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Improvement of Wood Surface by Inorganic Modification

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To improve the properties of wood, an inorganic modification with Si, Ti, Fe, Cu and Al was investigated. First, the wood surfaces were modified with a tetraethyl orthosilicate by the sol-gel process to prepare wood-inorganic composite material. By this treatment, Si was covalently bonded as Si-O or Si-C to wood components, i.e., polysaccharides and lignin. This silicate treatment improved the wood properties, for example, dimensional stability, fire-resistance and durability, without any significant increase in weight. On the other hand, considering the efficient use of wood materials in life environment, wood/TiO_2 composite material was investigated, because TiO_2 catalyzed the degradation of various organic toxics by the photocatalytic reaction. TiO_2 modified wood catalyzed the degradation of some organics, however, wood components were also degraded by photocatalytic reaction with TiO_2. Thus, wood/SiO_2/TiO_2 composite, which is modified with tetraisopropyl titanate by gas phase reaction after silicate treatment, was investigated. Consequently, we succeeded the addition to wood surface of both degradation of organic toxics and protection of wood base. Besides, transport of metal components (Fe, Cu, or Al) from the molding block or metal plate to wood surface was investigated during compressive molding process with high-pressure steam. In effect, improvements in the physical properties of wood surface were derived.
Keywords: wood-inorganic composite / SiO_2 / TiO_2 / photocatalysis

1.INTRODUCTION

Wood has many good characters for human life, e.g., ratio of dynamic modulus, moisture control and physiological comfort etc. However, it has disadvantageous characteristics also, e.g., combustion, dimensional instability by water, and biodegradation. Thus, we attended to wood-inorganic composite for the leverage to overcoming these disadvantages.

Chemical or composite treatment for wood was carried practically by polyethylene glycol treatment, wood plastic composite, or acetylation.[1] However, these treatments cause often the gain of weight and the damage on the advantages of wood. Then, we have tried the application of sol-gel process.[2] This process is effective method for wood-inorganic composite. We further tried with small amount of inorganic compound to avoid the gain of weight.

In this report, we firstly cleared the production of chemical bond with tetraethyl orthosilicate (TEOS) and wood components to improve combustion, dimensional instability by water, and biodegradation. Second, we investigated the wood-TiO_2 composite with tetraisopropyl titanate (TIOT), because TiO_2 catalyzed the degradation of various organic toxics by the photocatalytic reaction[3]-[6]. By this treatment, however, it is unavoidable the degradation of wood components by photocatalyzation. Then, we developed the sandwiched wood/SiO_2/TiO_2 composite that is firstly covered with SiO_2, and following TiO_2 is reacted to the surface. Finally, transport of metal components (Fe, Cu, or Al) from the molding block or metal plate to wood surface was investigated during compressive molding process with high-pressure steam.

2.MATERIALS AND METHODS

2.1 Evidence of covalent bond between inorganic and wood components

To evidence the covalent bond between inorganic and wood components, the reaction between TEOS and model compound of wood components was investigated.

First reaction, 40 mg coniferyl alcohol were dissolved in 2 ml dried dioxane in flask. 99 µl TEOS and about 10 mg D-camphor-10-sulfoic acid were added in this solution. It was refluxed in oil bath at 120 °C for 15 minutes with Liebig condenser. The products were separated with TLC, and the chemical structures were determined by ^{1}H-NMR, ^{13}C-NMR, and MS spectra. Vanillyl alcohol and methyl 4-O-methyl-α-D-glucopyranoside was reacted with TEOS by same method.

2.2.1 Gas phase reaction with TEOS and TIOT

Specimens [50(R) × 50(T) × 5(L)mm] obtained from the Japanese Cypress which compressed in half size by compressive molding apparatus.[7]

After dried at 105 °C for 24 hours, specimens were put into 500 ml separable flask without touch each other. The flask was heated at 160-170 °C in vacuo.

After pre-heating, 20 ml of TEOS was dropped slowly into bottom of flask, and then the vapor of TEOS was reacted to wood with gas phase reaction. After 4-20 hours of reaction, unreacted TEOS was evaporated from the flask, and returned to atmospheric pressure. After this reaction with TEOS, sample was treated with TIOT or tetraethyl titanate (TEOT) by same method. These samples named TEOS-TIOT and TEOS-TEOT samples, respectively.

2.2.2 Weight Percent Gain and ash content

To measure the Weight Percent Gain (WPG), the samples [20(R) × 20(T)] were dried at 105 °C for 24 hours, and weighted in before and after the reaction.

To measure the ash content, weighted samples were completely burned to ash in electric furnace at 600 ± 25 °C.

