CHARACTERISTICS OF SILVERGRASS AND FEASIBILITY OF SILICA AS A WATERPROOF AGENT IN SILVERGRASS PARTICLEBOARD

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Abstract. Silvergrass is a natural biological material and, in this study, the feasibility of it being used as raw material for particleboard was investigated. The results of pH value, buffering capacity, and surface wettability determinations indicated silvergrass could be glued with urea–formaldehyde resin. The main elements of silvergrass stalk, which included carbon, oxygen, and silicon, were determined by energy dispersive analysis of X-rays. Silicon occurs in silvergrass stalk as compound silica, and the silica content of stalk was 3.49%, which indicated silica may play the role of a waterproof agent in particleboard. Feasibility of silica being used as a waterproof agent of silvergrass particleboard was analyzed, and results showed silica actually functioned as a waterproof agent, therefore wax was not needed in silvergrass particleboard manufacture.

Keywords: Elemental analysis, physical and mechanical properties, pH value, silica, surface wettability.

INTRODUCTION

The great challenge of the global wood-based panel industry is to address and overcome declining raw material supplies. Decreasing raw materials and the need to conserve natural resources led to research on efficient use of trees. In some countries, environmental pressures have managed to prohibit forest harvesting, resulting in expected opposition as a consequence of wood shortage,

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shutdown of wood industries, unemployment, etc (Nemli and Aydın 2007). In 2010, global production of particleboard was 94 Mm^3 (FAO 2010). Decreases in world forest resources, high demand for wooden materials, and increases in forest fires have increased the importance of particleboard manufacturing from agricultural fibers and wood residues as a substitute for the use of solid wood. There is a growing trend in using raw material from nonwood and agroforest waste to produce composite panels. Fast-growing species, agricultural crops, etc, will play an important role in manufacture of composite panels such as particleboard. The efficient use of agricultural residual fiber resource 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 2009).

Silvergrass possesses high strength parallel to the fibers and low strength perpendicular to the fibers (Liao et al 2012). It can be very popular in countries in which wood resources are scarce and silvergrass is readily available, especially in China. Silvergrass is an East Asian species found in China, Japan, North Korea, and Siberia (Yang et al 2009). In China, silvergrass is used as an industrial raw material for paper-making, and in 2007, the Institute of Nuclear Energy Research of Taiwan 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). 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). Nanoscale structure and mechanical properties of the cell wall of silvergrass fibers were characterized by nanoindentation, and silvergrass fibers had better mechanical properties than wood fibers at the cell wall level (Liao et al 2012). Silvergrass is a good potential raw material for particleboard manufacturing.

Silvergrass stalk has a mineralized layer on the surface. It is hydrophobic and hinders adhesive contact with the inner layer of silvergrass stalk. Silica is the main component of the mineralized layer. Urea–formaldehyde (UF) resin was used as the adhesive in manufacturing silvergrass particleboard. UF was considered to have poor strength in gluing strawboard. Adhesive addition is a process of adsorption and desorption of adhesive on the surfaces of particles. Adhesive bonding strength depends on surface wettability, pH, and buffering capacity.

To use silvergrass efficiently in wood-based composites, UF resin was investigated as a possible adhesive by determining the properties of silvergrass, such as pH, buffering capacity, and surface wettability. The content of silica in silvergrass stalk was determined, and a contrast test was done to evaluate the feasibility of silica as a waterproof agent in silvergrass particleboard manufacture. Within this context, this study aimed at characterizing feasibility of silvergrass used as raw material for particleboard by determining pH, buffering capacity, and surface wettability; analyzing effects of silica and wax addition on physical and mechanical properties of silvergrass particleboard; and evaluating the feasibility of silica used as a waterproof agent in silvergrass particleboard manufacture.

