Mechanisms and Properties of Chitosan-Assisted Bamboo Dyeing

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Acid dyes are often used to improve the decorative properties of bamboo products. However, the use of these dyes is problematic because they run easily. This study examined the use of chitosan as a fixing agent to address this issue. The study also investigated the interaction between dyed bamboo powder and dyed veneers pre-treated with chitosan. Powder was dyed at various pH values with acid scarlet GR and soaked in various solvents. Analyses were conducted using Fourier transform infrared spectroscopy, a zeta potential measurement analyzer, UV-visible spectroscopy, and a color measuring instrument. Pre-treated bamboo veneers were also dyed with acid scarlet GR and evaluated with the color measuring instrument, a scanning electron microscope, and an optical microscope. Chitosan functioned as a bridge and immobilized dye on the bamboo. This occurred through a chemical reaction and opposite charge attraction under acidic conditions. Pretreated dyed bamboo veneers demonstrated excellent dye uptake, color-fastness, and levelness. Therefore, chitosan shows promise for use as a fixing agent in dyed bamboo.

Keywords: Acid dye; Bamboo; Chitosan; Fixing agent

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INTRODUCTION

Bamboo has attracted considerable attention in a variety of fields in recent years, including architecture (Miyamoto et al. 2014), sewage treatment (Jiang et al. 2012; Suwanasing and Poonprasit 2014), smart materials (Bashar et al. 1996), and textiles (Liu et al. 2011). Bamboo is abundant in tropical and subtropical regions and has fast growth rates and short rotations (Hu and Yu 2014). In addition, bamboo processing requires minimal energy expenditure (Marinho et al. 2013) and has high annual productivity. Bamboo is well-known for its superior bending properties as a raw material (Zhao et al. 2010; An et al. 2011).

In industry, the flat color of bamboo limits its decorative use. To add color, bamboo is often dyed with acid dyes (Hu and Yu 2014). Many studies have investigated wood and bamboo dyeing (Dogu and Grabner 2010; Li et al. 2011). However, they have focused primarily on dyeing technology and the dyeing process; few have investigated color-fastness. Acid dyes are easily released from bamboo because of their small molecular weights and lack of chemical reaction with the material.

Fibers such as wool, silk, and nylon contain some free amino -NH₂ groups, while acid dyes contain acidic groups, usually -SO₃H. By forming salt linkages between acid and basic groups, dyes and fibers can easily bond (Perkins 1996).
In this study, chitosan was used as a fixing agent to immobilize dye on bamboo because it contains multiple -NH₂ groups. Chitosan is also known as poly-(1→4)-2-amino-2-deoxy-β-d-glucose and is derived from chitin, the second-most naturally abundant class of polysaccharide on Earth after cellulose and hemicellulose (Kadir et al. 2011; Vakili et al. 2014). It is nontoxic (Yang et al. 2014), renewable, and inexpensive. Chitosan is widely used as an alternative adsorbent because it has good adsorption capacity while still being low-cost (Wan Ngah et al. 2011).

In this study, an approach to immobilize chitosan and prepare it for bamboo dyeing was employed. Fourier transform infrared spectroscopy (FTIR), a zeta potential measurement analyzer, UV-visible spectroscopy (UV-vis), and a color measuring instrument were used to explore interactions between chitosan and bamboo. The effect of chitosan on bamboo dyeing, in terms of leveling tendency, light-fastness, wash-fastness, and color differences, were examined with a color measuring instrument, scanning electron microscope (SEM), and optical microscope.

**EXPERIMENTAL**

**Bamboo Powder Dyeing with Chitosan**

In this study, bamboo veneers (220 mm × 220 mm × 0.44 mm) were supplied by a furniture company in Hubei Province, China. The veneers were optionally ground with a high-speed grinder to obtain 200-mesh powders. Five grams of bone-dry bamboo powder was mixed with 100 mL of 1 wt. % chitosan solution (using 0.5 wt. % acetic acid solution as the solvent), stirred for 30 min, and ultrasonicated for 30 min. The mixture was separated by centrifugation for 10 min. The sediment was filtered and dried at 102 ± 5 °C for 48 h to obtain pure chitosan-bamboo powder.

The molecular structure of chitosan is shown in Fig. 1 (a).

