Effects of Ultraviolet Irradiation Treatment on the Surface Properties and Adhesion of Moso Bamboo (*Phyllostachys pubescens*)

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ABSTRACT: The poor adhesion of bamboo coatings is a serious issue in the bamboo industry. To overcome this problem it is necessary to modify the actual surface of the bamboo before finishing. A study on the surface properties and adhesion of moso bamboo (*Phyllostachys pubescens*) were investigated with various UV irradiation conditions including irradiation time and dose using different UV lamps. Two types of wood coatings, i.e., solvent-borne nitrocellulose (NC) lacquer and waterborne polyurethane (PU) coating, were used in the study, and 180° peel strength and shear strength tests for measuring adhesion of films were conducted. The results revealed that the wettability and the carbonyl group concentration of the bamboo surface were increased. This was particularly apparent for an irradiation time less than 15 s with a mercury UV lamp (H-lamp), rated at an intensity of 100 W/cm kept at a distance of 15 cm. In all the treatments, the greenish appearance of moso bamboo was retained and the adhesion was improved. Especially, using solvent-borne NC lacquer finishing, the higher-dose (under a mercury UV lamp combined with metal halide lamp; H + M-lamps) irradiated bamboo had the best adhesion, while, for waterborne PU coating, the H-lamp irradiated one showed the best improvement. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2037–2044, 2008

Key words: adhesion; coatings; surfaces; FTIR

INTRODUCTION

Natural materials are attracting 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, as it grows faster than any other woody plant on earth. There are many genera of bamboos cultivated in Taiwan. The total area of bamboos is about 152,300 hectares, which is 7.24% of the total forest area in Taiwan.[1] Among them, moso bamboo (*Phyllostachys pubescens*) is one of the most popular and valuable bamboo species and is widely used as a raw material for furniture, construction, and handcrafts. However, bamboo has little decay-resistance and without protective treatment it becomes susceptible to attack by fungi and insects, to discolor and deteriorate because of ambient environment such as moisture and sunlight, and thus shortens its service life and also reduces its value. Many methods could be used to treat bamboo to prevent deterioration.[2–7] Using a coating finish designed for wood on the bamboo surface is the simplest and the most economical method. However, according to Chang and Yeh,[8] the capes of silica cell abound in the cuticular layer and the waxes cover the surface layer of moso bamboo culms. The report also states that the main components of fresh bamboo waxes are long-chain fatty acid, pentacryclic triterpeniods, steriols, and flavonoids. These hydrophobic materials should interfere with the adhesion properties of the coatings. The poor adhesion of coating is always a problem in 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 modify the actual surface of the bamboo before coating. To ensure good adhesion of a coating to a substrate, good wettability of its surface is required. The wettability of bamboo surface is improved most effectively by irradiating with a hydrogen ion beam,[9] and plasma treatments are proven to be greatly effective for the adhesion of varnish to bamboo surfaces.[10] Simple and economical pretreatments used on the bamboo surface including sanding treatment,[11] alkali solution soaking treatment,[12] heating treatment,[13] and hydrogen peroxide solution soaking treatment,[14] that would be even cheaper than using a plasma or ion beam treatment, were studied in our previous reports and for each study, the optimum condition was obtained. In this study, we will focus on the ultraviolet (UV) irradiation treatments on bamboo surface.

