STUDY ON THE SWELLING CHARACTERISTICS OF BAMBOO BASED ON ITS GRADED HIERARCHICAL STRUCTURE

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Abstract. To understand the swelling characteristics of bamboo under its gradient structure, different parts of bamboo specimens have been soaked in solutions of different electrolytes. The results showed that the swelling extent of bamboo in solution is mainly influenced by chemical activity and molecular dimension of the solute. The dimensional increase in bamboo after swelling is mainly observed in the tangential and radial direction, and the largest dimensional increase as a result of swelling occurred in intermediary bamboo. High-concentration strong electrolytes will cause a certain degree of recrystallization in the bamboo specimen, especially in intermediary bamboo, resulting in an increase in its mass. In summary, the conclusion is that the removal of wax and tabaxir before swelling and the avoidance of using strong electrolytes as swelling solutions tend to improve the efficiency of swelling bamboo.

Keywords: Phyllostachys pubescens swelling characteristics, maximum percentage swelling, mass loss, hierarchical structures.

INTRODUCTION

The phenomenon of swelling is characteristic of all elastic materials but differs somewhat for different types of materials (Mantanis et al 1994a, 1994b). Wood swelling in liquid has been studied for the past 70 yr. West (1988) assumed that wood swelling was a bimolecular reaction merely requiring the collision of liquid molecules with wood. A number of scientists have made attempts to determine the factors that influence wood swelling in liquid. Actually, wood swelling is a complex process, and its influencing factors include wood substrate and solvents, none of which can be used to extrapolate conclusions individually. As for solvents, there are three main factors that influence wood swelling (Mantanis et al 1994b). The first is the dimensions of the molecule. The molecule size is in inverse proportion to the rate of swelling, and any increase in the molecular size of the swelling liquid will result in a consequent decrease in the degree of swelling.
the swelling (Nakatani et al. 2010). In addition, the molecular shape and branching and steric hindrance also affect the swelling effect. The second factor is the hydrogen bond. According to Ishimaru et al. (2001), a correlation existed between the degree of swelling and the extent of hydrogen bonding between the constituents of wood and those of the swelling agent. Mantanis et al. (1994b) found a strange phenomenon in the study of the effect of the molecular size on the degree of wood swelling. Benzyl alcohol, despite having a rather large molecular size, has strong swelling ability for hardwood, which might be accounted for by its high hydrogen bonding capability. The third factor is basicity. Mantanis et al. (1994b) placed several specimens of North American wood species in sealed weighing bottles with 40 different organic liquids to evaluate the influence of a wide variety of solvent factors. He found that the maximum tangential swelling for all the wood species was linearly correlated with the solvent basicity. As for wood substrates, density and extractives are two main factors that influence swelling. Wood density has been found to be an important factor that significantly influences the swelling of wood (Mantanis et al. 1994a). In general, the hardwoods such as maple (Acer saccharum) swelled to a much greater extent compared with the softwoods such as Douglas fir (Pseudotsuga menziesii). This is likely due to the greater density of hardwoods (Mantanis et al. 1994a). Wood extractives are substances that can be extracted with organic liquids, such as resin acids, fats, terpenes, lignans, flavonoids, tannins, stilbenes, etc., or hot water (Jankowska et al. 2016). A number of scientists have made attempts to determine the reason why the removal of extractives greatly increased the degree of the wood swelling. Mantanis and Papadopoulos (2010) suggested that cell wall disruption could be the main reason behind the phenomenon: the extraction process expands the size of the microscopic capillaries and accelerates the diffusion of the swelling liquid into the cell wall structure of wood. In addition, Mantanis et al. (1995a) found that the rate of wood swelling in organic liquids demonstrated a strong dependence on temperature (20-100°C). More specifically, the correlation between temperature and wood swelling suggests that the phenomenon of wood swelling is similar to a chemical reaction. This may be linked to minor changes in the cell wall structure when wood is treated with high-temperature liquids (Xing et al. 2016; Tanaka et al. 2017). Based on this, Mantanis et al. (1994a) first proposed the concept of activation energies, which represents the energy required to break the wood’s hydrogen bonds to allow for wood swelling in water. The removal of extractives or a drop in temperature can increase activation energies.