![Chemical structure of chitosan (a) and acid scarlet GR (b)](image)

**Fig. 1.** Chemical structure of chitosan (a) and acid scarlet GR (b)

Acid scarlet GR (C.I. Acid red 73, λ_{max} 510 nm) was used as the colorant, and its structure is shown in Fig. 1 (b). One gram pure chitosan-bamboo powder was gradually added into 20 mL of 1 wt. % dye liquor under pH values of 1, 4, 7, or 13. The mixture was then heated in a water bath (80 °C) and stirred for 1 h. Next, the dyed chitosan-bamboo powder was separated by suction filtration and washed with distilled water repeatedly until no floating color remained. The filtrates from different pH values were collected separately and diluted to 100 mL. The powder was dried to an absolutely dry state for future use.

For comparison purposes, the acid dye solution was mixed with bamboo powder or chitosan solution. The resultant samples were denoted dyed bamboo and dyed chitosan, respectively.
Bamboo Veneer Dyeing with Chitosan

In this study, bamboo veneers were cut to dimensions of 80 mm × 10 mm × 0.44 mm and divided into three groups weighing 11.50 ± 0.05 g each. The veneers in one group were painted with chitosan solution evenly on both sides, dried to 8% moisture content (according to the local relative humidity), and soaked in 1 wt.% acid dye liquor for 1 h at 80 °C at pH 4. The liquor-to-solids ratio was 20 to 1, which was the same as what was used for bamboo powder dyeing. The veneers were successively washed with distilled water until the washing water was colorless and then dried to local relative humidity. The veneers in the second group were dyed with Acid scarlet GR under the same conditions, air-dried, painted with chitosan solution, and dried to 8% again. Veneers in the last group were dried directly to the same state without chitosan or dye.

Analytic Methods to Determine Immobilization Mechanisms

To ensure that chitosan is a suitable fixing agent and analyze the immobilization mechanisms of chitosan and bamboo, chitosan and dye, the zeta potential values of the dye solution, the bamboo powder suspension, and the chitosan solution at pH values of 1, 4, 7, and 13 were determined using a zeta potential analyzer (Nano ZS90 Malvern, England). The FTIR spectra of bamboo, chitosan, dyestuff, chitosan-bamboo powder, dyed powder, dyed chitosan, and dyed chitosan-bamboo powder were recorded using KBr pellets in the spectral range of 400 to 4000 cm\(^{-1}\) by Fourier transform infrared spectroscopy (Nicolet 6700 Thermo Scientific, USA) at 4 cm\(^{-1}\) resolution for 32 scans.

The effect of chitosan on bamboo dying was evident in the amount of dye uptake. The dyeing percentage at pH values of 1, 4, 7, and 13 of the dyed chitosan-bamboo powders, dyed chitosan powders, and dyed bamboo powders were measured with UV-visible spectroscopy (721 ApL, China) at \(\lambda_{\text{max}} 510\) nm. The rate of dyeing was calculated according to the following equation,

\[
E\% = \frac{C_0 - C_f}{C_0} \times 100\%
\]

where \(C_0\) and \(C_f\) represent the concentrations of the dye bath before and after dyeing.

The endurance of the chitosan linkage to dyed bamboo was tested for the decolor rate according to Duan’s method (Duan et al. 2003). The dry, dyed chitosan-bamboo powders produced at pH 4 were immersed into six kinds of solvents (0.1 g/100 mL), including alcohol, hydrochloric acid (2 M), acetic acid (2 M), NaOH solution (2 M), ammonium hydroxide (2 M), and distilled water. Before filtration, they were heated in a water bath for 30 min. The sediments were then washed and dried.

The \(K/S\) value of six types of powder was tested with a color measuring instrument (Dataflash 110 Datacolor, USA) under the illuminant D65 using a 10° standard observer. These measurements were taken five times for each sample. \(K/S\) comes from the Kubelka-Munk equation, which provides a calculation of the ratio,

\[
K/S = \frac{(1-R)^2}{2R}
\]

where \(K\) is the coefficient of absorption and \(S\) is the coefficient of scattering. The quantity \(R\) is the fractional reflectance at a specific wavelength (Perkins 1996). Color strength was denoted by the \(K/S\) value (Yu et al. 2013).
Characterization of Dyed Chitosan-Bamboo Veneer

The surface appearance of the dyed chitosan-bamboo veneers prepared via different processing methods was observed with a scanning electron microscope (SEM).