MATERIALS AND METHODS

Materials

Silvergrass particles from Poyang Lake, Jiangxi province, China, were used for board manufacturing. Particles were dried to a target moisture content of 5%. UF and wax provided by Huaneng Co., Ltd., Chuzhou, China, were used in silvergrass particleboard manufacturing. Solid content of UF was 65%. Poplar veneer and wheat straw from Suqian, Jiangsu province, China, were used for surface wettability determination. They were also dried to a target moisture content of 5%.

pH Value

pH of silvergrass and poplar was determined according to the methods given in China National

Standard (1999a). Silvergrass stalk and leaf and poplar were ground into powder and screened between 0.3 and 0.45 mm. Then, 3 g of powder was placed in a 50-mL beaker, 30 mL of boiled distilled water was added, and the solution was mixed for 5 min with a glass rod. After standing 15 min, mixing 5 min, and another 5 min standing, pH measurements of samples were determined with an acidometer (PHS-3C; Leici, Shanghai, China).

Buffering Capacity

Buffering capacity of silvergrass was determined according to the methods given in China National Standard (1999b). Silvergrass stalk and leaf were ground into powder. The grain diameter of the powder was between 0.3 and 0.45 mm, and the weight was 500 g. The powder was placed in a jar with a frosted glass plug for testing after 48 h.

First, specimen moisture content was determined. Twenty-five grams oven-dry weight of specimen was placed in a 500-mL flask, and 250 mL of boiled distilled water was added to the flask. The solution was extracted for 20 min by boiling and refluxing, and then it was filtered. Two 50-mL samples of filtrate were moved into two 80-mL beakers. They were titrated by 0.0125 mol/L H_2SO_4 and 0.0250 mol/L NaOH until pH reached 3 and 11, respectively. The dosages of H_2SO_4 and NaOH were acid and alkali buffering capacities, respectively.

Surface Wettability

The wetting behavior of the particleboard samples conditioned at 65% RH and 20°C was characterized by the contact angle method (goniometer technique). Contact angles were obtained using a contact angle tester (JC2000A; Zhongchen Company, Shanghai, China).

Silvergrass stalks and wheat straw were cut along the shaft to a length of 50 mm (width and thickness were the natural sizes of the stalks). Specimens of silvergrass stalk were divided into two groups, those from the upper part and those from the lower part of the stalk. The pith had to be removed if the specimen was taken from the upper part. Poplar specimens of 50 × 10 × 4 mm were taken from poplar veneer.

The specimen was put in the contact angle tester. Then, distilled water (about 5 μL) was placed on the specimen surface using a 0.005-mL microsyringe. The figure of the specimen was caught by the tester about 10 s after the distilled water was dropped. Thus, the contact angle was obtained by the contact angle measuring software. Fifteen specimens were measured for each material.

Elemental Analysis of Silvergrass Stalk by Energy Dispersive Analysis of X-Rays

Samples were selected from the lower and upper parts of the stalk. They were cut to 4 × 5 mm (width × length) using a sharpened blade. Thickness was left as the naturally occurring thickness of the silvergrass stalk. Each sample was sputtered with a gold–platinum coating in the cross-section by a sputter coater. Elemental analysis was performed by an environment scanning electron microscope (Quanta200; FEI, Hillsboro, OR), which was equipped with energy dispersive analysis of X-rays (EDAX). Ten samples on each part of stalk were examined.

Feasibility of Silica as a Waterproof Agent for Silvergrass Particleboard

Feasibility of silica as a waterproof agent of silvergrass was analyzed by studying the effect of silica on physical and mechanical properties of particleboard. Particleboards were manufactured with wax and without wax. Solid loading level of wax was 1.5% based on oven-dry weight of the particles for the particleboard with wax. Sample boards of 300 × 300 × 10 mm were manufactured with target density of 0.75 g/cm^3 and 14% UF adhesive content. One percent (w/w) NH_4Cl based on the solid weight of UF was used as a curing agent.

