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Effects of hydrogen peroxide treatment on the surface properties and adhesion of ma bamboo (*Dendrocalamus latiflorus*)

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Abstract The poor adhesion of bamboo coatings is a serious issue in the bamboo industry. To develop a pretreatment method that improves the adhesion of films and increases the economic value of bamboo products, a study of hydrogen peroxide treatment with solutions of various pH (pH 4–9) on bamboo surfaces was conducted. Five-year-old ma bamboo (*Dendrocalamus latiflorus* Munro), and nitrocellulose lacquer were used in the study. Surface properties of the bamboo such as contact angle and color were evaluated, and 180° peel strength and shear strength tests for measuring adhesion of films were conducted. The results showed that the wettability of water droplets and the carbonyl group concentration on the bamboo surface were increased significantly by alkaline (pH 8 and 9) hydrogen peroxide treatments. There was only minor color variation and the outer wax layer of bamboo was etched to form additional recesses after hydrogen peroxide treatment. It was also found that all hydrogen peroxide treatments improved the adhesion of bamboo coating; bamboo treated with hydrogen peroxide at pH 7 showed the greatest improvement. The enhanced adhesion was attributed to the mechanical interlocking of the film on the treated bamboo rather than to surface activation.

Key words Ma bamboo · Hydrogen peroxide · Surface properties · Adhesion

Introduction

Natural materials are gathering more attention as environmental protection is becoming more and more important. Bamboo, a perennial lignified plant that belongs to Bambusoideae, is one of the most important forest resources because it grows faster than any other woody plant on earth. Most species reach their maximum height of 15–30 m in 2–4 months and reach full maturity in about 3–8 years.[1] Because of its rapid growth rate, excellent specific strength, and easy machinability, it is used widely as a raw material for furniture, construction, handicrafts, and pulp. Approximately 1500 commercial applications of bamboo have been identified.[2]

Ma bamboo (*Dendrocalamus latiflorus* Munro) is one of the most popular and valuable bamboo species in Taiwan. Without protective treatment, it becomes susceptible to attack by fungi and insects, resulting in degraded performance, shortened service life, and reduced value. Thus, it is necessary to apply coatings, preservatives,[3] or other treatments[1,4–7] to bamboo to prevent deterioration. Among the available methods, use of a coating finish designed for wood on the bamboo surface is the simplest and the most economical. However, it is well known that a natural siliceous wax covers the surface layers of bamboo culm and interferes with the adhesion properties of coatings. The poor adhesion of coatings on bamboo is a constant problem of the bamboo industry.

To overcome this problem and to encourage the bamboo industry to explore the potential utilization and increased economic value of bamboo products, it is necessary to use surface treatments to increase the polarity of the bamboo surface and improve their ability to be coated. The wettability of bamboo surface is improved most effectively by irradiation of a hydrogen ion beam,[8] and plasma treatments are proven to be greatly effective for the adhesion of varnish to bamboo surfaces.[9] Simple and economical pretreatments used on the bamboo surface include sanding, alkali solution soaking, thermal treatment, ultra-violet light exposure treatment, hydrogen peroxide solution soaking, and chitosan treatment. In this study, the effects of a hydrogen peroxide oxidizing agent on the surface properties of bamboo and its improvement of adhesion of coated bamboo have been investigated.

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Theory

Hydrogen peroxide (H_2O_2) is a powerful oxidizing agent in either alkaline or acidic conditions, Eq.1, and is also used as a reducing agent, Eq. 2. Although the decomposition of H_2O_2 is complicated, the overall reaction gives up one mole of molecular oxygen for every two moles of H_2O_2, Eq. 3. Furthermore, H_2O_2 tends to form the hydroperoxide ion (OOH^-), Eq. 4, which has an effective bleaching ability.[10] Thus, hydrogen peroxide is widely used as a bleaching agent for furniture woods to remove the natural colorants by oxidizing them to colorless forms.