Bamboo is a tree-like giant grass composed of hollow culms and separated by nodes along its height (Sharma et al. 2015). It is a unique bio-composite like wood, but with vascular bundles as the reinforcement and parenchyma cells as the matrix (Zhang et al. 2017). The nonuniform distribution of vascular bundles embedded in the matrix makes it a functionally graded material (Silva et al. 2006; Li et al. 2018) (similar to the variations between wood growth rings in the radial direction). This means that the fiber distribution on the cross-section of bamboo is not as uniform as that of wood. Moreover, the fibrous sheath of bamboo is also changing along the radial direction. Based on this, bamboo can be divided into three parts from the outside to the inside, namely, the outer part, the intermediary part and, the inner part (Zhang et al 2014). Mantanis et al (1994b) suggested that cellulose is the primary wood polymer responsible for the most part of wood swelling in his research on the influence of basicity (donor number), molecular volume, and hydrogen bonding on the swelling of wood. Presumably, the swelling of bamboo should have characteristics different from those of wood because of its uniquely graded structures. Surprisingly, detailed data on the swelling of bamboo have not yet been collected extensively. Further development in the new solvent pulping processes requires more detailed information on the effects of chemical reagents on bamboo, which has great significance in commercial exploitation and more pioneering experiments.
In an attempt to narrow this gap, this study focuses on the swelling characteristics of bamboo based on its special structure. First, we compared the structural differences of wood and bamboo, and then, based on the gradient structure of bamboo, we studied its swelling characteristics in solutions of different electrolytes.

**MATERIALS AND METHODS**

**Materials**

*Bamboo specimens.* Moso bamboo (*Phyllostachys pubescens* Mazei ex H. de Lebaie) of 5 yr of age was collected from a bamboo plantation located in Anhui Province, China. All the specimens used for the swelling experiment were prepared from a height of 1.5 m above the ground of the same moso bamboo culm. Care was taken during the selection of bamboo specimens to reduce the influence of the variation of the specimens itself on the experiment. The specimens were divided into two groups. Group one was a bamboo block with a final dimension of 10 mm (*L*, longitudinal) × 10 mm (*T*, tangential) × *t* (*R*, radial; thickness of the bamboo culm wall) by split and was processed further. Group two was the group one block further evenly divided into three pieces in the radial direction, namely, outer bamboo, intermediary bamboo, and inner bamboo with a dimension of 10 mm (*L*) × 10 mm (*T*) × *t/3*.

The solutions were divided into nine types of chemical reagents under three categories, each of which (except for deionized water) consists of three different concentration levels, and each concentration level contains three specimens to reduce errors. So, there were 9 × 3 × 3 = 81 specimens in group one and 9 × 3 × 3 × 3 = 243 specimens in group two. A total of 324 specimens were used in the experiments.

**Methods**

*SEM observation.* The cross-sectional structure of moso bamboo was observed by using a scanning electron microscope (FEI-ESEM, XL-30, FEI, Inc, Hillsborough, OR). with an accelerating proportion voltage of 7 kV. For comparison, the cross-sectional structures of poplar and Chinese fir were also observed.

**Swelling experiment.** Experimental reagents include strong electrolytes: NaOH, Na₂CO₃, and NaCl; weak electrolytes: ice-cold acetic acid, quinine, pectase; and nonelectrolytes: deionized water, ethanol, and glycerin. The preparation of the solutions was carried out delicately at room temperature. More details of the nine types of chemical reagents are shown in Table 1. The specimens from group one and group two were soaked in the 27 types of prepared solutions in sealed weighing bottles placed in a thermostatically controlled bath for 10 d at the temperature of 25°C.