Two kinds of silvergrass particleboards were made from the same silvergrass particles. Proportions of screening value (S) of the particles were 7.6% in S < 60 mesh, 26.2% in 60 mesh < S < 30 mesh, 38.7% in 30 mesh < S < 10 mesh, and 27.5% in 10 mesh < S. The silvergrass particles were oven-dried to a target moisture content of 5%, and then UF resin was blended with particles by spraying. The silvergrass particles with UF resin were prepressed into a single layer mat in a 300- × 300-mm wood mold. Then the mat was hot-pressed to make the final board, and two 10-mm-thick steel rods were used to achieve a constant particleboard thickness. Pressure, temperature, and time were set at 3.5 MPa, 180°C, and 6.5 min, respectively.

Physical and mechanical properties including modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding strength (IB), and thickness swelling (TS) are very important specifications for silvergrass particleboard. They were measured according to the methods described in the following.

Mechanical properties were conducted on a mechanical testing machine (Model 8104; SANS, Shenzhen, China). Capacity of the load cell was 10 kN, and the movable crosshead speed was 5 mm/min for MOR, MOE, and IB tests. Finished particleboards were cut to various specifications according to China National Standard (1999c). Rectangular 50- × 250-mm pieces were cut for three-point bending measurement of MOR and MOE, and 50- × 50-mm pieces were used for IB determination.

For TS determination, silvergrass particleboards were cut into 50- × 50-mm squares and soaked in water at 20 ± 2°C for 2 h. Sample thickness was measured before and immediately after soaking. TS was calculated as ratios of increased thickness to the value before soaking and expressed as percentages.

Also, density profile of these two kinds of particleboards across the thickness direction was determined on a vertical density profile instrument (DENSE-LAB; Electronic Wood Systems, Hameln, Germany). Fifty- × 50-mm pieces were used for determination.

RESULTS AND DISCUSSION

pH Value and Buffering Capacity

pH of silvergrass was represented by the pH of water extractives of silvergrass, including cell cavity extractives and cell wall extractives pH. It is an important factor of wood-based panel bonding and affects the addition of curing agent. Acidic substances help UF to cure rapidly and properly. pH of the particles may influence the curing rate of formaldehyde-based resin (Nemli et al 2006). Table 1 shows the pH value of the whole plant was about 5.82, and it was lower than 6.95 for poplar. Silvergrass was weak acidic and more favorable for improving the bond quality of UF, which is a pH-sensitive resin. As a result, silvergrass could be bonded by UF, and UF was fit to be used as adhesive in silvergrass particleboard manufacture.

Buffering capacity represents the ability of silvergrass to keep its pH stable. Table 1 shows acid buffering capacity of silvergrass stalk was 6.97, which was lower than the 17.50 of poplar. Thus, the addition of curing agent (NH_4Cl) in silvergrass particleboard manufacture was lower than that in poplar. Alkali buffering capacity of silvergrass stalk was 23.21, which was close to that of poplar, and silvergrass stalk had higher resistant ability of alkali than of acid. Buffering capacity of the leaf was higher than that of the stalk. It can be predicated that including leaves in silvergrass particleboard manufacture may increase the need for a curing agent for UF bonding.

Surface Wettability

Contact angle θ was determined to estimate surface wettability of silvergrass. Surface wettability

Table 1. pH value and buffer capacity of silvergrass and poplar.

Property	Stalk	Leaf	Whole plant	Poplar[a]
pH value	5.78	5.87	5.82	6.95
Acid buffer capacity (mL)	6.97	12.04	—	17.50
Alkali buffer capacity (mL)	23.21	58.16	—	20.50

[a] Acid and alkali buffer capacities of poplar were from Li et al (2009).

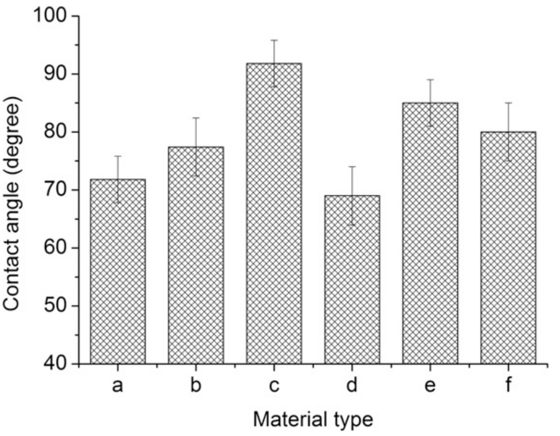

Figure 1. Wettability of silvergrass, poplar, and wheat straw (a) poplar; (b) wheat straw (internal surface); (c) wheat straw (external surface); (d) silvergrass (internal surface of stalk); (e) silvergrass (external surface of stalk); (f) silvergrass (leaf).

