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Investigation into the deterioration process of archaeological bamboo strips of China from four different periods by chemical and anatomical analysis

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ABSTRACT

The chemical and the anatomical features of the archeological bamboo strips of China from four different periods were compared with the non-degraded fresh bamboo to understand the deterioration process. Unprocessed bamboo strips, isolated hemicelluloses and lignin fractions were analyzed with wet chemical analysis, GC, FTIR, UV and XRD to investigate the chemical degradation. It was found that the crystalline cellulose and the polyxylose degraded with increasing age, leaving the amorphous cellulose and the lignin with syringyl moieties modified as the main residual cell wall materials. Serious degradation of *p*-coumaric acid and ferulic acid were detected and indicated the cleavage of the linkage between the lignin and the carbohydrate, which might facilitate the degradation of carbohydrate. The anatomical analysis with SEM and TEM revealed the vanishing of the parenchymatous ground tissue and vessels and the cellulose microfibrils in the multilayered secondary wall. The differences in lignin content and in tissue density (cell thickness/cell size) between the parenchyma cells and the sclerenchymatous fiber cells fundamentally led to the formation of the unique anatomical structure of the archeological bamboo strips which was composed of parallel solid bundles. The effects of the chemical and the anatomical degradation on the mechanical properties were also discussed.

1. Introduction

Bamboo strips were the main media for literacy before the invention of paper in ancient China and were of great importance in the research of Chinese history. However, as shown in Fig. 1, unearthed archaeological bamboo strips often exhibit literature-covering dark color and twisted and curled appearances, implying chemical modification and serious loss of mechanical strength and rigidity which were caused by gradual natural aging. This is unfavorable for display and long-term preservation.

Unfortunately, up to now, the degradation of the archaeological wood has been widely researched [1–4] while research about the degradation of archaeological bamboo is quite limited. Although the main chemical composition of bamboo is similar to wood, over 90% of which consists of cellulose, hemicelluloses and lignin [5,6], bamboo exhibits quite different chemical and physical characteristics from wood due to the differences in types and contents of extractives and in anatomical structure. Thus the deterioration behavior of bamboo is possibly different from wood, which means that the conclusions and methodology for archaeological wood cannot be directly applied to archaeological bamboo. On the other hand, past researches mainly focused on the deterioration behavior, attention to the deterioration process over time was limited. In this paper, we investigated the archaeological bamboo strips of four different periods, trying to clarify the deterioration process.

Chemical degradation is an important part of the deterioration of archaeological bamboo. Many researches concerning archaeological wood pointed out that the decay of wood was mainly due to the action of microbial including fungi and bacteria originated from soil or air contamination [1,7–10]. Due to the high content of starch (2–6%), sugar (2%) and protein (1.5–6%) and the low content of resin, wax and tannin, bamboo is more susceptible to microorganisms and insects [11] than wood. In fact, it has been pointed out

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Fig. 1. Photographs of the air-dried bamboo strips dated from the Three-Kingdom Dynasty (A.D. 220–280) and excavated from Zoumalou, Changsha, China.

that white-rot fungi can preferentially degrade the lignin of bamboo [12–15] and brown-rot fungi preferentially degrade hemicelluloses [15,16]. Cha et al. observed bacterial tunneling at the waterlogged archeological bamboos excavated from the shipwrecks [17] and considered erosion bacteria as the most important degraders.