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \quad E_0 = 1.77\,V\ (\text{H-accepter}) \tag{1}$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e \quad E_0 = -0.68\,V\ (\text{H-donor}) \tag{2}$$

$$H_2O_2 \rightarrow H_2O + 1/2\,O_2 + 23.5\ \text{kcal} \tag{3}$$

$$H_2O_2 \leftrightarrow H^+ + OOH^- \tag{4}$$

Hydrogen peroxide used alone is not effective. It must be combined with an activator such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), ammonium hydroxide (NH_4OH), or ammionium carbonate [$(NH_4)_2CO_3$]. The most effective and widely used activators contain NaOH as an essential ingredient.[11] The amount of alkali left is small and is not considered dangerous. Thus, there is no need for neutralizing or washing. In this study, the bamboo surfaces were activated by hydrogen peroxide pretreatment. Oxidation processes, performed in with molecular oxygen or the hydroperoxide ion, introduce a range of functionality at the bamboo surface, therefore increasing the surface polarity. The treatment may also be accompanied by topographical changes and removal of weakly cohesive surface material. All of the results improve the adhesion of bamboo coatings.

Materials and methods

Materials

Five-year-old ma bamboo (*Dendrocalamus latiflorus* Munro) was obtained from Luh-Guu village in Nan-Tou County, Taiwan. The 15-cm-long fresh bamboo sections cut from each culm were washed with water and then dried in an oven at 60°C for 24 h. The samples were cut into pieces (60 × 25 × 3 mm) to be used as specimens. Hydrogen peroxide (28% w/v) was supplied by Union Chemical, Taiwan. Six H_2O_2 solutions with various pH values, i.e., pH 4, 5, 6, 7, 8, and 9, were prepared using NaOH activator to adjust the pH. Nitrocellulose lacquers (NC lacquer), the most common and widely used wood coatings, including sanding sealer and clear topcoat were purchased from Kuo-Roung Paint, Taiwan.

Hydrogen peroxide treatments

The bamboo specimens were soaked in hydrogen peroxide solutions at various pH for 30 min and were then dried at room temperature for 24 h. At least five samples were used in each treatment.

Wettability of treated bamboo

The wettability of bamboo surfaces was investigated by measuring the contact angle with pure water as the wetting liquid, using a contact-angle meter (Kyowa). The results obtained were the average values from five measurements.

FT-IR spectroscopy analysis

To analyze the chemical structure of treated bamboo surfaces, Fourier transform-infrared (FT-IR) spectroscopy was carried out using a Mattson Genesis II FT-IR spectrophotometer incorporating a Spectra Tech diffuse reflectance accessory unit. The samples were mixed with KBr in a weight ratio of 1:100, and were ground into a pellet. Data were collected from 4000 to 400 cm^{-1} with 16 scans for each sample. The resolution was 4 cm^{-1} and the obtained spectra were expressed in Kubelka-Munk (K-M) units.

Measurement of the bamboo surface color

The changes in color of specimens were measured with a spectrophotometer (CM-3600d, Minolta) fitted with a D_{65} light source with a measuring angle of 10 degrees and a test-window diameter of 8 mm. The tristimulus values X, Y, and Z of all specimens were obtained directly from the colormeter. The CIE L^*, a^*, and b^* color parameters were then computed, followed by calculating the brightness difference (ΔL^*), the difference of a^* component (Δa^*), the difference of b^* component (Δb^*), the color difference (ΔE^*), the chroma difference (ΔC^*), and the hue difference (ΔH^*) directly from the Minolta MCS software system.

SEM inspection

The bamboo surface textures before and after hydrogen peroxide treatment were examined by scanning electron microscopy (SEM, Topcon ABT-150S). The specimens were dried in a vacuum oven at 25°C for 24 h and were then gold-coated prior to examination.

Bamboo finishing

The viscosity of sanding sealer and topcoat of NC lacquer was adjusted to 20 s with thinner by using No.4 Ford cup at room temperature. Two coatings of sanding sealer and then one coating of clear topcoat were applied to the bamboo

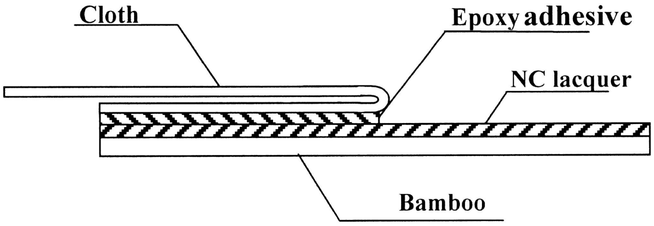

Fig. 1. Peel test specimen. *NC*, nitrocellulose

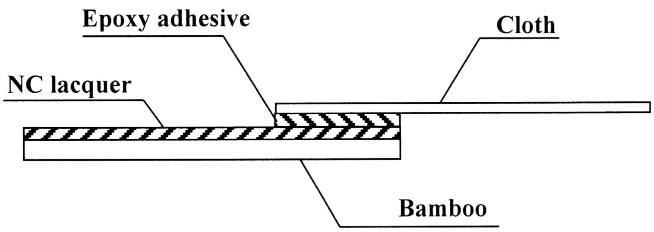

Fig. 2. Shear test specimen

surfaces using an air spray gun with the ratio of compressed air and fluid coatings adjusted to obtain a smooth pattern of spray flow and even thickness of films. The coated bamboo was then reconditioned at 27°C with 65% relative humidity for 1 week prior to the adhesion test.

