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Reaction Characteristics on the Green Surface of Moso Bamboo (*Phyllostachys pubescens* Mazel) Treated with Chromated Phosphate

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Keywords

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Summary

Standing moso bamboo (*Phyllostachys pubescens* Mazel) culm is attractive to many people for its green color, but it fades readily if it is not chemically treated. Chromated phosphate (CP) has been successfully used to protect the green color of bamboo. In order to understand the mechanisms of such protection with CP, this study was performed using various surface analytical methods (FTIR, ESCA, and ESR) to examine the characteristic structures on the CP treated bamboo surface. The results revealed that pigments remaining in the bamboo epidermis did not affect the color of bamboo during subsequent green-color-protection treatment. After CP treatment, chromium and phosphorous from CP were located in the epidermis and cortical parenchyma of bamboo epidermal tissue. CP oxidized the chemical components on the bamboo surface and consequently generated a large number of carbonyl groups and radicals. Meanwhile, the valence states of Cr were reduced from Cr(VI) to Cr(V) and then to Cr(III).

Introduction

In many countries, especially in those in Asia, bamboo is an enormous natural resource and plays an important role in people's daily lives and culture. This is due to its rapid growth rate, excellent flexibility and excellent machinability. It is used widely as a material for construction, furniture, pulping and handicraft works. Without any preservation or protective treatment, bamboo culm is susceptible to attack by fungi and insects, resulting in degradation of its performance, shortening of its service life and reduction of its value.

To extend the service life and increase the utility and economic value of bamboo, many researchers have used chemicals such as acid copper chromate (ACC), Tanalith C (CCA type preservative), Boliden K-33 (CCA type preservative), nickel nitrate and copper sulfate to evaluate effects on green-color protection and green-color fastness of bamboo culms (Lee and Chang 1990; Chang and Chang 1994; Chang and Lee 1996; Chang 1997). Among these, Boliden K-33 has been demonstrated to be the most effective, both in preserving the green color on the culm surfaces and having good lightfastness and weathering durability (Chang and Lee 1996; Chang 1997). Unfortunately, the arsenic component in Boliden K-33 has been recognized to be harmful to human health and to have an adverse impact on the environment. Hence, many countries such as Indonesia and Germany have banned or restricted the use of this compound.

About 30 years ago in Sweden the arsenic-free wood preservative known as Boliden P50 was developed with a phosphoric component (P_2O_5 belonging to the same VA group as arsenic in the periodic table) replacing the arsenic component (As_2O_5) in CCA (Richardson 1993). Taking advantage of this, two arsenic-free preservatives were developed by the authors, chromated copper phosphate (CCP) and chromated phosphate (CP), and have been proven to be effective green-color protectors for ma bamboo (*Dendrocalamus latiflorus* Munro), one of the most popular and valuable species in Taiwan (Chang and Wu 2000 a). Ma bamboo culms treated with CCP or CP exhibited excellent color fastness (Chang and Wu 2000 b).

Besides ma bamboo, recent research has found that using the same chemical treatments can also effectively protect the green color of moso bamboo (*Phyllostachys pubescens* Mazel), another important economic species of bamboo in Taiwan. The treated specimens exhibit excellent green color fastness in both accelerated UV lightfastness testing and outdoor weathering exposure (Chang and Yeh 2001).

Even though some research has been done on the effects of alkali pretreatment on green color conservation of bamboo (Chang and Yeh 2000) and effects of environmental factors such as oxygen and light on the color variation of CrO_3-treated bamboo (Chang and Wu 2000 b), the mechanisms of green-color conservation are still unclear. To further understand the mechanisms of protection by chromium-based green-color-protecting agents, various analytical methods, including spectroscopy, were used.

Materials and Methods

Sample preparation

Three-year-old moso bamboo (*Phyllostachys pubescens* Mazel) culms were obtained from the Forest Land of Taiwan Forest

Research Institute in Nan-Tou County. The bamboo culms were cut into strips (100 mm (longitudinal) × 15 mm (tangential) × 40 mm (radial)) and stored at 4 °C in the dark prior to use. Before treatment with the green-color protection reagents, the bamboo specimens were pretreated at 80 °C with a mixture of 2 % potassium hydroxide and 3 % surfactant for 30 min to remove the waxes from the moso bamboo surface and provide better penetration (Chang and Yeh 2000).

