MICROSTRUCTURE AND MECHANICAL PROPERTIES OF SILVERGRASS FIBER CELL WALLS EVALUATED BY NANOINDENTATION

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Abstract. Silvergrass is a natural biological material with high mechanical strength and toughness and has potential as a raw material in wood-based composites. Structure and mechanical properties of fiber cell walls of silvergrass stalk in nanoscale were measured by nanoindentation. Silvergrass fiber cells have multilayered structure and diameter between 5 and 20 μm. Nanoscale mechanical tests showed that fibers of the upper stalk of silvergrass had better mechanical properties than those of the lower stalk and silvergrass fibers had better mechanical properties than wood fibers at the cell wall level. Macrohardness of the silvergrass stalk was 0.330 GPa evaluated from nanoindentation tests. Results found by nanoindentation were also verified by longitudinal tensile strength testing and particleboard manufacture.

Keywords: Cell wall, fiber, longitudinal tensile strength, mechanical properties, nanoindentation, silvergrass.

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INTRODUCTION

The great challenge of the global wood-based panel industry is to address and overcome declining raw material supplies, to fully use available resources, and to take advantage of innovations in wood processing. A growing number of timber producers are facing raw material shortages, and some wood processors are now operating below 50% capacity. This problem is expected to worsen (Setunge et al 2009). Developing wood-based composites from renewable available fiber resources would be an efficient way to solve the problem. In recent years, some countries, such as the US, Japan, Germany, England, Canada, and Sweden, have focused on research on waste agricultural raw materials for panel production, such as wheat straw board and rice straw board. High-quality straw boards have been developed and manufactured (Zhang et al 2003). Efficient use of agricultural residual fiber in manufacturing wood-based composites is of great interest today because of the decrease in supply of conventional raw materials from forests (Wu et al 2010).

Silvergrass (*Miscanthus sacchariflorus*, Family: Poaceae) is a tall, upright perennial grass with a stem height of 1.5-7.5 m and a diameter of 5-35 mm (Liu 1997; Hata et al 2010). Silvergrass is an East Asian species found in China, Japan, North Korea, and Siberia (Yang et al 2009). In China, silvergrass is used as industrial raw material for paper-making (Liu et al 2001). In Germany, as a perennial grass with high biomass, silvergrass has been studied as an energy plant and has great potential (Gao et al 2009). Silvergrass also grows abundantly throughout Taiwan. Since 2007, the Institute of Nuclear Energy Research of Taiwan has attained funding to develop cellulosic ethanol production using locally abundant agriculture residues, including silvergrass. Silvergrass is being studied as an energy crop for ethanol production through conversion technology including pretreatment, enzymatic saccharification, and fermentation (Guo et al 2008, 2009). However, before this study, application of silvergrass in the wood-based panel industry had not been studied and silvergrass composites had not been manufactured. Being a typical natural biological material with superior mechanical properties, silvergrass has the potential to be used as raw material in the wood-based panel industry.

To use silvergrass efficiently in wood-based composites, it is necessary to understand the properties of silvergrass at the microscopic level. Mechanical properties of silvergrass vary significantly between the bottom and top sections of the stalk. The upper part is solid with pith in it, but the lower part is hollow. Mechanical properties depend on such factors as density and diameter of fibers, thickness of fiber cell walls, and moisture content (Low et al 2006). Furthermore, silvergrass has high strength in the direction parallel to fibers and low strength perpendicular to fibers.

In the manufacture of wood-based composites, it is important to understand the mechanical properties of silvergrass fibers. Nanoindentation is a technique used to determine mechanical properties of a material at the submicron or nanoscale. The test involves penetration of a sample material using an indenter, and penetration depth and load are recorded, allowing relative elastic modulus and hardness of the material at the indented location to be subsequently calculated (Wu et al 2009).

