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EFFECT OF STEAM EXPLOSION AND GRINDING ON BINDERLESS BOARD MADE FROM RICE STRAW

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ABSTRACT

The purpose of this study was to examine the effects of pretreatments such as steam explosion and grinding on the properties of binderless boards. Steam-exploded rice straw was ground and hot-pressed to make binderless boards. The internal bonding (IB), thickness swelling (TS) and water absorption (WA) of the boards were measured and discussed, along with the results of chemical analyses. Chemical modifications such as hemicellulose decomposition to monosaccharides and lignin reconstruction might have occurred during steam explosion, consequently increasing IB. Defibration occurred during steam explosion, causing an increase in bonding area and a reduction of the disadvantages of trichomes and protuberances that are characteristic to rice straw. Self-bonding also increased. Grinding the steam-exploded rice straw further improved IB by increasing the effective bonding area. Pretreatment combining steam explosion and grinding was the most effective way to increase self-bonding in this study. TS was also improved by steam explosion and grinding.

KEY WORDS: Binderless, fiberboard, rice straw, *Oryza sativa*, steam explosion.

INTRODUCTION

Nowadays, the use of non-wood biomass like annual crops are accelerated for essential lignocellulosic materials. Rice straw is an agricultural by-product of rice production, but has not been effectively used. In a previous study, we reported that binderless boards were successfully manufactured from rice straw (Kurokochi and Sato 2015). However, despite high water resistance, their internal bonding was very low. It is necessary to improve this internal bonding.

Steam explosion is one method to improve properties of boards regardless of addition of any chemicals. Binderless boards having good mechanical properties were reportedly made from steam-exploded non-wood biomass like oil palm frond (Suzuki et al. 1998, Laemsak and Okuma 2000), *Mischanthus sinensis* (Velasquez et al. 2002), banana brunch (Quintana et al. 2009). Binderless fiberboard from steam exploded bamboo was also reported (Luo et al. 2014).

However, Fenton's reagent was added during steam explosion, it was not strictly binderless board as a consequence.

In the process of steam explosion, samples are subjected to steam at high temperature and high pressure to accelerate hydration at first. When the pressure is released suddenly, the samples are defibrated to pulp and black liquor. Suzuki et al. (1998) concluded that released lignin and furfural derivatives generated during steam explosion contributed to self-bonding. There has been little information about chemical composition of black liquor. Shao et al. (2008) analyzed that the powdery portion of steam-exploded pulp, however it was not clear that whether the powder portion of steam-exploded pulp was derived from black liquor or not. To examine the chemical modification of rice straw during steam explosion, not only pulp but also black liquor should be analyzed.

Meanwhile, Velasquez et al. (2002) reported that the addition of a grinding process after steam explosion further improved internal bonding strength owing to the segregation of packages of fibers. With this manufacturing method, it was possible to improve the internal bonding strength with a mild pretreatment.

In rice straw, the influence of steam explosion has been investigated mainly for ethanol production. By steam explosion, ethanol was produced effectively from holocellulose of rice straw (Sawada et al. 1997). Moreover, epoxy resin could be produced from methanol-soluble lignin, and the yield was increased by steam explosion. Acetic hydration of hemicellulose and lignin depolymerization and re-concentration occur during steam explosion (Ibrahim et al. 2011). Such chemical changes would increase self-bonding.

Therefore, the purpose of this study was to examine the effects of steam explosion and grinding on the properties of binderless boards. Firstly, rice straw was pretreated with steam explosion to generate a pulp. Second, binderless boards were manufactured from the ground pulp by hot-pressing. Finally, the mechanical and physical properties of boards were measured and chemical characteristics of raw materials and black liquor were analyzed.

MATERIAL AND METHODS

Steam explosion pretreatment

Rice straw (*Oryza sativa* L. cv. *Dontokoi*) was obtained from the experimental farm of the University of Tokyo (Institute for Sustainable Agro-ecosystem Services, Tokyo, Japan), and air dried. Whole rice straw was cut with scissors into chips shorter than 50 mm (Fig. 1a).

These chips were subjected to a steam explosion digester with 2.5 L volume (Nittoukouatsu Co. Ltd., Tsukuba, Japan), 100 g dry material per batch. The conditions for steam explosion were pressure of 2 MPa for 5 min at 205°C. Steam-exploded rice straw was a mixture of solid and liquid products. They were sieved with a 1-mm screen, dividing them into pulps and black liquor; pulps were retained on the sieve, and black liquor passed thorough the sieve. The amount of black liquor was approximately 2 L. Pulps were not rinsed by water, in accordance with the method of Shao et al. (2008). All pulps were air dried for several weeks (Fig. 1c).