Chemical treatments

Alkali-pretreated moso bamboo specimens were treated at 60 °C with 2 % (W/W) chromated phosphate (CP) for 6 h (ratio of CrO_3 to H_3PO_4 was 1) followed by a water rinse and then dried at 60 °C for 12 h.

Analytical methods

The color measurements were conducted using a Micro Color Meter (Dr. Lange Co., Germany). The light source was D_{65} and the diameter of measuring window was 10 mm. Specimens were placed directly at the measuring window and the tristimulus values X, Y, and Z of the specimens were obtained directly from the colorimeter. The test was conducted according to TAPPI T524 om-79, the parameter of CIE LAB color system, a*(a* = 500[(X/94.81)$^{1/3}$– (Y/100)$^{1/3}$]), was calculated. The value of a* is the best parameter to show the colors red and green. A positive a* value denotes a red sample and a negative value indicates a green sample. The smaller the value of a*, the greener the sample.

The bamboo surface morphologies, elements mapping and line scanning were examined by a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDX, Hitachi S-2400, Japan). The critical point-dried specimens were taped on circular holders and coated with carbon. Carbon-coated samples were imaged at 15 kV.

The detection of residual chromium (VI) ions in bamboo epidermis was done by titration based on a colorimetric assay described by Forsyth and Morrell (1990). CP treated bamboo epidermis (0.2 g) was reacted with chromotropic acid (20 ml) for 30 min at room temperature. The solutions were filtrated (3G4 filter cup) and the filtrates analyzed by ultraviolet-visible (UV/Vis) spectrophotometry (Jasco V-550, Japan) at 350 nm.

Chemical analysis of bamboo epidermis was carried out using Fourier transform infrared spectroscopy (FTIR, Bio-rad FTS-7, USA). The specimen (1 mg) was mixed with KBr (200 mg), ground into powder and then pressed into a disc for FTIR analysis. Data were collected from 400 cm^{-1} to 4000 cm^{-1} with 64 scans for each sample. The resolution was 8 cm^{-1}.

After the bamboo culm was dried in a vacuum desiccator, the surface chemical compositions of specimens were analyzed using an electron spectroscopy for chemical analysis spectrometer (ESCA, Perkin-Elmer PHI-1600, USA) equipped with a magnesium (Mg) anode (15 kV). Survey scan and detail scan, with pass energy being set at 117.40 eV and 11.75 eV, were applied to the bamboo surface and curve fitting was used to deconvolute the $C_{(1S)}$ peak. The corrected binding energy was calculated. The full width at half maximum (FWHM) height of C1, C2, C3 and C4 were restricted to 1.51 ± 0.20 eV.

The valences of chromium ions and free radicals of bamboo were recorded on an X-band electron spin resonance spectrometer (ESR, Brucker EMX-10, USA). The ESR measurements were carried out at a microwave frequency of 9GHz. All spectra were measured at 25 °C. DPPH (α,α'-diphenyl-β-picrylhydrazyl) was used as the standard reference.

Results and Discussion

The green color of the surface of bamboo is mainly due to chlorophylls in the epidermis. A recent study on the green color protection of moso bamboo revealed that chlorophylls a and b in the bamboo epidermis were modified during the brief hot KOH pretreatment (Chang and Yeh 2000). The remaining pigments were mainly lutein and chlorophyll a-1. The surface color of KOH-pretreated bamboo was still green after CP treatment. However, it is not clear whether the composition of this green color is still related to pigments in bamboo epidermis after KOH pretreatment. In order to answer this question, one KOH-pretreated bamboo sample was extracted thoroughly with acetone and the other was not. Both specimens were then treated with CP for 6 h. The color parameters of both specimens are compared (see Table1). For the KOH pretreated bamboo without acetone extraction, the a* value is –4.5 and then becomes –13.3 after CP treatment. However, the a* values of acetone extracted bamboo before and after CP treatment are –0.8 and –13.5, respectively. It is obvious that both CP treated specimens exhibit similar green color. This revealed that the pigments remaining in the bamboo epidermis did not affect the color of bamboo during green-color-protecting treatment.

