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Development of Photocatalytic Wooden Binderless-boards

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Photocatalytic wooden binderless boards were developed by using TiO_2 and unutilized wooden materials like sawdust. According to our findings, only a little amount of TiO_2 powder addition to wooden board was enough to decompose VOCs, and pretreatment (UV irradiation) is required to activate the surface of prepared boards. We accomplished the following; boards possessed antibacterial ability and VOC decomposition activity by the addition of TiO_2 powder. Silicate was coated to boards to prevent the wooden component from degrading photocatalytically, thus strengthening the boards. Also copper addition to boards maintained antimicrobial activity in case of absence of lights.
Key words: Titanium Dioxide, Photocatalyst, Acetaldehyde, Interior Material, High Pressure Steam

1. INTRODUCTION

In recent years, we often hear about VOCs (Volatile Organic Compounds) which are harmful to human-beings. Many successful works on VOC decomposition have been accomplished by using the photocatalyst, titanium dioxide (TiO_2).[1] Many researchers have succeeded by coating TiO_2 on inorganic materials[2],[3] or making thin TiO_2 films. However, these methods are costly from the commercial production point of view. Consequently we used affordable anatase TiO_2 powder which also has a high photocatalytic activity. For the base material, we used Japanese cedar (*Cryptomeria japonica,* D.Don) sawdust which is unutilized wooden material from lumber production. The high-pressure steam technique was used to fabricate the TiO_2-containing wooden boards. The boards are environmentally friendly materials as no chemical binders such as phenol-formaldehyde resins were used. The purpose of TiO_2 addition to the wooden board is to use them as interior wall or ceiling materials, thereby purifying interior environmental air and disinfecting the surface of walls.

2. MATERIAL AND METHODS

2.1 Board fabrication methods

The apparatus used to fabricate the board is an airtight autoclave with six compressing cylinders in it. High-pressure steam is filled into the autoclave. Boards were fabricated with oven-dried Japanese cedar sawdust screened to 1.68 mm or 10 mesh. Our molding jig allows to make 185 cm (width) × 28.5 cm (length) × 1.0 cm (thickness) board by putting 600 g of sawdust into it. The brief fabrication process has been listed bellow:

(1) Softening stage

The temperature in the autoclave is raised up to 120 °C by filling it with high pressure steam and this stage lasts for 20 minutes.

(2) Compressing stage

Softened material is compressed by pressing component with molding surroundings. The compressing stroke is controlled to obtain a target density of approximately 1.0 g/cm^3.

(3) Fixation stage

Board shape of compressed material is fixed by high-pressure steam at 180 °C and lasts for 10 minutes. Fixation here was caused by the structural change of cellulose non-crystalline region, and the transformation of crystalline region.[4] These phenomena mainly cause adhesion between wooden particles.

2.2 TiO_2–containing wooden boards

2.2.1 Fabrication of the TiO_2–containing wooden boards

The TiO_2 used in the entire experiment is ST-01 made by Ishihara Sangyo Kaisha LTD. 60.0 g, 120.0 g or 300.0 g of TiO_2 powder was added to 600 g of sawdust and mixed in a plastic container. Board fabrication followed the method described in 2.1.

2.2.2 Pretreatment of the fabricated board

TiO_2-containing wooden boards immediately after fabrication had no photocatalytic activity and activation is required. Thus the activation of the board was accomplished by irradiating UV to the board surface for 7 days. Black light (Toshiba Lightec Co., 20W) as used the UV source. Lighting intensity was 2.5 mW/cm^2 at sample surface.

2.3 Strengthening TiO_2–containing wooden boards

Boards were made with two layers, one with TiO_2 powder and one without. Between these layers, TiO_2 concentration was reduced gradually. Its strength was compared with normal one layer TiO_2–containing boards.

Test pieces were made by cutting each sample to 3.0 cm x 3.0 cm for internal bonding test and 3.0 cm x 15.0 cm for bending test.