Untreated rice straw and pulps were ground in a Wiley mill (WT-150; Miki Seisakusho, Tokyo, Japan) to pass through a 1-mm screen. Original powder (Fig. 1b) and pulp powder (Fig. 1d) were produced, respectively. Black liquor was gathered by freeze-drying, and freeze-dried black liquor is also referred to as black liquor in the present study.

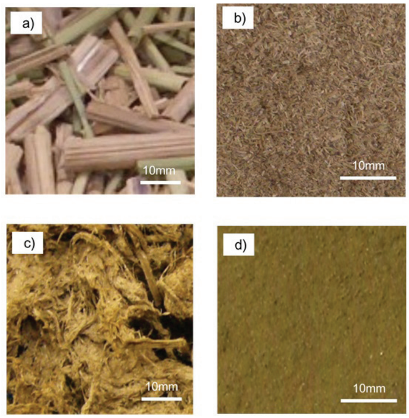

Fig. 1: Photographs of raw materials. a) Chips. b) Original powder. c) Pulp. d) Pulp powder.

Board manufacture

Original rice straw (≤1 mm), pulp (≤50 mm) and pulp powder (≤1 mm) were prepared as raw materials for board manufacture. These raw materials were stored in an air-dried state and the moisture contents were 6-9 %. Binderless boards were manufactured under the pressing conditions shown in Tab. 1. The target density was 0.8 g.cm^{-3}. The board size was 300 × 300 × 5 mm and the pressing procedure was as described in our previous study (Kurokochi and Sato 2015). Two boards were manufactured from each raw material, respectively.

Tab. 1: Manufacturing conditions of each board type.

Board type	Pretreatment	Pressing conditions		
		Temperature	Pressure	Time
-	-	°C	MPa	min
Original	Grinding	200	7	10
Pulp	Steam explosion			
Pulp powder	Steam explosion & Grinding			

Evaluation of mechanical and physical properties of boards

Experimental boards were tested according to JIS A5905-2014 procedure. The main purpose of this study was to examine the self-bonding between fibers. Thus, the internal bonding strength (IB) was evaluated with nine specimens from each board type. Additionally, 24-hour thickness swelling (TS) and water absorption (WA) were measured using six specimens from each board type to determine water resistance.

Chemical analysis

Sample preparation

Original rice straw (≤1 mm), pulps (≤1 mm) and black liquor were Soxhlet extracted with an ethanol-benzene mixture (1:2, v/v) for six hours until the solvent was clear of any color. These samples were subjected to analyses except for neutral sugar composition. For the analysis of neutral sugar composition, the extracted samples were further ground in a ball mill (MM200; Retch, Germany) after grinding to pass through a 500-µm screen with a Wiley mill.

Neutral sugar composition

Neutral sugar compositions were determined by the alditol-acetate procedure modified from Blakeney et al. (1983). Neutral sugars were released by hydrolysis with 4 % sulphuric acid for 1 hour at 121°C after treatment with 72 % (w/w) sulfuric acid for 1 hour at room temperature. Monosaccharides were reduced with a solution of sodium borohydride in dimethyl sulphoxide for 30 min at 70°C. The alditol acetylates were quantified by gas liquid chromatography (GC-1700; Shimadzu, Kyoto, Japan) with a TC-17 capillary column (30 m × 0.25 mm i.d.). The column temperature was 200°C, both injection and detector temperatures were 250°C, and the detector was FID.

Klason lignin

Klason lignin and acid-soluble lignin were determined using the method modified from Rabemanolontsoa et al. (2011). In brief, 10 ml of 72 % sulphuric acid was added to 1 g of extract-free samples and left to react at room temperature for 3 hours. The mixture was autoclaved at 121°C for 30 min after diluting to 3 % sulphuric acid and filtered to obtain crude Klason lignin plus contaminating inorganics. The residue was combusted for 3 h at 700°C to determine the amount of acid-insoluble ash. The corrected Klason lignin content was determined by subtracting ash from the crude Klason lignin.

Acid-soluble lignin content was measured from UV absorbance at 205 nm, using an absorptivity value of 110 l $g^{-1}cm^{-1}$.

Ash

Ash and acid insoluble ash (silica) were determined by the method proposed by Park et al. (1999). The samples were combusted at 700°C for 3 hours to determine ash content. Silica content was determined gravimetrically after boiling the ash in 1M HCl for 30 min. The silica remained as an insoluble residue.

