Holzforschung
54 (2000) 327–330

Stabilizing Effect of Chromated Salt Treatment on the Green Color of Ma Bamboo (*Dendrocalamus latiflorus*)

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Keywords

Dendrocalamus latiflorus
Munro
Green color fastness
CCP (chromated copper phosphate)
CP (chromated phosphate)

Summary

Processed bamboo culms capable of maintaining the greenish color in their skin have increased economic value. The use of protectors to preserve the green color and to improve the color fastness of bamboo culms has, therefore, attracted great interest in the industry. In this paper three exposure tests, including accelerated UV lightfastness, outdoor weathering, and indoor exposure, were used to evaluate the color fastness of ma bamboo (*Dendrocalamus latiflorus* Munro) treated with chromium based reagents. Experimental results revealed that bamboo culms treated with CCP (chromated copper phosphate) or CP (chromated phosphate), both homemade by the authors, exhibited excellent color fastness. Among all inorganic salt-treated bamboo culms the CP-treated samples had the brighter greenish skin and also provided the best green color fastness. It was further noticed that ultraviolet light plays an important role on the color conversion of CrO_3-treated bamboo. The green color becomes significantly enhanced with increased exposure time.

Introduction

Bamboo, a perennial lignified plant which belongs to *Bambusoideae*, is one of the most important forest resources as it grows faster than any other woody plant on earth (Liese 1987). In many countries, especially in China, bamboo is a vast natural resource and plays an important part in the daily life and in cultures, as well. Because of its rapid growth rate, excellent flexibility, and easy machinability, it is used widely as an industry material for pulping, furniture, and construction.

Among the varieties of bamboo in Taiwan, ma bamboo (*Dendrocalamus latiflorus* Munro) is one of the most popular and valuable species. It exhibits a fascinating greenish skin, thanks to the abundant chlorophyll in its epidermis. However, it is generally known that after harvest, plants and organisms with green appearance are susceptible to discoloration resulting from the degradation of chlorophyll. Numerous studies had reported that light, oxygen (Llewellyn *et al*. 1990a; 1990b; Struck *et al*. 1990), and enzymes (Yamauchi and Watada 1991) played an important role during chlorophyll degradation, both *in vitro* and *in vivo*. Unfortunately, similar to the plants with green appearance, the green color of bamboo culm fades as a result of deterioration of chlorophyll when exposed at ambient conditions.

To develop a method that prevents the fading of green color of bamboo culms and that the bamboo industry becomes motivated to explore potential applications, and subsequently increase the economic value of bamboo products, a study of chemical treatments was initiated. Chemical reagents including chromates, nickel salts, and copper salts *etc*. were used as protectors in our previous paper (Lee and Chang 1990; Chang and Chang 1994; Chang and Lee 1996; Chang 1997). Among these chemicals employed, CCA (chromated copper arsenate) such as Boliden K-33 produced excellent green color conservation results. The 45.4 % arsenic contained in CCA, however, has been recognized as having an adverse impact on the environment. To develop an arsenic-free formula, phosphoric (belonging to the same VA group as arsenic in the periodic table) compounds were tested. It demonstrated, as reported in another paper by us (Chang and Wu 2000), that green color conservation was indeed achieved when the arsenic component in CCA was replaced by phosphoric compound. CCP (chromated copper phosphate) and CP (chromated phosphate) were two successfully developed examples in which the H_3PO_4 replaced As_2O_5 and both proved to be good green color protectors.

To further understand the effectiveness of green color fastness using these treatments, a special study was conducted and is reported in this paper. In addition, the effects of environmental factors such as light and oxygen on the color of CrO_3-treated bamboo were also investigated.

Materials and Methods

Materials

Three year-old ma bamboo (*Dendrocalamus latiflorus* Munro) was obtained from the experimental forest of National Taiwan University. The green bamboo was cut into 4 cm × 1.5 cm × 0.4 cm pieces to be used as specimens. Four inorganic salts, including CCA (chromated copper arsenate; 19.6 % CuO, 35.3 % CrO_3, 45.1 % As_2O_5), CCP (chromated copper phosphate; 33.3 % CrO_3, 33.3 % $CuSO_4$, 33.3 % H_3PO_4), CP (chromated phosphate; 50 % CrO_3, 50 % H_3PO_4) and chromium trioxide (CrO_3) were used

Table 1. Controlled exposure conditions for studying the effect of environmental factors on the color of ma bamboo treated with CrO_3

Abbr.	Environmental factors Light	Oxygen	Exposure conditions
Control	✗	✗	Specimens were covered with aluminium foil and put into a closed quartz tube which was purged with nitrogen
UVN	✓	✗	Specimens were put into a closed quartz tube which was purged with nitrogen and irradiated with UVA-340
UVO	✓	✓	Specimens were put into an open quartz tube and irradiated with UVA-340

as protectors in treating the samples. The concentration of each reagent preparation was 2 %, and in addition 5 % CCA was also examined.