of silvergrass stalk and leaf was measured and compared with that of poplar and wheat (Fig 1). Contact angle of the external surface of silvergrass stalk was close to 90°, which was higher than that of the internal surface. Silica covered almost all the external surface of the stalk, which lowered wettability of that surface. A nonpolar waxy external surface makes it hard for the adhesive to wet and penetrate into the cellular structure, resulting in poor bonding strength between UF and active hydroxyl groups of the cellulose of the silvergrass stalk (Ayrilmias et al 2012). Contact angles of the external surface of silvergrass stalk and leaf were both lower than that of the external surface of wheat. Also, the internal surface of the silvergrass stalk had better wettability than poplar. The outer thin waxy layer accounted for little proportion of the stalk, therefore the negative effect of silica on the bonding strength of UF was also weakened.

Main Elements of Silvergrass Stalk Determined by Energy Dispersive Analysis of X-Rays

The main elements of silvergrass stalk were also measured by EDAX. Regions of cross-section in the lower stalk and upper stalk were selected for measurement as shown in Figs 2 and 3, and the result is listed in Table 2. EDAX results clearly showed the presence of carbon and oxygen in silvergrass stalk, because carbon and oxygen photoelectron peaks were clearly resolved. Only these two elements were present in a noticeable amount, because silvergrass is a cellular biomaterial with an intricate structure principally consisting of cellulose, hemicelluloses, and lignin. Small peaks caused by silicon were also present in the survey spectra.

Atomic percentages of silvergrass stalk are presented in Table 2. The oxygen-to-carbon atomic ratio was of particular interest. This ratio was

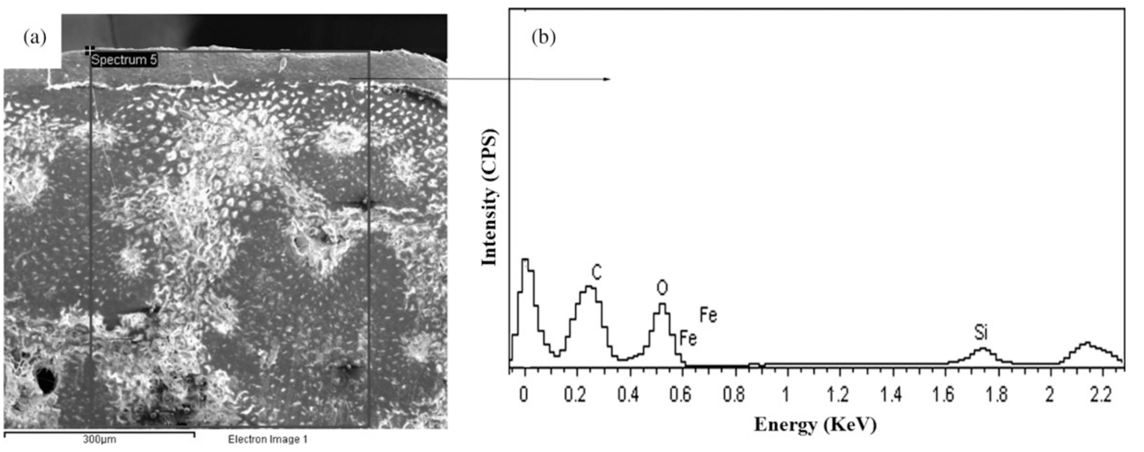

Figure 2. Energy dispersive analysis of X-rays (EDAX) analysis of lower silvergrass stalk (a) region selected for elemental analysis in lower stalk; (b) EDAX spectrum of lower stalk.