In this study, nanoscale structure of the cell wall of silvergrass fibers was characterized by scanning probe microscopy (SPM) assembled in the TriboIndenter system (Hysitron, Inc., Minneapolis, MN). Hardness and elastic modulus of the fiber cell wall were measured by a nanoindenter, and indentation deformation mechanisms are discussed with reference to its nanoscale structure, hardness, and elastic modulus. The macrohardness value of silvergrass stalk was approximated from nanoindentation tests. In macromechanical property, longitudinal tensile strength of silvergrass was determined and particleboards were made to verify results measured by nanoindentation.

MATERIALS AND METHODS

Nanoindentation Test

The silvergrass stalk varies significantly between the bottom and the top; the upper part is solid with pith in it, and the lower part is hollow. The silvergrass used in this study was taken from Poyang Lake, Jiangxi province, China. Samples for nanoindentation were selected from the lower and upper parts of stalk, respectively. They were cut into 2 × 5-mm samples (width × length), and the thickness was the natural thickness of the stem. A novel method for sample preparation suitable for silvergrass chips or a single fiber without resin application was developed. The procedure uses plastic sealing and embedding. Specimens were cut into small pieces and sealed in polymer film in a FoodSaver vacuum sealer (Sunbeam Products, Inc., Jarden Corporation, Rye, NY). A small silvergrass block was placed between two films and pressed by an electric iron at 160°C. Then, presealed samples were embedded in epoxy resin using the aforementioned procedure.

Misalignment between the longitudinal cell axis and indentation direction will introduce a test value bias caused by the artificial change of microfibril angle. This sealing procedure makes it easier to mount the silvergrass inside the embedding mold parallel to the longitudinal axis of the silvergrass cell wall. The sample was mounted into a special metal sample holder for the ultramicrotome. Cell walls with empty lumen were obtained by diamond knife cutting. Although there was some polymer penetration between the bond line of the silvergrass cell wall and the thin film used for isolating, the majority of cell walls were protected well enough for indentation testing.

The nanoindentation test was conducted using the TriboIndenter system. A Berkovich indenter, three-sided pyramid with an area-to-depth function was used for all experiments (Oliver and Pharr 1992). An indentation experiment consists of four steps: approaching the surface; loading to peak load; holding the indenter at peak load for 5 s; and unloading completely (Zou et al 2009). An indenter displacement rate of 10 nm/s was used until the tip contacted the sample surface; then the displacement rate was kept constant at 5 nm/s until a target indentation peak load of 150 μN was obtained. Peak load was held for 5 s. The hold was used to minimize the creep effect. Finally, unloading was executed at 5 nm/s. After indentation, specimens were examined by SPM assembled in the TriboIndenter system, which is capable of accurately positioning the fiber cell walls' S_2 layer.

Hardness and elastic modulus were calculated from load-displacement data as determined by nanoindentation based on the Oliver–Pharr method (Oliver and Pharr 1992). Nanoindentation hardness is defined as indentation load divided by projected contact area of indentation:

$$H = \frac{P_{\max}}{A} \tag{1}$$

where $P_{\max}$ is peak load and A is the projected contact area.

Nanoindentation elastic modulus was calculated using the Oliver–Pharr (Oliver and Pharr 1992) data analysis procedure beginning with fitting the unloading curve to a power–law relation. Unloading stiffness (S) can be obtained from the slope of the initial portion of the unloading curve. The geometry-independent relation involving contact stiffness, contact area, and elastic modulus can be derived as follows:

$$S = 2\beta E_r\sqrt{\frac{A}{\pi}} \tag{2}$$

where β is a constant that depends on geometry of the indenter (β = 1.034 for a Berkovich indenter) and E_r is the decreased elastic modulus that accounts for the fact that elastic deformation occurs in both the tested specimen and the indenter.

