallel correlation between the mean heat release rates over the period to 60 and 300 s combustion (*HRR*₆₀ and *HRR*₃₀₀ shown in Table 2) and the amount of HAp contents.

Figure 5 shows the total heat release (*THR*) at lapse of 600 s burning. The *THR*s were also decreased with increased amount of the HAp injection in a reflection of *HRRs* reduction, and the declining rate of the *THR*s is similar between the HAp composites with Japanese cedar and those with Japanese cypress. These results indicate that the HAp treatment contributes to decrease the flammability of the treated woods, and these results from the cone calorimeter study are consistent with those from the OI measurement.

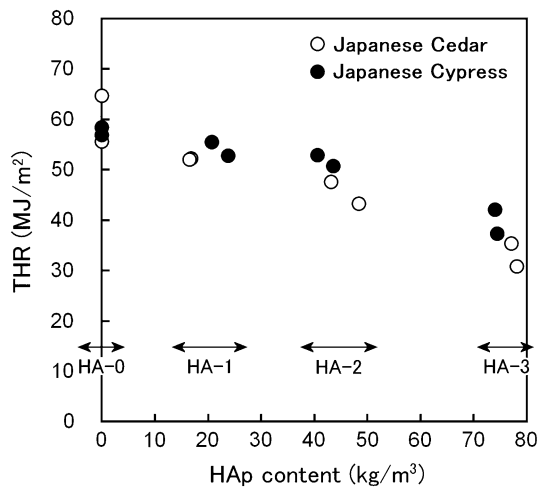


Fig. 5 Total heat release (*THR*) at lapse of 600 s combustion from HAp composites with Japanese cedar (*open circles*) and Japanese cypress (*filled circles*). See Table 1 for symbols HA-0 to HA-3

Conclusions

It has been found that the wood ash-based amorphous HAp suspension has flame retardant effect on the HAp-treated woods. The HAp produces characteristic alterations as phosphoric agents in the thermogravimetric properties of the HAp-treated woods; the exothermic and weight loss peaks due to their significant thermal decomposition were weakened and peak temperatures were shifted to the lower. The OI measurements indicate that with the increase in the amount of HAp injection, it was becoming difficult to keep the combustion of the HAp composites without raising the oxygen concentration. Also in cone calorimeter study, the HRRs and THRs of the HAp composites tend to be decreased and the second HRR peak risings due to their gradual burning after the initial charred layers tend to be delayed with increasing amounts of the HAp contents. These results indicate that the HAp treatment contributes to decrease the flammability of the treated woods.

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