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Polymer Degradation and Stability 74 (2001) 551–557

Polymer Degradation and Stability

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Mechanisms for the surface colour protection of bamboo treated with chromated phosphate

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Received 11 June 2001; accepted 6 July 2001

Abstract

The attractive green appearance of bamboo culm discolours easily without any protective treatment. Chromated phosphate (CP) was used successfully to protect the green surface of bamboo. To further understand the mechanisms of this protective treatment, three model compounds including cellobiose, arabinose and guaiacol, in place of the chemical components of bamboo, were used to react with CP. FTIR with liquid attenuated total reflectance accessory (liquid ATR) was conducted to investigate the reaction between the model compounds and CP. The results revealed that guaiacol had the greatest reactivity toward CP, followed by arabinose and cellobiose. Green precipitates were formed in the solution, as reaction time increased. This green complex was similar to a green pigment, chromic phosphate ($CrPO_4$), in chemical structure. This green complex contributed to the green-colour protection of bamboo treated with CP by precipitation and chemical bonding to its epidermis. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Discolouration; Green-colour protection; Bamboo; Chromated phosphate (CP); FTIR; Model compound

1. Introduction

People, especially those in Asia, are fascinated by bamboo for its green appearance. But without any protective or stabilization treatment, bamboo culms which are rich in chlorophyll and carbohydrates are very susceptible to attack by fungi or insects, and hence discolour easily. This degrades its performance, shortens its service life, and reduces its value. The fading of the greenish colour due to degradation of chlorophyll is known to be caused by light, oxygen [1–3], and enzymes [4].

To inhibit the discolouration and extend the service life of bamboo, some researchers have used chemicals, such as acid copper chromate (ACC), Tanalith C (CCA type wood preservative) and Boliden K-33 (CCA type wood preservative), for green-colour protection of bamboo culms [5–8]. Among these chemicals, Boliden K-33 has been demonstrated to be the most effective, both in protecting the green colour on bamboo culm and in having good lightfastness and weathering durability [7,8]. Unfortunately, many countries such as Indonesia and Germany have banned the use of this compound because of the harmful arsenic component.

In the development of the arsenic-free wood preservatives as known as Boliden P50, a phosphoric component [belonging to the same group (VA) as arsenic in the periodic table], P_2O_5, has replaced the arsenic component (As_2O_5) in CCA about 30 years ago in Scandinavia [9,10]. Taking advantage of this, two arsenic-free bamboo green-colour protectors developed by the authors, chromated copper phosphate (CCP) and chromated phosphate (CP), have been proven to be much superior green-colour protectors than Boliden K-33 both for ma bamboo (*Dendrocalamus latiflorus* Munro) and moso bamboo (*Phyllostachys pubescens* Mazel) [11,12]. For example, the CIE LAB colour parameters of fresh moso bamboo were 40.9 (L^*),−6.7 (a^*), and 17.6 (b^*), respectively. The parameters of CP treated moso bamboo were 41.1 (L^*),−6.6 (a^*), and 21.5 (b^*) with a slight colour difference ($\Delta E^* = 3.9$). Further-

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PII: S0141-3910(01)00192-6

more, these two bamboo culms treated with CP or CCP exhibited excellent colour fastness both in accelerated UV lightfastness and outdoor weathering exposure [12,13].

Although some recent studies [13–15] have tried to examine the mechanism of green-colour protection of bamboo, such as effects of environmental factors (oxygen and light) on the colour variation of chromated salts treated bamboo, changes in the surface property of CP-treated moso bamboo culms, and effects of CP treatment processes on the bamboo green-colour protection, the actual mechanism involved remains unclear. Findings from these previous studies showed that the chlorophyll in the bamboo epidermis was not involved in green-colour protection reaction. After CP treatment, chromium and phosphorous, the main components in CP solution, were located in the epidermis and cortical parenchyma of bamboo epidermal tissue. Fourier transform infrared spectroscopy (FTIR) analysis of the bamboo surface showed that the characteristic absorptions of lignin and carbohydrates were changed greatly [14]. Therefore, we speculate that the chemical components of bamboo might play an important role in green-colour protection of CP-treated bamboo.