Elastic modulus of specimen (E_s) was given by the following equation:

$$E_s = \left(1 - v_s^2\right)\left(\frac{1}{E_r} - \frac{1 - v_i^2}{E_i}\right)^{-1} \tag{3}$$

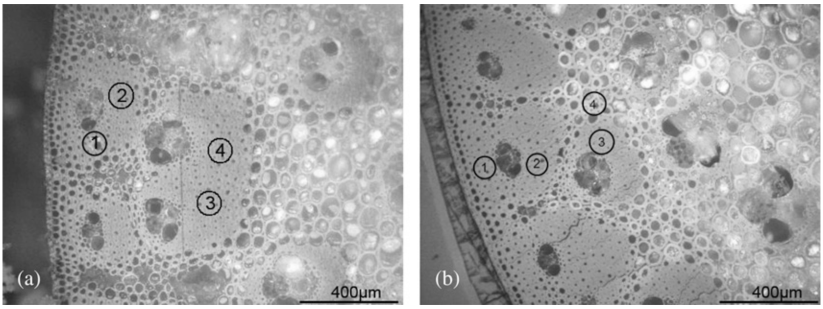

Figure 1. Regions in silvergrass stalk selected for nanoindentation: (a) lower stalk and (b) upper stalk.

where E_s and v_s are elastic modulus and Poisson's ratio for the specimen, and E_i and v_i are the same quantities for the indenter, respectively. For diamond, $E_i = 1141$ GPa and $v_i = 0.07$, v_s was assumed to be 0.25 for silvergrass.

Tensile Strength Test

Tensile measurements were conducted on a mechanical testing machine, Model 8104 (SANS, Shenzhen, China). Specimens were cut to shapes with a width of 4 mm for the narrow portion and total length of 20 mm. Fifteen specimens for each group were tested using standard GB1938-1991 (China National Standard 1991).

Particleboard Manufacture and Mechanical Properties Tests

Silvergrass particleboards were made from the upper and lower parts of the stalk. Upper and lower particles are manufactured by the same process. Proportions of upper particle screening value (S) were 8.4% in S < 60 mesh, 25.2% in 60 mesh < S < 30 mesh, 38.1% in 30 mesh < S < 10 mesh, and 28.3% in 10 mesh < S, respectively. Screening value of lower particles was 8.3, 25.4, 38.2, and 28.1% for each mesh section. Therefore, upper and lower particles were similar in size. Sample boards of 300 × 300 × 10 mm were formed with a target density of 0.75 g/cm^3. Urea–formaldehyde resin adhesive content was 14%, and solid content was 65%. All mats were pressed at 3.5 MPa in a hot press at 180°C. Hot-press time was 30 s/mm. Mechanical properties were measured according to China National Standard (1999) GB/T17657-1999.

Table 1. Length and longitudinal tensile strength of silvergrass stalk.[a]

Silvergrass stalk	Length (mm)	Longitudinal tensile strength (MPa)
Upper part	1118 (102)	185.1 (14.1)
Lower part	442 (38)	118.6 (8.7)

[a] Standard deviation shown in parentheses.

RESULTS AND DISCUSSION

Microscopic Structure of Silvergrass Fiber

Figures 1a and b are cross-section images of silvergrass fibers from the lower and upper parts of the stalk, respectively. Regions marked in Fig 1 were selected for nanoindentation. Vascular bundles were dispersed in ground parenchyma cells, both in the upper and lower parts. Each vascular bundle consisted of 2-3 vessel elements and fiber cells. Table 1 shows the length of upper and lower stalk parts, which was measured from 60 silvergrass stalks. Approximately 70% of the whole stalk had pith tissue.

Figures 2a and b show the nanoscale structure of the silvergrass fiber cell and the indentations on it. The fiber is an irregular polygonal with a diameter of 5-20 μm. The multilayer feature of the silvergrass fiber cell wall with the primary wall in the outer layer and the secondary wall in the inner layer is shown. The primary wall is thin (about 0.5 μm thick). The secondary wall also