Testing the adhesion of coated bamboo

The adhesion of the NC lacquer to the bamboo surfaces was measured by two different tests, namely the 180° peel test and the shear test,[12,13] using an EZTest tester (Shimadzu). To have a full attachment to a rigid and slightly curved bamboo surface, and to fix tightly in the jaws of the EZTest tester, a flexible cloth was required. The composition of the cloth was 50% polyester and 50% cotton, the weight specification was 187.0 g/m^2, and the cloth dimensions were 100 × 25 × 0.02 mm. The cloth was glued onto the coated bamboo with a lap joint (25 × 20 mm) as shown in Figs. 1 and 2 for the peel and shear tests, respectively. The adhesive was a solventless dual-component epoxy resin (Nan Pao-Bond, no. 906), which was mixed with a hardener in a weight ratio of 1:1 before use. The crosshead speed of testing was 20 cm/min.

Durability of coated bamboo

The durability of film was evaluated using a hot and cold cycle test, in which one test cycle required placement of the sample in a –20°C refrigerator for 2 h before transfer to a 50°C oven for 2 h. The cycle number was recorded if the sample films were cracked.

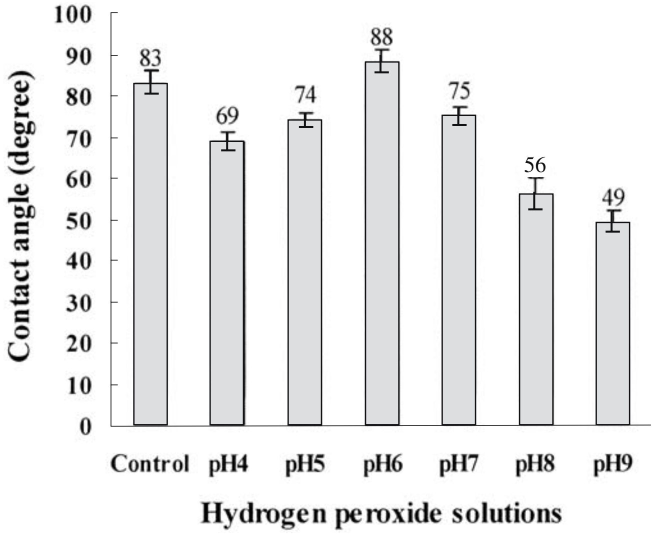

Fig. 3. Contact angle of ma bamboo before (*control*) and after hydrogen peroxide treatments. *Error bars* show standard deviations

Results and discussion

Surface properties of ma bamboo

Figure 3 shows the effect of pH of the H_2O_2 pretreatment solution on the contact angle of ma bamboo. The contact angles of treated bamboo were lower than those of untreated bamboo except for the sample treated at pH 6. This means that the wettability of bamboo is increased by H_2O_2 solution treatment. Among these treatments, the alkaline hydrogen peroxide showed higher enhancement of wettability than acidic solutions. For example, the contact angle of bamboo treated with pH 9 H_2O_2 solution decreased from its original 83° to 49°, whereas it decreased to 69° with pH 4 solution.

FT-IR analysis was employed to examine the chemical functionality of the bamboo surface after hydrogen peroxide treatment. The FT-IR spectra of treated specimens are shown in Fig. 4. The absorption bands at 1730 cm^{-1} and 2900 cm^{-1} were due to the carbonyl group (C=O) and C—H stretching, respectively. The ratios of absorbance at 1730 cm^{-1} to that at 2900 cm^{-1} (A_{1730}/A_{2900}) on the bamboo surfaces before and after treatment are listed in Table 1; the ratio can be used to identify the activation effects of the treated bamboo surfaces. The surface activation is found to favor the formation of hydrogen bonds at active sites to bond with the NC lacquer film. The results showed that treatment with alkaline hydrogen peroxide solutions of pH 8 and pH 9 gave A_{1730}/A_{2900} ratios of 0.95 and 0.94, respectively, which are higher than that of the untreated bamboo (0.92). This indicates that the treatments can introduce more carbonyl groups to the bamboo surface and the results are in accordance with the trends in contact angle as shown in Fig. 3. Treatments with hydrogen peroxide solutions of pH 4–7 gave A_{1730}/A_{2900} ratios that were lower than that of untreated bamboo. Other research of hydrogen peroxide treatment of moso bamboo (*Phyllostachys*