2.3.1 Bending strength (modulus of rupture, MOR)

Bending strengths were measured with multi-strength

testing machine (Imada Seisakujyo Co., LTD. SV55) and Data Logger (Tokyo Sokki Kenkyujo Co., LTD. TDS-601). Testing method was central concentric loading (3 point load) and the maximum stress at the breaking point and strain at the center and the stress were reordered every second by a Data Logger. This data was substituted into equation 1 and calculated bending strength was calculated (MOR in Pa). Five test pieces were prepared for each sample to obtain accurate data.

$$MOR = \frac{3Pl}{2bh^2} \qquad (1)$$

P : ultimate load (N), l : distance (m),
b : sample width (m), h : sample height (m)

2.3.2 Internal bonding (IB)

The sample has adhered to metal plate and pulled with same machine as 2.3.1. The loading speed was set to 10mm/min and recorded until delamination fracturing. IB strength in Pa was calculated using the formula below (2). Five test pieces were prepared for each sample to obtain an accurate data.

$$IB = \frac{P_{max}}{b \times L} \qquad (2)$$

P_{max}: ultimate load at delamination fracture (N),
b: width of the sample (m),
L: length of the sample (m)

2.4 Acetaldehyde (CH_3CHO) decomposition test

In order to test the VOC decomposition ability of the board, gaseous acetaldehyde was selected as common example of VOCs. Prior to CH_3CHO decomposition test, adsorption ability of the wooden board was tested by closed-system using a gas bag. The gas bag was filled with pure air and CH_3CHO concentration was adjusted to 100ppm. The temperature was kept at 23 °C.

The experimental set-up for photocatalytic activity test is shown in Fig.1. Photocatalytic decomposition of acetaldehyde was performed with it in pure air (13 ppm), and the gas flow rate was 1.0 litter / min. The gap between samples and the glass cover is set to 2mm. For the light source, a black light type (Toshiba Lightec Co., 20 W) were used. Lighting intensity was 1.5 mW/cm^2 at sample surface. The temperature was kept at 23 °C. Gas samples collected from inlet and outlet were injected into Shimadzu GC-18A gas chromatography (GC) with F.I.D. as a detector and the concentrations were measured. Concentration measurements were started 30min after gas introduction to the reaction vessel, because wooden boards adsorb important amounts of CH_3CHO and concentration is unstable. The column used for GC was PorapakQ (Shinwa Chemical Industries, LTD.) and is 2.6 mm (I.D.) × 2 m (Length). GC analysis conditions were set to the following; Column temperature: 140 °C, injection block: 180 °C, Detector block: 180 °C, carrier gas: He (30 ml/min.), hydrogen pressure: 70 kPa, air pressure: 50 kPa. Photocatalytic activity (R) was compared after calculating decomposition rate with equation 3.

$$R = \frac{C_{UV\,OFF} - C_{UV\,ON}}{C_{UV\,OFF}} \times 100 \qquad (3)$$

$C_{UV\,OFF}$: CH_3CHO concentration without irradiation
$C_{UV\,ON}$: CH_3CHO concentration with irradiation

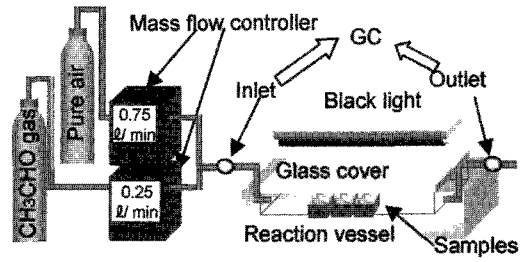

Fig.1 Experimental set-up for photocatalytic activity test

2.5 Antimicrobial ability test

0 wt%, 0.1 wt%, 1 wt%, 5 wt%, 10 wt%, and 20 wt% TiO_2-containing boards were prepared for antimicrobial ability test. Fabricated boards are pretreated for 7 days as shown in 2.2.2

