Development of High-Performance Reed and Wheat Straw Composite Panels*1

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Introduction

In the production of composite panels from the annual crop and plant straws, some problems still exist in seasonality, storage, scattering sources, and bondability1). Among these factors, bondability remains a major unsolved technical problem, especially when urea-based resins are applied2)-4). It has been reported that UF-bonded straw boards have inferior properties, and the high quality boards could be produced by using isocyanate resin5)-8). But the application of isocyanate is hindered by its high cost, hence it is not commonly used, especially in developing countries. The poor properties of UF-bonded straw boards are related to a range of factors. The straw materials in general contain a substantially higher proportion of thin walled parenchymatic cells which are crashed to dust during mechanical processing9,10). The excessive extractives may influence the curing behavior of UF resin11). Higher pH and buffering capacity of some straws result in longer gel time of UF resin12). Of all the causes, extremely high silica and wax contents mainly concentrated on the surface of straws are considered to be major factors. This surface layer deteriorates the moisture absorbency of straw from water-based adhesives like UF resin, it hence acts as a barrier to the bonding13)-16). The removing of this bonding barrier layer from straw materials has been a technical problem in the performance enhancement of straw panels.

The objectives of this study were to first assess the fundamental properties of UF-bonded reed and wheat straw particleboards; then investigate the effects of silane coupling agent and ethanol/benzene extraction on the board properties; to clarify the improvement mechanism of bondability by physical and chemical treatments, the silicon distribution in the straws by ESCA and wettability before and after treatments as well as the curing behavior.
of UF resin were also investigated; finally, UF-bonded straw MDF was manufactured to explore an economical and feasible product for utilizing the straw materials.

Chapter 1 Manufacture of reed and wheat straw particleboards

The natural characteristics of reed and wheat straw materials make them difficult to bond with urea-formaldehyde (UF) resin, an adhesive popularly used in panel manufacture. The inherent non-polar, hydrophobic characteristics of the cuticles of straw caused by silica and wax, and the polar, hydrophilic nature of urea-based resins result in the difficulties in adhesion between these two components\(^{17}\). Silane coupling agents are generally applied for improving the adhesion between organic and inorganic materials. There are at least two functional groups in their molecules: one is methoxyl or ethoxyl-group which decomposes in water or reacts with some groups of inorganic material, and another amino-, epoxy-group which can react with organic materials. In this regard, silane coupling agents are used to modify the characteristics of inorganic surface by fixing some organic functional groups onto it\(^{18}\). This chapter discusses and compares the effects of silane coupling agent and ethanol/benzene extraction treatments on the properties of reed and wheat particleboards.

1.1 Effects of the types of silane coupling agents on board properties

1.1.1 Materials and methods

(1) Materials

Reed (Phragmites communis Trin.) and wheat (Triticum aestivum L.) straws with air-dry densities of 0.57 and 0.31 g/cm\(^3\), respectively, were obtained from northeastern China. A commercial urea formaldehyde (UF) resin (Zheng Yang He Wood Processing, China) with a solid content of 65% and a U: F ratio of 1.0: 1.4 was used. Three types of silane coupling agents (SCA), namely, vinyl silane, amino silane, and epoxide silane, were supplied by Gai Xian Chemical, China. A commercial urea formaldehyde (UF) resin were also investigated; finally, UF-bonded straw MDF was manufactured to explore an economical and feasible product for utilizing the straw materials.

Chapter 1 Manufacture of reed and wheat straw particleboards

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1.1 Effects of the types of silane coupling agents on board properties

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Vinyltriethoxysilicone (SiVN1): \(CH_2=CH-Si(OC_2H_5)_3\)

Vinyltris(\(\beta\)-methoxyethoxy)silane (SiVN2): \(CH_2=CH-Si(OC_2H_5OC_2H_5)_3\)

Amino silane (SiNH):

\(\gamma\)-Aminopropyltriethoxysilane: \(NH_2-C_3H_6-Si(OC_2H_5)_3\)

Epoxide silane (SiEP):

\(\gamma\)-Glycidoxypropyltrimethoxysilane:

\(H_2C-CH=CH-O-C_3H_6-Si(OCH_3)_3\)

Some basic properties of these silane coupling agents are shown in Table 1.1

(2) Method

Table 1.1. Some basic properties of silane coupling agents.

<table>
<thead>
<tr>
<th>Coupling agent</th>
<th>Molecular weight</th>
<th>Specific gravity at 25°C</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyltriethoxysilane (SiVN1)</td>
<td>190.3</td>
<td>0.90</td>
<td>161</td>
</tr>
<tr>
<td>Vinyltris((\beta)-methoxyethoxy)silane (SiVN2)</td>
<td>280.4</td>
<td>1.04</td>
<td>285</td>
</tr>
<tr>
<td>(\gamma)-Aminopropyltriethoxysilane (SiNH)</td>
<td>221.4</td>
<td>0.94</td>
<td>217</td>
</tr>
<tr>
<td>(\gamma)-Glycidoxypropyltrimethoxysilane (SiEP)</td>
<td>296.3</td>
<td>1.07</td>
<td>290</td>
</tr>
</tbody>
</table>

Table 1.2. Composition of fine and coarse particles based on mesh analysis.

