Micromorphological and chemical characteristics of waterlogged archaeological bamboo

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Abstract

Waterlogged archaeological bamboo works such as bamboo slips and bamboo baskets, etc. were unearthed during excavations of the Mado shipwreck No. 1 excavation in 2009. Despite the number of bamboo artefacts recovered from underwater sites, the characteristics and conservation of waterlogged archeological bamboo unearthed from the sea have not been studied sufficiently.

Following examinations of waterlogged archaeological bamboo using optical, scanning electron and transmission electron microscopy, it was found that waterlogged archaeological bamboo has been invaded by soft rot fungi and erosion and tunneling bacteria. This is similar to the usual micromorphological decay characteristics of waterlogged archaeological wood. Unlike waterlogged wood however, waterlogged bamboo demonstrated differences in aspects of decay in the interlayer structure of the fibre cell and in the degree of decay, depending on the parts of the bundle sheath examined.

Chemical analyses suggested that, as in waterlogged archaeological wood, cellulose and hemicellulose were significantly degraded and the content of lignin was relatively high in waterlogged bamboo.

1. Introduction

Many bamboo artefacts have been recovered from shipwrecks in Korean waters. Excavations of the Mado No. 1 shipwreck in 2009 uncovered waterlogged archaeological bamboo artefacts such as bamboo slips, chopsticks and baskets (Figure 1; National Research Institute of Maritime Cultural Heritage 2010). Large numbers of waterlogged bamboo artefacts were also recovered from the Mado shipwreck No. 2 in 2010 and from the Mado shipwreck No. 3 that is still being excavated (National Research Institute of Maritime Cultural Heritage *in press*).

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Figure 1. Bamboo slips from Mado shipwreck No. 1
(National Research Institute of Maritime Cultural Heritage, 2010)

Bamboo artefacts are very important, particularly the bamboo slips that were found with rice seeds, buck wheat and millet because the writing on them provides valuable archaeological information about trade and the date of the shipwreck. The year that the goods were packed, the names of the senders of the goods and the people to whom they were despatched were given on these slips. Ceramics found on the same shipwreck could then also be easily dated.

Despite the large amount of bamboo that has been excavated from Asian shipwrecks, very little work has been done to characterise the type and extent of deterioration of these archaeologically valuable material types. This knowledge is very important as a guide to the best conservation method for the long-term stabilisation of these artefacts.

On the other hand, the deterioration of waterlogged wood has been extensively studied. Waterlogged archaeological wood, excavated after being buried for long periods in boggy marshes, lakes or the marine environment, is usually deteriorated due to attack by non-biological and/or biological agents. In the case of wood that has been buried in the ocean for hundreds of years, the wood breaks down due to attack by marine organisms such as Teredo navalis or by the chemical actions of sea water and the attack of soft rot fungi, erosion bacteria and tunneling bacteria. Changes induced by microbiological attack can be verified through microscopic and chemical analyses.

Decay of wood by soft rot fungi mainly occurs in the thick cell walls of the latewood and a cavity is formed in the middle layer of the secondary cell wall. Soft rot fungal decay also occurs in the cell wall of the cell lumen. Decay of the secondary wall is usually widespread while that of middle lamella is quite insignificant by comparison.

When examined using optical microscopy, evidence of bacterial decay of the secondary wall is provided by the appearance of a form of granulates. It is possible to differentiate between attack by erosion and tunneling bacteria by examining the pattern of decay in the cell wall. Erosion bacteria decay the S2 layer, penetrating into the S3 layer and attack the secondary wall. They do not attack the middle lamella. On the other hand, tunneling bacteria attack the S2 layer as well as the S1 layer, penetrating the middle lamella and leaving a crescent-shaped decay pattern in the area in which wood cell wall was decayed (Eriksson et al 1990; Hoffmann and Jones 1990:35-65; Kim and Singh 2000:135-155; Singh and Butcher 1991:143-157).

Chemical and microbiological attack on wood has the biggest impact on the cellulose and hemicellulose components. These polysaccharide components are more easily degraded than the polyphenolic lignins, leading to significant decreases in the polysaccharide content and a corresponding relative increase in the amount of lignin retained in waterlogged wood (Hedges 1990:111-140; Hoffmann and Jones 1990:35-65; Kim 1993; Kim, *et al.* 1990:3-7).