Pretreatment

Results in our previous studies indicated that before treating with inorganic salts, alkali pretreatment was required to achieve green color conservation of bamboo culms (Chang and Lee 1996; Chang 1997). Therefore, the bamboo specimens were pretreated at 80 °C in 4 % potassium carbonate containing 1 % surfactant for 30 min. to remove the wax layer on the outer surfaces, and then carefully rinsed with water.

Chemical treatments

After alkali-pretreatment, the samples were soaked in one of the four reagent (CCA, CCP, CP, and CrO_3) baths at 60 °C for 6 h, then dried at 60 °C for 12 h.

Measurement of surface color

The color change of specimens was measured with a color and color difference meter (Dr. Lange Co.) equipped with a D_{65} light source and a 5 mm diameter test-window. The tristmulus values X, Y, Z of all specimens were obtained directly from the colorimeter. Then the recommended CIE (Commission Internationale d'Eclairage) L*, a* and b* color parameters were computed. The brightness difference (ΔL*), the difference of a* component (Δa*), and the difference of b* component (Δb*) were then calculated based on the following formulas (Chang 1986; Chang and Lee 1996):

$\Delta L^* = L_t^* - L_0^*$, $\Delta a^* = a_t^* - a_0^*$, $\Delta b^* = b_t^* - b_0^*$; where L_t^*, a_t^*, and b_t^* = L*, a*, and b* of the treated (or exposed) sample, respectively; L_0^*, a_0^*, and b_0^* = L*, a*, and b* of the control reference, respectively; L* = the value on the white/black axis; a* = the value on the red/green axis; b* = the value on the blue/yellow axis.

Exposure test

Ma bamboo samples treated with different chromium based reagents were exposed to various conditions in the color fastness study. The exposure conditions include an artificially accelerated lightfastness tester made by Q-Panel Co. It uses a light source of UVA-340 sunlamp and the temperature of the black panel is 60 ± 2 °C. An outdoor weathering rack was also used. It was positioned at a 45° angle facing the South. For comparison, also an indoor exposure rack was used. The samples were exposed to these conditions for 32, 42, and 70 days, respectively. In addition, the effects of environmental factors such as light and oxygen on the green color were also investigated. Specimens were placed in a quartz tube and then exposed to three different conditions as summarized in Table 1.

Results and Discussion

Color variations of ma bamboo treated with chromium based reagents were evaluated using the CIE LAB color specifications. The CIE LAB color parameters L*, a*, and b* of fresh ma bamboo culm were 32.7, –5.3, and 16.7, respectively. The a* value is a color parameter on the red/green axis. Positive a* value represents red color, whereas negative a* value represents green color. In general, a more negative a* value means a deeper green color. Hence, as described in our previous paper (Chang and Wu 2000), it is rather easy to evaluate the effectiveness of green color development by looking at the a* value. Results from Figure 1 showed that the a* value of alkali-pretreated ma bamboo, without inorganic salt treatment, was –1.5 and those treated with 5 % CCA, 2 % CCA, 2 % CCP, 2 % CP, and 2 % CrO_3 were –5.5, 4.5, –0.3, –16.6, and 10.5, respectively. Comparison of the a* values of specimens treated with two different concentrations of CCA (2 % and 5 %) showed that 2 % CCA was ineffective on green color conservation, whereas the 5 % CCA group exhibited excellent green color performance with a* = –5.5. The best green color conservation result, among all of the reagents employed, however, was obtained (Fig. 1) by 2 % CP treatment. The L*, a*, and b* color parameters of 2 % CP-treated ma bamboo culm were 48.8, –16.6, and 17.4, respectively. Differences in the color parameters between 2 % CP-treated bamboo and fresh specimen were 16.1 (ΔL*), –11.3 (Δa*), and 0.7 (Δb*). It is shown that the treated color was not only greener but also brighter. In order to evaluate their color fastness, three different exposure tests including accelerated UV lightfastness, outdoor weathering, and indoor exposure were employed.