The color difference between dyed chitosan-bamboo veneers and dyed bamboo was determined with a color measuring instrument (Dataflash 110 Datacolor, USA) via CIELAB color coordinates. $L^*$ (lightness and darkness), $a^*$ (redness and greenness), $b^*$ (yellowness and blueness), and $C^*$ (saturation) were all tested. The difference in the color parameters $\Delta L^*$, $\Delta a^*$, $\Delta b^*$, $\Delta C^*$, and $\Delta E$ (total color difference) was determined at five positions in each veneer (Romagnoli et al. 2013).

\[
\begin{align*}
\Delta L^* &= L_1^* - L_0^* \\
\Delta a^* &= a_1^* - a_0^* \\
\Delta b^* &= b_1^* - b_0^* \\
\Delta C^* &= C_1^* - C_0^* \\
\Delta E &= \left(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\right)^{1/2}
\end{align*}
\]

To test light fastness, half of each groups’ veneers were exposed to YG611 light and a weather fastness tester (Changzhou No.2 Textile Instrument Factory, China) under a xenon lamp for 4 h. The remaining veneers were maintained in 80 °C water for 4 h. The color differences comparing the specimens before ($L_0$, $a_0$, $b_0$, $C_0$) and after ($L_1$, $a_1$, $b_1$, $C_1$) treatment were calculated with Eqs. 3 through 6, and the total color differences were calculated with Eq. 7.

RESULTS AND DISCUSSION

Zeta Potential Analysis of the Immobilization Mechanism

The zeta potentials of dye solution, chitosan solution, and the bamboo powder suspension are shown in Table 1. The zeta potentials of dye and bamboo were negative at any pH value. Little negatively charged dyestuff was able to attach to the bamboo because of the electrostatic repulsion from the same charge. The chitosan, on the other hand, had positive charge and could therefore attach to the bamboo easily via electrostatic attraction. It follows that the adsorption between bamboo and chitosan was stronger than that between bamboo and dye.

<table>
<thead>
<tr>
<th>pH value</th>
<th>Zeta potential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bamboo</td>
</tr>
<tr>
<td>1</td>
<td>-1.1±0.76</td>
</tr>
<tr>
<td>4</td>
<td>-12.2±1.81</td>
</tr>
<tr>
<td>7</td>
<td>-11.8±1.25</td>
</tr>
<tr>
<td>13</td>
<td>-13.6±1.37</td>
</tr>
</tbody>
</table>

*Chitosan was dissolved with acetic acid solution, so the zeta potentials at 7 and 13 were not tested.
FTIR Analysis of Immobilization Mechanisms

The FTIR spectra of bamboo and dyed bamboo are shown in Fig. 2. The two spectra were so similar that they indicated no significant chemical reaction between the dye and bamboo. Thus, there might be no strong bonding between the dye and bamboo. So multiple interactions between a single dye molecule and bamboo are needed to ensure a strong bonding.

![FTIR spectra of bamboo and dyed bamboo](image1)

**Fig. 2.** FTIR spectra of bamboo and dyed bamboo

Typical FTIR spectra of bamboo, chitosan-bamboo, dye and dyed chitosan-bamboo are shown in Fig. 3. The FTIR spectra of bamboo and chitosan-bamboo looked similar which proved bamboo did not react with chitosan. So they bonded by electrostatic attraction, which is consistent with the zeta potential results.

![FTIR spectra of bamboo, chitosan-bamboo, dye, and dyed chitosan-bamboo](image2)

**Fig. 3.** FTIR spectra of bamboo, chitosan-bamboo, dye, and dyed chitosan-bamboo
An absorption peak of chitosan-bamboo at 1657 cm\(^{-1}\), attributed to the primary amine, disappeared from the spectrum of the dyed chitosan-bamboo. This indicates that some \(-\text{NH}_2\) groups in the chitosan reacted in the dye solution. Furthermore, peaks at 1500 cm\(^{-1}\) in the spectra of dyed chitosan-bamboo and dye were ascribed to aromatic groups. The typical sulfonate peak at 1208 cm\(^{-1}\) appeared in the spectra of both the dye and the dyed chitosan.

These results indicate that a chemical interaction between chitosan and dye occurred. Because, according to Figs. 2 and 3, bamboo did not interact to a significant extent with dye or chitosan under acidic conditions. It follows that the effect was due to the presence of both chitosan and dye. The amino group of chitosan (CTS-\(\text{NH}_2\)) bonded with the sulfonic group of the dye (HSO\(_3\)-GR) under acidic conditions (H\(^+\)), producing sulphonate sediments (CTS-\(\text{NH}_3^+\text{SO}_3\)-GR). The chemical equations are shown below,

\[
\text{GR} - \text{SO}_3\text{Na} + H^+ \rightarrow \text{GR} - \text{SO}_3H + \text{Na}^+ \quad (8)
\]
\[
\text{CTS} - \text{NH}_2 + \text{HSO}_3 - \rightarrow \text{CTS} - \text{NH}_3^+\text{SO}_3 - \text{GR} \quad (9)
\]

where GR-SO\(_3\)Na represents acid scarlet GR with plenty of sulfonate groups.