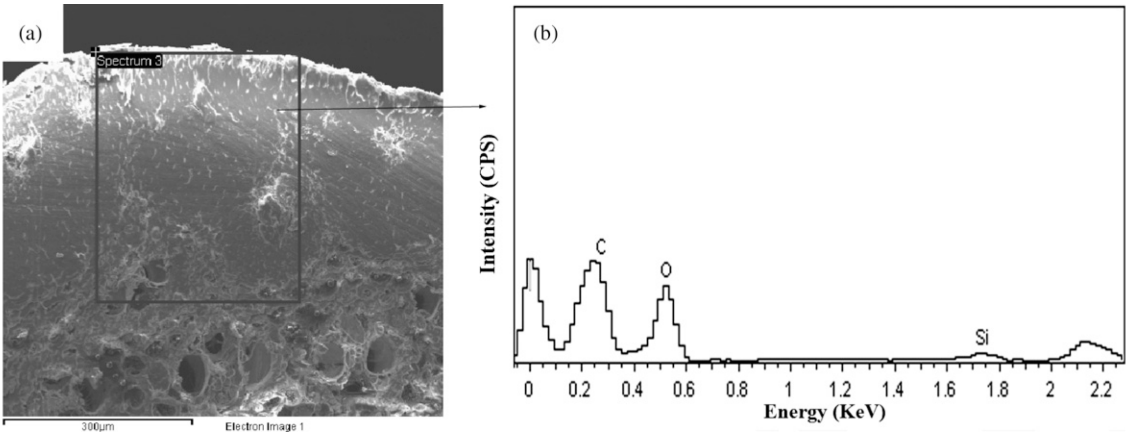

Figure 3. Energy dispersive analysis of X-rays (EDAX) analysis of upper silvergrass stalk (a) region selected for elemental analysis in upper stalk; (b) EDAX spectrum of upper stalk.

0.90 for both upper and lower stalk (Table 2). Weight percentages of main elements in lower and upper stalks are also shown in Table 2. According to results, approximately 70% of the stalk was upper stalk and 30% lower (Liao et al 2012). Average weight percentages of the main elements in silvergrass stalk could be calculated from the EDAX results of silvergrass stalk, which indicated carbon content of 44.63% and oxygen content of 53.53%. These elements occupy 98.16% of the weight of silvergrass stalk. This result proved that silvergrass is a biological material, and its main chemical components are carbon and oxygen. The weight percentage of silicon in the lower stalk was 2.28%, which was higher than the 1.35% for the upper stalk. The higher content of silicon in the lower stalk could be explained by the fact that silicon is mainly absorbed from the soil and it partly participates in the mineral cycle in reed stalk through diffusion and transpiration (Pan 2004). Silicon content of silvergrass stalk can also be calculated using the EDAX data in Table 2. Average silicon content of silvergrass stalk was about 1.63%. Silicon occurs in silvergrass stalk as compound silica. Silica content can be evaluated according to the following equation:

Table 2. Element analysis of silvergrass stalk by energy dispersive analysis of X-rays.

	Lower stalk		Upper stalk	
Elements	Weight percentage	Atomic percentage	Weight percentage	Atomic percentage
Carbon	44.06	51.85	44.88	52.24
Oxygen	53.03	46.85	53.75	46.92
Silicon	2.28	1.15	1.35	0.68

$$C_{Silica} = C_{Silicon} \times \frac{60}{28} \quad (1)$$

where C_{Silica} is content of silica and $C_{Silicon}$ is content of silicon.

Therefore, silica content of the stalk was 3.49% calculated from Eq 1. Surface wettability of silvergrass stalk is poor because silica is the main component of the mineralized layer and it is more hydrophobic than cellulose. Therefore, in silvergrass particleboard manufacturing, silica affects bonding strength of UF, but it may play the part of a waterproof agent. However, silica content of stalk was higher than addition of waterproof agent, which was 1-2%. Wax is the waterproof agent frequently used in particleboard manufacturing. It has fluidity and can prevent water-sensitive hydrogen groups of silvergrass particles from absorbing water. Silica is solid and has less fluidity, so the 3.49% content of silica in particleboard manufacturing could have a similar waterproofing effect to 1-2% content of wax.