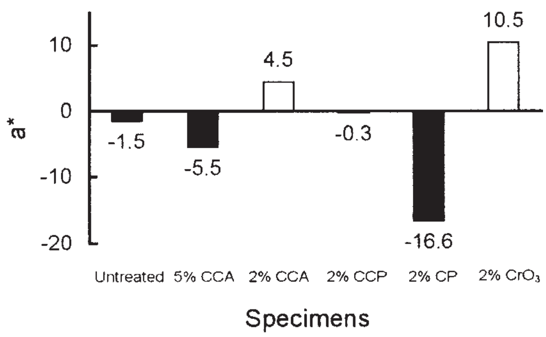

Fig. 1. The a* values of ma bamboo culms treated with CCA, CCP, CP, and CrO_3.

Accelerated UV lightfastness test

Ma bamboo culms treated with different inorganic salts were irradiated with ultraviolet light for 32 days. After irradiation the color fastness of the specimens was evaluated by comparing changes in their a* values. The results demonstrated that, except CrO_3, the other three inorganic salts employed all provided quite effective color fastness for alkali-pretreated ma bamboo (Fig. 2). Among the inorganic salts used, CCP- and CP-treated bamboo specimens possessed better color fastness than the others did. The Δa* values of ma bamboo specimens treated with CCP or CP ranged between 0 and -5 after the 32 day exposure period. The untreated and the CrO_3-treated samples showed the most significant variation in a* values. Their Δa* values were between 10 ~ 16 and –7 ~ –17, respectively. Another finding is that the a* value of CrO_3-treated bamboo decreases with increased exposure time, changing from an initial 10.5 to –6.4 after 32 days of exposure. This indicates that, after irradiation, bamboo specimens treated with CrO_3 surprisingly become greener. A similar result was obtained on CCA-treated wood (Dahlgren 1973). It was suggested that photo-activation before the fixation of reagents in specimens was the cause for the color change on CCA-treated wood. Pigmentation happened when reagents migrated to the surface of specimens and precipitated subsequently.

To study the effects of environmental factors such as oxygen and light on the color variation of CrO_3-treated bamboo, some specimens were exposed in a Q-UV accelerated lightfastness tester under three different environmental conditions, as summarized in Table 1, including Control, UVN, and UVO. The a* value of specimen, exposed to an environment without oxygen and light (Control) for 24 days changed from an initial value of 7.8 to 4.3, as shown in Figure 3. This result indicated that CrO_3-treated ma bamboo only showed a slight green color variation when exposed in the absence of oxygen and light. On the other hand, the a* values of specimen exposed to nitrogen (UVN) or air (UVO) were –4.0 and –6.8, respectively after 24 days of UVA-340 sunlamp irradiation. Although the strength of green color was significantly enhanced by increasing the exposure time (Fig. 3), the change in the a* value became small following 4 days of irradiation. The comparison of the a* values of two different exposure conditions (UVN and UVO) is shown in Figure 3. The results revealed that the oxygen concentration had little influence on the a* value of CrO_3-treated bamboo. Results in Figure 3 also reveal that ultraviolet light plays a much more important role than oxygen and, therefore, is the key factor in influencing the color of CrO_3-treated bamboo.

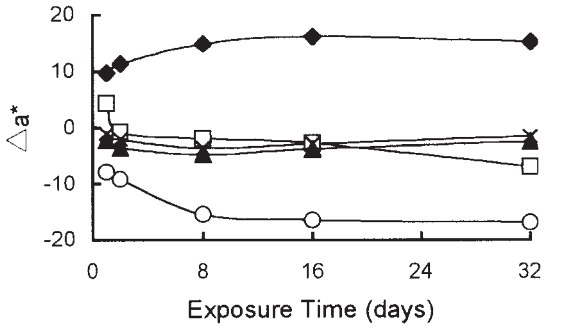

Fig. 2. Change in Δa* of bamboo culms after exposure to an accelerated UV lightfastness test for 32 days. (◆: Untreated; □: 5% CCA; ▲: 2% CCP; ✕: 2% CP; ○: 2% CrO_3).

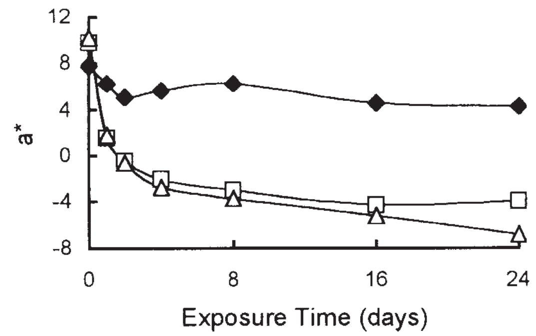

Fig. 3. Effect of light and oxygen on the discoloration of bamboo culms treated with CrO_3 (◆: Control; □: UVN; △: UVO).