**Data measurement.** Specimens were oven-dried at 60°C for 24 h and then cooled in a desiccator; then the cooled oven-dry weights and dimensions were quickly measured. After the swelling experiment, specimen dimensions were measured again in a humid state, and then the cooled oven-dry weights after the swelling were measured after the specimens were dried in the oven at 60°C for 24 h. All the measurements were made at room temperature by using a micrometer caliper accurate to ±0.01 mm and a scale balance accurate to ±0.01 g. To further improve the accuracy of the measurement size, five points on the cross-section were selected as the measurement points (one point is in the center and four points are in the four corners), and the average value was finally taken. The maximum percentage swelling was calculated by the use of the equation (Mantanis et al 1994a, 1994b):

\[
\text{Maximum percentage swelling} = \frac{\text{Swollen dimension}-\text{Oven dry dimension}}{\text{(Oven dry dimension)}} \times 100\%.
\]

Mass loss was calculated by the use of the equation:
Mass loss

\[ \text{Oven dry weight}\cdot\text{Oven dry weight after swelling} = \ \text{Oven dry weight} \times 100\%. \]

**RESULTS AND DISCUSSION**

**Microstructure Differences between Bamboo and Wood**

Figure 1 shows the hierarchical structures of bamboo. Obviously, bamboo is a unique annular culm with hollow structure (Fig 1(a) and (b)); its outer surface was covered with wax, inner surface was covered with tabaxir, and its middle part was composed of vascular bundles and parenchyma tissue (Fig 1(c)). Among them, vascular bundle consists of fibers (Fig 1(j)) and vessel (Fig 1(i)), and parenchyma tissue consists of parenchyma cells (Fig 1(h)). Compared with Chinese fir tracheid (Fig 2(b)) and poplar fiber (Fig 2(d)), fiber distribution on the cross-section of bamboo is not as uniform as that of wood, making its structure more special; moreover, moso bamboo fibers have almost no cell wall lumen (Fig 1(j)).

Furthermore, the vascular bundles in bamboo is also nonuniform along the radial direction. Based on this, bamboo can be divided into outer bamboo (Fig 1(e)), intermediary bamboo (Fig 1(f)), and inner bamboo (Fig 1(g)) from the outside to the inside, which is similar to the difference between the early and late wood of Chinese fir (Fig 2(a)) and poplar (Fig 2(c)). The radial distribution of vascular bundles in bamboo shows a graded hierarchical structure (Fig 1(d)).

**Maximum Percentage Swelling of Bamboo Block in Different Solutions**

Most solutions seem to swell the bamboo to an almost consistent extent, although variations in different solutions did occur. Figure 3 is a graph of the swelling degree of the bamboo block in different solutions. Results indicated that sodium hydroxide, glacial acetic acid, and ethanol swelled the bamboo block more than water, but sodium carbonate, sodium chloride, quinine, pectase, and glycerin were less capable than water in terms of swelling bamboo. The largest amount of bamboo swelling was caused by sodium hydroxide.

Mantakis et al (1994b) suggested that the strong basic nature of solutes is significant for the degree of swelling. This may explain that sodium hydroxide resulted in the highest level of swelling of bamboo because of its strong base with high chemical activity. The microstructure of bamboo can be understood in a way that the combination of cellulose is the strengthened ligand, hemicellulose is the connecting substance, and lignin is the filling material, whereas extractives (terpenes, fats, phenols, fatty acids, tannins, etc.) do not count as structural components. Sodium hydroxide not only has strong chemical activity (Nguyen et al 2018) but also has a strong extraction influence on bamboo, especially for hemicellulose and extractives. Hemicellulose and

<table>
<thead>
<tr>
<th>Experimental reagents</th>
<th>Concentration level</th>
<th>Molecular formula</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide</td>
<td>1%, 2%, and 4%</td>
<td>NaOH</td>
<td>AR</td>
<td>Qiangsheng Biochemical Co. Ltd., Jiangsu, China</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>1%, 2%, and 4%</td>
<td>Na₂CO₃</td>
<td>AR</td>
<td>Qiangsheng Biochemical Co. Ltd., Jiangsu, China</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>1%, 2%, and 4%</td>
<td>NaCl</td>
<td>AR</td>
<td>Qiangsheng Biochemical Co. Ltd., Jiangsu, China</td>
</tr>
<tr>
<td>Glacial acetic acid</td>
<td>5%, 10%, and 20%</td>
<td>C₄H₄O₂</td>
<td>AR</td>
<td>RichJoint Chemical Reagents Co. Ltd., Shanghai, China</td>
</tr>
<tr>
<td>Quinine</td>
<td>1%, 2%, and 4%</td>
<td>C₂₀H₂₄N₂O₂</td>
<td>AR</td>
<td>Macklin Biochemical Co. Ltd., Shanghai, China</td>
</tr>
<tr>
<td>Pectase</td>
<td>1%, 2%, and 4%</td>
<td>C₂₀H₄₃N</td>
<td>AR</td>
<td>Macklin Biochemical Co. Ltd., Shanghai, China</td>
</tr>
<tr>
<td>Deionized water</td>
<td>100%</td>
<td>H₂O</td>
<td>EW-II Laboratory provided</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>25%, 50%, and 100%</td>
<td>C₃H₆O₃</td>
<td>AR</td>
<td>SuYi Chemical Reagent Co. Ltd., Shanghai, China</td>
</tr>
<tr>
<td>Glycerin</td>
<td>25%, 50%, and 100%</td>
<td>C₃H₈O₃</td>
<td>AR</td>
<td>SuYi Chemical Reagent Co. Ltd., Shanghai, China</td>
</tr>
</tbody>
</table>