Extensive research has been done to study the fixation between wood (or model compounds) and chromium salts in CCA wood preservative [9, 16–23], but little information was related to CP or CCP treated wood except the work of Pizzi and Kubel [9]. They studied the kinetic behaviour of CCP wood preservative in its fixation reactions onto wood and calculated its constituents on wood.

Our study, therefore, was designed to confirm whether the chemical components of bamboo reacted with CP and even bonded with CP. Three model compounds, cellobiose, arabinose and guaiacol, representing three main components of bamboo, cellulose, hemicelluloses and lignin, respectively, were reacted with CP. Reactions were detected by FTIR with liquid attenuated total reflectance accessory (liquid ATR). Results of this study can contribute to a better understanding of the mechanisms involved in green-colour protection of CP-treated bamboo.

2. Materials and methods

2.1. 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 with a dimension of 100 mm (longitudinal) × 15 mm (tangential) × 40 mm (radial) and stored at 4 °C in the dark prior to use. Before being treated with the green-colour protection reagent at 60 °C for 6 h, the bamboo specimens were pretreated at 80 °C with a mixture of 2% potassium hydroxide and 3% sodium lauryl sulfate for 30 min. This pretreatment removes the waxes from the moso bamboo surface and ensures better penetration and reaction for the subsequent green-colour protection treatments [24].

2.2. Chemicals

The green-colour protection reagent used in this experiment was 2% (w/w) chromated phosphate (CP) with a 1:1 ratio of CrO_3 to H_3PO_4.

In order to simulate the reaction between CP and the three main chemical components of bamboo, cellulose, hemicelluloses and lignin, three model compounds, namely cellobiose, arabinose and guaiacol, were dissolved in distilled water with the concentrations of 0.5, 0.5 and 0.16 M, respectively. The mole ratio reacted with CP was 1:1.

2.3. Precipitate isolation

During the reaction of CP and model compounds, the solutions of reaction mixtures were centrifuged at 8000 rpm for 5 min to obtain the precipitates. The collected precipitates were resuspended in 20 ml of distilled water, and then placed in an ultrasonic bath for extraction for 3 min. After extraction, the solution was centrifuged at 8000 rpm for 5 min again, and the supernatant was removed. These procedures for centrifugation and ultrasonic extraction were repeated five times to remove the unreacted model compounds and CP residues in the precipitates. The precipitates were dried in a vacuum oven at 60 °C for 24 h, and then placed in darkness until the spectroscopic analyses were carried out.

2.4. FTIR spectroscopy analysis

Analyses of the chemical structure of precipitates obtained from the reaction of CP and model compounds were carried out using Fourier transform infrared spectroscopy (FTIR, Bio-rad FTS-7, USA). One milligram of the precipitate mixed with 200 mg of KBr was ground into a powder and then pressed into a disc under high pressure before FTIR analysis. Data were collected from 400 to 4000 cm^{-1} with 64 scans for each sample. The resolution was 8 cm^{-1}.

The analyses of liquid samples were also conducted by Fourier transform infrared spectroscopy (FTIR, Bio-rad FTS-7, USA) equipped with liquid attenuated total reflectance accessory (liquid ATR, Graseby Specac Co., USA). The crystal used was ZnSe. Data were collected from 800 to 4000 cm^{-1} with 64 scans for each sample. The resolution was 4 cm^{-1}.

3. Results and discussion

3.1. The reaction of CP with guaiacol

To profile the mechanisms involved in green-colour protection of bamboo afforded by CP treatment, three model compounds, cellobiose, arabinose and guaiacol, were chosen to react with CP solution, and the reactions were monitored using FTIR with liquid ATR accessory. The result implies that guaiacol has the greatest reactivity to CP solution since the solution colour changed immediately. After mixing guaiacol solution with CP, the colour of the solution turned from orange-yellow to reddish-brown, and then to purple-brown. Simultaneously, purple-brown precipitates were also formed in the solution and their colour turned green gradually over 2 weeks. Compounds which are similar to these highly insoluble brown precipitates were also investigated by Pizzi and Kubel [9]. They mixed guaiacol with both CrO_3 and H_3PO_4 solution for 3 h, but no green precipitates were detected. It is probable that the reaction time was not long enough to form green precipitates. Schmalzl et al. [20] mixed guaiacol with only a CrO_3 solution but no green precipitate was formed.