<table>
<thead>
<tr>
<th>Mesh size (mm)</th>
<th>Fine</th>
<th>Coarse</th>
<th>Fine</th>
<th>Coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\geq 4.76)</td>
<td>0</td>
<td>0.65</td>
<td>0</td>
<td>0.19</td>
</tr>
<tr>
<td>4.76-2.00</td>
<td>0.50</td>
<td>31.61</td>
<td>35.30</td>
<td>60.75</td>
</tr>
<tr>
<td>2.00-1.00</td>
<td>20.84</td>
<td>54.76</td>
<td>62.80</td>
<td>37.01</td>
</tr>
<tr>
<td>1.00-0.25</td>
<td>68.35</td>
<td>12.90</td>
<td>1.90</td>
<td>2.05</td>
</tr>
<tr>
<td>0.25-0.125</td>
<td>8.17</td>
<td>0.07</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\leq 0.125)</td>
<td>1.94</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Components are expressed as percentage based on the total weight.

Board manufacture

Reed and wheat straws were first cut into 15- to 20-cm length by a drum chipper and further produced into particles by using a ring flaker. The particles were then screened into two groups of fine and coarse particles. Table 1.2 summarizes the composition of fine and coarse particles based on mesh analysis. All particles were dried at 80°C to about 3% moisture content (MC) before board fabrication. The UF resin was sprayed onto the particles in a blander at 13% resin content based on the oven-dried weight of particles. For the board incorporation with SCA made from coarse particles, 2% of silane coupling agent was mixed with the UF resin prior to blending, based on the weight of resin solid. One percent of NH\(_4\)Cl, based on the weight of resin solid, was added as the curing catalyst.

The hand-formed mats were pressed into 8 mm thick boards using distance bars at 150°C for 7 minutes. A three-step pressing schedule was used to avoid blistering. The specimens were cut from the boards after conditioning at 20°C and 65% RH for 2 h. Four to eight replicates were used for each condition.

Thickness swelling was determined by measuring the changes of board thickness after immersing in 20°C water for 2 h. Four to eight replicates were used for each condition.
Table 1.3. Densities of particleboards manufactured.

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Without coupling agent (g/cm(^3))</th>
<th>With coupling agent (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiVN1</td>
<td>SiVN2</td>
</tr>
<tr>
<td>Reed board</td>
<td>0.55</td>
<td>0.60</td>
</tr>
<tr>
<td>Fine</td>
<td>0.68</td>
<td>0.90</td>
</tr>
<tr>
<td>Coarse</td>
<td>0.66</td>
<td>0.75</td>
</tr>
<tr>
<td>Wheat board</td>
<td>0.55</td>
<td>0.60</td>
</tr>
<tr>
<td>Fine</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>Coarse</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.1.2 Results and discussion

(1) Fundamental board properties

Figures 1.1 and 1.2 show the MOR and IB of reed and wheat straw particleboards at different densities. Similar to conventional wood-based particleboard, both MOR and IB increased with increasing board densities. The IB values of the straw boards were much lower than those of conventional wood particleboard. This was true especially in the case of reed and wheat boards made from coarse particles, where the IB values were only 0.16 and 0.10 MPa, respectively, at a high density level of 0.80 g/cm\(^3\). It is obvious from the figures that for both reed and wheat particleboards, the MOR and IB of board produced from fine particles are better than those from coarse particles at the same board density level. It is well known that the size and configuration of particles have great effect on board properties\(^{19}\). Generally, small particles result in low MOR and high IB of particleboards. The results of this experiment may be attributed to the inherent characteristics of the raw materials. Like other non-wood lignocelluloses, both reed and wheat straws have higher hemicellulose and ash contents than wood. The outer surfaces of these two straws are covered with much silica and wax\(^{3,6,20}\). In the case of smaller particles, the specific surface of the particles is increased with a reduction in the surface containing silica and wax. This results in a reduced bonding inhibition effect caused by silica and wax, and so higher MOR and IB are obtained when fine particles were used as raw materials.

Figure 1.3 shows the TS of the straw boards at different densities. In general, the TS after a long duration of water immersion would have a tendency to increase with increasing board density because of the greater springback of compacted particles in boards of higher density\(^{21}\). However, in this study, the TS values of both reed and wheat boards were found to decrease with an increase in board density, especially in reed board. The reduction in TS in this case might be due to the following causes: The
water immersion time was rather short. Although the sample size was small, a 2-h immersion may be too short to allow thorough penetration of water into the board; hence most of the compacted particles did not experience complete springback. There are more voids in the low-density boards than in the high-density boards. Consequently, more water was being absorbed, resulting in a greater springback. At high density, the higher bonding strength may play a more dominant role than compaction ratio where water absorption is concerned during such short immersion.

The TS values of boards with fine particles tended to be lower than those made from coarse particles. This may be caused by the closer structure of the board, where the contact among the fine particles is better. Higher IB strength may also contribute to the reduction in water penetration. Figure 1.3 also shows that the TS of wheat boards is much greater than that of reed boards, which may reflect the higher IB values of reed boards with the same densities as shown in Fig. 1.2.

(2) Effects of various silane coupling agents on board properties

The results above indicate that the board properties are not satisfactory and must be improved. Figure 1.4 and Table 1.4 show the effects of various silane coupling agents on the properties of reed and wheat particleboards. All the property values were corrected to a board density of 0.70 g/cm³, based on the linear equations obtained from the correlation between board density and properties.