Feasibility of Silica as a Waterproof Agent for Silvergrass Particleboard

To investigate the feasibility of silica as a waterproof agent of silvergrass particleboard, a comparison experiment was designed. Physical and mechanical properties including IB, MOR, MOE, and TS were determined, and results are displayed in Table 3.

Internal bonding strength is an important specification for silvergrass particleboard, and it is affected by the adhesive property and wettability of particles. The adhesive property was formed by crosslinking between UF and active hydroxyl groups of silvergrass particles, and wettability of particles affected IB directly. Table 3 shows that IB of the particleboard without wax was 0.62 MPa. The hydrophobic substance contained in silvergrass particleboard was silica, and its content was 3.49%. IB of the particleboard without wax was 0.55 MPa, which was 3.1% lower than that with wax. This decrease in IB strength was mainly caused by another hydrophobic substance, wax, being added to the silvergrass particleboard. Wax hindered UF contact with active hydroxyl groups of silvergrass particles, and the adhesive property was weakened. Also, wax was dispersed on particle surfaces, and wettability of particles was lowered. All this indicated that wax had a negative effect on IB and silvergrass as a raw material for particleboard without wax was feasible. Wheat is also a straw material with silica in the stalk. Silicon contained in wheat was 2.09-8.49%, which was higher than the 1.63% of silvergrass (Su et al 2002). Excessive silica in wheat stalk lowered IB of wheat particleboard significantly, therefore wheat could not be used to manufacture particleboards bonded by UF. This finding agrees with a previous study (Mo et al 2003).

MOR measures the maximum bending load that a board can support. Its value indicates the stress required to cause failure (Pan et al 2006). Table 3 shows the change in MOR was not significant after wax was added because MOR was highly related to key factors, such as particle size, adhesive addition, density profile, etc. Particleboards with and without wax had similar "M" type density profiles and density values (Fig 4). Consequently, the similar MOR values of these two kinds of particleboards were caused by the fact that they had similar density profiles and the same particle sizes and adhesive addition. The effect of adding wax on MOR was negligible.

Table 3. Results of particleboard physical and mechanical properties.[a]

Particleboard type	IB (MPa)	MOR (MPa)	MOE (MPa)	TS (%)
With wax	0.55 (0.03)	18.46 (1.1)	3366.9 (99)	6.3 (0.3)
Without wax	0.62 (0.04)	18.74 (0.9)	3453.2 (91)	6.5 (0.5)

[a] Values in parentheses are standard deviations.

IB, internal bonding strength; MOR, modulus of rupture; MOE, modulus of elasticity; TS, thickness swelling.