Lignin structure

The aromatic composition of lignin was examined by the alkaline nitrobenzene oxidation procedure (Iiyama and Lam 1990) using a gas chromatograph (GC-17A; Shimadzu, Kyoto, Japan) with a NB-1 capillary column (30 m x 0.25 mm i.d.). Both injector and detector temperature were 280°C. The column temperature was 150°C for 15 min, then programmed at 5°C min^{-1} to 280°C, and kept for 4 min at 280°C.

RESULTS AND DISCUSSION

Effect of steam explosion on self-bonding

In our previous study, binderless boards could not be manufactured from untreated rice straw chips (Kurokochi and Sato 2015). In contrast, binderless boards were successfully manufactured from steam-exploded chips. Moreover, Fig. 2 shows that the IB met the requirement for MDF Type 5 (JIS A5905, 2014).

Some chemical modifications were detected in the pulp along with the color change to dark brown. From Tab. 2, the xylose content was decreased in pulp compared to the original rice straw, whereas the xylose content was increased in black liquor. Arabinose and galactose showed the same trend as xylose. Considering that black liquor was approximately pH 3-4, these changes suggested that the release of acetyl groups in hemicellulose occurred, and then hemicellulose was hydrolyzed to sugar and became soluble in black liquor during steam explosion. This phenomenon was already reported by Moniruzzaman (1996). Shao et al. (2008) expected that xylan was significantly hydrolyzed and produced furfural from xylosyl residues during steam explosion by acetic acid. Suzuki et al. (1998) suggested that the furfural contributed to self-bonding. However, the pressing temperature of 200°C in the present study was higher than the boiling point of furfural, 167°C. If the furfural were derived from xylose, it might vaporize during hot-pressing. Therefore, we considered that furfural might not have contributed to the self-bonding in the present study. Lamaming et al. (2013) reported that sugar played the major role in the bonding of binderless boards. Our study also showed that the decomposition of hemicellulose to simple sugar increased self-bonding.

Tab. 2: Chemical compositions of raw materials.

Types of raw materials		**Original**	**Pulp**	**Black liquor**
Conditions of steam explosion		-	**2.0 MPa / 5 min**	
Weight ratio (wt %)		100.0	65.4	20.9
Neutral sugar (wt %)	Rhamnose	0.0	0.0	0.0
	Aranobise	3.1	0.6	2.8
	Xylose	16.2	7.6	21.7
	Mannose	0.6	0.0	0.9
	Glucose	34.2	50.0	20.4
	Galactose	1.7	0.5	2.4
	Total	55.7	58.7	48.3
Lignin (wt %)	Klason lignin	17.6	25.0	13.2
	Acid soluble lignin	3.0	1.4	3.8
	Total	20.6	26.4	17.0
Ash (wt %)	Silica	22.0	27.0	15.0
	Total	23.1	27.3	21.1

From Tab. 2, the Klason lignin content increased by steam explosion. Shao et al. (2008) reported that this relative increase of lignin content could be due to the decrease of cell wall polysaccharides, especially xylan. This discussion also applied to our results. IB values increased with increasing Klason lignin content (Fig. 2 and Tab. 2). Mancera et al. (2011) reported that the addition of lignin to steam-exploded pulp increased bonding strength. The present study also showed a positive effect of lignin in pulp on self-bonding. Additionally, the acid soluble lignin content of black liquor was higher than those of both the original rice straw and pulp (Tab. 2). The reason was that Klason lignin was depolymerized by acidic hydrolysis and could be dissolved in the black liquor due to its low pH.

Tab. 3 shows the alkaline nitrobenzene oxidation products in raw materials. The yield is the weight percent of benzaldehyde derivatives based on the Klason lignin content. S/V ratio is the syringyl nuclei/guaiacyl nuclei molar ratio. From Tab. 3, the yield increased by steam explosion, indicating that condensation of lignin occurred by steam explosion.

The S/V ratio also increased by steam explosion. The same trend has been shown in bamboo (Shao et al. 2008). Okuda et al. (2006) reported that the yield was decreased and the S/V ratio was increased during hot-pressing. They suggested that this change might contribute to self-bonding. Consequently, our research indicated that the progress of lignin concentration in the pretreatment procedure also influenced self-bonding.

Tab. 3: Alkaline nitrobenzene oxidation products in raw materials.

Types of raw material	Original	Pulp	Black liquor
Conditions of steam explosion	-	**2.0 MPa / 5 min**	
Yield (wt %)	12.00	6.35	10.70
S/V ratio (molar ratio)	1.46	1.93	1.42
V : S : H (molar ratio)	1 : 1.2 : 0.5	1 : 1.9 : 0.7	1 : 1.4 : 0.7

V, Guaiacyl unit; S, Syringyl unit; H, p-Hydroxyphenyl unit.