The board properties were generally improved by the addition of silane coupling agents. For reed board, even though there was no substantial increase in MOR, the IB was improved significantly. After adding SiEP the IB value was twice as much as that of the control. It was also found that the TS decreased by about 30% compared to that of the control. For wheat board, incorporation of SiNH resulted in IB of 0.19 MPa, which is more than 2 times that of the control. SiNH also reduced the TS of wheat board to about 1/3 of that of the control, resulting in a final TS of 17%.

The improvement caused by each coupling agent was different. The addition of SiNH results in great improvement in IB in wheat board, but SiVN1 and SiVN2

![Fig. 1.3. Thickness swelling (TS) of reed and wheat particleboards made from fine and coarse particles at different densities.](image)

![Fig. 1.4. Effects of various silane coupling agents on the properties of reed and wheat particleboards. Refer to Table 1.1. for explanation of various silane coupling agents.](image)

### Table 1.4. Improvement of board properties using various silane coupling agents.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Wheat board</th>
<th>Reel board</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiVN 1</td>
<td>SiVN 2</td>
</tr>
<tr>
<td>MOR</td>
<td>1.70</td>
<td>1.08</td>
</tr>
<tr>
<td>IB</td>
<td>2.14</td>
<td>1.92</td>
</tr>
<tr>
<td>TS</td>
<td>0.89</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Improvement is expressed as ratio of the properties of board with silane coupling agent to that without silane coupling agent (control). MOR, modulus of rupture; IB, internal bond; TS, thickness swelling.
were not so effective. This difference may be related to the difference in chemical structure and the optimal adhesive type in which they can function. SiVN1 and SiVN2 are compatible with polyethylene and polyester resins, respectively, and SiNH and SiEP are compatible with formaldehyde and epoxy resins.

Epoxy silane (SiEP) is considered to be more effective for reed board, whereas the properties of wheat board were greatly improved by adding SiNH. This improvement could be due to reactions among coupling agent, UF resin and the particles. There are two functional groups in the SiEP molecule: the methoxysilane group and the epoxy group. The methoxysilane is readily hydrolyzed, and the silanols formed may react with silica on the material surface to form strong siloxane bonds. It is speculated that the reactions between the epoxy and amide groups in the resin molecules could also have taken place, and the amido formed is capable of reacting with the hydrate of formaldehyde. Ethoxysilane and amino are the two main functional groups of SiNH molecule. Ethoxysilane may experience a reaction similar to that of methoxysilane, and the reaction between amino and hydroxyl groups in UF resin may occur. The curing reactions of UF resin after adding silane coupling agents could be more complicated, and the above reactions must be further investigated.

1.2 Effects of the contents of silane coupling agents on board properties

1.2.1 Materials and methods

(1) Materials

Reed and wheat straws used were the same as in this chapter 1.1. Urea formaldehyde resin with a solid content of 65% and a U : F ratio of 1.0 : 1.4 was formulated by Oshika Shinko, Japan. Epoxide and amino silanes were obtained from Shin-Etsu Chemical, Japan.

(2) Methods

Board manufacture

The straws were first cut to about 8 cm length by using a hand-cutter, followed by disintegration in a hammer-mill. The hammer-milled particles were then screened through an 8 mm sieve, where particles retained on the screen and passing through the screen were classified into coarse and fine particles, respectively. The corresponding particle geometry is summarized in Table 1.5. The particles were dried to 2–5% moisture content (MC) at 60°C prior to board fabrication.

The particles were sprayed with UF resin in a rotating drum blender, at a resin content of 12% based on the oven-dried weight of the particles. The resin was applied by means of a spray gun. Based on the conclusion of this chapter 1.1 on the types of SCA, SiEP and SiNH were used for reed and wheat particles, respectively, in this study. For coarse particles, the SCA was incorporated into the resin solutions at 2, 5, and 7%, based on the resin solid content. For fine particles, only 2% of SCA was added. Table 1.6 summarizes the processing parameters for reed and wheat particleboards. The resin-sprayed particles were then hand-formed in a forming box, and hot pressed at 130°C for 6 min. The boards were manufactured to \( 350 \times 400 \times 9 \text{ mm} \), at a targeted density of 0.7 g/cm\(^2\). A maximum pressure of about 3.0 MPa was applied during hot pressing. Due to the inferior permeability of straw mat, the breathing period at the end of the hot pressing cycle was monitored carefully, in order to prevent delamination.

Board evaluation

Prior to the conventional evaluation of mechanical properties and dimensional stability, the particleboards were conditioned for 2 weeks under 20°C and 65±5% relative humidity (RH). The boards were tested in accordance with the JIS for Particleboards (JIS A 5908, 1994). The static bending test in the dry condition was conducted for four specimens of \( 50 \times 200 \text{ mm} \) each board, using a three-point bending test over an effective span of 150 mm at a loading speed of 10 mm/min. Five \( 50 \times 50 \text{ mm} \) specimens were prepared from each board for internal bond (IB) and thickness swelling (TS) tests, respectively.