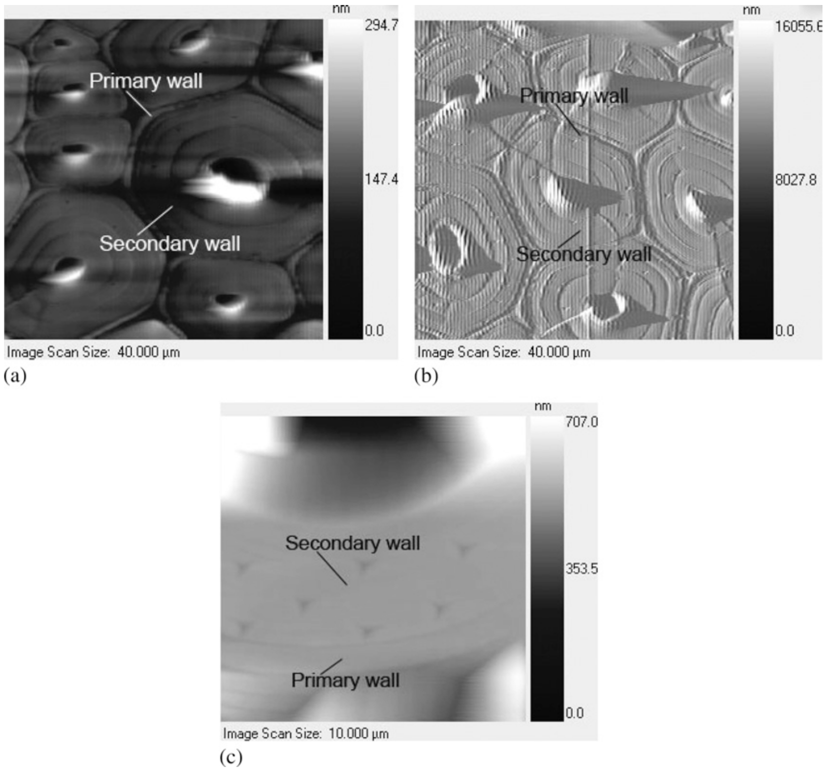

Figure 2. Scanning probe microscopy (SPM) images of silvergrass fibers and parenchyma cell: (a) nanoscale structure of silvergrass fiber cells; (b) indentations on silvergrass fiber cell walls; (c) SPM image of silvergrass parenchyma cell in upper stalk.

exhibited a multilayered structure with 3-4 layers, each layer about 2 µm thick. Figure 2c is a SPM image of an indentation on the parenchyma cell wall. The parenchyma cell wall was about 5 µm thick, much thinner than that of fiber. This is one of the reasons that mechanical properties of parenchyma cells were lower than those of fiber cells.

Mechanical Properties of Silvergrass Fiber Cell Wall

Nanoindentation test results represent the natural properties of fiber cell walls. Nanoindentations were made at different locations on the cross-section of silvergrass fibers. Figure 3 is a representative nanoindentation load-displacement curve. The load-displacement curve shows typical characteristics of elastic–plastic deformation. Indentation loading and unloading curves are smooth without any discontinuities. There were also no cracks at the corners of these indents (Fig 2b), and mounding could be seen around the nanoindentation impression. These observations indicate that the cell wall of silvergrass fiber was ductile.

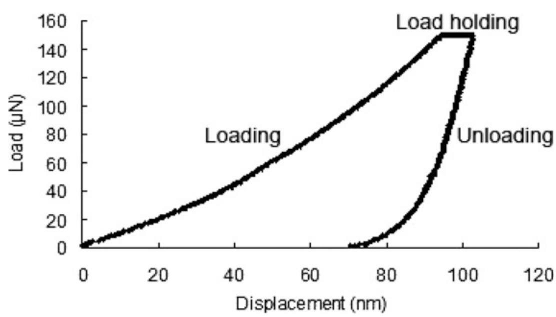

Figure 3. Representative nanoindentation load-displacement curve drawn from a result of nanoindentation.

Table 2 shows elastic modulus and hardness values of silvergrass determined by nanoindentation. These two mechanical properties of the fiber cell wall in the upper stalk were 11.9 and 9.4% higher than those in the lower stalk. The upper stalk presented higher nanoscale mechanical properties than the lower part. Compared with the elastic modulus of hardwoods (20.2 GPa) and softwoods (16.2 GPa) (Wu et al 2010), elastic modulus of silvergrass fiber in the upper stalk was 11.4 and 38.9% higher than that of hardwoods and softwoods, respectively. Elastic modulus of silvergrass fiber in the lower stalk was close to that of hardwoods and 24.1% higher than that of softwoods. Hardness of the fiber cell wall in the lower stalk was 8.2 and 29.3% higher than hardwoods (0.49 GPa) and softwoods (0.41 GPa), respectively. For the upper stalk, hardness values were much higher than those for hardwoods (18.4%) or softwoods (41.5%). Therefore, silvergrass fibers had better mechanical properties than wood fibers at the cell wall level.