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UV irradiation is an electromagnetic irradiation of a wavelength shorter than that of visible light. The UV spectrum extends from 200 to 400 nm and it has an energy of 70–142 kcal/mol. Sufficient amount of UV energy is available to break many of chemical bonds in organic compounds.[15] Furthermore, the most important components of the chemical environment that influence the polymer are oxygen and ozone. Oxygen is involved in a number of photochemical reactions that result in the degradation of the organic material.[16] Although most polymers react very slowly with atmospheric oxygen, oxidation is greatly promoted by elevated temperature and UV irradiation.[15] When a UV lamp is operated, it produces a considerable amount of heat and a small amount of ozone in its vicinity.[17] We hope that direct exposure of bamboo surface to UV light within a very short time causes a synergistic effect of oxygen, ozone, and heat, which can modify the waxy layer of bamboo surface by oxidative activation. Therefore, the wettability of bamboo surface and good adhesion of a coating can be improved. The most important parameters of the UV irradiation, such as irradiation time and dosage, will be examined in this study. In addition, two types of wood coatings were used in the study. One of them was solvent-borne nitrocellulose (NC) lacquer, which is the most common and widely used wood coating. For a considerable reduction in the emission of volatile organic compounds to limit industrial health hazards and to prevent environmental pollution, the other coating used was waterborne polyurethane (PU) coating.

EXPERIMENTAL

Materials

Five-year-old moso bamboo (*Phyllostachys pubescens*) was obtained from the Luh-Guu Village in Nantou County. The 15 cm-long fresh bamboo sections cut from each culm were washed with water and dried in an oven at 60°C for 24 h. The final moisture content of the bamboo was 10.95%. The samples were cut into pieces (60 mm × 25 mm × 3 mm), which were to be used as specimens. Two wood coatings were used in this study. The solvent-borne NC lacquers including sanding sealer and clear topcoat were supplied by Kuo-Roung Paint Manufacture, Taiwan. The waterborne PU coating was purchased from Becker Industrial Coatings in Taiwan.

UV irradiation treatments

Two UV irradiation sources, including a high-pressure mercury vapor lamp (H-lamp; the major wavelength was 365 nm) and a metal halide lamp (M-lamp, the major wavelengths were 420, 365, and 250 nm) rated at 100 W/cm, were used. The UV equipment (UVC-326) was supplied by C-SUN MFG, Taichung, Taiwan. Two experiments were performed with different irradiation times and doses. In the first one, the moso bamboo samples were irradiated with the H-lamp, keeping at a constant distance of 15 cm, by varying the conveyor speed which was set to 1, 3, 5, 7, and 9 m/min corresponding to irradiation time of 65, 25, 15, 10, and 7 s, respectively.

In the second experiment, the effect of irradiation dose was examined. The samples were irradiated with the H-lamp, M-lamp, and the H-lamp combined with M-lamp (H + M lamps) corresponding to the UV energies of 405.00 mJ/cm^2, 1.08 J/cm^2, and 1.54 J/cm^2, respectively. The irradiation distance was kept at 15 cm and the conveyor speed was 5 m/min.

Wettability of treated bamboo

The wettability of the bamboo surfaces before and after UV irradiation was investigated by measuring the contact angle with pure water and waterborne PU as the wetting liquid, respectively, using a contact-angle meter (CBVP-A3, Kyowa, Japan). The results obtained were the average values from five measurements.

SEM Inspection

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

Fourier transform-infrared spectroscopy analysis

To analyze the chemical structure of treated bamboo surfaces, Fourier transform-infrared (FTIR) spectroscopy was carried out using a Mattson Genesis II spectrophotometer incorporating a Spectra Tech diffuse reflectance accessory unit. The samples were then mixed with KBr with the 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 the specimens were measured with a spectrophotometer (CM-3600d, Minolta, Osaka, Japan) fitted with a D_{65} light source with a measuring angle of 10° 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

TABLE I
Contact Angles of Moso Bamboo Surfaces Before and After UV Irradiation

Irradiation time (s)	Contact angle of the droplet[a] (°)	
	Water	Waterborne PU
Control	88	60
7	77	33
10	78	41
15	75	43
25	89	55
65	99	58

[a] The surface tension of water and waterborne PU were 73 and 31 dyne/cm, respectively, by using Kyowa CBVP-A3 meter, Japan.

then computed, followed by calculating the brightness difference (ΔL^*), the difference of a^* component (Δa^*), and the difference of b^* component (Δb^*) directly from the Minolta MCS software system.