Antibacterial ability test followed the JIS L 1902 standardized antimicrobial testing method. *Klebsiella pneumoniae* were used as the test bacteria,. Samples and standard cotton cloth (no antibacterial activity was detected) was cut down to 0.4 g and put into vial container (n=2×2 pairs, total of 4) and autoclaved (121 °C) for 15minutes to be sterilized. Cultured bacteria was transplanted into Nutrient liquid medium using platinum loop and shaking cultured for 24 hours at 37 °C. Preincubated bacteria were diluted by Nutrient liquid medium diluted by 5% and viable bacteria adjusted to 4.12×10^6 bacteria/ml (emulsion of sample bacteria) 1.0 ml of this emulsion was put into vial container and the cap tightened. Two vial containers had wrapped with aluminum foil to shield fluorescent light irradiation, while the other two were unwrapped to irradiate to the light. Fluorescent light was installed in the incubator and samples were stationary cultured for 24 hours at 37 °C with fluorescent light irradiation (2 μW/cm^2). After incubation, bacteria were washed away using saline solution. Diluting sequence was made using ten times dilution method and plate incubated using nutrient agar. The number of colonies were counted after 48 hours to calculate the number of viable bacteria and activity value.

Activity values (L) were calculated by following equation 4.

$$L = M_a - M_b \qquad (4)$$

L: Antimicrobial activity value
M_a: Viable cell count on unwrought samples immediately after inoculation (common logarithm)
M_b: Viable cell count on treated samples immediately after inoculation (common logarithm)

2.6 Addition of Cu to maintain antimicrobial activity under dark condition

Two ways of Cu addition were conceived. One was to simply add Cu powder and the other was transcription

from Cu plate during fabrication of the board. The transcription of Cu to wood lumber surface from Cu plate was determined in a previous experiment.[5] Cu can be transcripted from underlayed Cu plate to wooden material during high pressure steam process. Board containing Cu powder was fabricated by adding 15.0 g of Cu powder (Kanto Chemical Co., INC.) into 600g of sawdust. The rest of the fabrication processes were carried out as shown in 2.1.

2.7 Protection of wooden base by silicate coating

Wooden material coating was succeeded by Tetraethyl Orthosilicate (TEOS) in our laboratory.[5] TEOS (Tokyo Kasei Kogyo Co., LTD.) was coated to oven dried sawdust. 20 ml TEOS and 600 g sawdust are heated to 170 °C. Desiccator containing sawdust was evacuated. By opening both cocks, TEOS vapor was infused into the sawdust. This reaction was repeated for 7 times and finally air dried for 5 days. Silicate coated sawdust was mixed with TiO_2 powder, and fabricated by the same method as shown in 2.1.

Protection of wooden base was evaluated by measuring CO_2 production caused by photocatalytic degradation of wooden base. 10.0 cm × 10.0 cm of test piece was put into a gas bag. The gas bag was filled with pure air. Initial and final CO_2 concentration was measured with infrared CO_2 monitor (Riken Keiki Co., LTD, RI-85). As the light source, a black light type (Ultra Violet Products, 100W) was used. Lighting intensity was 5.0 mW/cm^2 at sample surface. The temperature was kept at 23 °C.

3. RESULTS

3.1 Strength of the TiO_2-containing boards

Bending strength (MOR) of boards is shown in Table I. Double layer board was more than 2 times stronger than single layer board. We expect that the layer without TiO_2 in double layer boards reinforced the TiO_2 containing portion of the board. Double layer boards were almost as strong as board without TiO_2.

IB of boards is shown in Table I. Double layer boards were found to be more than 1.6 times stronger. It is said to be middle part of fabricated board is weakest thorough out the board. Because midst part of double layer boards were non-TiO_2 containing portion, IB of double layer boards with gradient was strengthened than single layer boards. In addition, the amount of TiO_2 powder to fabricate boards had reduced.