In addition, the linear expansion (LE), thickness changes (TC), and equilibrium moisture content (EMC) of two \( 50 \times 200 \text{ mm} \) specimens from each board were examined after exposure to an RH cycle of 33, 66% and 98%. The initial and final dimensions of the specimens were measured after oven-drying until they reached a constant weight at 60°C; the specimens were then cooled in a desiccator at 20°C (8% RH). The RH in the desiccator was recorded through an RH recording meter. The corresponding changes in length, thickness and weight were determined after the samples were conditioned to equilibrium at 33, 66% and 98% RH over saturated solutions of MgCl\(_2\), NaN\(_2\)O\(_2\) and Ca\(_2\)SO\(_4\), respectively, in air-tight moisture chambers at 20°C. The length was measured to the nearest 0.01 mm. After the RH cycle and measurements, the samples were subjected to drying again at 105°C until a constant weight was reached and then weighed to determine the EMC.

1.2.2 Results and discussion

(1) Mechanical and physical properties

Figures 1.5 and 1.6 show the effects of SCA levels on the MOR and MOE of reed and wheat particleboards. Irrespective of the addition level, SCA was found to have very little effects on the MOR and MOE of both reed and wheat boards. Similar to conventional particleboard, the bending properties of boards made from fine particles were comprising of elastic wheat straw had higher MOE.

| Table 1.5. Geometry of reed and wheat particles of different sizes. |
|---------------------------|----------------|----------------|----------------|
|                          | Reed           | Wheat          |                |
| Length (mm)              | 12.7 – 28.8    | 2.5 – 6.0      | 9.8 – 23.1     | 2.8 – 7.5      |
| Width (mm)               | 0.8 – 1.6      | 0.4 – 1.0      | 0.8 – 2.3      | 0.5 – 1.4      |
| Thickness (mm)           | 0.17 – 0.39    | 0.08 – 0.22    | 0.16 – 0.42    | 0.08 – 0.28    |
Table 1.6. Processing variables for reed and wheat particleboards.

<table>
<thead>
<tr>
<th>Code</th>
<th>Particle types</th>
<th>SCA addition levels (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>C</td>
<td>-</td>
</tr>
<tr>
<td>SCA/2</td>
<td>C</td>
<td>2</td>
</tr>
<tr>
<td>SCA/5</td>
<td>C</td>
<td>5</td>
</tr>
<tr>
<td>SCA/7</td>
<td>C</td>
<td>7</td>
</tr>
<tr>
<td>Control-F</td>
<td>F</td>
<td>-</td>
</tr>
<tr>
<td>SCA/2-F</td>
<td>F</td>
<td>2</td>
</tr>
</tbody>
</table>

a C, coarse particles; F, fine particles. b Based on the solid weight of resin; SCA, silane coupling agent.

Fig. 1.5. Effects of silane coupling agent (SCA) addition level on moduli of rupture (MOR) of reed and wheat particleboards. Refer to Table 1.6. for the explanation of legend. Vertical lines through the bars represent the standard deviation from the mean value.

Fig. 1.6. Effects of SCA addition level on moduli of elasticity (MOE) of reed and wheat particleboards. Refer to Fig. 1.5. for other explanations.

Fig. 1.7. Effects of SCA addition level on the IB of reed and wheat particleboards. Refer to Fig. 1.5. for other explanations.

Fig. 1.8. Effects of SCA addition level on the TS of reed and wheat particleboards. Refer to Fig. 1.5. for other explanations.

relative low compared to those composed of coarse particles. Based on the inherent characteristics of the raw materials, the high-strength reed straws contributed to superior MOR of reed board, whereas the wheat board.

The IB strengths of reed and wheat boards with different SCA contents are shown in Fig. 1.7. The IB values of both reed and wheat boards were found to increase with higher SCA content. The IB improved significantly when up to 5% of SCA was incorporated, but the effectiveness of treatment kept constant at above 5%. Similar to the earlier study, the IB values of both reed and wheat boards fabricated from fine particles were superior to those produced from coarse particles.

Figure 1.8 indicates the effects of SCA levels on the TS of reed and wheat boards produced from fine and coarse particles. Generally, TS decreased with increasing SCA content. This reduction in TS was significant when SCA content was below 5%, but the significance of treatment didn't vary much at above 5% SCA content. The TS values of wheat boards were generally higher compared to those of reed boards. This is related to the inherent characteristics of the raw materials, where reed straw is more water-resistant compared to wheat straw. This superior water-repellence property of reed straw is due to its higher silica content. Besides, Fig. 1.8 also shows the TS of wheat boards produced from fine particles to be higher than those made from coarse particles, whereas the TS of reed boards was not affected by particle size. This may be attributed to the superior water resistance of reed straw, which prevented thorough penetration of water into the board, despite immersion in water for 24 h. Consequently, most of the compacted particles might not have experienced complete springback, making it not possible to determine the true effect of particle size on the...
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(2) Dimensional stability under varying relative humidity

Figures 1.9, 1.10 and 1.11 show the LE and the corresponding TC of reed and wheat boards with different SCA level during moisture absorption and desorption processes under different RH. Both LE and TC of the boards improved with increasing SCA content. Generally, the LE and TC increased gently when RH was increased up to 66%, but recorded exceedingly high values after attaining equilibrium at 98% RH. For reed and wheat boards:

Fig. 1.9. Linear expansion (LE) of reed particleboard under different relative humidity (RH) during moisture absorption (left) and desorption (right) processes. Refer to Table 1.6. for the explanation of legend.