Bamboo finishing

The viscosity was adjusted to 20 s with mixed solvent for NC lacquer (including sanding sealer and topcoat) and 15 s with mixed water for waterborne PU by using No. 4 Ford cup at room temperature. The bamboo finishing with NC lacquer was performed using two coatings of sanding sealer, followed by sanding with No. 180 sand paper after drying and then one coating of clear topcoat; the waterborne PU followed the sequence of one coating, sanding, and then one more coating. All coatings were applied to the bamboo 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 films with even thickness. The coated bamboo was then reconditioned at 27°C with 65% relative humidity for 1 week before the adhesion test.

Testing the adhesion of coated bamboo

The adhesion of the NC lacquer or PU coating to the bamboo surfaces was measured by two different tests, namely 180° peel and shear tests[18,19] using an EZTest tester (Shimadzu, Tokyo, Japan). To have a full attachment to a rigid and slightly curved bamboo surface and to fix tightly to the jaws of the EZTest tester, a flexible cloth was required. The composition of cloth was 50% polyester and 50% cotton, the weight specification was 187.0 g/m^2, and the cloth dimensions were 100 mm × 25 mm × 0.02 mm. The cloth was glued onto the coated bamboo with a lap joint of 25 mm × 20 mm for peel and shear tests, respectively. The adhesive was a solventless dual-component epoxy resin (Nan Pao-Bond, No. 906, Tainan, Taiwan), which was mixed with a hardener in a weight ratio of 1 : 1 before use. Samples were placed between the jaws, and a load was applied at a rate of 20 cm/min until failure occurred. Five samples were used and the results were averaged for each data point.

RESULTS AND DISCUSSION

Effects of irradiation time on the surface properties and adhesion of moso bamboo

The moso bamboo surfaces were irradiated with a high-pressure mercury vapor lamp (H-lamp) rated at 100 W/cm and kept at a distance of 15 cm. The effect of irradiation time on the wettability of moso bamboo is shown in Table I. Irrespective of whether pure water or waterborne PU was used as the wetting liquid, the contact angles increased with an increase in the irradiation time. However, the contact angles of treated bamboo within 15 s irradiation time were significantly lower than those of untreated bamboo. For example, the contact angle of bamboo with 15 s irradiation time decreased from its original value of 88° to 75° when water droplet was used and from 60° to 43° when waterborne PU droplet was used. This means that the wettability of moso bamboo is enhanced by UV irradiation, especially during an irradiation time of less than 15 s. It may be due to the oxidative activation of organic components from the bamboo surface waxes during UV irradiation.

FTIR analysis was employed to examine the chemical functionality of the bamboo surface after UV irradiation. The FTIR spectra of treated specimens are shown in Figure 1. 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 UV irradiation are listed in Table II. The ratio can be used to identify the oxidative activation effects of

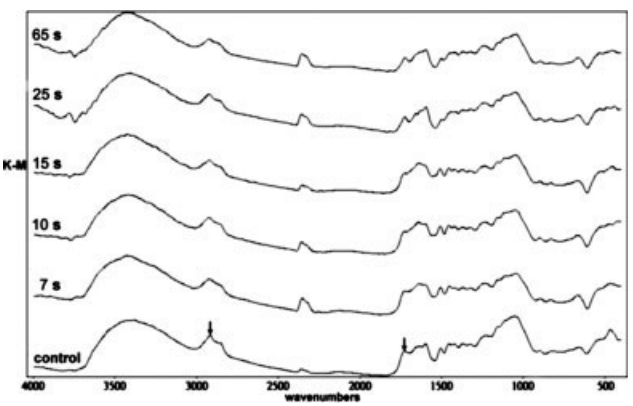

Figure 1 FT-IR spectra of moso bamboo before and after UV irradiation.