After our precipitates were isolated by centrifugation, the remaining solution was analyzed by liquid ATR. The time-dependent spectra of this solution are shown in Fig. 1. Assignments of the absorption peaks to guaiacol in liquid ATR are also listed in Table 1. The spectrum of guaiacol changed immediately with CP, showing that the aromatic C=C stretching at 1504 cm^{-1} and the C–O–CH_3 vibration at 1264 cm^{-1} reduced (Fig. 1B). Also, the conjugated C=C absorption at 1467 cm^{-1} and the CH bending at 1366 cm^{-1} decreased. However, the aromatic C=C stretching at 1596 cm^{-1} and the C–OH vibration at 1217 cm^{-1} increased. The reason why the 1504 cm^{-1} band was weakened but the 1596 cm^{-1} band was intensified is that the band modes were affected by different substitution changes in the benzene ring as mentioned by Michell [19], who mixed only guaiacol and CrO_3 with 1:1 mole fraction.

The broad peak at 1070 cm^{-1} in Fig. 1B was attributed to the phosphate group absorption in CP solution. The new peak at 1630 cm^{-1} was probably due to the alkene double bond from the ring-opening or ring-substitution reaction between guaiacol and the strong oxidation agent, chromic acid, in CP solution. Kaldas et al. [21] proposed a similar ring-opening and alkylation scheme in lignin and chromium interaction. Jorge et al. [23] also pointed out some evidence of the reaction between CrO_3 and the hydrogen of the benzene ring of guaiacol. But this compound seems to be a transition product because such an absorption peak at 1630 cm^{-1} was not observed in the spectrum of 0.5 h reaction time (Fig. 1C). Both absorption peaks of guaiacol and the phosphate group were weakened after reaction for 0.5 h, demonstrating that guaiacol reacted with CP. As the reactions progressed, the phosphate content of solution was decreased. These results indicated that the reaction positions were in the methoxy or hydroxyl groups on guaiacol, and that the ring-opening or *ortho*-, *meta*-substitution of benzene ring might be another reaction position.

FTIR analysis was employed to examine the chemical structure of the precipitate in this reaction, and the result is shown in Fig. 2. This precipitate (Fig. 2A) had a broad absorption in the range of 3000–3500 cm^{-1}, indicating the existence of some strong intermolecular hydrogen bonds. There was also a phosphate absorption at around 1070 cm^{-1}. This spectrum was similar to that of a green pigment, chromic phosphate ($CrPO_4$), as shown in Fig. 2B, except that some small peaks

Table 1
Assignments of the absorption peaks to guaiacol in the liquid ATR spectrum

Wavenumber, cm^{-1}	Peak assignments
1596	C=C Str. (ar. ring)
1504	C=C Str. (ar. ring)
1467	Conjugated C=C
1366	CH bending
1264	C–OCH_3 Str.
1217	C–OH Str.