As seen above, much research has been devoted to the analysis and preservation of waterlogged archaeological wood. Unfortunately, probably because of the relative scarcity of bamboo on many shipwreck sites, the pattern of decay and changes in the chemical characteristics of waterlogged archaeological bamboo have not been adequately determined. The archaeological significance of bamboo artefacts however, demands that a study of the nature of their deterioration be conducted. This study aimed therefore to analyze the micromorphological characteristics and the changes in the chemical components of waterlogged archaeological bamboo and compare these with the characteristics of both modern, undegraded bamboo and with waterlogged wood. It was hoped that this comparison would provide information that could be used to guide conservation treatments of waterlogged archaeological bamboo.

2. Methods and materials

Examinations were conducted of the micromorphological characteristics and changes in the chemical characteristics of waterlogged archaeological bamboo unearthed as part of the Mado shipwreck No. 1 underwater excavations in 2009. The Mado shipwreck No. 1 is estimated to have sunk in coastal waters near Mado island, Taean in the spring of 1208 (National Research Institute of Maritime Cultural Heritage 2010). As there is no anatomical difference between *Phyllostachys bambusolides*, *Phyllostachys nigra* var. *henonis* and *Phyllostachys pubescens* which grow in Damyang, Korea (So, *et al.* 1999:7-14), this study used 3 year old, undegraded *Phyllostachys bambusolides* as a control group for comparison. The species of waterlogged archaeological bamboo unearthed in the Mado shipwreck excavations could not be precisely determined.

2.1 Micromorphological characteristics

Collected samples were embedded in Spurr's resin after being fixed and dehydrated. Semi-thin sections were observed with an optical microscope (Olympus BX50) after being were dyed with Toluidine blue. Ultra-thin sections were observed with a transmission electron microscope (TEM, JEM-1400; JEOL Ltd., Japan) after being were dyed with $KMnO_4$ and UALC.

2.2 Chemical characteristics

Waterlogged archaeological bamboo samples used in this experiment were freeze-dried prior to characterisation to minimize changes that may have otherwise occurred during drying.

2.2.1 Material composition

Prior to chemical component analysis, the bamboo samples were ground with a Wiley mill, producing a wooden powder of 60~80 mesh. Organic solvent extractives, holocellulose, Klason lignin, and ash were analyzed according to TAPPI standards while the monosaccharide components were analyzed by gas chromatographic techniques.

2.2.2 Chemical analysis

Powder samples of less than 300 mesh were analyzed with FT-IR after mixing them with KBr in the proportion 100:0.05 and producing a pellet. For X- ray diffraction analysis, CuKα radiation was used at 40 kV and 20mA. The relative crystallinity was determined using the Segal method (Lee and Kim 1992:28-37)

$$Cr. (\%) = [(I_{200} - I_{am}) / I_{200}] \times 100$$

I_{200} : diffraction intensity of (200) (2)

I_{am} : diffraction intensity of non-crystalline region (2)

3. Results and Discussion

3.1 Micromorphological characteristics

Bamboo fibres have a polylaminated structure in which narrow and wide layers are repeated (Cho, *et al.* 2008:261-265; Liese 1987:196-208). Examination with an optical microscope showed that there were differences in decay between the layers. Decay of the bamboo fibres near parenchyma cells was more advanced than that of bamboo fibres near vessels. Cavities were found in bamboo fibres and the presence of granulates showed that they were attacked by soft rot fungi and bacteria.

Observations using a TEM showed that there was difference in decay between the narrow layers and the broad layers in the polylaminated bamboo fibres. Although the waterlogged archaeological bamboo was attacked by both bacteria and soft rot fungi, most of the decay was caused by bacteria. Because the decay was so advanced it was impossible to clearly observe the exact nature of the decay of the bamboo samples. It was possible however, to observe the damage caused by tunneling bacteria. In some bamboo fibres, the deterioration of the cell lumen is similar to that of the middle lamella.