Ash and silica content of pulp were both slightly higher than that of the original rice straw (Tab. 2). Considering that silica was not influenced by the pretreatment temperature in the present study, these relative changes of ash and silica content were caused by changes of the other components such as hemicellulose. The IB of pulp powder was higher than that of the original rice straw regardless of the high silica content (Fig. 2). When UF (Urea- formaldehyde) resin was used as a bonding agent, resin could not effectively wetten and penetrate the rice straw surface due to silica. Hence, silica is considered to have a negative effect to bonding (Li et al. 2010). However, the influence of silica on binderless boards made from rice straw has not been examined in detail. It will be necessary to examine the effect of silica on the properties of binderless boards in future investigations.

These chemical changes caused physical changes to rice straw. The release of pressure after exposure to steam at high pressure and temperature caused effective defibration of rice straw. Cellulose fibers became exposed by steam explosion. This change increased the available bonding area. Kurokochi and Sato (2015) showed that the trichomes and wart-like protuberances that exist on the epidermis of rice straw might inhibit the bonding between particles. The proportion of the original surface area occupied by trichomes and wart-like protuberances was decreased by defibration. This might have contributed to effective self-bonding.

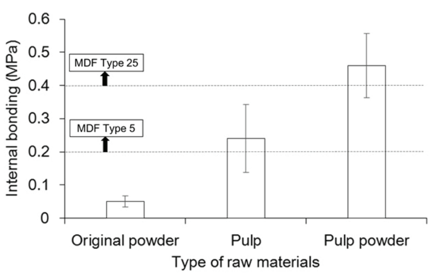

Fig. 2: Internal bonding of each board type.

Effect of grinding on self-bonding

From Fig. 2, IB was further improved by grinding pulp. The IB value met the requirement for MDF Type 25 (JIS A5905, 2014). Kurokochi and Sato (2015) reported that grinding increased the IB of board made from untreated rice straw because of the increase in bonding area. In pulp, Velasquiez et al. (2002) suggested that grinding to a pulp improved IB because the segregation of packages increased the inter-fiber bonding area. In fact, most fibers were segregated to single fibers in the ground rice straw. Using the same grinding process, the pulp became finer than untreated rice straw, because the pulp became fragile and its cellulose fibers became exposed. Epidermal tissue was cut into small pieces, with their sizes being smaller than the original powder. These physical changes might be effective in self-bonding.

Effect of pretreatment on water resistance

From Fig. 3, binderless boards made from pulp had low TS that met the requirement for MDF, 17 % (JIS A5905, 2014). The TS of pulp powder was further decreased due to the grinding process increasing the available bonding area. TS was originally low for the boards made from untreated rice straw because of wax-like substances on the epidermis of rice straw (Kurokochi and Sato 2015). Steam explosion further improved the water resistance of boards.

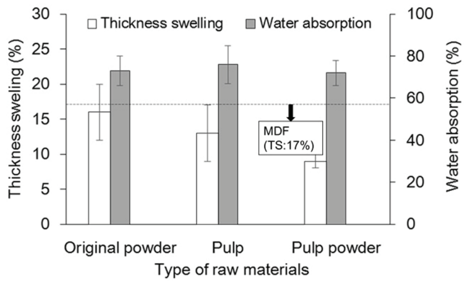

Fig. 3: Thickness swelling and Water absorption of each board type.

In contrast, WA values were not affected by pretreatment. When the binderless boards made from rice straw were soaked in water, the particles did not absorb water due to the presence of wax-like substances. Instead water entered cavities in the board. Hence, WA tended to be constant when the target density was constant (Kurokochi and Sato 2015). In the present study, WA showed a constant value regardless of pretreatment. In wheat straw, partial removal of wax by steam explosion was reported by Kristensen et al. (2008). It was suggested that the remained wax-like substances still contributed to water resistance of pulps. The role of the wax-like substances on water resistance of the binderless boards made from rice straw was not negligible. It will be necessary to examine this point in further detail in the future.

CONCLUSIONS

Steam-exploded rice straw was hot-pressed to make binderless boards. The properties of boards such as IB, TS and WA were measured and chemical analyses were carried out. Steam explosion increased the IB and TS of binderless boards made from rice straw, because chemical modifications such as hemicellulose decomposition to monosaccharides and lignin reconstruction occurred during steam explosion. Defibration also contributed self-bonding by increasing the bonding area and decreasing the disadvantage of trichomes and protuberances. Grinding further improved IB and TS by increasing the bonding area. Pretreatment combined with steam explosion and grinding was the most effective way to improves self-bonding.

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