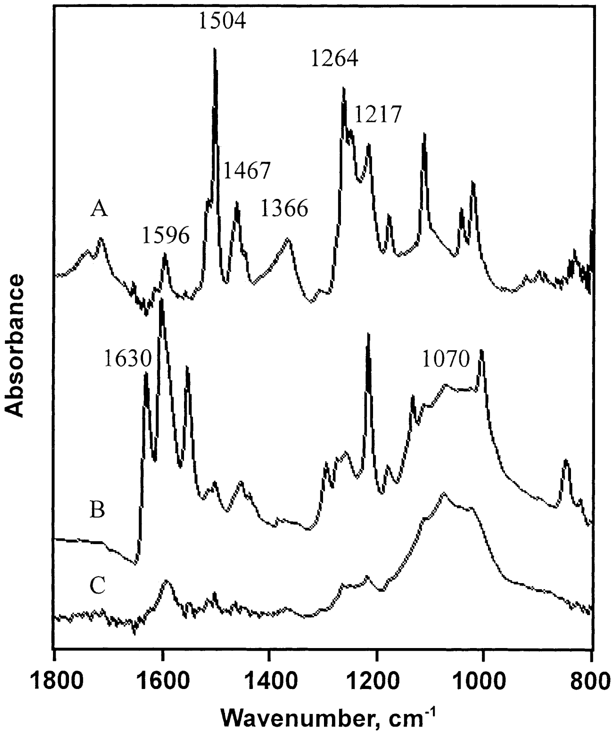

Fig. 1. Liquid ATR spectra of the reaction solution of guaiacol and chromated phosphate (CP). A: guaiacol, B: solution right after reaction, C: solution after 0.5 h reaction.

appeared at 800–1600 cm^{-1} in the spectrum of the precipitate. The precipitate was extracted thoroughly with ethanol to remove the unreacted guaiacol and then analyzed by FTIR. The result revealed no difference between the spectrum of the extracted precipitate and that shown in Fig. 2A. Hence, these small peaks may be due to the cross-linked products from guaiacol and CP reaction.

Furthermore, comparing the spectrum in Fig. 2A with guaiacol (Fig. 2C), no significant guaiacol functionalities were found in Fig. 2A except at 1596, 1504, 1264, and 1217 cm^{-1}. The former two peaks arise from the aromatic ring structure of CP-guaiacol complex and the latter two peaks should arise from this complex structure which chromate ester bonded directly to the unsubstituted carbon position *ortho* and *meta* to the phenolic hydroxy group. Pizzi [18] examined the precipitated complex from guaiacol and CrO_3 reaction and reported a similar type of compound. Hence, guaiacol indeed reacted with CP and some chemical bonds were formed during this reaction.

3.2. The reaction of CP with cellobiose or arabinose

As for the reactions of CP with cellobiose or arabinose, the reactivities of these two model compounds were lower than that of guaiacol, and the reactivity of cellobiose was much lower than that of arabinose. After these two model compounds were reacted with CP, the colour of their solutions turned from orange to yellowish-green (2–3 days), green (4–5 days), followed by formation of green precipitates in both solutions (6–8 days). Pizzi and Kubel [9] mixed glucose (though not the same carbonhydrate here) with CrO_3 and H_3PO_4, and a dark-green precipitate was obtained. They also mentioned the possible existence of $CrPO_4$ in this green precipitate.

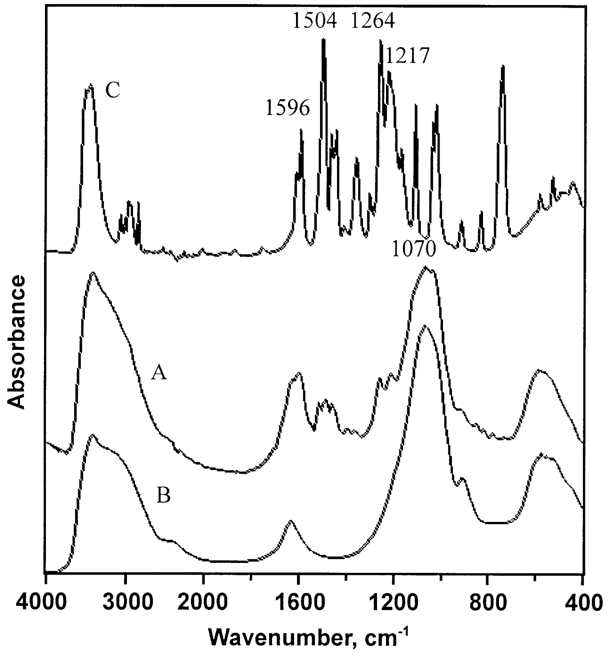

Fig. 2. FTIR spectra of the precipitate generated from the reaction of guaiacol with CP (A), chromic phosphate (B) and guaiacol (C).

In order to understand the reactions of CP with these two model compounds, liquid ATR analysis was employed to examine the supernatant of our reaction mixtures. The spectra showed that the characteristic absorption of each model compound was decreased as time increased, and there was no new absorption peak formed during the reaction (spectra not shown). This revealed that both model compounds were consumed in the reaction.