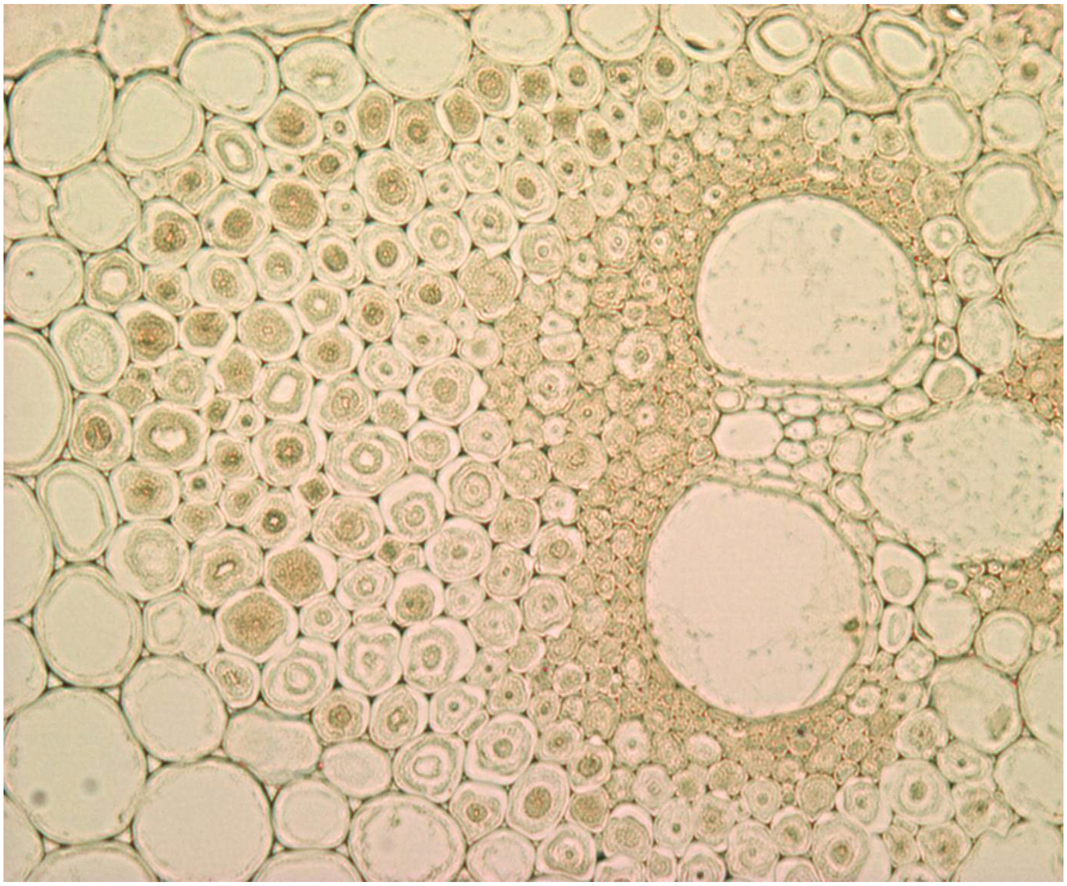

Figure 2. Bundle sheath of waterlogged archaeological bamboo(x200)
(photo by author).

3.2 Chemical characteristics

3.2.1 Material composition of waterlogged archaeological bamboo

The chemical composition of waterlogged archaeological bamboo is shown below (Table 1). It is reported that unlike lignin, polysaccharides are easily decayed, especially in waterlogged archaeological wood (Hedges 1990:111-140; Fujii, *et al.* 1988:261-265; Kim, *et al.* 1990: 3-7; Kim 1993; Seifert and Jagels 1984:269-297; Taniguchi, *et al.* 1986:738-743). It was revealed that the ratio of holocellulose to lignin was 0.1 to 1, due to preferential decay of the polysaccharides compared to lignin in waterlogged archaeological bamboo, a result similar to that which has been previously demonstrated in waterlogged archaeological wood. The ratio of holocellulose to lignin was 3.1 to 1 in the bamboo control group. These results compare favourably with the results of earlier research on waterlogged archaeological wood (Hedges 1990:111-140; Hoffmann and Jones 1990:35-65; Kim, *et al.* 1990:3-7; Kim 1993).

Assuming that all the glucose determined and reported in Table 1 originated from cellulose, the amount of cellulose and hemicellulose in degraded waterlogged archaeological bamboo is 8.1% and 8.4% respectively (Kim 1988:3-9). Based on the expected yields of glucose and hemicellulose sugars from undegraded bamboo, approximately approximately 76.7 % of the bamboo cellulose and 79.3 % of the bamboo hemicellulose has therefore been lost from the waterlogged archaeological bamboo. The amount of organic solvent soluble material also deceased. It was difficult to clearly judge whether the loss of organic soluble extractives like resin, was caused by activities of marine microorganisms or by chemical degradation and dissolution into the sea water.

The ash content of the waterlogged archaeological bamboo was 4.2 times greater than that of the control group. This result is not unexpected and is consistent with earlier reported results for waterlogged archaeological wood unearthed from marshes or underwater sites (Cha, *et al.* 2006:19-30; Hedges 1990:111-140; Hoffmann and Jones 1990:35-65; Kim, *et al.* 1990:3-7; Kim 1993).