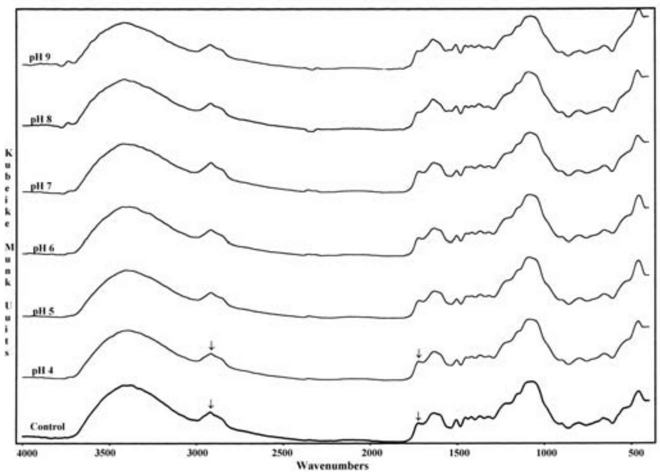

Fig. 4. Fourier transform-infrared spectra of the ma bamboo surfaces before (*control*) and after hydrogen peroxide treatments

Table 1. Absorbance ratio (A_{1730}/A_{2900}) of ma bamboo surfaces before and after treatments with hydrogen peroxide solution

	$H_2O_{2(aq)}$ treatment					
Control	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9
0.92	0.91	0.91	0.90	0.91	0.95	0.94

Table 2. Changes in color parameters of ma bamboo surfaces after treatment with hydrogen peroxide solutions of various pH

Treatment	ΔL^*	Δa^*	ΔC^*	ΔH^*	ΔE^*
pH 4	5.7	–0.4	–1.7	0.8	6.0
pH 5	5.3	–0.5	–2.0	1.0	5.7
pH 6	1.7	–0.6	–3.6	1.3	4.1
pH 7	5.1	0.2	0.3	–0.4	5.1
pH 8	2.3	0.4	–3.0	–1.2	3.8
pH 9	0.4	0.9	0.8	–2.0	1.2

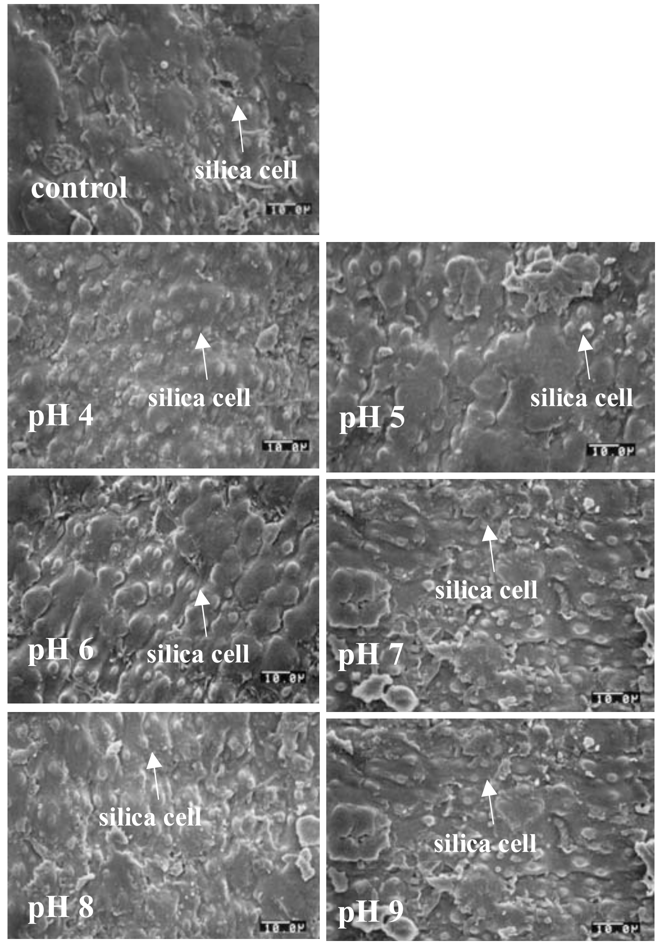

Fig. 5. Scanning electron micrographs of the ma bamboo surfaces before (*control*) and after hydrogen peroxide treatments