Fig. 1.10. Linear expansion (LE) of wheat particleboard under different relative humidity (RH) during moisture absorption (left) and desorption (right) processes. Refer to Table 1.6. for the explanation of legend.

Fig. 1.11. Thickness changes (TC) of reed and wheat particleboards under different RH during moisture absorption and desorption processes. Refer to Table 1.6. for explanation of legend.
The ethanol/benzene (EB) solution was prepared by mixing one volume of 95% ethanol with two volumes of benzene. The coarse particles, the same as in this chapter 1.2, were used. The particles were first dried at 60°C for 72 h, and then immersed in EB solution in a glass container placed in a 50°C waterbath for 24 h. The treated particles were dried again at 60°C to 2-3% MC prior to board manufacture. The UF resin addition content, board manufacture and evaluation were the same as in this chapter 1.2.

1.3.2 Results and discussion
Figures 1.13 to 1.15 show the effects of EB treatment on the mechanical properties of reed and wheat particleboards and comparison with SCA addition. EB treatment improved the MOR and MOE of wheat board by about 70%, but had no significant effect on reed board. A significant improvement of IB was observed in EB-treated wheat board, where the IB value was four times that of control. Since the EB extractive content of wheat particles was about 7%, and negligible in reed particles, the significant improvement of IB in wheat particleboard could be attributed to the removal of wax-like substances from the straw surface[30], hence facilitating the adherence of UF resin to the active hydroxyl sites of the cellulose.

Comparing the effectiveness of SCA and EB treatment,
The effect of EB treatment on the TS of the straw boards and the comparison with SCA addition is shown in Fig. 1.16. The TS values of EB-treated reed and wheat boards were reduced by about 30% and 50%, respectively. EB treatment was more effective for reducing the TS of both straw surfaces, which will be discussed in detail in next chapter.

Fig. 1.15. Effects of EB treatment on the IB of reed and wheat particleboards and the comparison with SCA addition. Refer to Fig. 1.5 for other explanations.

SCA was more effective for reed board while EB treatment was better for wheat board. In the board production, the SCA added resin-coated particles and EB-treated particles became less sticky and had better resin penetration than the untreated particles. The improvement of the properties of reed and wheat particleboards using SCA and EB treatment suggests the improved wettability of the straw surfaces, which will be discussed in detail in next chapter.

Fig. 1.16. Effects of EB treatment on the TS of reed and wheat particleboards and the comparison with SCA addition. Refer to Fig. 1.5 for other explanations.

Fig. 1.17. Linear expansion (LE) of reed and wheat particleboards after EB treatment under different RH, and comparison with the effect of SCA addition. Refer to Table 1.6 for other explanations.

Fig. 1.18. Thickness changes (TC) of reed and wheat particleboards after EB treatment under different RH, and comparison with the effect of SCA addition. Refer to Table 1.6 for other explanations.
reed and wheat boards compared to SCA addition. This is attributed to improved interparticle bonding after EB-treatment which resulted in lower water penetration into the board.

Figure 1.17 and 1.18 show the dimensional stability of the EB-treated and SCA-added boards during moisture absorption and desorption processes under different RH. The LE and TC of both the reed and wheat boards improved with EB treatment. The LE of the board with EB treatment was superior to that added with SCA. The LE of the EB-treated board was completely reversible upon oven-drying at the end of the RH cycle. This superior LE could be attributed to the stronger interelement bonding in EB-treated board.

1.4 Summary

The properties of UF-bonded reed and wheat particleboards manufactured from 2 types of particle at different densities were determined. Particle size was found to have a profound effect on the board properties. The properties of both reed and wheat boards produced from fine particles were better than those from coarse particles.

The board properties are closely related to the board density. An increase in board density resulted in higher mechanical properties and dimensional stability. However, the properties of UF-bonded straw particleboards were rather lower compared to conventional wood particleboards, the IB and TS of the boards at 0.50-0.80 g/cm³ densities could not meet the requirement of Chinese Particleboard Standard (GB/T 4897-92).

Silane coupling agents (SCA) can be used to improve the board properties of reed and wheat particleboards. The improvement was more obvious in IB than in MOR and TS. It seems that epoxide silane was more effective for reed board, whereas amino silane was better for wheat board.

With the effects of SCA addition levels on board properties, the IB and TS of both reed and wheat particleboards increased significantly when SCA was incorporated up to 5%, but the improvement didn’t vary much at above 5%. Ethanol/benzene treatment was found to improve the IB and TS of wheat board significantly, whereas SCA incorporation was more effective for reed board. The dimensional stability of the boards under various RH conditions was also improved with increasing SCA content. Ethanol/benzene treatment resulted in greater improvement in board dimensional stability compared to SCA.

Chapter 2 Improvement mechanism of bondability by physical and chemical treatments

The previous study showed that the properties of UF-bonded reed and wheat straw particleboards could be improved by the addition of silane coupling agent and ethanol/benzene extraction treatment. However, the improvement mechanism of bondability was not yet clear. This chapter discusses the effects of silane coupling agents and ethanol/benzene extraction treatments on the wettability of the straw surfaces. The distribution of silicon along the thickness of straws was analyzed by electron spectroscopy for chemical analysis (ESCA). In addition to the effects of hot-water extractives and addition of silane coupling agents on the gel time of UF resin were also examined.