Table 1. Information of chemical reagents.

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the extractive would dissolve partly when bamboo is being soaked in the sodium hydroxide solution, and the strong-acting force between microfibrils inside the cytoderm is weakened. So, it is easier for the microfibrils to expand and swell, and both the degree of swelling and the macroscopic volume of the cytoderm will increase as a result. Similarly, glacial acetic acid...
and ethanol also have a strong extraction effect on the extractives, but not on hemicelluloses. Mantanis et al. (1994a) reported that the removal of extractives has been found to enhance swelling significantly. In addition, it was found that the removal of extractives from wood even with mild procedures caused a large decrease in the activation energy, $E_a$, which represents the energy required to break the wood (Mantanis et al. 1994a). In other words, the removal of extractives makes the network structure of the cell wall more easily damaged by the invading external molecules. Compared with wood, bamboo has higher extractives and hemicellulose content (Table 2), which indicated the removal of extractives and hemicellulose may be more significant for bamboo swelling. Furthermore, the strong swelling ability of ethanol compared with water can also be explainable by its very high hydrogen-bonding capability. In addition, the surface tension of ethanol (21.97 mN/m) is less than that of deionized water (72.00 mN/m) and glycerin (63.30 mN/m) at a temperature of 25°C possibly because it is easier for ethanol to go into the interior of bamboo and participate in the expansion of microfibrils. Similarly, as for glycerin, both its density (1.263 g/cm$^3$) and viscosity (945 Pa·s) are higher than those of deionized water (1 g/cm$^3$, 0.894 Pa·s) and ethanol (0.789 g/cm$^3$, 1.074 Pa·s), so it should be more difficult for glycerin to penetrate the interior of bamboo. Mantanis et al. (1994b) suggested that any increase in the molecular dimensions of the

![Figure 2. Chinese fir and poplar structure.](image)

![Figure 3. Dimensional change of bamboo when soaked in different solutions.](image)
liquid will cause a consequent increase in the $E_a$ of wood swelling, which may account for the stronger swelling ability of ethanol than glycerin, and similarly why sodium carbonate, sodium chloride, quinine, and pectase are less capable in swelling wood. Nakatani et al (2010) and Kucharczyková et al (2017) assumed that wood swelling was a bimolecular reaction merely requiring the collision of liquid molecules with wood. Because it is more difficult for larger molecules to enter the interior of bamboo, the degree of bimolecular reaction is very low.

We can also find that the swelling ability of the solutions do not correlate directly with its ability to ionize, ie whether it is a strong electrolyte, weak electrolyte, or nonelectrolyte. As shown in Fig 3, electrolysis (except sodium hydroxide) has very little effect on the swelling of bamboo. However, it is highly probable that more complex mechanisms are behind this phenomenon that awaits further exploration.