Also, nanoindentation tests were carried out on silvergrass parenchyma cell walls in the upper stalk. They could not be carried out for the lower stalk, because parenchyma cell walls were too thin and had poor strength. Table 2 lists hardness and elastic modulus values of silvergrass fiber cell walls and parenchyma cell walls in the upper stalk. It also shows that the parenchyma cell has lower hardness and elastic modulus than those of fiber cells. In the silvergrass stalk, fibers act as reinforcements and parenchyma cells are matrix, which simulates a composite material. Therefore, silvergrass fibers mainly contribute to stiffness and toughness of the silvergrass stalk.

Table 2. Values of hardness and elastic modulus determined by nanoindentation.[a]

Silvergrass component	Hardness (GPa)	Elastic modulus (GPa)
Fiber cell wall (lower)	0.53 (0.04)	20.1 (1.02)
Fiber cell wall (upper)	0.58 (0.04)	22.5 (1.87)
Parenchyma cell wall (upper)	0.53 (0.03)	20.6 (1.34)

[a] Standard deviation shown in parentheses.

Evaluation of Macrohardness of Silvergrass Stalk from Nanoindentation Tests

Macrohardness values of silvergrass stalk can be extracted from nanoindentation tests. Effectiveness of the method relies on the relationship between the ratio of nanoindentation hardness to macrohardness and some indentation parameters. Macrohardness values of a material can be approximated using the following equation:

$$H_0 = H/[k_1 - k_2(X + k_3 E_r)] \tag{4}$$

where k_1, k_2, and k_3 are fitting coefficients equal to 6.7986, 3.8303, and 3.7162×10^{-4} GPa^{-1}, respectively. According to regression analysis, H_0 is macrohardness, H is nanoindentation hardness, X is the power-law exponent, and E_r is decreased elastic modulus (Ma et al 2005).

In this study, maximum indentation depth, h_m, was equal to five times $\triangle h$, where $\triangle h$ is the absolute bluntness of the indenter defined as distance from the apex of the ideal pyramidal shape and the top of the real indenter ($\triangle h =$ 40.4 nm). Maximum indentation depth of these nanoindentation tests was 102 nm, which does not agree with the requirement of the expression. However, it does not affect calculation of the power-law exponent, X. The power-law exponent X can be extracted from fitting nanoindentation loading curves according to a power-law function:

$$P = Ch^X \tag{5}$$

where P is indentation load, C is fitting coefficient, and h is indentation depth.

In this test, X equals 1.3196. H is 0.565 GPa, which is a mean value calculated from nanoindentation hardness values of the upper and lower stalks. The mean value of E_r is 21.8 GPa. Silvergrass stalk can be considered a composite material because fibers act as reinforcements and parenchyma cells are matrix.

To simplify the problem, parenchyma cells are treated as a uniform matrix (Zou et al 2009), and silvergrass stalk is assumed to be a homogeneous material of fiber cells. Based on results, elastic modulus of parenchyma cells (20.6 GPa) was similar to the mean value of fiber cells (21.8 GPa). Macrohardness was approximated in the previous assumptions. The calculated value for macrohardness of silvergrass stalk (Eq 4), H_0, equals 0.330 GPa.

Longitudinal Tensile Strength of Silvergrass Stalk

Nanoindentation test results showed that the upper part of the stalk presented higher nanoscale mechanical properties than the lower part. The macromechanical property was also determined in the study to verify nanoindentation results. Longitudinal tensile strength of the two stalk parts was determined (Table 1). The macromechanical property of the upper stalk was 66.5 MPa higher than that of the lower stalk. This result agreed with mechanical properties measured by nanoindentation. Properties of the upper stalk were better than those of the lower stalk, both in nanoscale and at the macroscopic level.