2.2.3 Demonstration of decomposition of pollutant by UV irradiation

TEOS-TEOT samples were painted with 50μl/cm^2 Patentblau V (0.1% in water), and irradiated by UV-ray (B-100A, 352nm) for 1 week after drying in dark place. Distance of between samples and UV-lamp was 10 cm.

2.2.4 Effect on degradation resistance of SiO_2 layer

To investigate the resistance by SiO_2 layer to degradation by photocatalysis with TiO_2, the change of Vickers hardness to base on Japan Industry Standard (JIS) B 7774 was measured and compared in before and after irradiation.

2.2.5 Combustion test

The combustion test of TEOS-TEOT sample was carried out by D-style Candle System Fire Testing Machine with JIS K 7201. In this test, the oxygen index (lowest concentration of oxygen for combustion) and the growing combustion time were measured.

2.3.1 Production of compressed wood with metal plates

Specimens [300(R) × 200(T) × 15(L)mm] of Japanese Cypress were compressed to 7.5mm thickness by compressive molding apparatus. These productions were compressed with various metal plates (Fe, Al, Cu or Stainless steal) put on wood surface.

2.3.2 Surface analysis

To measure the transcription of metals, the surfaces of compressed wood were analyzed by JASCO-850. These were also measured the Brinell hardness test for sample to base on JIS Z 2101.

2.3.3 Color change of wood by compressing with metal plates

Change of wood surface color by treatment in 2.1 was measured by colorimeter ND-300A (NIPPON DENSYOKU), and expressed as L*, a* and b*.

3 RESULTS AND DISCUSSION

3.1 Evidence of covalent bonding between inorganic and wood components

Figure 1 shows the chemical structures of compounds after reaction of vanillyl alcohol, coniferyl alcohol or methyl 4-O-methyl-α-D-glucopyranoside with TEOS. Former alcohols and later saccharide were model compounds for lignin and saccahrides, respectively, in wood components. By this result, it was found that TEOS covalently bonded to alcoholic hydroxyl group and aromatic ring in wood component.

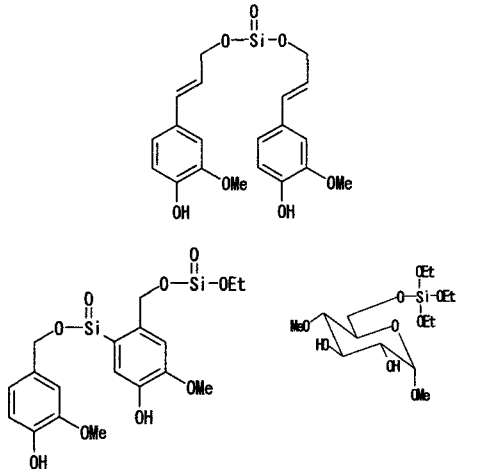


Fig.1 Typical examples of chemical structures of products in model reaction of wood components with TEOS

3.2.1 WPG and ash content

Table 1 shows the results of WPG and ash content in samples prepared at various reaction times. WPG of all samples increased to 1- 3 % comparing with untreated sample because of production of composite materials with inorganics. However, WPG reduced with increase of treatment time. It suggested that hemicellose containing in wood cell wall was extracted by long time treatment.

On the other hand, ash content increased from 0.4 % of untreated wood to 2-5 %. These high values indicate the TEOS and TIOT were reacted with wood components whereas small increase of WPG. It seems that the ash content depends on the reaction time. This suggests the existence of best condition of the reaction.

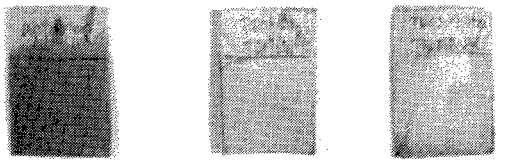
3.3 Decomposition of pollutant on wood surface by UV irradiation

Photo 1 shows the result of after UV irradiation for 1 week. For TEOS-TEOT samples, Patentblau V on the surface was completely decolorized whereas it was incomplete without TEOS-TEOT treatment.

Consequently, the addition of photocatalysis to wood surface was succeeded by TEOS-TEOT treatment.

Table 1 WPG and ash content in sample prepared by various methods

	WPG (%)	Ash content (%)
Untreated	-	0.40
TIOT5h	3.25	2.93
TEOS5h-TIOT5h	2.65	1.89
TEOS8h-TIOT8h	1.01	4.65
TEOS20h-TIOT20h	0.95	3.21



Untreated TEOS 8h TEOT 8h TEOS 4h TEOT 8h

Photo. 1 Result of color degradation after irradiation in UV-ray for 1 week

3.4 Effect on degradation resistance of SiO_2 layer

Table 2 shows the results of Vickers hardness examination by before-and-after UV irradiation. In before irradiation, the hardness of all samples were improved more than double to compare with untreated wood. It was suggested that Si and Ti compounded to wood components and linked them.