2.1 Materials and methods

 Reed and wheat straws were ground into powder for extraction test and cut into 50 mm length for wettability measurement. The UF resin, ethanol/benzene (EB) solution and silane coupling agents (SCA): epoxide silane (SiEp), amino silane (SiNH), and vinyl silane (SiVN), were the same as in chapter 1. NH4Cl solution of 20% concentration was used as the hardener.

2.1.1 Extraction test

The reed and wheat straws of 50 mm length were extracted with EB solution for 24 h using the Soxhlet extraction method. Oven-dried reed straw meal (32-70 mesh, 100 g) was extracted with boiling water for 8 h. The filtrate was dried by freeze-drying method. The extractives obtained were prepared for gel time experiments.

2.1.2 Silane coupling agent treatment

Reed and wheat samples were kept in a desiccator and then weighed and soaked in SCA solutions of various concentrations from 0.1% to 100% for 30 s. The samples were then dried, reconditioned to the initial moisture content (prior to treatment), and weighed again. The weight gain (WG) of the sample was calculated as follows: where W1 is the weight of treated sample after drying and reconditioning, and W0 is the weight before treatment. EB-extracted straws were treated with SCA using the same procedure.

2.1.3 Measurement of wettability

Wettability is expressed as the advancing contact angle of distilled water on the outer surface of the straw. The contact angle was measured with a M-2010 B contact anglemeter (Erma Optics, Japan). An aliquot (6 μl) of distilled water was dropped onto the surface with a micropipette. A photograph was taken 10 s after the water had been dropped. The contact angle was then calculated with the height and chord of the droplet measured. Five measurements were made for each sample.

2.1.4 Electron spectroscopy for chemical analysis (ESCA)

Samples of 7×7×0.2-0.3 mm were cut by a microtome from three positions along the thickness of straw: outer, sectioned and inner surfaces. The presence of silicon (Si2p) on these surfaces were detected by X-ray photoelectron spectroscopy at a current of 10 mA and a voltage of 15 kV.

2.1.5 Measurement of gel time and pH of UF resin

Hot-water extractives and SCA were added to 10 g of the UF resin at 1, 2 wt% and 3 wt% and at 2, 4, 6 wt% and 10 wt% based on its resin solid, respectively. After adding 1 ml of NH4Cl solution, the gel times of the resin-extractive system at 70°C and 90°C and that of the resin-SCA system at 90°C were measured according to the procedure described in JIS K 6801. The pH of these two systems was measured at 25°C by using a pH meter immediately after adding extractives and SCA. Two replicates were
HAN: Development of High-Performance Reed and Wheat Straw Composite Panels

125
100
75
50
25
0

Control SiEP SiNH SiVN
Silane coupling agent

Fig. 2.1. Effects of silane coupling agents on the contact angles of reed straw outer surface. SiEP, epoxide silane; SiNH, amino silane; SiVN, vinyl silane.

The untreated specimen (control) had a large contact angle, indicating relatively low surface wettability of the reed straw. This poor wettability may interfere with the spreading and penetration of resin, thereby affecting the bond formation between the resin and particles. After treating with SCA, the contact angles were reduced by about 66% and 36% for SiEP and SiNH, respectively. SiVN had almost no effect on the contact angles, which could be due to the insoluble characteristic of SiVN.

Considering the fact that low contents of SCA were used for board manufacture in the earlier studies, the SCA was diluted into various concentrations of aqueous solutions. Reed and wheat straws were then treated with these different concentrations of SCA solutions to obtain various weight gains of the treated samples. Because the contact angle was not affected by SiVN, only SiEP and SiNH were used in this experiment. Figure 2.2 expresses the relation between the contact angles of straw outer surfaces and the weight gain of the treated samples. For both reed and wheat straws, the contact angles generally decreased with increasing weight gain. SiEP was more effective in reducing the contact angles for reed straw, and SiNH was better for wheat straw.

It was also found that SCA reduced the contact angles to a greater extent in reed straw than in wheat straw. This wettability improvement after SCA treatment could be attributed to some hydrophilic components exposed on the straw surfaces, which might have resulted from some reactions between SCA and the straw surfaces.

The results of this experiment indicate that the wettability of straw outer surfaces was improved by treating with SCA, which may be one of the reasons why the board properties were improved by the SCA addition. The reduction of contact angle achieved by each SCA shows good correlation with the improved board properties in the previous studies.

### 2.2.1 Effects of silane coupling agents on the wettability of straw surfaces

It has been reported that bond strength is dependent on wetting, spreading and surface tension. Wettability evaluation is of great importance since bond quality in composites is affected by the contact of the resin with wood and is a good indicator of the resin penetration into the wood. The previous study showed that the inferior properties of reed and wheat straw boards were improved using SCA; SiEP was more effective for reed board while SiNH was better for wheat board. To confirm the effects of SCA on the straw materials, reed straw was treated with SCA at 100% concentration. Figure 2.1 shows the effects of SCA on the straw materials, reed straw was treated with SCA at 100% concentration. Figure 2.1 shows the effects of SCA on the contact angle of reed straw outer surface. The untreated specimen (control) had a large contact angle, indicating relatively low surface wettability of the reed straw. This poor wettability may interfere with the spreading and penetration of resin, thereby affecting the wettability of straw outer surfaces. The presence of extractives can also influence the wettability of materials. It has been reported that low wettability is related to the existence of nonpolar extractives.

