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Photostable wood-inorganic composites prepared by the sol-gel process with UV absorbent

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Abstract To enhance the photostability of wood against ultraviolet (UV) light, a UV absorbent, 2,2',4'trihydroxy-4-[2-hydroxy-3-(3-trimethoxysilylpropoxy) propoxy]benzophenone (BP), was applied to the reaction system for preparing SiO₂ wood–inorganic composites by sol–gel reaction. The BP–SiO₂ wood–inorganic composites obtained were examined for photostability by scanning electron microscope observations, color changes, and diffuse reflectance infrared fourier transform analyses. The results clearly indicated that compared with SiO₂ composites, BP–SiO₂ composites improved the photostability of wood. In addition, BP was stable against UV light without degradation so that the BP–SiO₂ composite should provide sustainable and high photostability of treated wood.

Key words Wood-inorganic composites \cdot Sol-gel process \cdot Photostability \cdot UV absorbent

Introduction

Recently, wood has been utilized as an environmentally friendly material in indoor and outdoor applications. However, wood has some unfavorable end-product properties such as biodeterioration, combustibility, and photodegradability. In particular, photodegradability against ultraviolet (UV) light is one of the drawbacks of wood when used outdoors. To overcome such disadvantageous characteristics of wood, a sol–gel process has been used in our laboratory to prepare wood–inorganic composites,^{1–10} and inorganic substances were found to be distributed differently in wood as different metal alkoxides when used with

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Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Kyoto 606-8501, Japan Tel. +81-75-753-9116; Fax +81-75-753-9116 e-mail: miyafuji@energy.kyoto-u.ac.jp moisture-conditioned wood or water-saturated wood.^{1,2,5} From a comparative study that used weathering tests of several composites, SiO_2 wood–inorganic composites were found to be one of the most promising materials because of enhanced photostability. Specifically deposited SiO_2 gels have been observed within the wood cell walls and cell lumens.¹¹ However, cell lumens in such composites were filled with SiO_2 gel so that the porous structure of the wood was lost.

In this study, therefore, to enhance the photostability of wood against UV light irradiation, we have applied UV absorbent which bears a silicon alkoxide residue so that the UV absorbent moiety is covalently bonded with SiO_2 gel in the composites. The prepared SiO_2 wood–inorganic composites with UV absorbent were then studied to determine their photostability to UV irradiation, and the effects of the UV absorbent on the photostability of wood were evaluated.

Materials and methods

Wood specimens

The specimens $[30(R) \times 30(T) \times 5(L) \text{ mm}]$ obtained from the sapwood portions of western hemlock (*Tsuga heterophylla* Sarg.) were extracted with acetone for 24 h and subsequently with water for another 24 h in a Soxhlet apparatus. Extracted wood specimens were then oven-dried, and their oven-dried weights were measured. To prepare the wood specimens with 20%–25% moisture content, ovendried specimens were placed in a desiccator for 3 weeks at 20°C in which the relative humidity was controlled at 98% with a saturated salt solution of K₂SO₄.

Preparation of wood-inorganic composites

A solution was prepared with a molar ratio of 1:10:0.01 tetraethoxysilane (TEOS), tetrahydrofuran (THF), and acetic acid (AcOH) for preparing the SiO₂ wood–inorganic composites. To this solution, 2,2',4'-trihydroxy-4-

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[2-hydroxy-3-(3-trimethoxysilylpropoxy) propoxy] benzophenone [(BP), C₆H₃(OH)₂COC₆H₃(OH)CH₂ $CH(OH)CH_2O(CH_2)_3Si(OCH_3)_3$] was added as a 50 wt% solution in *n*-butylacetate to give molar ratios of 0.002, 0.010, and 0.100 to TEOS to prepare BP-SiO₂ woodinorganic composites. TEOS and BP were obtained from Shin-Etsu Chemicals. For comparison, BP-treated woods were also prepared with several solutions of BP in THF and AcOH with molar ratios of 0.002, 0.010, and 0.100 BP in 10:0.01 molar ratio THF/AcOH. To achieve the same volume concentrations of BP as in the reaction mediums for the BP-SiO₂ composites, the previously used volume of TEOS was replaced with an equal volume of THF.

The prepared solutions were impregnated into moistureconditioned specimens at 20°C under reduced pressure (15mmHg) for 3 days. The impregnated specimens were then placed in an oven controlled to at 60°C for 24h and 105°C for a further 24h for aging of the gels.

Evaluation of wood-inorganic composites

The weight percent gain (WPG) of the composites was determined, on an oven-dried weight basis, by measuring the oven-dried weights of the specimens before and after treatment. The bulking coefficient (B) was also determined for the prepared composites.