TABLE II
Absorbance Ratio (A_{1730}/A_{2900}) of Moso Bamboo Surfaces Before and After UV Irradiation

Irradiation time (s)	Absorbance ratio
Control	0.853
7	0.929
10	0.912
15	0.924
25	0.840
65	0.856

the treated bamboo surfaces.[10] The UV irradiation with irradiation time of 7, 10, and 15 s gave A_{1730}/A_{2900} ratios of 0.929, 0.912, and 0.924, respectively, which were higher than those of the untreated bamboo (0.853). This indicated that the shorter time of UV irradiation could introduce more carbonyl groups to the bamboo surface, and the results are in accordance with the trends in the measurement of contact angle as shown in Table I. The longer the irradiation time (i.e., 25 and 65 s), the larger the contact angle and lesser the carbonyl groups obtained. It is well known that when a UV lamp is operated, it also develops a considerable amount of heat and the wax layer on the bamboo surface could be melted. Figure 2 illustrates the surface morphologies of bamboo treated with UV irradiation. We can see that a denser layer has been formed and that the capes of silica cells in the cuticular of bamboo are more distinct at a irradiation time of 25 and 65 s. Because the surface provided a higher contact angle and a lower A_{1730}/A_{2900} ratio, the results may cause poor wettability and less oxidative activation on the bamboo surfaces.