**SEM Analysis of the Immobilization Mechanism**

The appearance of dyed chitosan-bamboo (a), chitosan-bamboo (b), and dyed bamboo (c) was observed by SEM (Fig. 4). Dyed bamboo and chitosan-bamboo had smooth surfaces and exhibited even distributions of chitosan or dye bonded by weak, secondary interactions. However, the surface of the dyed chitosan-bamboo was rough, indicating that the dye reacted with chitosan, which is consistent with sulphonate sediments.

**Fig. 4.** SEM micrographs of (a) dyed chitosan-bamboo, (b) chitosan-bamboo, (c) dyed bamboo

**Chemical Scheme of Pretreated Dyed Bamboo**

The chemical scheme of pretreated dyed bamboo is shown in Fig. 5, displaying the interactions between the dye, chitosan, and bamboo. According to FTIR spectra, which were shown before, salt linkages formed between chitosan and dye through the chemical reaction of \(-\text{SO}_3\text{H}\) and \(-\text{NH}_2\) groups. And the sediments that were observed by SEM also confirmed the production of salt linkages. Physical bonds were formed by electrostatic forces on the interface between chitosan and bamboo powder under acidic conditions. The electric property of chitosan was positive and opposite to dye, which were shown by the
analysis of zeta potential. As a result it can be concluded that the chitosan and bamboo were combined by electrostatic force.

Fig. 5. Chemical scheme of chitosan modification of dyed bamboo particles

**Effects of Chitosan on the Bamboo Dye Uptake**

The extent of dye uptake onto untreated bamboo and chitosan-treated bamboo are shown in Table 2. The addition of chitosan significantly increased the dyeing rate at pH 1, 4, and 7. According to the data in Table 2, stronger acidity of the dye solution facilitated higher dyeing rate. The dyeing rate improved after bamboo was soaked in a 21.31% chitosan solution at pH 1, 16.59% at pH 4, and 17.11% at pH 7, but declined in an alkaline environment. Under acidic conditions, chitosan helps maintain the dye in the bamboo and provides dye sites for SO$_3^-$+. Without H$^+$, the dye and chitosan are barely reactive and the interaction between dye and chitosan consists of physical adsorption only.

**Table 2. Dyeing Rate (%) of Bamboo and Chitosan-Bamboo at Different pH Values**

<table>
<thead>
<tr>
<th>pH value</th>
<th>Bamboo (%)</th>
<th>Chitosan-bamboo (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.40 ± 2.57</td>
<td>59.71 ± 2.60</td>
</tr>
<tr>
<td>4</td>
<td>37.97 ± 1.40</td>
<td>54.56 ± 6.25</td>
</tr>
<tr>
<td>7</td>
<td>35.32 ± 0.70</td>
<td>52.43 ± 3.64</td>
</tr>
<tr>
<td>13</td>
<td>19.82 ± 6.11</td>
<td>13.72 ± 1.09</td>
</tr>
</tbody>
</table>

*Dyeing rate (%) was calculated using Eq. 1.

**Stability of Dyed Chitosan-Bamboo under Various Conditions**

Figure 6 displays the color concentrations of dyed chitosan-bamboo powders after they were soaked in various solvents. Powder did not dissolve or fade in the organic solvent or acid solution. However, they decreased in the alkaline solution for both NaOH and ammonium hydroxide because of the precipitation of dissolved sulfonate.

$$\text{CTS}^-\text{NH}_3^+ + \text{SO}_3^- - \text{DYE} + \text{NaOH} \rightarrow \text{CTS}^-\text{NH}_2 + \text{CTS}^-\text{SO}_3^-\text{Na} + \text{H}_2\text{O} \quad (10)$$

The alkalinity of the NaOH solution is stronger than that of chitosan. This indicates that sulfonate produced by chitosan and dye (CTS-NH$_3^+$-OS-DYE) can react with NaOH.

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and produce a weak base with new salts (CTS-SO₃Na). Although ammonium hydroxide is less alkaline than NaOH, it is more alkaline than chitosan and can support the replacement.

![Graph showing K/S values of dyed chitosan-bamboo after soaking](image)

**Fig. 6.** K/S values of dyed chitosan-bamboo after soaking

The present findings show that dyed chitosan-bamboo is stable in organic solvents and acid solutions and easily degrades under alkaline conditions. This indicates that chitosan can be used as a fixing agent for acid dye except in an alkaline environment.