Table 1. Effect of acetone extraction on the a* value of moso bamboo treated with CP

Specimens	Acetone extraction	
	No	Yes
Before CP treatment	–4.5	–0.8
After CP treatment	–13.3	–13.5

To understand the distribution of green-color-protecting agent on the bamboo surface, SEM-EDX was used to examine the elemental constituents of CP. The result showed that chromium and phosphorus were distributed evenly over the CP treated bamboo surface. From the SEM-EDX line scanning diagram (Fig. 1) of the radial section of CP treated bamboo, chromium was principally distributed in the epidermis cells and cortical parenchyma of bamboo epidermal tissue, but rarely found in the interior vascular tissue of bamboo. Phosphorus showed a similar pattern.

Because all the constituents of CP were located in the bamboo epidermal tissue, some chemical reactions may

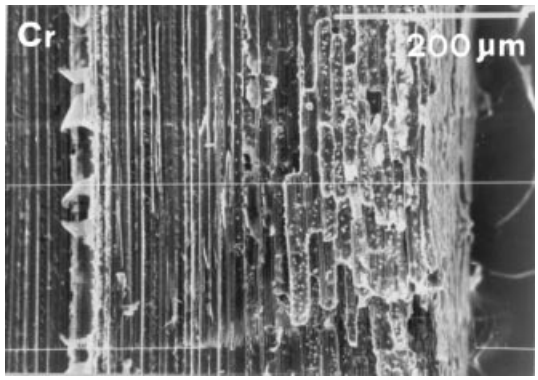

Fig. 1. SEM-EDX line scanning diagram of chromium in a radial section of CP treated moso bamboo.

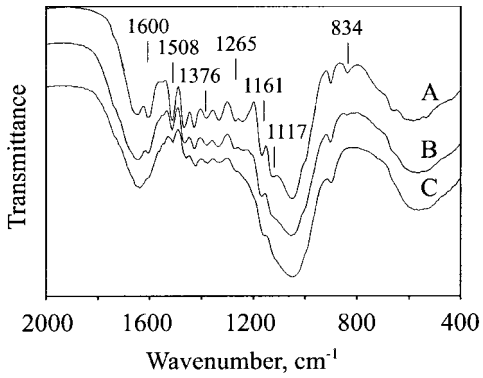

Fig. 2. FTIR spectra of pretreated bamboo epidermis after reaction with CP. A: pretreated, B: CP treated for 1 h, C: CP treated for 6 h.

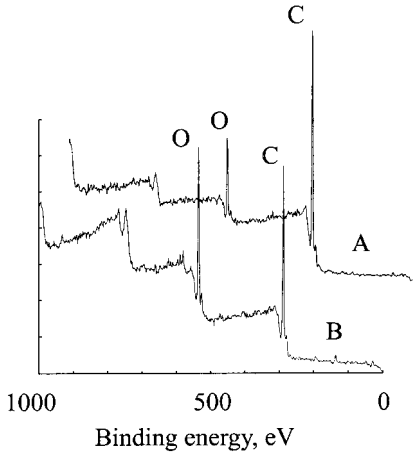

Fig. 3. ESCA survey scan spectra of pretreated bamboo epidermis after reaction with CP. A: pretreated, B: CP treated for 6 h.

have taken place. FTIR spectroscopy was used to profile any chemical structural changes in the bamboo epidermis. The time-dependent FTIR spectra of CP treated bamboo are shown in Figure 2. After reaction for 1 h (Fig. 2B), the characteristic absorption of the lignin aromatic ring at 1600 cm^{-1} and 1508 cm^{-1}, and C-H out-of-plane vibration absorption of lignin at 834 cm^{-1} were reduced significantly. An accompanying reduction can also be found at 1265 cm^{-1}, C-O absorption of lignin. As for the intensities of C-O peaks of cellulose and hemicelluloses at 1161 cm^{-1} and 1117 cm^{-1}, they were also decreased but the extent of diminution was less than that of lignin. However, after reaction for 6 h (Fig. 2C), the related peaks of lignin, C-O peaks of cellulose and hemicelluloses at 1161 cm^{-1}, C-H deformation at 1462, 1423, 1376, and 1329 cm^{-1} all became weakened. The carbonyl absorption near 1640~1730 cm^{-1} became broader after reaction for 6 h. These results revealed that, in the process of CP treatment, lignin was oxidized first, followed by carbohydrates, as observed by an increase in carbonyl bands.