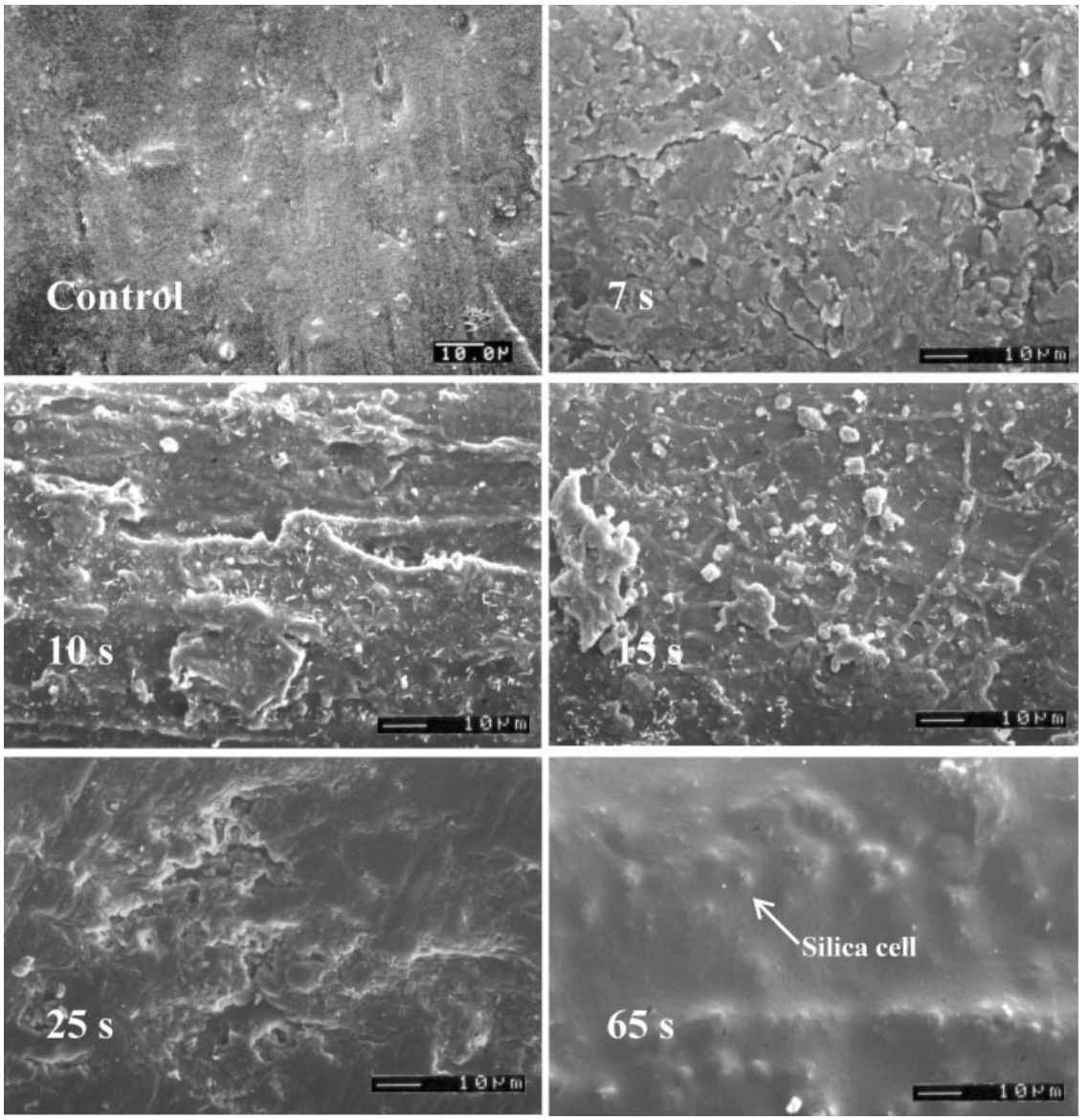

Figure 2 Scanning electron micrographs of the moso bamboo surfaces before and after UV irradiation (×1000).

TABLE III
Change in Color Parameters[a] of Moso Bamboo Surfaces After UV Irradiation

Irradiation time (s)	Color parameters		
	ΔL^*	Δa^*	Δb^*
7	0.54	−0.40	−0.47
10	−0.05	−0.03	0.22
15	−0.33	−0.01	0.11
25	−3.16	0.82	0.56
65	−1.82	1.01	1.13

[a] ΔL^*, the brightness difference; Δa^*, the difference of a^* component; Δb^*, the difference of b^* component; where L^* is the value on the white/black axis, a^* is the value on the red/green axis, and b^* is the value on the blue/yellow axis.

For versatile utilization of bamboo, it is desirable that there is little color variation after UV irradiation. Table III shows the changes of color parameters on moso bamboo surfaces after various durations of UV irradiation time. Compared with untreated moso bamboo, except for the irradiation time of 7 s, all the ΔL^* values of the treated bamboo were negative. This means that the bamboo treated with UV irradiation showed darker surfaces, especially for the irradiation time of 25 s for which the ΔL^* value was −3.16. The results also indicated that the Δa^* values of irradiation time less than 15 s were negative so as to obtain a deeper greenish skin. However, with the longer irradiation time of 25 and 65 s, more reddish color was observed in the bamboo (the Δa^* values were positive). Furthermore, the Δb^* values of specimens of various irradiation time were positive, except for the one with 7 s irradiation, meaning that a more yellowish color of bamboo was obtained after UV irradiation. In spite of the results mentioned earlier, in fact, only a minor variation was apparent, i.e., the greenish appearance of moso bamboo was retained, even after the longest irradiation time of 65 s.

In this study, the 180° peel test and the shear test were used to evaluate the influence of UV irradiation on the adhesion of solvent-borne NC lacquer and waterborne PU coated on moso bamboo. The results of adhesion testing of various UV irradiation time are listed in Table IV. For NC lacquer coating, both the 180° peel strength and shear strength of specimens treated at various UV irradiation time were higher than those of the untreated bamboo. This means that the adhesion of NC lacquer coated bamboo could be improved by UV irradiation. Among all the treatments, the highest peel strength of 36.95 N/25 mm and shear strength of 0.43 MPa were obtained for bamboos treated with an irradiation time of 15 and 10 s, respectively. The results show that shorter the UV irradiation time, better the adhesion of NC lacquer. The results may be attributed to the fact that the shorter irradiation time introduces functional groups such as C=O to the bamboo surface, therefore, increasing the surface polarity and providing additional physical or chemical bonding opportunities for the solvent-type coatings.