To study the photostability of the composites, the transverse section of the composite specimens was surfaced with a freeze microtome, and then exposed to UV light $(2 \text{ mW/} \text{ cm}^2 \text{ intensity})$ at 352 nm for 144 h. The intensity of sunlight irradiation at 352 nm in Kyoto was 0.5 mW/cm^2 . The surfaces of the transverse sections were directly studied before and after UV irradiation without any destruction procedures using diffuse reflectance infrared fourier transform (DRIFT) spectroscopy with a fourier transform infrared (FT-IR) spectrophotometer (Shimadzu FTIR-8300) coupled with a diffuse reflectance unit (Shimadzu DRS-8000). All spectra were measured at a resolution of 4 cm^{-1} throughout the spectra ranges ($4000-400 \text{ cm}^{-1}$) with 100 times accumulation. The obtained spectra were calculated in Kubelka-Munk (K-M) units.

To study the chemical changes of the components in the BP-SiO₂ wood-inorganic composites caused by UV irradiation, milled wood lignin, glucomannan, cellulose (avicel), SiO₂ gel, and BP gel were analyzed by FT-IR spectroscopy using the KBr pellet method at a resolution of 4 cm⁻¹ throughout the spectra ranges $(4000-400 \text{ cm}^{-1})$ with 100 times accumulation. SiO₂ gel and BP gel were prepared by the following procedure: a solution with the same contents as that used for the SiO₂ wood–inorganic composites was prepared. To this solution, distilled water was added to give a molar ratio of 4 to TEOS to prepare the SiO₂ gel. A solution with the same contents as that used for the BPtreated woods with a molar ratio of 0.1 BP was also prepared. To this solution, distilled water was added to give a molar ratio of 0.4 to prepare the BP gel. These solutions were stored at 20°C for 3 days and were then placed in an oven controlled at 60°C for 24h and 105°C for a further 24h for aging of the gels.

To evaluate the color changes of composite specimens after UV irradiation, samples were studied with a color difference meter (Nippon Denshoku Kogyo Z-1001DP) according to the L*a*b* system. Measurements were made on three specimens for each treatment. The color differences (ΔE^*) were calculated by the following formula:

$$\Delta E^* = \left[\left(\Delta L^* \right)^2 + \left(\Delta a^* \right)^2 + \left(\Delta b^* \right)^2 \right]^{1/2} \tag{1}$$

where ΔL^* is the difference in brightness of the composites before and after UV irradiation, and Δa^* and Δb^* are the differences in chroma of the composites before and after UV irradiation.

To study the morphological changes of the composites specimens after UV irradiation, samples were studied with a scanning electron microscope (SEM) (JEOL JSM-T330A) at an accelerating voltage of 10kV.

Results and discussion

BP-added wood-inorganic composites

Table 1 shows the weight percent gain (WPG) and bulking coefficient (*B*) for the BP-added wood–inorganic composites obtained in this study. WPG and *B* increased with increasing molar ratio of BP in the reaction mediums. For these composites, SEM observations were made and the results are shown in Fig. 1. In the BP wood and BP–SiO₂ composites, the inorganic gel could not be observed in the cell lumens as in the untreated wood, and the porous structure of the wood was retained. From these results, the inorganic gel is considered to form in the cell walls in the composites. The photostabilities against UV irradiation were evaluated for the composites.

Photostability of BP-added wood-inorganic composites

Figure 2 shows the SEM micrographs for the BP-added wood–inorganic composites after UV irradiation. For comparison, results for the untreated wood and SiO_2 composites are also shown in Fig. 2. Erosions of the middle lamella, and

Table 1. Weight percent gain (WPG) and bulking coefficient (B) of various BP-added wood-inorganic composites

Composites ^a	WPG (%)	B(%)
SiO ₂	3.5	2.9
0.002BP	2.7	0.7
0.01BP	3.6	1.0
0.1BP	10.3	2.4
0.002BP-SiO ₂	4.1	3.7
0.01BP-SiO ₂	5.2	4.3
0.1BP-SiO ₂	14.3	4.9

^a 0.002, 0.01, and 0.1 indicate the molar ratios of BP to tetraethoxysilane in the reaction mediums

distortions and degradations of cell walls were found in the untreated wood. These were observed less in the SiO_2 composites. From this result, the SiO_2 composites are thought to have some photostability, as reported previously.¹¹ How-



Fig. 1a,b. Scanning electron microscopy (SEM) micrographs for 0.1BP-added wood–inorganic composites. **a** BP wood (10.3 WPG), **b** BP–SiO₂ composite (14.3 WPG)

ever, the BP wood and BP–SiO₂ composites clearly showed high photostability without any morphological changes.

Figure 3 shows the color difference (ΔE^*) for the BPadded wood–inorganic composites, compared with the untreated wood and the SiO₂ composites. Although the SiO₂ composites were slightly lower in ΔE^* compared with the untreated wood, the BP wood showed much smaller ΔE^* , indicating its color changes were restrained to some extent. In the BP–SiO₂ composites, small color changes were observed. Therefore, it is obvious that the BP–SiO₂ composites have enhanced photostability against UV light. These results agree well with the results of SEM observations shown in Fig. 2.