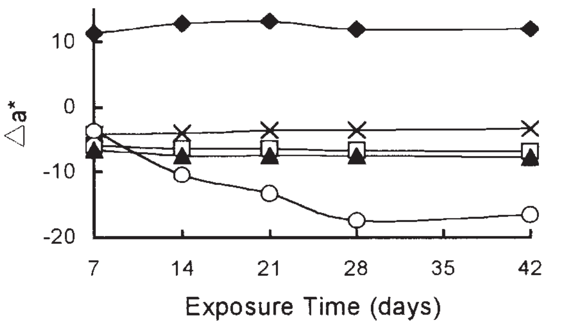

Fig. 4. Change in Δa* of bamboo culms after weathering outdoors for 42 days. (◆: Untreated; □: 5% CCA; ▲: 2% CCP; ✕: 2% CP; ○: 2% CrO_3).

Outdoor weathering

The results of outdoor weathering on the green color fastness were shown in Figure 4. The Δa* variations of specimens, after exposure to outdoor environment for 42 days, were similar to that under accelerated lightfastness test. Among all the inorganic salt-treated bamboo, the CrO_3-treated sample showed the most significant Δa* variation. Its a* value varied from 10.5 down to –6.6 after 42 days of exposure and the sample color was transformed from its original dark brown color to dark green.

Using the Δa* values in Figure 4 as a green color variation index, it was noticed that the green color of all the treated samples, except the CrO_3-treated one, became greener shortly after the exposure began and then remained quite flat for the rest of the 42 days of exposure. This phenomenon demonstrated their eminent color fastness property against weathering. Among them, the CP-treated bamboo sample showed the slightest difference in a* value and, thereby, exhibited the best green color fastness.

Indoor exposure

Only the portion of the light with long wavelengths ($\lambda > 300$ nm) is transmitted through a window glass filter and irradiates on specimen surfaces. Therefore, the discoloration was less significant when the specimens were exposed indoors. A comparison of the Δa* values in Figure

5 showed that after indoor exposure the difference in the a* value of CrO_3-treated specimen was the smallest. In fact, the a* value remains as high as 8.3 after 70 days of exposure. The color of bamboo culm still remained dark brown and this result confirmed that ultraviolet light played a key role on the color conversion of CrO_3-treated bamboo. Besides, the Δa* values that varied between –4 and –6 were almost the same for other specimens treated with inorganic salts. In this respect, the CP treated sample showed the same results as in the accelerated UV lightfastness and weathering resistance tests and the difference among the a* values was the smallest after exposure. This allows the conclusion that ma bamboo culms treated with CP solution possessed the best green color fastness when exposed to oxygen and light.

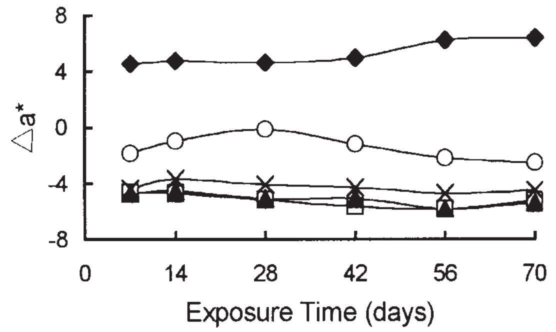

Fig. 5. Change in Δa* of bamboo culms after indoor exposure for 70 days. (◆: Untreated; □: 5% CCA; ▲: 2% CCP; ✕: 2% CP; ○: 2% CrO_3).

Conclusions

Ma bamboo culms treated with different types of chromium-based reagents exhibited a distinct color appearance. From the results of accelerated UV light fastness, outdoor weathering and indoor exposure tests, it was concluded that the CCP (chromated copper phosphate) and CP (chromated phosphate) treated ma bamboo had excellent color fastness. As for the CrO_3 salt, ultraviolet light has a strong effect on its green color conservation. However, its green color is significantly enhanced with increased exposure time. The results, as demonstrated in this paper, show that a durable green color on ma bamboo culm surface can be achieved using 2% CrO_3 treatment and followed by exposure to sunlight or ultraviolet light. Finally, among all of the chemical reagents tested in this study, CP is the most effective one in making the bamboo greener and it also imparted the best green color fastness.

Acknowledgements

This work was carried out as part of a research project (NSC-86-2313-B-002-096) funded by the National Science Council. We would like to thank NSC for the financial support of this project.

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Received April 16th 1999

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