However, for waterborne PU coating, bamboo irradiated with UV light for 65 s showed the greatest adhesion, as confirmed by both 180° peel test and the shear test. In spite of the contact angle and A_{1730}/A_{2900} ratio of these specimens being similar to that of untreated bamboo, the wettability and oxidative activation on the bamboo surfaces did not even improve by the longest UV exposure time. However, from the SEM inspection (see Fig. 2), we can see that a smoother surface was obtained after UV irradiation for 65 s. The smooth surface may be providing more opportunity for van der Waals interactions or hydrogen bonds with the waterborne type coating film.[20,21] Furthermore, interfacial failure between film and bamboo surface for all test specimens was found by the microscopic examination.

Effects of irradiation dose on the surface properties and adhesion of moso bamboo

In this section, the moso bamboo surfaces were irradiated with three UV-lamps including H-lamp, M-lamp, and H + M-lamps, corresponding to the UV energies of 405.00 mJ/cm^2, 1.08 J/cm^2, and 1.54 J/cm^2, respectively. The irradiation distance was kept

TABLE IV
Peel and Shear Strength of Coated Moso Bamboo Before and After UV Irradiation

Irradiation time (s)	NC lacquer		Waterborne PU	
	180° peel strength (N/25 mm)	Shear strength (MPa)	180° peel strength (N/25 mm)	Shear strength (MPa)
Control	10.00 ± 3.52	0.30 ± 0.02	15.29 ± 0.20	0.30 ± 0.01
7	20.48 ± 5.78	0.39 ± 0.03	16.66 ± 2.94	0.42 ± 0.04
10	24.99 ± 7.45	0.43± 0.06	23.03 ± 8.82	0.32 ± 0.06
15	36.95 ± 11.27	0.32 ± 0.08	21.66 ± 3.43	0.33 ± 0.06
25	22.44 ± 2.55	0.38 ± 0.04	14.70 ± 4.61	0.34 ± 0.03
65	27.73 ± 7.25	0.39 ± 0.04	24.30 ± 4.70	0.44 ± 0.04

Data are given as mean ± SD (n = 5).

TABLE V
Contact Angles of Moso Bamboo Surface Before and After Exposure Using Different UV Lamps

	Contact angle of the droplet (°)	
	Water	Waterborne PU
Control	88	60
UV lamp[a]		
H	75	43
M	88	43
H + M	83	44

[a] H, mercury lamp; M, metal halide lamp.

TABLE VI
Absorbance Ratio (A_{1730}/A_{2900}) of Moso Bamboo Surfaces Before and After Exposure Using Different UV Lamps

	Absorbance ratio
Control	0.853
UV lamp[a]	
H	0.924
M	0.884
H + M	0.871

[a] H, mercury lamp; M, metal halide lamp.

at 15 cm and the duration of exposure was 15 s. The effect of irradiation dose on the wettability of moso bamboo is shown in Table V. When using water as a wetting liquid, the bamboo surface exposure using H-lamp had the lowest contact angle of 75°, indicating that better wettability was obtained using lower UV energy. However, using waterborne PU droplet, the contact angles were not significantly different among all the different UV-treated samples and the value of about 43°–44° was lower than that of untreated bamboo (60°). The absorbance ratios of A_{1730}/A_{2900} of the bamboo surfaces before and after exposure using different UV lamps are listed in Table VI. Irrespective of irradiation doses used, the ratios of A_{1730}/A_{2900} were higher than those of untreated bamboo (0.853), meaning that the bamboo surface could be activated after exposure using three UV lamps with different irradiation doses. Furthermore, among all of them, the bamboo surface exposure using H-lamp had the highest ratio of 0.924, indicating the formation of more carbonyl groups on the bamboo surface under this treated conditions.

The surface morphologies of bamboo treated with different UV radiation are shown in Figure 3. The smoother surface was obtained after exposing at a higher irradiation dose of H + M-lamps with an energy of 1.54 J/cm^2. It was due to the higher energy accompanied by a increased amount of heat at which the wax layer on the bamboo surface could be melted, while loose flake surfaces were observed upon exposing to a lower energy of H and M lamps.