**Difference on the Longitudinal, Tangential, and Radial Direction of Swelling of Bamboo**

Figure 4 shows the dimension change and the change rate of longitudinal, tangential, and radial direction of bamboo, which was soaked in different solutions. It shows that the increments are mainly reflected in the tangential and radial direction, but not in the longitudinal direction of bamboo blocks in any solution. In addition, the ratio of the tangential increment to radial increment is between 0.32 and 0.54. The dimensional change in the longitudinal direction was more affected by the microfibril angle. The reason why the longitudinal increment is less can be explained by its much smaller microfibril angle (about 9°) (Yu et al 2014). Normally, the ratio of the tangential increment to radial increment of swelling of wood is 2, which is drastically different from the data from the bamboo swelling experiment carried out in this study (Sopushynskyy 2017). There may be two reasons for this phenomenon. 1) Macroscopically, bamboo is characterized by a hollow structure (Fig 1(b)) with large tolerance inside the radial direction. Therefore, its congenital conditions allow for more radial increase to prevent cracking. 2) Microscopically, as shown in Fig

![Table 2. Chemical constituents of moso bamboo (Phyllostachys pubescen) and wood (Zhang et al 2005; Jiang et al 2006; Hong 2015; Meng et al 2016).]

<table>
<thead>
<tr>
<th></th>
<th>Cellulose %</th>
<th>Hemicellulose %</th>
<th>Lignin %</th>
<th>Extractives %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bamboo clock$^a$</td>
<td>41.54</td>
<td>25.51</td>
<td>22.06</td>
<td>6.27</td>
</tr>
<tr>
<td>Outer bamboo$^b$</td>
<td>45.27</td>
<td>22.04</td>
<td>27.90</td>
<td>5.23</td>
</tr>
<tr>
<td>Intermediary bamboo$^b$</td>
<td>41.23</td>
<td>27.15</td>
<td>24.01</td>
<td>7.39</td>
</tr>
<tr>
<td>Inner bamboo$^b$</td>
<td>39.01</td>
<td>24.01</td>
<td>23.68</td>
<td>7.18</td>
</tr>
<tr>
<td>Bamboo parenchyma cell$^c$</td>
<td>25.53</td>
<td>31.82</td>
<td>22.55</td>
<td>10.70</td>
</tr>
<tr>
<td>Bamboo fiber$^c$</td>
<td>46.74</td>
<td>20.93</td>
<td>20.83</td>
<td>5.06</td>
</tr>
<tr>
<td>Poplar$^d$</td>
<td>52.83</td>
<td>19.50</td>
<td>21.77</td>
<td>2.64</td>
</tr>
<tr>
<td>Chinese fir$^d$</td>
<td>47.40</td>
<td>10.65</td>
<td>32.94</td>
<td>4.31</td>
</tr>
</tbody>
</table>

$^a$ Meng et al (2016).
$^c$ Hong (2015).
1(d), the structure of bamboo results in huge variations in the radial direction, which is mainly reflected by the density and the size of the vascular bundles. Therefore, unlike the radial direction, the variation is smaller tangentially.

**Differences between Maximum Swelling Percentage of Outer, Intermediary, and Inner Bamboo in Different Solutions**

The results of the maximum percentage swelling with outer, intermediary, and inner bamboo in different solutions are shown in Fig 5. Results indicated that all agents are capable of swelling the three separate parts of bamboo better than they do with the bamboo block. The largest amount of outer bamboo, intermediary bamboo, and inner bamboo swelling was caused by sodium hydroxide, glacial acetic acid, and ethanol, which is similar to the results of the swelling of the bamboo block. In addition, the maximum swelling values for all solutions occur with intermediary bamboo, followed by outer bamboo and then inner bamboo.

The different extents of swelling of outer, intermediary, and inner bamboo can be directly related to its structure. Chuma et al (1990) reported the density of bamboo fibers is 1.57 g/cm³ and that of parenchyma cells is 0.45 g/cm³. Zhang et al (2017) suggested that the distribution density of vascular bundles increased radially from the interior to the exterior of the bamboo culm, which is also be seen in Fig 1. Higher density means a large proportion of vascular bundles exist in the outer bamboo and by contrast, lowest density means a very small proportion of vascular bundles exist in inner bamboo. In other words, outer bamboo is more compact than inner bamboo. Mantanis et al (1994b) noted that the wood swelling rate increased dramatically with the decreasing size of molecules. Nakatani et al (2010) also suggested that larger molecules encounter difficulties in diffusing into the fine capillary structure of wood. Bamboo swelling seems to be a bimolecular reaction that requires collisions between solute molecules and bamboo molecules; so, the structure of bamboo should have a great influence on its swelling. Solvent molecules have difficulties in diffusing into the...
capillary structure of outer bamboo because of its high density and the existence of wax (Fig 1(c)). As for inner bamboo, the density of vascular bundles is lower because the tissue proportion of the fibrous sheath here is very small, and a large number of parenchymal cells are present inside (Zhang et al 2017). In fact, inner bamboo is very loose because of its lower density; but solvent molecules also experience difficulties in diffusing into it because of its tabaxir, which is covered with more lignin that prevents the invasion of external particles. Mantanis et al (1994b) indicated that the cellulose polymer is possibly the primary cause for the maximum extent of wood swelling. The swelling effect of outer bamboo is stronger than that of inner bamboo as a result of its higher cellulose content, and that may also be due to its greater density. There is no wax and tabaxir of intermediary bamboo; therefore, the molecules of the solvent can easily diffuse into its structure. So, intermediary bamboo swells the greatest because it has an intermediate density and lacks substances that hinder swelling. The swelling effect of bamboo block is the poorest likely because it has wax and tabaxir at the same time. Therefore, for better effects, we suggest to remove the wax and the tabaxir before swelling bamboo.