DRIFT analyses were conducted to evaluate the chemical changes that occur in the prepared composites caused by UV irradiation. Prior to this evaluation, however, we studied the chemical changes of milled wood lignin, glucomannan, and cellulose (avicel) by FT-IR spectroscopy



Fig. 3. Changes in the color difference (ΔE^*) for 0.1BP-added wood-inorganic composites caused by UV irradiation

Fig. 2a–d. SEM micrographs for 0.1BP-added wood–inorganic compsoites after UV irradiation for 144 h. **a** Untreated, **b** SiO₂ composite (3.5 WPG), **c** BP wood (13.0 WPG), **d** BP–SiO₂ composite (14.3 WPG)







Fig. 4. Infrared spectra for milled wood lignin, glucomannan, and cellulose before (*a*) and after (*b*) UV irradiation for 144h

Fig. 5. Infrared spectra for SiO_2 gel and BP gel before (*a*) and after (*b*) UV irradiation for 144 h

after UV irradiation. SiO_2 gel and BP gel, as the inorganic components in the prepared composites, were also studied after UV irradiation. By doing so, the chemical changes of the prepared composites could be evaluated more clearly.

Figure 4 shows the infrared spectra obtained from milled wood lignin, glucomannan, and cellulose before and after UV irradiation. In the spectrum of milled wood lignin, the peaks at around 1515 cm^{-1} , derived from C=C in aromatic ring,¹² and around 1740 cm⁻¹, derived from C=O,¹³ were observed to decrease and increase in absorption, respectively. These results indicated that lignin was easily degraded and changed its chemical structure because of UV irradiation. In glucomannan and cellulose, on the other hand, abrupt changes in their spectra could not be observed before and after UV irradiation, indicating that glucomannan and cellulose have photostability against UV light. The characteristic peak for these materials at 895 cm⁻¹, derived from C—H in pyranose rings,¹⁴ was also found to be unchanged. Figure 5 shows the infrared spectra obtained from SiO₂ gel and BP gel used as inorganic components in the prepared wood-inorganic composites before and after UV irradiation. These gels were also found to be stable against UV light without any abrupt changes in their spectra.

From these results, the BP-added wood-inorganic composites prepared in this study should be evaluated for photostability against UV irradiation by comparing changes in the peaks at 1515 cm^{-1} and 1740 cm^{-1} relative to the absorption at 895 cm^{-1} .

Figure 6 shows the DRIFT spectra obtained for the wood-inorganic composites with an added BP molar ratio of 0.1 before and after UV irradiation. For comparison, the results of the untreated wood and SiO₂ composites are also shown. In the untreated wood, the peak at 1515 cm⁻¹ almost disappeared despite the appearance of a shoulder peak, while the peak at around 1740 cm⁻¹ became larger. This is caused by the degradation of lignin in wood by UV light as mentioned above. The SiO₂ composites showed that although the peak at 1515 cm⁻¹ was also weakened after UV irradiation, it was not as badly affected when compared with untreated wood. In the BP wood, the peak at $1515 \,\mathrm{cm}^{-1}$ was weakened and almost disappeared after UV irradiation. However, in the BP-SiO₂ composites, changes in the spectra before and after UV irradiation were hardly noticeable because of the protection against lignin degradation. These results clearly show that the BP–SiO₂ composites attained enhanced photostability against UV light. This is because BP has a benzophenone group that acts as a UV absorbent and a trimethoxysilyl group that can be bound covalently with TEOS by sol-gel reaction to form SiO₂ gel. Although a similar reaction can be expected in both BP wood and BP–SiO₂ composites, the photostability of the







Fig. 7. The mechanism of UV light absorption of benzophenone

latter is much higher than that of former. In our previous studies on enhancing water repellency by using a silicon alkoxide with a long hydrophobic alkyl chain,^{8,10} it was apparent that uniform distribution of the hydrophobic chain within the wood cells was significant for enhancing the properties of wood. Therefore, the difference of the photostability between the BP wood and BP–SiO₂ composites as seen in this study is probably because BP, with a functional group of benzophenone, is more soluble and less aggregated in the reaction medium of TEOS/THF/acetic acid, compared with that of THF/acetic acid, and thus is more uniformly distributed within the wood cells in the BP–SiO₂ composites.

In addition, the benzophenone group is thought to be stable against UV light because of the transformation of energy from UV light into heat emission as shown in Fig. 7.¹⁵ Therefore, the BP–SiO₂ wood–inorganic composites prepared in this study can be expected to maintain their high photostability for a long period.

Conclusions

It is noteworthy that the BP–SiO₂ wood–inorganic composites, with only 15% in WPG at most, are highly photostable while keeping the porous structure of wood. It is also emphasized that this high photostability of the BP–SiO₂ wood–inorganic composites would be sustainable for a long period.

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