Table I, MOR and internal bonding strength comparison between single and double layer gradient boards.

sample	MOR(MPa)	IB(MPa)
Single layer board	47.3	0.108
Double layer, TiO_2 containing layer and TiO_2-less layer	109.9	0.182
Sawdust only	125.2	0.777

3.2 Acetaldehyde (CH_3CHO) decomposition test

CH_3CHO adsorption rate is shown in Fig. 4. CH_3CHO concentration was greatly decreased within 2 hours. 90 % of CH_3CHO was adsorbed by wooden boards.

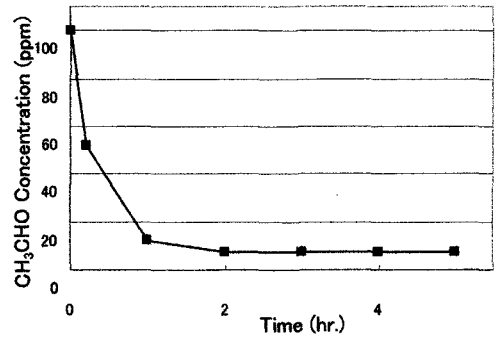

Fig. 4 Decrement of CH_3CHO concentration due to adsorption by wooden board. Gas bag capacity was 5 litters. Test piece was 15.0 x 15.0 x 1.0 cm.

CH_3CHO decomposition rates are shown in Fig. 5. Decomposition rates increased as TiO_2 increased. For comparison, a filter-type commercial product was tested for its decomposition ability. The decomposition rate of the commercial product was almost the same as 20 wt% TiO_2-containing boards. From that point of view, the developed TiO_2-containing wooden board has TiO_2 decomposition ability to meet commercial product standards.

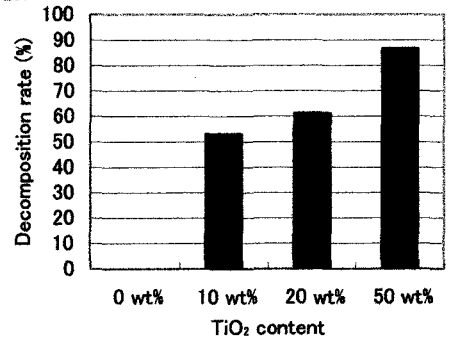

Fig. 5 CH_3CHO decomposition rates of TiO_2-containing boards.

3.3 Antibacterial ability test

Antimicrobial activity values of TiO_2-containing wooden boards are listed in Table II. As content of TiO_2 increases the number of antimicrobial activity value decreases with or without light irradiation. With irradiation, photocatalytic activity took place and bacteria were killed. In the case without irradiation, we expect that it would be crucial for bacteria to survive on the inorganic substance such as TiO_2.

Table II, Antimicrobial activity values of TiO_2-containing boards.

TiO_2 Content	With UV irradiation	Without UV irradiation
0%	0.98	0.98
0.10%	0.94	0.93
1%	3.29	1.99
5%	>5.25*	2.69
10%	>5.25*	3.04
20%	>5.25*	3.74

* Value above 5.25 could not be detected.

3.4 Addition of Cu

Antimicrobial activities for Cu-containing boards and Cu transcript boards are listed in Table III. Antimicrobial activity values for Cu powder and Cu transcript samples were at highest measuring limit. The addition of 2.5 wt% Cu powder addition may be too much. We anticipate that less amount of Cu powder to the board is enough to ensure antimicrobial ability. In the case of Cu transcription, the surface of boards had a metallic shiny look. It may be inferred from that point that transcription turned out well and antimicrobial activity value was also very high. Cu plate that was used in board fabrication is reusable, so it may be suitable for mass production.

Table III, Antimicrobial activity values of Cu added boards.