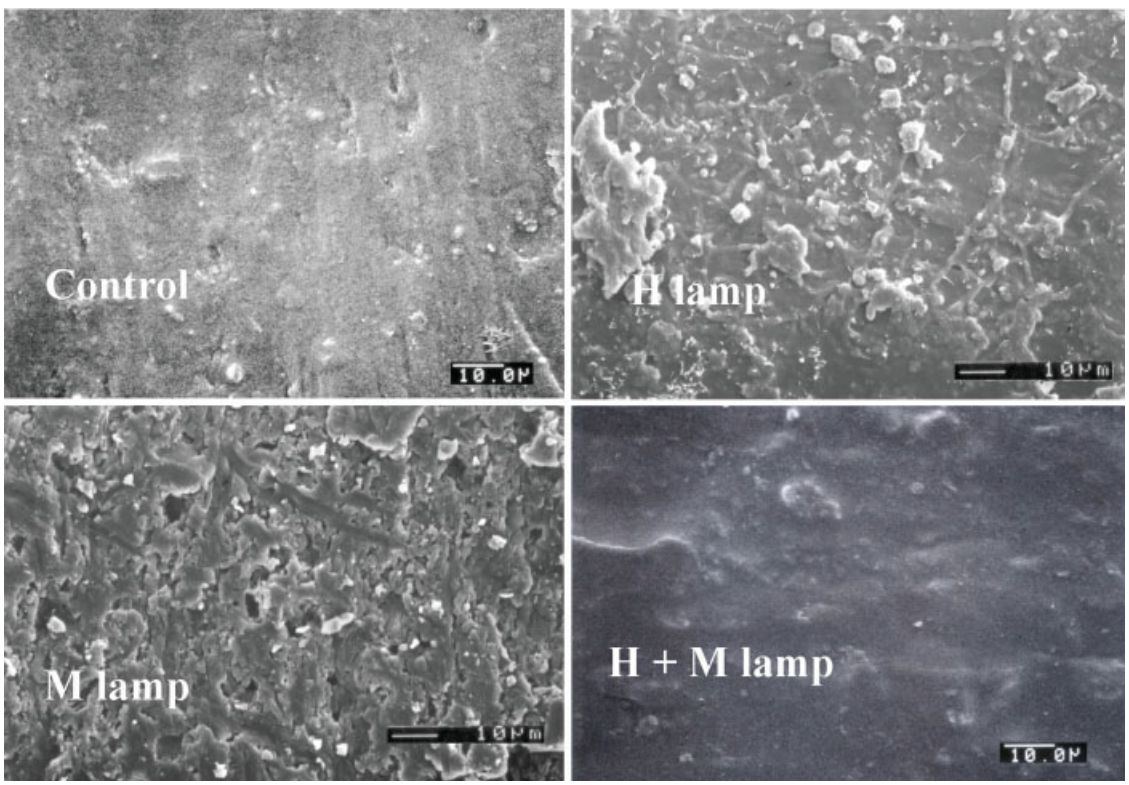

Figure 3 Scanning electron micrographs of the moso bamboo surfaces before and after exposure using different UV lamps (×1000).

TABLE VII
Change in Color Parameters of Moso Bamboo Surfaces After Exposure Using Different UV Lamps

	Color parameters[b]		
UV lamp[a]	ΔL^*	Δa^*	Δb^*
H	−0.33	−0.01	0.11
M	−0.31	0.06	0.12
H + M	−0.10	0.12	−0.19

[a] H, mercury lamp; M, metal halide lamp.
[b] ΔL^*, Δa^*, and Δb^* were the same as Table III.

Table VII shows the changes of color parameters on moso bamboo surfaces after exposure using different UV lamps. Whatever the UV irradiation doses applied, the ΔL^*, Δa^*, and Δb^* were changed only slightly compared with the untreated bamboo surface, meaning that the greenish appearance of moso bamboo was retained.