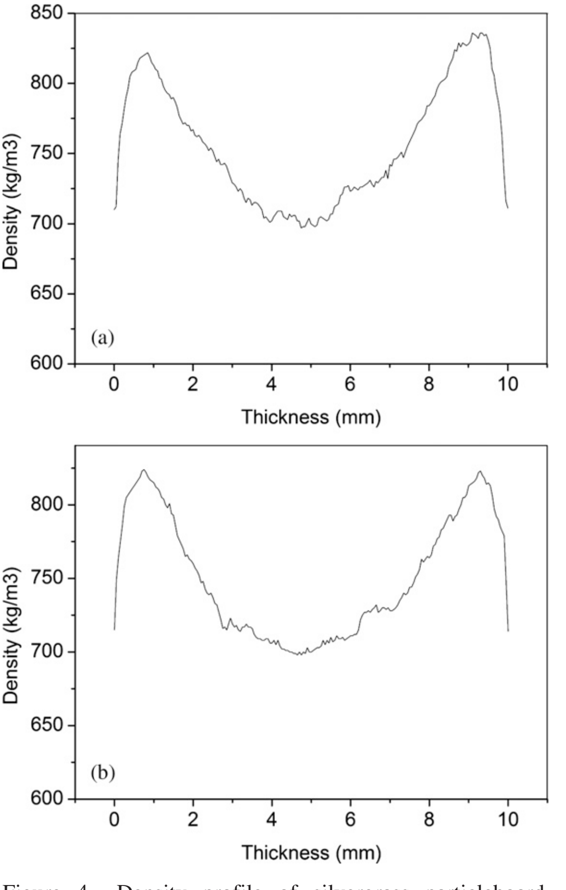

Figure 4. Density profile of silvergrass particleboard across the thickness direction (a) silvergrass particleboard without wax; (b) silvergrass particleboard with wax.

Also, MOR of particleboards without wax can reach the specified requirement of the China National Standard (2003).

Modulus of elasticity measures stiffness and indicates the ability to resist deflection. MOE of the particleboard without wax was 3.45 GPa, which was close to the 3.37 GPa of the particleboard with wax, meaning it can also reach the specified requirement of the standard. In general, MOE followed the same trend as MOR (Pan et al 2006).

Thickness swelling is a key parameter in describing dimensional stability of wood-based composites. The poor absorption resistance of the cellulosic material is mainly caused by the presence of polar groups, which attract water molecules through hydrogen bonding. This phenomenon leads to a moisture build-up in the fiber cell wall and also in the fiber–adhesive interface. This causes changes in the dimensions of wood-based panel composites, and as a consequence, outdoor applications are greatly affected (Tabarsa et al 2011). Water molecules are connected with hydroxyl groups of cellulose in the secondary cell wall of silvergrass (Nemli and Aydın 2007). TS of the particleboard without wax was 6.5%, which was lower than the standard value of 8% (Table 3) because silica was also a hydrophobic substance and decreased the TS. TS of the particleboard without wax was 6.3%, which was a little lower than that with wax. This was attributed to wax preventing polar groups from attracting water. After adding wax, TS of particleboard was improved, but the effect was not significant. Adding wax also increased production cost in industrial manufacture. Mechanical properties of silvergrass particleboard were also lowered to some degree. This agreed with Zheng et al (2006). Silica actually performed the function of a waterproof agent, and wax was not needed in silvergrass particleboard manufacture.

Physical and mechanical properties of the particleboard without wax could reach the specified requirement in the China National Standard (2003). Silica contained in silvergrass stalk was more hydrophobic than cellulose, and it was dispersed evenly in the silvergrass particleboard manufacture process. All this indicated that about 3.49% content of silica contained in silvergrass manufacture was capable of performing the role of the waterproof agent. It is feasible to manufacture silvergrass particleboard without adding wax.

CONCLUSIONS

Within the characteristics of silvergrass, main elements analysis, and physical and mechanical properties examined in this study, the following conclusions can be drawn:

(1) At pH and buffering capacity determination, silvergrass was weak acidic and beneficial to UF curing. Silvergrass could be bonded by UF, and UF was fit to be used as the adhesive in silvergrass particleboard manufacture. The acid buffering capacity of silvergrass stalk was lower than that of poplar.
(2) The internal surface of silvergrass stalk has greater wettability than poplar. However, contact angle of the external surface of silvergrass stalk was close to 90°. The outer thin waxy layer accounts for little proportion of the stalk, and the effect of the external surface of silvergrass stalk on bonding strength of UF was weakened.
(3) Based on EDAX, the main elements of silvergrass stalk were carbon, oxygen, and silicon. Silicon is the main elemental component of silvergrass stalk, and its content was 1.63%. Silicon occurs in silvergrass stalk as compound silica, and silica content (3.49%) of stalk was calculated from silicon content.
(4) Feasibility of silica as a waterproof agent of silvergrass particleboard was analyzed. Mechanical properties of silvergrass particleboard without wax were greater than those with wax, and TS of silvergrass particleboard without wax was lower than the standard value of 8%. After adding wax, TS of silvergrass particleboard improved, but the effect was not significant. As a result, silica could be used as a waterproof agent for silvergrass particleboard.

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