In comparing the effect of irradiation, the hardness of TIOT5h sample remarkably decreased to compare with TEOS-TIOT samples. By this result, it was found that the degradation of wood by photocatalytic reaction could be restrained by SiO_2-layer.

3.5 Combustion test

Table 3 shows the results of combustion test. In the case of without inorganic treatment, the oxygen index was 23.0 % and the growing combustion time was 79 seconds. In the case of TEOS treatment without TEOT, the oxygen index was higher than untreated sample, and the combustion time was decreased. Especially, for TEOS16h sample, the combustion time disappeared. By this result, improvement of fire-resistance was achieved by treatment with TEOS. It was suggested that Si was covalently bonded with lignin because lignin maintained growing combustion. Saka et al developed the fire-resistance by addition of inorganic compounds to lumens. However, their materials were high WPG over 10%. Wood-inorganic composite materials in our preparation were below 5 % and lower than theirs. Consequently, we succeeded the addition of fire-resistance for wood with small WPG. Our result shows that the addition of fire-resistance can be achieved by only chemical modification to cell wall.

Further, TEOS-TEOT samples also resisted the growing combustion time to 0 second, and the oxygen index more improved. By results of TEOS-TEOT samples, i.e., treated TEOT on SiO_2-layer, it was suggested that TiO_2- and SiO_2-layers restrain the thermal flowability and the supply of oxygen to inside of wood.

Table 2 Vickers hardness examination by before-and-after irradiation of UV-ray

	Before irradiation (MPa)	After irradiation for 1 week (MPa)
Untreated	219.1	171.4
TIOT5h	428.4	177.9
TEOS5h-TIOT5h	526.9	438.9
TEOS8h-TIOT8h	465.9	364.6
TEOS20h-TIOT20h	480.7	306.8

Table 3 Results of combustion test as expressed by oxygen index

	Oxygen index (%)	Combustion time (sec)
Untreated	23.0	78
TEOS8h	24.2	22
TEOS16h	24.8	0
TEOS8h-TEOT8h	25.2	0
TEOS16h-TEOT16h	25.2	0

3.6 Surface and depth analysis by ESCA

By the result of ESCA, it found that the contents of metallic elements increased for metal treated woods. By this result, it was found that metallic elements were transcribed to wood surface during compressively molding with high-pressure steam.

For the case of surface analysis, the content of oxygen was increased in all samples. It may be that oxygen atom increased by oxidation in heating and compressing with metal surface.

On the change of metal content, the amount of metals

were about 1 % for Cu, 3 % for Al, and 8 % for Fe. Especially, large amount of Fe was observed for compressing with Fe plate. This value was also observed in depth analysis for 70 min shaving. The content of Fe cannot be removed by acid and alkali cleaning. This suggests that Fe combined to oxygen of wood components.

Table 4 shows the result of Brinell hardness test. The hardness were not so changed for Cu and Al treatments, and bit large for Fe treatment. This small increases suggests that the modification with metal plates were produced the covalent bonds but less the linkage between wood components comparing with TEOS treatments.

Table 4 Result of Brinell hardness test

	KPa
Untreated	267.8
Cu	267.3
Al	254.7
Fe	297.1

3.8 Color change of wood surface by compressing with metal plates

The color of wood surface was changed to be dark by high-pressure steaming. In this report, the effect of species of metal block on it was discussed.[8] Table 5 shows the result of wood surface color. L* of samples compressed with Cu, Al and Stainless plates were not changed, but that of Fe was remarkably decreased. The decrease for Fe indicates that the surface color was changed to be dark by compressing with metal plates. This cause would be oxidation of Fe transcribed to wood surface.

For a* and b*, the values were not so changed with compressing. However, a* of Cu sample was higher than other samples. This increase of a* indicates that the color of Cu sample changed toward red. For Fe sample, both a* and b* were changed toward zero, and means toward color-less.

Consequently, we suggested that the change of color depend on the species of metal plates and the amount of transcribed elements.

4. CONCLUSION

We succeeded the development of wood material that shared good physical characteristics and new functions by inorganic modification with small weight gain. We present the new material with conjugation of wood and metal components. Further, we obtained the evidence of covalent bond in wood components with inorganic compounds.

Table 5 The change of surface color by compressing with various metal

	L*	a*	b*
Untreated	51.92	9.36	28.38
Cu	52.78	11.82	27.56
Al	58.49	8.37	28.00
Stainless	55.95	8.69	26.71
Fe	31.07	2.04	5.65

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