Figure 2.3 shows the effect of EB extraction on the contact angles of reed and wheat straw outer surfaces. The untreated specimen (control) had a large contact angle, indicating relatively low surface wettability of the reed straw. This poor wettability may interfere with the spreading and penetration of resin, thereby affecting the wettability of straw outer surfaces. The presence of extractives can also influence the wettability of materials. It has been reported that low wettability is related to the existence of nonpolar extractives.

Figure 2.3 shows the effect of EB extraction on the contact angles of reed and wheat straw outer surfaces. The untreated specimen (control) had a large contact angle, indicating relatively low surface wettability of the reed straw. This poor wettability may interfere with the spreading and penetration of resin, thereby affecting the wettability of straw outer surfaces. The presence of extractives can also influence the wettability of materials. It has been reported that low wettability is related to the existence of nonpolar extractives.

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Fig. 2.2. Relation between the contact angles of the straw outer surfaces and the weight gains of treated samples. Refer to Fig. 2.1 for the explanation of legends.
of straw surfaces extracted with EB. For reed straw, at a weight gain of less than 8% there was a great reduction in the contact angles of straw surfaces after treatment with SiEP, whereas at more than 8% weight gain only a slight change was observed in the contact angles. In the case of SiNH treatment, there was a clear decrease in contact angles when the weight gain was less than 5%. SCA had almost no effect on the contact angles when the weight gain exceeded 5%. For wheat straw, the contact angles of the EB-extracted specimens remained almost constant despite a hike in the weight gain.

It can be concluded that SCA was more effective in reducing the contact angle of reed straw both before and after extraction. However, EB extraction had a greater effect than SCA on improving the wettability of wheat straw. These results agree with the different effects of SCA and EB on the board properties in the earlier studies.

2.2.3 Analysis of silicon distribution in straws by ESCA

For further elucidation of the mechanism of bond formation, the reed and wheat straws were analyzed by ESCA. The distribution of silicon along the thickness of these straws is illustrated in Fig. 2.5. The silicon peaks are shown at a binding energy of 100–102 eV. Relatively high silicon peaks were observed on the outer surfaces of both reed and wheat straws; no peak was found on the sectioned surfaces. A high peak also appeared on the inner surface of reed straw but not on wheat straw. Reed straw seems to contain more silicon than wheat straw. Based on the speculation of some reactions among SCA, UF resin and the particles, the greater improvement of the properties of reed board achieved by SCA treatment might be related to the higher silicon content in reed straw. The superior bondability of wheat board by EB extraction is attributed to the greater improvement of wettability in wheat straw due to the removal of wax.

Generally, there is a waxy layer on the cereal straw surface. The wax on the straws which makes the UF resin chemically incompatible with straws is probably one of the main factors responsible for the reduction of bond quality. The bondability improvement of the EB-extracted particleboards is highly related to the upgraded wettability of the straw surfaces. Wax removal pretreatment of the straw materials is efficient to enhance strawboard performances. Further studies should be conducted to investigate other more economical and feasible pretreatments of the wax removal from straws.

Figure 2.4 shows the effect of SCA on the contact angles of straw surfaces extracted with EB. For reed straw, at a weight gain of less than 8% there was a great reduction in the contact angles of straw surfaces after treatment with SiEP, whereas at more than 8% weight gain only a slight change was observed in the contact angles. In the case of SiNH treatment, there was a clear decrease in contact angles when the weight gain was less than 5%. SCA had almost no effect on the contact angles when the weight gain exceeded 5%. For wheat straw, the contact angles of the EB-extracted specimens remained almost constant despite a hike in the weight gain.

It can be concluded that SCA was more effective in reducing the contact angle of reed straw both before and after extraction. However, EB extraction had a greater effect than SCA on improving the wettability of wheat straw. These results agree with the different effects of SCA and EB on the board properties in the earlier studies.

Figure 2.4 shows the effect of silane coupling agents on the contact angles of straw surfaces before and after ethanol/benzene extraction. The corresponding effects of epoxide silane (SiEP) and amino silane (SiNH) on contact angles before extraction. 

--- 30 ---
specific surface area of the particles is increased with a reduction in the surface containing silica and wax; and most of the silicon on the surface could be removed in the milling process\(^4\).

### 2.2.4 Effects of water extractives and silane coupling agent on gel time and pH of UF resin

Using gel test to determine the cure rate and degree of catalyzation of a resin is a common industrial procedure. It has been reported that hot-water extractives of wood have a significant effect on the gel time of UF resin\(^33\)\(^-\)\(^35\). UF resin is known to be acid-catalyzed and cannot attain an optimum state of cure in a low acid environment\(^36\).