The degradation of chemical components results in the decay of anatomical structure, which is closely related to the mechanical properties of wooden artifacts. For bamboo, its different anatomical structure from wood implies a different decay pattern which is important for the selection of a restoration method. The transverse sections of bamboo culms are characterized by numerous vascular bundles embedded in the parenchymatous ground tissue. The sclerenchymatous fibers locate at the periphery of the vascular bundles and form fiber caps, which account for about 40% of a culm by volume and contribute greatly to the excellent mechanical properties of bamboo culms [18–21]. Different from the secondary wall of wood fibers and tracheids, which is normally characterized by a two- to three-layered structure, the secondary wall of bamboo fibers consist of alternate wide and narrow layer and the number of cell wall layers can reach 9 or even more. The narrow layer is richer in lignin content and has transverse cellulose microfibril angle. Contrarily, the wide layer is less lignified and has oblique cellulose microfibril angle [18,21,22]. It is reported that the microfibril angle had more influence on the longitudinal modulus and the lignin level had more influence on the transverse rigidity [21]. Furthermore, the stiffness across the fiber caps, from the side adjacent to the vessels to the side adjacent to the ground tissue, was assessed and a gradual decrease trend was observed by researchers [21], which was thought to avoid stress discontinuities between the stiffening elements and the soft parenchyma tissues. Based on the above statements, we have reason to believe that the investigation into the anatomical structure will be helpful in the understanding of the deterioration of mechanical properties of archaeological bamboo.

In order to investigate the anatomical and chemical degradation process over time, the archaeological bamboo strips of four different periods were compared with the fresh bamboo. The chemical degradation was analyzed with wet chemical analysis, FTIR and XRD. Hemicelluloses and lignin fractions of each specimen were isolated and characterized with GC and UV respectively in order to complement the investigation on chemical degradation. The anatomy was observed with SEM and TEM techniques. The chemical and the anatomical results were combined to study the deterioration of mechanical properties.

2. Experimental

2.1. Materials and reagents

Fresh mature bamboo specimens were collected from Wuhan, Hubei Province, China. The archaeological bamboo strips excavated from the sites of the Song Dynasty (A.D. 960–1279), the Three-Kingdom Dynasty (A.D. 220–280), the Han Dynasty (B.C. 202~A.D. 220) and the Qin Dynasty (B.C. 221~B.C.206) were supplied by Jingzhou Preservation Center of Culture Relics (Jingzhou, Hubei, China). The approximate age of the archaeological bamboo strips was estimated from the distinguishable literature on the other bamboo strips recovered from the same site. They were denoted as Song-800, Wu-1700, Han-2000 and Qin-2200 (i.e. dynasity + approximate age) respectively. All the archaeological bamboo strips were waterlogged. Due to the serious collapse already happened and the low quantity of the archaeological bamboo strips, the basic physical parameters, such as water content, basic density and shrinkage, could not be determined. All the specimens were washed with an ultrasonic cleaner to remove the soil contamination and air-dried before analysis. All chemicals used were of analytical grade.

2.2. Wet chemical analysis of unprocessed bamboo specimens

Traditional wet chemical compositional analysis based on Van Soest method [23,24] was performed to investigate the compositional changes upon degradation. Neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL) and ash content of unprocessed fresh and archaeological bamboo specimens were determined. 0.5 *g* dried specimens were ground to pass the 0.8 mm screen and added to a flask. 50 ml of the neutral or acid detergent solution (prepared according to references [23,24]) were added. The mixture was heated to boil in 5–10 min and heated under reflux for 60 min from onset of boiling to get NDF or ADF (depended on the detergent solution). The obtained NDF or ADF was immediately washed with hot water (95–100 °C) until free of detergent solution, rinsed with acetone 3 or 4 times and oven-dried overnight at 100 °C. The dried NDF or ADF was weighed and the percentage was calculated. Then the ADF was immersed with 72% H_2SO_4 for 4 h and washed with hot water until acid free to get ADL. The obtained ADL was oven-dried overnight at 100 °C, weighed and the percentage was calculated. Finally, the ADL were heated at 500 °C in a furnace for 4 h. The obtained ashes were weighed and the ash content was calculated. Hemicelluloses, cellulose and lignin contents were calculated by the difference between NDF and ADF content, ADF and ADL content, ADL and ash content, respectively.

2.3. Isolation of hemicelluloses and lignin fractions

Hemicelluloses and lignin fractions were isolated from the fresh and the archeological bamboo specimens. The isolation process was based on references [25–27]. Each specimen was ground to pass a 0.8 mm screen and then extracted with toluene/ethanol (2:1, v/v) in a Soxhlet extractor for 6 h and dried in an oven at 60 °C for 16 h before use. The dried powder was treated with 0.2 M NaOH at 50 °C