The precipitates formed in the reaction were isolated, washed, dried, and then analyzed by FTIR. The results are shown in Fig. 3. The spectrum of the green precipitate obtained from the reaction of cellobiose with CP (Fig. 3B) is identical to that obtained from the reaction of arabinose with CP (Fig. 3D). Compared with the spectrum of chromic phosphate (Fig. 3A), the spectra of these two precipitates are also similar to that of chromic phosphate, except for small peaks at 810 and 1410 cm^{-1}. The broad band near 1700 cm^{-1} was probably caused by the carboxyl compounds formed from the reactions of model compounds with CP. Jorge et al. [23] used FTIR to detect the reaction product between methyl-β-cellobioside and CrO_3 and they reported that

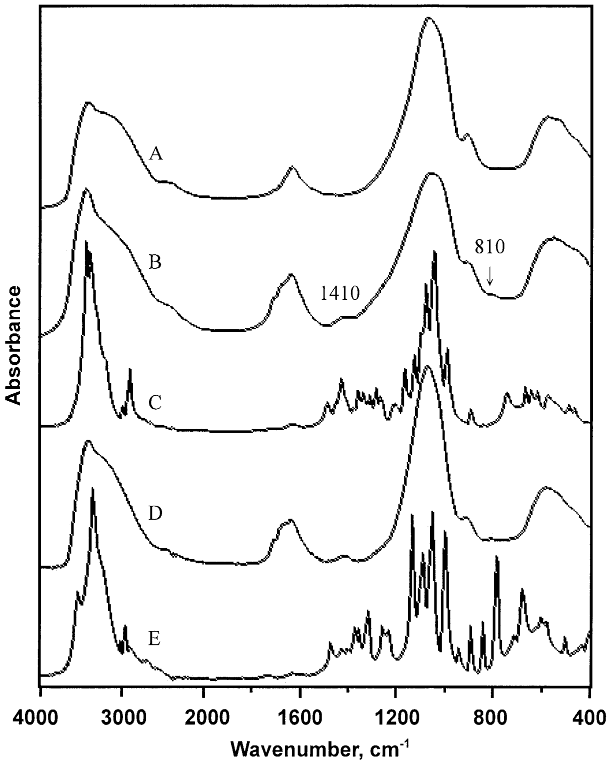

Fig. 3. FTIR spectra of chromic phosphate (A), the precipitate generated from cellobiose and CP reaction (B), cellobiose (C), the precipitate from arabinose and CP reaction (D), and arabinose (E).

the band at 1683–1681 cm^{-1} originated from the vibration of the carbonyl in conjugated ketones and the region of 1660–1647 cm^{-1} might be due to the Cr(III)-coordinated carboxyl group. Hence the broadening here (Fig. 3B and Fig. 3D) might be due to $CrPO_4$-coordinated carboxyl group. The two green precipitates also had broad absorptions between 3000 and 3500 cm^{-1}, which showed that these compounds were also rich in intermolecular hydrogen bonding.

To further simulate the actual reaction between the chemical components of bamboo and CP, three model compounds blended with the ratio of 4(cellobiose): 3(arabinose): 3(guaiacol) were reacted with CP. The result was similar to those of individual reactions as mentioned above. Guaiacol was reduced quickly during the initial stage of reaction and purple-brown precipitates were formed. As the reaction time increased, some green precipitates were formed in the solution, and all the precipitates turned green eventually. The longer the reaction time, the greener the precipitates became. Our findings revealed that the green-colour protection of the bamboo surface afforded by the CP treatment might be due to the formation of green complexes during the reaction of CP and the chemical components of bamboo, such as cellulose, hemicelluloses and lignin.

3.3. The reaction of CP with bamboo epidermis

Although chromic phosphate cannot be easily dissolved by organic solvents, it can dissolve in acids or bases [25,26]. Thus, 10% NaOH with heating at 60 °C for 10 min was employed to dissolve the green pigments in this experiment. This short hot NaOH treatment would not cause any obvious chemical change in the pretreated moso bamboo surface. The green epidermis of CP-treated moso bamboo was scratched off and milled to powder with a vibration mill. After this green powder was dissolved in 10% NaOH and filtrated through a 3G4 filter cup, the filtrate and sludges were analyzed by FTIR and compared with chromic phosphate. Meanwhile, the dissolution rates of chromic phosphate and the green epidermis powder in 10% NaOH solution were also compared.