Sample	Antimicrobial activity value*[1]
Only sawdust	0.98
2.5 wt% Cu powder	>5.25*[2]
Cu transcript	>5.25*[2]

*[1] Lights were not irradiated.
*[2] Value above 5.25 could not be detected.

3.5 Protection of wooden base by silicate coating

Results of wooden base protection by TEOS are shown in Fig. 6. The 10 wt% TiO_2-containing boards produced more than 8050 ppm CO_2 in the gas bag while non TiO_2-containing boards produced only 720 ppm. By coating TEOS on board sawdust, CO_2 production was suppressed to 1870 ppm even for boards containing TiO_2. This value is close to the non TiO_2-containing boards, a result which indicates that the wooden base was protected by silicate bonded chemically to it.[5]

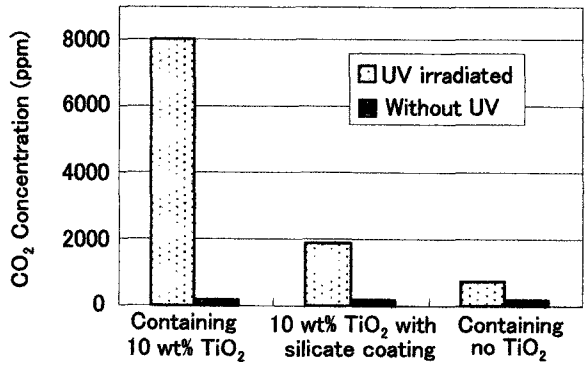

Fig. 6, Increment in CO_2 concentration from 10 wt% TiO_2 board surface after 72 hrs of UV irradiation (5 mW/cm^2). Initial CO_2 concentration was between 90-100 ppm.

4. DISCUSSIONS

TiO_2 powder addition to the board makes the board antimicrobial and also effective for VOC decomposition.

Wooden boards adsorb important amounts of VOCs and TiO_2 can effectively decompose VOCs, while TiO_2 coated glass for example, can adsorb only few amounts of VOCs and only decompose VOCs close to the TiO_2 coated glass.

TiO_2-containing wooden boards immediately after fabrication had almost no photocatalytic activity, even TiO_2 raw material itself had important photocatalytic activity. This phenomenon occured because extractives were covering the surface of TiO_2. To solve this problem, UV irradiating pretreatment is necessary to activate the fabricated boards.

Because sawdust is an organic material, it was expected that TiO_2 would degrade the base material and weaken it. To avoid this problem, it is expected that protection of the base was necessary. We thought of silicate coating to the surface of sawdust. Silicate coating to wood lumber has been successful by using TEOS in our laboratory. We thought this technique will work for protection from photocatalytic activity, because photocatalytic degradation would not work against inorganic materials like silicate. Therefore silicate coating was expected to work as a binder. As a result, TEOS treatment is necessary and it can prevent the deterioration of base materials. This technique might be also applied for other organic material protection.

In order for TiO_2 board to have antimicrobial activity, UV irradiation (less than 380 nm of wavelength [1]) was necessary. To achieve practical uses of TiO_2, boards should be expected to have antimicrobial activity all the time. Because Cu compounds themselves have antimicrobial activity, we have suggested the addition of Cu to the board to maintain antimicrobial activity. Cu addition and Cu transcription to the board both helps maintaining antimicrobial activity. From the result, the amount of Cu powder addition can be reduced, but it will still possess antimicrobial activity. Furthermore, Cu addition to the board promotes more antimicrobial activity. Cu addition, as a matter of course, has no effect on VOC decomposition.

TiO_2 powder addition weakened the board strength. Strength of the board would become to important factor when the boards are to be used as building material such as wall or ceiling. To solve this problem, boards were made with 2 layers, one with TiO_2 powder and one without. This method worked and strengthened bending strength, though internal bonding strength was weakened considerably. Therefore, we made a concentration gradient of TiO_2. This method resulted in a strengthened board in both bending and internal bonding strengths.

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