bambusoides Sieb. et Zucc.) to obtain activated surfaces has been reported by Kawamura and Kotani.[9] They reported an A_{1730}/A_{2900} ratio of 0.79 for bamboo treated with a 1:1 mixture of H_2O_2 (3.5%) and NH_4OH (2.8%) at 20°C for 30 min, which was slightly higher than the ratio of 0.73 for untreated bamboo. The same study also reported absorbance ratios for bamboo soaked in 1:1 mixtures of H_2O_2 (3.5%) + NH_4OH (2.8%) and H_2O_2 (35%) + NH_4OH (28%) at 20°C for 10 min of 0.71 and 0.72, respectively, which are both lower than that of untreated bamboo. These results indicated that the surface activation of bamboo could be affected by different pH or concentration and treatment time.

For versatile utilization of bamboo, it is desirable that there is little color variation after hydrogen peroxide treatment. Table 2 shows the changes of color parameters on ma bamboo surfaces after being treated with H_2O_2 solutions of various pH. Compared with untreated ma bamboo surfaces in which L^*, a^*, and b^* were 51.4, 0.7, and 24.8, respectively, all the ΔL^* values of the treated bamboo were positive. This means that all bamboo treated with hydrogen peroxide showed brighter surfaces, especially for the pH 4, 5, and 7 hydrogen peroxide solutions for which the ΔL^* values were 5.7, 5.3, and 5.1, respectively. The results also indicated that the value of Δa^* was negative when the bamboo was treated with acidic hydrogen peroxide. A deeper greenish skin was obtained, particularly for those samples treated with pH 6 H_2O_2 solution, even though the Δa^* was only –0.6. However, with alkaline hydrogen peroxide treatment, a more reddish color was observed in the bamboo (the Δa^* values were positive). In spite of the results mentioned above, a slight chroma difference (ΔC^* from –3.6 to 0.8), a hue difference (ΔH^* from –2.0 to 1.3), and a color difference (ΔE^* from 6.0 to 1.2) were also obtained. Generally speaking, only a minor variation was apparent, i.e., the greenish appearance of ma bamboo was retained and brighter color was obtained after treating with hydrogen peroxide solutions of different pH.

Figure 5 illustrates the surface morphologies of bamboo treated with hydrogen peroxide solutions of varying pH and that of untreated bamboo (control). It is known that there are many capes of silica cells in the cuticular layer of bamboo.[5] No significant differences in morphology after

Table 3. Peel and shear strength of coated untreated ma bamboo and coated ma bamboo previously treated with hydrogen peroxide

Treatment	180° Peel strength (kgf/25 mm)	Shear strength (kgf/cm^2)
Control	1.13 ± 0.51	1.89 ± 0.80
pH 4	1.38 ± 0.36	2.60 ± 0.40
pH 5	1.19 ± 0.36	2.42 ± 0.50
pH 6	1.19 ± 0.37	2.27 ± 0.58
pH 7	1.70 ± 0.60	2.81 ± 0.75
pH 8	1.03 ± 0.47	2.38 ± 0.61
pH 9	1.19 ± 0.25	1.89 ± 0.27

Data are given as mean ± SD ($n = 5$)

treatment with hydrogen peroxide were found. However, the capes of silica cells are more distinct in treated bamboo than those of untreated bamboo. This may be due to the wax layer being etched and the clogged dust on the bamboo surface being removed by the oxidative and bleaching action of hydrogen peroxide. The result is more recesses on the bamboo surface and this is beneficial for the adhesion of coatings.

Coating adhesion on ma bamboo

Peel and shear tests have been used successfully to give quantitative measures of the adhesion of coatings. The tests are less subject to human error and provide more information about adhesion and/or cohesion of coatings when compared with the most commonly used ASTM D3359 tape test method.[13] In this study, the 180° peel test and the shear test were used to evaluate the influence of hydrogen peroxide treatments on the adhesion of NC lacquer coated on ma bamboo.