Table 1. Chemical composition *of Control(Phyllostachys bambusolides) and WAB (Waterlogged archaeological Bamboo).*

(% of dry matter)	*OSE*	*HL*						*KL*	*Ash*
		Rham	Ara	Xyl	Man	Gal	Glu		
Control	4.4	75.2						24.3	1.3
		0	3.5	36.0	1.0	0	34.7		
WAB	2.3	16.5						62.1	5.4
		0.1	0.6	7.3	0.3	0.1	8.1		

Abbreviations used: Rham (rhamnose), Ara (arabinose), Xyl (xylose), Man (mannose), Gal (galactose), Glu (glucose), HL (holocellulose), KL (Klason lignin), OSE (organic solvent extractives).

3.2.2 Fourier transform infrared (FTIR) and XRD analyses

When analyzing the chemical characteristics of waterlogged archaeological bamboo with FT-IR, it was revealed that all components in the waterlogged archaeological bamboo sharply decreased. Cellulose absorptions at the 895, 1050 and 1160 cm^{-1} bands either disappeared or decreased. The 1730 cm^{-1} band corresponding to hemicelluloses disappeared and the combined cellulose/hemicellulose band at 1315~1335 cm^{-1} band sharply decreased. In the control group, one band (1251 cm^{-1}) was found while in waterlogged archaeological bamboo, two bands at 1225 cm^{-1} and 1266 cm^{-1},were found. Absorptions at the 1220~1230 cm^{-1} band and at approximately 1270 cm^{-1} are attributed to guaiacyl lignin and it was found that the guaiacyl lignin component was less decayed than the syringyl type. This result supports the argument that as lignin decays, the decay resistance of guaiacyl lignin is greater than that of the syringyl type (Hedges 1990:111-140).

The results of X- ray diffraction analyses are presented in Table 2. The diffraction intensity corresponding to crystalline cellulose (I_{200}), sharply decreased while the diffraction intensity , corresponding to amorphous cellulose (I_{am}) decreased. When measuring the degree of relative crystallization according to the Segal method, it was revealed that crystallization sharply decreased by over 4.7 times.

Table 2. Relative crystallinity of Control(*Phyllostachys bambusolides*) and WAB (Waterlogged archaeological Bamboo).

	Relative crystallinity(%)
Control	51.8%
WAB	10.9%

4. Implications for Conservation Treatment of Bamboo

The aim of this study was to determine the degree of degradation of waterlogged archaeological bamboo as a precursor to the determination of the most appropriate conservation treatment for these material types. The polysaccharide content, as found by the chemical determination of holocellulose (Table 1), corresponds to a maximum water content of approximately 700 % (Wilson, *et al.* 1993:599-610), indicating that the waterlogged archaeological bamboo is extremely degraded. Such extreme degradation would normally imply that PEG 4000 should be used to treat these materials. However because of the differences in the structures of wood and bamboo such a treatment would not necessarily be the best. It was also important to find a treatment that would stabilise the bamboo for eventual display in the high relative humidity conditions that exist in the Korean summer.

Experiments are in progress therefore, in which different consolidants (PEG, sucrose and cetyl alcohol) are being used to determine the most effective treatment for these materials. For these consolidants different molecular weights (PEG), different concentrations and varying treatment times are being tested. Treated archaeological bamboo will be freeze-dried after consolidation. An analysis of the treatments, based on shrinkage data, colour, extent of cracking and checking and general aesthetic appearance will be used to determine the most effective treatment or treatments. The results of these tests and the conclusions drawn will be reported at a later date when all experiments have been completed.

5. Conclusions

When observing waterlogged archaeological bamboo with an optical microscope and a TEM, it was revealed that waterlogged archaeological bamboo was decayed by soft rot fungi and bacteria, in a manner similar to the micromorphological decay of waterlogged archaeological wood. It was found that unlike the decay of wood however, in waterlogged bamboo, there were differences in aspects of decay of the layer structure in the fibrous cells of bamboo and in the degree of decay in the vascular regions of the plant.

As with waterlogged archaeological wood, there is a relative increase in the lignin content compared to the holocellulose that degrades more readily.

Research on changes in the chemical characteristics according to patterns and processes of decay was not conclusive because the decay of the waterlogged archaeological bamboo used in this study was very highly advanced. Further research will be conducted into the changes in the chemical characteristics according to patterns and processes of decay.

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