ESCA was used to evaluate the changes in carbon and oxygen elements in the pretreated bamboo surface during CP treatments. The result is shown in Figure 3. The oxygen to carbon ratio (O/C) of pretreated bamboo was 0.18 and after reacting with CP for 6 h became 0.34, suggesting the bamboo surface was oxidized. The high resolution scan of the $C_{(1S)}$ peak of the pretreated bamboo after CP reaction was carried out, and deconvoluted by curve fitting into C1 (285.00 eV), C2 (286.54 eV), C3 (288.15 eV) and C4 (289.23 eV) bands, with the ratios of 61 : 29 : 7 : 3, respectively (Fig. 4B). In comparison to the pretreated specimen (C1 : C2 : C3 = 75 : 23 : 2) (Fig. 4A), the C1 component decreased, whereas the C2 and C3 components increased, and C4 was generated simultaneously. The C4 is assigned to a carbon bearing three oxygens (*e. g.* carboxylic acid or ester) (Dorris and Gray 1978 a, b). This was confirmed by the appearance of a broader IR absorption peak near 1640 ~ 1730 cm^{-1} of CP treated bamboo (Fig. 2C). This result is similar to that reported by Ostmeyer *et al.* (1988) who studied the reaction of southern yellow pine with CCA. It also coincides with the results obtained from the formation of an activated bamboo surface by treating it with chromic acid (Kawamura and Kotani 1992).

Since oxidation/reduction reactions occur together, it was necessary to observe the reduction reaction. Chromium in CrO_3 is in VI state and is diamagnetic. During the reaction with bamboo, Cr(VI) may be reduced to Cr(V) or Cr(III), both of which are paramagnetic and these changes

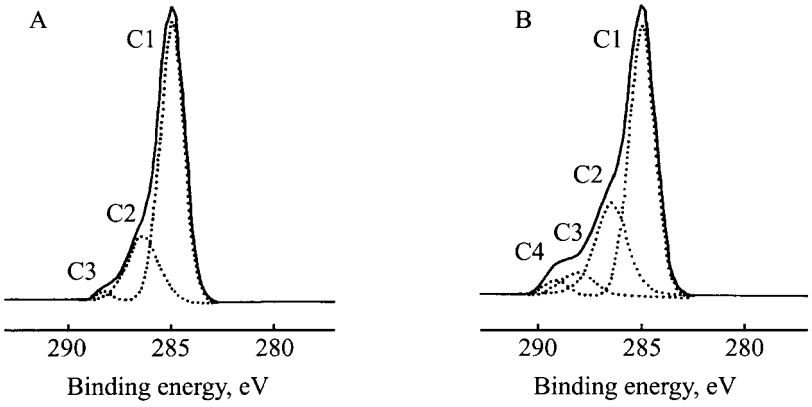

Fig. 4. Curve fitting of $C_{(1S)}$ core level in the ESCA spectra of pretreated bamboo epidermis after reaction with CP for 6 h. A: pretreated bamboo, B: pretreated bamboo reacted with CP for 6 h.

can be observed by ESR spectroscopy. The free radicals formed on the bamboo surface were also examined. The ESR spectra of pretreated bamboo culms after reaction with CP for 1, 3 and 6 h are shown in Figure 5. All spectra lines can be observed as a signal at ca. 3200~3800 Gauss with a line width of ca. 580 Gauss and a g-value of ca. 2.0. This is the characteristic signal of Cr(III) and the peak intensity increases and broadens as the reaction proceeds. It was observed that a large quantity of Cr(III) was produced as the reaction proceeded and that more than one Cr(III) species was formed as seen during the fixation process of CCA-treated wood (Ruddick *et al.* 1994).

In the center of the Cr(III) signal in Figure 5, there were two sharp signals at ca. 3500 Gauss. After expanding this region, as shown in Figure 6, the left peak, g = 2.0044 with a line width of 15 Gauss, was clarified. The intensity of this peak was shown to increase as CP treatment proceeded. A similar signal was detected from CP treated milled wood lignin, but not from CP treated filter paper (cellulose). Hon (1992) analyzed milled wood lignin and lignin model compounds by ESR and reported that the g-value of phenoxy radical was 2.0024 with a line width of 16 Gauss. In addition, Hon and Feist (1992) also used ESR to detect the phenoxy radical, with a g-value of 2.0023 and a line width of 15 Gauss, in southern yellow pine after photo-irradiation. Hence, the left peak signal in CP treated bamboo was due to the phenoxy radical of bamboo.