The results of adhesion testing for 180° peel strength and shear strength are listed in Table 3. Except for ma bamboo treated with pH 8 hydrogen peroxide solution, the peel strengths of samples treated at various pH levels were higher than that of the untreated bamboo. Among all samples, the highest peel strength of 1.70 kgf/25 mm was for bamboo treated with pH 7 H_2O_2 solution as compared with 1.13 kgf/25 mm for the untreated bamboo. The results of the shear strength tests also confirmed better coating adhesion on bamboo treated with hydrogen peroxide than on untreated bamboo. Among all the treatments, bamboo treated with pH 7 H_2O_2 solution had the highest shear strength of 2.81 kgf/cm^2; the untreated sample had a shear strength of 1.89 kgf/cm^2. Interfacial failure between film and bamboo for all test specimens was found by microscopic examination.

The mechanism of adhesion can be divided into three groups: (1) mechanical interlocking, (2) physical bonding, and (3) chemical bonding. In all substrate–coating systems as well as in general joining technology, these mechanisms individually or together are responsible for adhesion. Very often, one of the mechanisms plays a dominant role.[14] Coatings with better penetration and substrate wetting show superior adhesion. As a consequence, good surface wetting and capillary penetration is generally considered to be the prerequisite for good adhesion of a coating. In this study, the goal was to activate the bamboo surfaces by oxidation with hydrogen peroxide and to introduce functional groups such as C=O to the bamboo surface, thereby increasing the surface polarity and providing additional physical or chemical bonding opportunities. Comparing the six hydrogen peroxide treatments used, the alkaline H_2O_2 solutions, i.e., pH 8 and pH 9, were the most efficient in activating the bamboo surface as shown in Table 1. However, the coating adhesion for both treatments was inferior to the other treatments. The results suggest that improved wettability does not indicate whether interfacial bonding actually takes place. Sato[15] suggested that if a coating has difficulty in wetting the substrate thoroughly, increasing the wettability of the substrate can provide better adhesion. However, if a coating can adequately wet the substrate, the relation between adhesion and wettability is less pronounced. In this study, although the alkaline hydrogen peroxide treatment showed higher enhancement of bamboo wetting than acidic treatments, in practice, NC lacquer finishing readily wetted all the treated and untreated bamboo surfaces.

Some researchers[16,17] and our previous report[18] indicate increased adhesion strength of a coating with increased surface roughness. Thus, it can be assumed that mechanical anchoring or hooking plays an important role in the adhesion of coatings to a substrate surface. Meijer and Militz[16] examined the adhesion of coatings on wood and showed that adhesion was clearly higher in the deeply penetrated earlywood cells in comparison with the less penetrated latewood cells. In the present study, the SEM micrographs of the surface of bamboo treated with H_2O_2, given in Fig. 5, show that the weakly cohesive surface material such as the wax layer and dust on the bamboo surface can be etched and removed to thereby roughen the bamboo surface as mentioned above. The recesses produced result in an increase in the real surface area, which in turn increases the potential for mechanical interlocking between coating and bamboo. This is the major reason that the H_2O_2-treated bamboo had a higher peel strength and higher shear strength than those of the untreated bamboo. Furthermore, bamboo treated with pH 7 H_2O_2 solution showed the greatest adhesion, as confirmed by both the 180° peel test and the shear test. In spite of the best wettability of the bamboo specimens and the increase in the bamboo surface area achieved by treatment with pH 8 and pH 9 H_2O_2 solutions, it is hypothesized that the significant vigor of these treatments may damage the cellular structure of bamboo and reduce the opportunity for hydrogen bonds or van der Waals forces to influence surface bonds with the NC lacquer film. From the observed results mentioned, it is apparent that the mechanical interlocking of film plays a dominant role for the improvement in coating adhesion rather than surface activation.

In addition, the durability of coated film for each of the test specimens was also examined using a hot–cold cycle test. Film cracking was observed on the untreated sample after three test cycles, whereas all of the samples treated with H_2O_2 solutions retained a perfect film appearance after ten test cycles. This result shows that all ma bamboo treated with hydrogen peroxide had better durability of coated films than that of untreated bamboo.

Conclusions

Ma bamboo samples treated with hydrogen peroxide solutions of various pH showed increased wettability and carbonyl group concentration compared with untreated bamboo. These effects were particularly apparent for treatments with alkaline H_2O_2 solutions. In all the treatments, only slight chroma and hue differences were observed and improvement in coating adhesion, especially for samples treated with hydrogen peroxide solution at pH 7, was demonstrated by peel and shear tests. It was revealed that the improvement in coating adhesion was due to the mechanical interlocking of film rather than surface activation.

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