Mechanical Properties of Particleboard Made from Silvergrass Stalk

Particleboards were made from the upper and lower parts of the stalk, respectively. Mechanical properties, including modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond strength, were determined to evaluate particleboard quality. Values for mechanical properties measured in this experiment all reached the specified minimum values in the China National Standard (2003) GB/T 4897.3-2003. Figure 4 shows that mechanical properties of boards made from the upper stalk were all higher than those of boards made from the lower stalk, with the ratios of 15.6, 12.1, and 11.0%, for MOR, MOE, and internal bond strength, respectively. Therefore, mechanical properties of particleboard made from the upper stalk were better than those of particleboard made from the lower stalk, and silvergrass particleboard can be successfully manufactured using urea–formaldehyde resin.

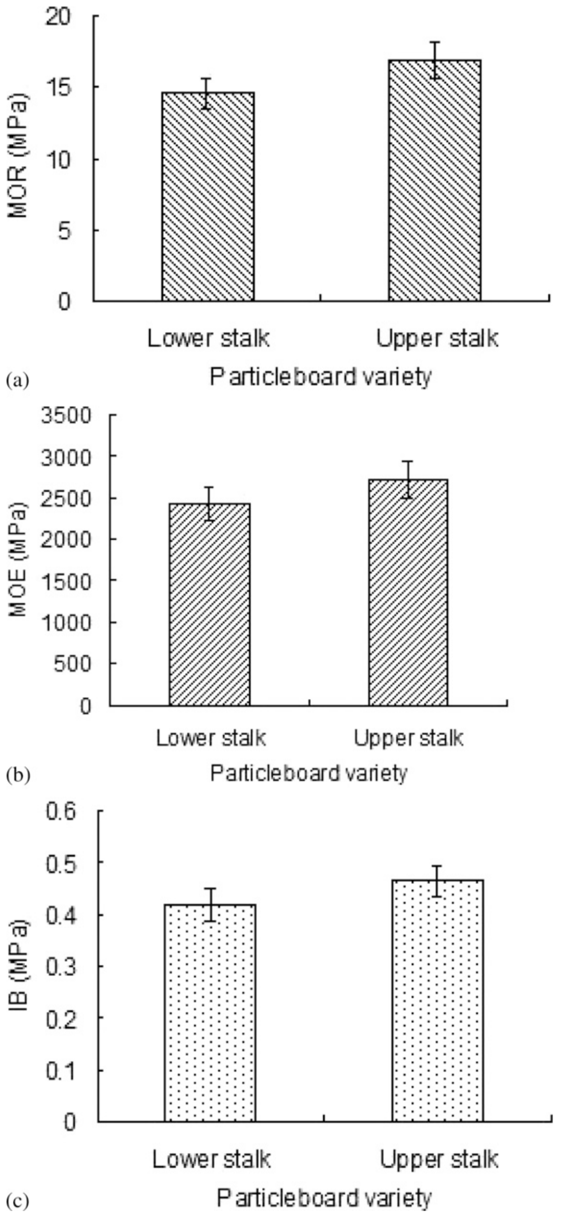

Figure 4. Mechanical properties of particleboard made from silvergrass stalk: (a) modulus of rupture (MOR); (b) modulus of elasticity (MOE); (c) internal bond strength (IB).

CONCLUSIONS

The structure and mechanical properties of fiber cell walls of silvergrass stalk in nanoscale were measured by nanoindentation. The fiber cell is an irregular polygonal with a diameter of 5-20 μm and has a multilayered structure. Nanoindentation hardness values of the fiber cell wall in lower and upper stalks were 20.1 and 22.5 GPa, and elastic modulus values were 0.53 and 0.58 GPa, respectively. Fibers of the upper stalk of silvergrass had better mechanical properties than those of the lower stalk in nanoscale. Macrohardness value of silvergrass stalk was 0.330 GPa evaluated from nanoindentation tests. Results of longitudinal tensile tests at the macroscopic level and particleboards made from the two parts of silvergrass stalk also agreed with results of nanoindentation tests. Based on the properties determined, silvergrass is a good potential raw material for particleboard manufacturing.

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