The results showed that the dissolution rate of chromic phosphate was slower, but more complete than that of the green powder of CP-treated bamboo epidermis. In spite of the fast dissolution rate of green powder of bamboo epidermis, there were green insoluble sludges left on the filter. The FTIR spectrum of the green insoluble sludges (Fig. 4C) is similar to that of CP-treated moso bamboo epidermis without NaOH extraction (Fig. 4B), except that the absorption bands in the range of 500–1600 cm^{-1} decreased in intensity. The absorption peak of the phosphate group at 1070 cm^{-1} was weakened and the broad peak of the carboxyl group near 1640 cm^{-1} was narrowed, as was the highly hydrogen-bonded absorption peak at 3000–3500 cm^{-1}. The cellulose absorption peaks at 1161 and 896 cm^{-1} became much more prominent and similar to those of the pretreated moso bamboo (Fig. 4A). Some researchers reported that the broad band at 540–550 cm^{-1} is due to the asymmetric stretching vibration of the bent Cr–OH–Cr group [20,23]. Hence, all these weakened peaks in Fig. 4 revealed that some chromic phosphate complexes, especially those loosely bonded to bamboo or precipitated on it, were indeed dissolved by NaOH extraction. But some residual green complexes were still bonded on the bamboo epidermis. Therefore, it seems that two possible types of green complexes are formed in the green-colour protective treatment of bamboo.

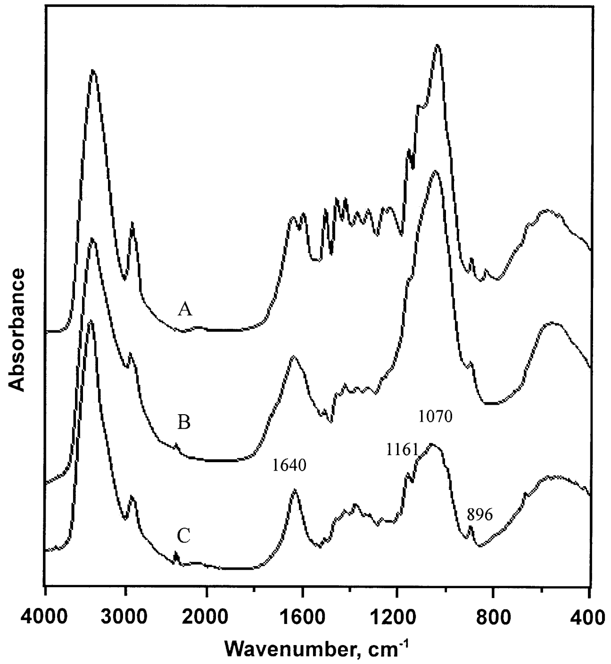

Fig. 4. FTIR spectra of CP treated moso bamboo epidermis after dissolution with 10% NaOH. A: pretreated moso bamboo epidermis, B: CP treated moso bamboo epidermis, C: CP treated moso bamboo epidermis after dissolution with 10% NaOH.

Considering the results all above and some reaction mechanisms of wood and chromium (VI) wood preservatives [9,16–18,21–23], we propose the possible formation scheme of these two types of green complexes as shown in Fig. 5. One complex (Fig. 5A) precipitates on or bonds weakly to the bamboo surface, while the other one (Fig. 5B) forms strong chemical bonds with the components of bamboo. Both green complexes contribute to the green-colour protection of CP-treated bamboo and also due to the inorganic component of $CrPO_4$, CP-treated bamboo culms have good light-fastness and weathering durability. As for the actual chemical structures of these two types of complexes, work is in progress to provide a more realistic elucidation in the near future.