Different Mass Loss of Outer, Intermediary, and Inner Bamboo in Different Solutions

Figure 6 shows the differences of the mass loss in outer, intermediary, and inner bamboo in different solutions. All solutions seem to cause a change in the weight of bamboo, although the extent of the change varies among the bamboo block, outer bamboo, intermediary bamboo, and inner bamboo. The mass loss in outer bamboo and the bamboo block is slighter than that in intermediary bamboo. In addition, there appears to be an increase in weight in the specimens when being soaked in a strong electrolyte with high concentration, especially for intermediary bamboo.

Mantanis et al (1995a) indicated that the phenomenon of wood swelling is similar to a chemical reaction. It is clear that the mass loss of bamboo is directly affected by its chemical
composition. Jiang et al (2006) showed that the cellulose content continuously decreases from outer bamboo to inner bamboo, whereas the content of hemicelluloses, lignin, and extractives shows a rising trend (Table 2), which is speculated to be linked with the distribution of fibers similar to its structural variation. Hemicelluloses, lignin, and extractives would dissolve partly when the bamboo specimens are soaked in solutions. For example, sodium hydroxide can dissolve part of the hemicellulose and extractives (Sun et al 2013), and glacial acetic acid can partially dissolve lignin and extractives (Wang et al 2017). But, such solutions generally have less effect on the cellulose. The mass loss in outer bamboo and bamboo block is less than that in inner bamboo, which can be explained by its larger proportion of cellulose (Table 2). There is a special phenomenon worth paying attention to, which is that bamboo specimens tend to demonstrate an increase in weight when the solution is a strong electrolyte with high concentration. Strong electrolytes are usually heavy metal salts, which are completely ionized in solution. Following their entrance into the interior of bamboo, they can be recrystallized after drying, leading to a weight increase. The swelling effect of intermediary bamboo is the most obvious because more molecules can enter into its structure. Consequently, the weight gain rate is the highest. Glacial acetic acid and ethanol are volatile and, therefore, do not cause any weight gain. In conclusion, strong electrolytes are not suitable for swelling bamboo because of the side effect, ie mass increase, caused by recrystallization.

CONCLUSION

The swelling characteristics of the bamboo block, outer bamboo, intermediary bamboo, and inner bamboo have been obtained in solutions of different electrolysis. The extent of swelling is mainly influenced by two solution properties: the chemical activity that determines the ability of the solution to interact with bamboo and the molecular dimension that determines whether the molecules can enter the interior of the bamboo or not. In addition, the dimension increase in bamboo after swelling is mainly reflected in the tangential and radial direction, and the ratio of the tangential increment to radial increment is between 0.32 and 0.54, which is drastically different from the corresponding data from wood swelling. Furthermore, the largest dimension increases occur in intermediary bamboo, which can be explained by the absence of wax in outer bamboo and tabaxir in inner bamboo. Moreover, high concentration of strong electrolytes will cause a certain degree of recrystallization in bamboo, especially for intermediary bamboo, resulting in an increase in its mass. In summary, we conclude that removal of wax and tabaxir before swelling and avoidance of using strong electrolytes as swelling solutions tend to improve the efficiency of bamboo swelling.

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