### Performance of Dyed Chitosan-Bamboo

**Color differences and fastness of dyed chitosan-bamboo veneer**

#### Table 3. Color Differences of Dyed Chitosan-Bamboo and Dyed Bamboo

<table>
<thead>
<tr>
<th>Color parameters</th>
<th>Dyed Bamboo</th>
<th>Dyed Chitosan-bamboo</th>
<th>Magnitude (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L^*)</td>
<td>38.88 ± 1.07</td>
<td>38.68 ± 2.32</td>
<td>1.33 ± 0.48</td>
</tr>
<tr>
<td>(a^*)</td>
<td>47.15 ± 3.68</td>
<td>47.36 ± 4.71</td>
<td>1.31 ± 0.74</td>
</tr>
<tr>
<td>(b^*)</td>
<td>39.61 ± 3.18</td>
<td>41.95 ± 6.35</td>
<td>3.83 ± 2.04</td>
</tr>
<tr>
<td>(C^*)</td>
<td>61.59 ± 4.80</td>
<td>63.30 ± 7.67</td>
<td>3.37 ± 1.67</td>
</tr>
</tbody>
</table>

\(\Delta E^{*b}\) 4.46 ± 1.70

\(^a\) Magnitude was calculated with Eqs. 3, 4, 5, and 7.

\(^b\) \(\Delta E^*\) (total color difference) was calculated with Eq. 8.

The relationship between the color of dyed bamboo and dyed chitosan-bamboo, as determined by CIELAB colorimetric analysis, is presented in the Table 3. With chitosan, the total color difference (\(\Delta E^*\)) was small. Saturation (the magnitude \(C^*\)) was improved slightly, indicating that the chemical reaction between chitosan and dye barely changed the color of the bamboo.

Due to chitosan, color fastness markedly improved (Table 4), especially the changes in brightness (\(\Delta L^*\)) and saturation (\(\Delta C^*\)). Chitosan worked as a bridge linking bamboo and dye, stabilizing it such that the water fastness and light fastness improved. The chitosan outside of the bamboo also plays a role in protecting dye from oxygen and preventing photooxide and photofade reactions.
Table 4. Color Fastness of Dyed Chitosan-Bamboo and Dyed Bamboo

<table>
<thead>
<tr>
<th>Color Parameter</th>
<th>Water-fastness</th>
<th>Light-fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dyed Chitosan</td>
<td>Dyed Bamboo</td>
</tr>
<tr>
<td></td>
<td>Bamboo</td>
<td></td>
</tr>
<tr>
<td>△L*</td>
<td>1.73 ± 1.13</td>
<td>11.94 ± 1.26</td>
</tr>
<tr>
<td>△a*</td>
<td>-7.34 ± 1.99</td>
<td>-21.45 ± 2.14</td>
</tr>
<tr>
<td>△b*</td>
<td>-9.37 ± 4.13</td>
<td>-23.19 ± 0.59</td>
</tr>
<tr>
<td>△C*</td>
<td>-11.76 ± 4.17</td>
<td>-31.34 ± 1.91</td>
</tr>
<tr>
<td>△E*&lt;sup&gt;b&lt;/sup&gt;</td>
<td>12.11 ± 4.4</td>
<td>33.99 ± 2.04</td>
</tr>
</tbody>
</table>

<sup>a</sup>Color parameter was calculated using Eqs. 3, 4, 5, 6, and 7.
<sup>b</sup>△E* (total color difference) was calculated with Eq. 8.

**Levelness of dyed chitosan-bamboo veneer**

Figure 7 illustrates the penetration of dyed chitosan-bamboo and dyed bamboo as determined with an optical microscope. The penetration of the dyed chitosan-bamboo was affected by the sediment. Some cells of chitosan-bamboo were not dyed or were brighter than those in dyed bamboo. The chitosan coating may prevent penetration by interacting with dye first and blocking some penetration pathways into the bamboo. It affected the levelness of dyed chitosan-bamboo veneer. However, the chitosan-bamboo that was immersed in acid dye produced sediments that enhanced immobilization of the dyestuff in the acidic solution. Future research on dye penetration of chitosan in bamboo is warranted.

![Image of optical micrographs](image_url)

**Fig. 7.** Optical micrographs of (a) dyed chitosan-bamboo and (b) dyed bamboo

**CONCLUSIONS**

1. Chitosan is a promising fixing agent for bamboo dyeing, except in alkaline conditions.
2. Chitosan functions as a bridge that links acid dyestuff and bamboo through chemical reactions and electrical attraction.
3. Chitosan modification improved the dyeing rate, wash-fastness, and light-fastness of dyed bamboo.
4. Future research on dye penetration in pretreated bamboo is warranted.
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