As for the right peak at g = 1.979 in Figure 6, it is known to be the signal of Cr(V). Hughes *et al.* (1994) reported the appearance of Cr(V) signal at g = 1.974 ~ 1.978 from CCA-treated Scots pine (*Pinus sylvestris*). Ruddick *et al.* (1994) also found a similar peak at g = 1.980 from CCA-treated Ponderosa pine (*Pinus ponderosa* Laws). As the treatment time increased, the intensity of Cr(V) signal became weaker. This shows that the Cr(V) content of CP treated bamboo reduced gradually and Cr(III) compounds were formed, as demonstrated by the enhanced Cr(III) signal (Fig. 5).

Because the Cr(VI) is diamagnetic in the treatment process, ESR cannot be used to detect the signal and hence chromotropic acid procedure (Forsyth and Morrell 1990) was used to titrate the amount of Cr(VI) of the CP treated bamboo epidermis. The principle of this method is to detect the absorption peak at 350 nm from the solution of chromotropic acid reacted with CP treated bamboo epidermis. The results obtained are shown in Figure 7. The intensity of 350 nm became weaker as the reaction time increased. The Cr(VI) content of bamboo CP treated for 6 h decreased to 36 % in comparison with the original amount at the initial stage. Thereby during the reaction of CP and moso bamboo, the chromium oxidizes the chemical constituents of bamboo with the production of phenoxy radical compounds and, consequently, the valence states of chromium are reduced from Cr(VI) to Cr(V) and finally to Cr(III).

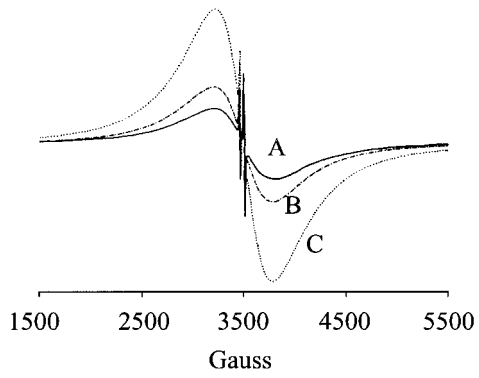

Fig. 5. ESR spectra of pretreated moso bamboo after reaction with CP for different times at 25 °C. A: reaction for 1 h, B: reaction for 3 h, C: reaction for 6 h.

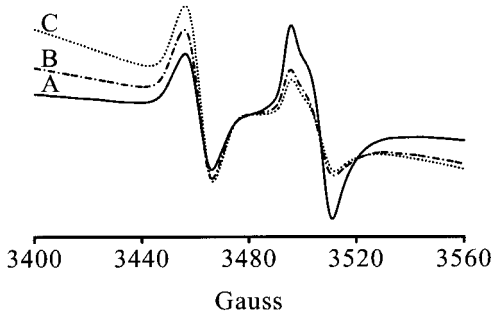

Fig. 6. ESR spectra of pretreated moso bamboo after reaction with CP for different times at 25 °C. A: reaction for 1 h, B: reaction for 3 h, C: reaction for 6 h.

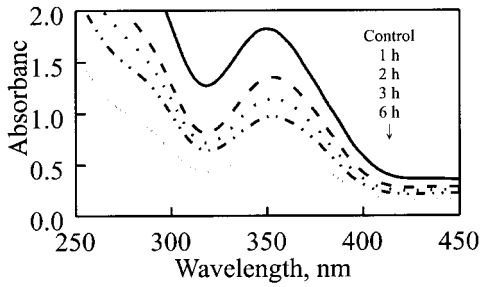

Fig. 7. Changes of Cr (VI) remained in bamboo epidermis after treatment with CP for different times.

Conclusions

To understand the mechanisms of green-color protection of moso bamboo afforded by chromated phosphate (CP), this study was carried out using various surface and chemical analytical methods to evaluate the characteristic structure variations on the CP treated bamboo surface. The results revealed that pigments remaining in the alkali-pretreated bamboo epidermis after acetone extraction did not affect the color of bamboo in the subsequent green-color protection treatment. After the treatment with CP, chromium and phosphorous were evenly distributed in the epidermis and cortical parenchyma of bamboo epidermal tissue. The chromic acid and phosphate reacted with the bamboo epidermis, leading to oxidation with the formation of a certain amount of carbonyl derivatives and radicals. The valence states of chromium were then reduced from Cr(VI) to Cr(V) and finally to Cr(III). Experiments on compounds causing the green surface of moso bamboo culms after reaction with CP are still in progress.

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