Table VIII shows the adhesion testing for 180° peel strength and shear strength of coated moso bamboo before and after exposure using different UV lamps. For solvent-borne NC lacquer, bamboos irradiated with different irradiation doses showed superior adhesion to untreated bamboo. Among all the samples, the highest 180° peel strength of 39.98 N/25 mm and shear strength of 0.48 MPa were for bamboo exposed at the highest irradiation dose of H + M-lamps when compared with 10.00 N/25 mm and 0.30 MPa for the untreated bamboo. However, for waterborne PU coating, the H-lamp treated sample had the highest 180° peel strength of 21.69 N/25 mm when compared with the untreated sample that had a 180° peel strength of 15.29 N/25 mm. In addition, the M-lamp treated sample had the highest shear strength of 0.39 MPa, followed by the H-lamp treated one of 0.33 MPa. As a conclusion, the best adhesions of NC lacquer- and PU-coated bamboo were for the H + M-lamps and H-lamp treated samples, respectively.

The mechanism of adhesion can be divided into three groups: (1) mechanical interlocking, (2) physical bonding, and (3) chemical bonding. In all the substrate-coating systems as well as in general joining technology, these mechanisms individually or together are responsible for adhesion.[22] In this study, the aim was to activate the bamboo surface by oxidation with different UV irradiation doses. The H-lamp and M-lamp irradiated bamboo surfaces had the highest activated effects (see Table VI) with more rough recesses (see Fig. 3), favoring the opportunity for chemical bonding and mechanical anchoring of coating to the bamboo surface. However, the smoother surface obtained from H + M-lamp irradiation (see Fig. 3) increased the physical bonding such as hydrogen bonds and van der Waals forces to increase surface bonds. In addition, the difference of adhesion between solvent-borne type and waterborne type coatings on bamboo surface with the same UV-treated conditions may also be due to the different viscoelasticities of coating.[23] However, it has not proven to be the link between adhesion and viscoelasticity of coating and it will be studied in detail in future steps.

CONCLUSIONS

Moso bamboo samples treated with UV irradiation for different durations and dosages showed increased wettability and carbonyl concentration compared with untreated bamboo. These effects were particularly apparent for the irradiation time less than 15 s with an H-lamp rated at 100 W/cm and kept at a distance of 15 cm. In all the treatments, the greenish appearance of moso bamboo was retained. The improvement in coating adhesion was demonstrated by peel and shear tests. Especially, using solvent-borne NC lacquer, the H + M-lamp irradiated bamboo had the best adhesion, while, for waterborne PU coating, the H-lamp irradiated one displayed the best improvement. The results from this work indicate that the UV irradiation processing is suitable for the wettability and adhesion enhancement process of moso bamboo surface. If only adjusting to an appropriate configuration of UV lamp, the processing also

TABLE VIII
Peel and Shear Strength of Coated Moso Bamboo Before and After Exposure Using Different UV Lamps

	NC lacquer[b]		Waterborne PU[b]	
UV lamp[a]	180° peel strength (N/25 mm)	Shear strength (MPa)	180° peel strength (N/25 mm)	Shear strength (MPa)
Control	10.00 ± 3.52	0.30 ± 0.02	15.29 ± 0.20	0.30 ± 0.01
H	36.95 ± 11.27	0.32 ± 0.08	21.69 ± 3.43	0.33 ± 0.06
M	18.62 ± 4.51	0.37 ± 0.05	18.62 ± 4.61	0.39 ± 0.02
H + M	39.98 ± 3.04	0.48 ± 0.09	18.23 ± 3.63	0.31 ± 0.02

[a] H, mercury lamp; M, metal halide lamp.
[b] Data are given as mean ± SD (n = 5).

shows promise as a cheap, environmentally friendly technique that can easily be adapted to inline treatment of bamboo with flat, slight curve figures and even with a cylindrical shape.

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