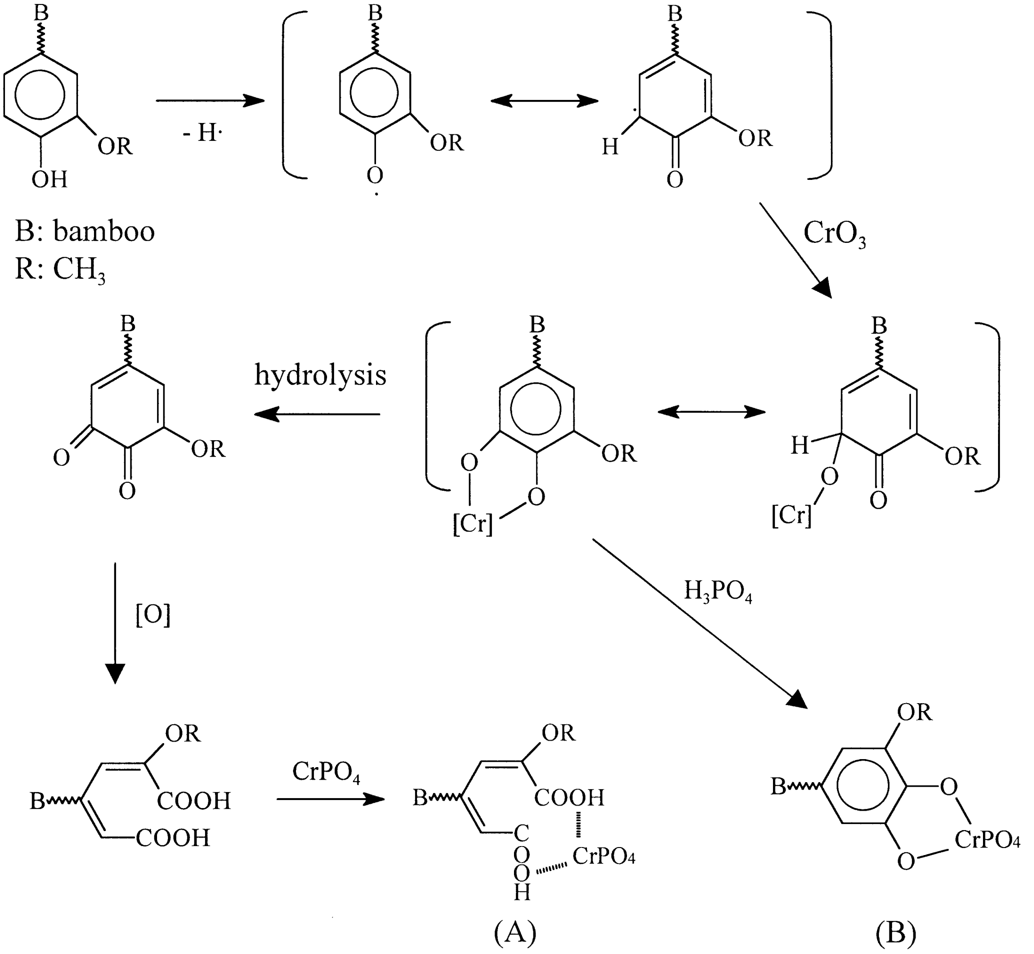

Fig. 5. Possible structures of green complexes formed during the green-colour protective treatment of bamboo. A: weak bonding or precipitate type, B: strong bonding type.

4. Conclusions

To understand the mechanisms involved in green-colour protection of moso bamboo treated with chromated phosphate (CP), three model compounds, cellobiose, arabinose and guaiacol, were chosen to represent bamboo's main chemical constituents, cellulose, hemicelluloses and lignin, respectively. These model compounds were reacted with CP and the reactions were examined by FTIR. The results showed that the reactivities of model compounds with CP were in the order guaiacol > arabinose > cellobiose. As the reaction time increased, green precipitates were formed in the solution. The chemical structure of these green precipitates was similar to that of chromic phosphate ($CrPO_4$), a green pigment. These green complexes not only precipitated on bamboo epidermis but also bonded to it. Hence, these green complexes might contribute to the green-colour protection of CP-treated bamboo.

Acknowledgements

This work was supported in part by a grant from the National Science Council (NSC-88-2313-B-002-017). We thank the NSC for the financial support.

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