In this study the hot-water extractives of reed straw and SCA were added to UF resin, and their effects on the gel time and pH of the resin were examined. As seen in Table 2.1 and Fig. 2.6, a higher extractive addition resulted in longer gel time at both 70°C and 90°C, which indicates that the extractives retarded the gelation of UF resin. Therefore a longer hot-pressing time would be necessary to achieve complete curing of the resin. The pH values at 25°C decreased slightly with an increased extractives content in the UF resin. It is well known that pH plays an important role in the curing of UF resin; a lower pH usually brings about a shorter gel time. The pH descent was reported to be retarded by the addition of water extractives of wood in UF resin\(^33\)\(^,34\). In this experiment the presence of extractives in the UF resin may also retard the rate of pH decrease during the curing process, and this showing of the pH decrease seemed to prolong the gel time.

The effects of SCA on the gel time and pH of UF resin are shown in Table 2.2 and Fig. 2.7. The gel time was prolonged with an increase of SiNH content in the resin, but it was not affected by the addition of SiEP and SiVN. The pH of the mixture increased with the amount of SiNH added. The pH values of the resin after adding SiEP and SiVN remained unchanged. SiNH seems to retard the
The wettability of treated samples was evaluated. The upgraded properties of straw MDF and particleboards are compared with each other.

### 2.3 Summary

The poor wettability of reed and wheat straw surfaces was improved by SCA and EB treatments. The improvement due to SiEP was more obvious for reed straw, whereas SiNH was more effective in wheat straw. In addition, EB extraction resulted in a greater increase in the wettability of wheat straw than reed straw. SCA improved the wettability to a greater extent in reed straw over wheat straw. SCA and EB treatments improved the wettability of reed straw more than in wheat straw. The wettability improvements show good correlation with the upgraded board properties by ESCA addition and EB extraction can improve the wettability of the straw surfaces, resulting in enhanced board performances. However, the bond formation between the resin and straws may be more complicated, and subjected to the influences of many factors.

### Chapter 3 Manufacture of reed and wheat straw medium density fiberboards

The previous studies reported that proper treatment like ethanol/benzene extraction improved the wettability of reed and wheat straw surfaces. The upgraded properties of UF-bonded straw particleboards could be attributed to the improved wettability, which was due to the removal of wax from the straw surfaces. Based on these results, it was considered that the wax layer would be destroyed by proper thermal-mechanical refining process. The objective of the study in this chapter was to investigate the effects of steam cooking treatment on the wettability and weight losses of the treated straws. The effect of steaming condition in refining process on the properties of medium density fiberboard (MDF) was examined. Finally, the properties of straw MDF and particleboards are compared with each other.

### 3.1 Materials and methods

Reed and wheat straws, UF resin and its hardener used were the same as in the previous studies.

#### 3.1.1 Preliminary experiment

Oven-dried reed and wheat straws of 10-cm length (about 5 g) were cooked with steam using a thimble filter. The steam cooking was conducted by using a special experimental apparatus designed for this purpose. The thimble filter was loosely tied with a wire before putting into a cooking cell to prevent the straw blocks from bursting out of the filter. The steam pressures were 2, 4, 6 atm and 10 atm. The cooking times for each pressure level were 5 and 10 min. The weight of samples after oven drying at 105°C for 24 h were measured before and after cooking, and the weight losses were then calculated. The wettability of treated samples was evaluated. Wettability is expressed as the advancing contact angle of distilled water on the outer surface of the straw.

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**Table 2.2. Gel time and pH of UF resin with silane coupling agents.**

<table>
<thead>
<tr>
<th>Silane coupling agent added (%)</th>
<th>SiNH+UF Gel time (min)</th>
<th>pH</th>
<th>SiEP+UF Gel time (min)</th>
<th>pH</th>
<th>SiVN+UF Gel time (min)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (control)</td>
<td>1.41 (100)</td>
<td>6.70</td>
<td>1.41 (100)</td>
<td>6.70</td>
<td>1.41 (100)</td>
<td>6.70</td>
</tr>
<tr>
<td>2</td>
<td>2.07 (147)</td>
<td>8.22</td>
<td>1.51 (107)</td>
<td>6.75</td>
<td>1.40 (99)</td>
<td>6.74</td>
</tr>
<tr>
<td>4</td>
<td>2.37 (168)</td>
<td>8.85</td>
<td>1.44 (102)</td>
<td>6.80</td>
<td>1.34 (95)</td>
<td>6.71</td>
</tr>
<tr>
<td>6</td>
<td>2.80 (198)</td>
<td>9.14</td>
<td>1.43 (101)</td>
<td>6.71</td>
<td>1.38 (98)</td>
<td>6.72</td>
</tr>
<tr>
<td>10</td>
<td>4.06 (288)</td>
<td>9.38</td>
<td>1.48 (105)</td>
<td>6.73</td>
<td>1.24 (88)</td>
<td>6.73</td>
</tr>
</tbody>
</table>

SiNH, amino silane; SiEP, epoxide silane; SiVN, vinyl silane. *The gel time was measured at 90°C; pH was measured at 25°C. The amount of silane coupling agent added was based on the weight of the resin solid.
Table 3.1. Experimental variables of the cooking conditions in refining processes.

<table>
<thead>
<tr>
<th>Code</th>
<th>Straw types*</th>
<th>Steam pressure (atm)</th>
<th>Steaming time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/ 5</td>
<td>W</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>4/10</td>
<td>R</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>6/ 3</td>
<td>R, W</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>6/10</td>
<td>R, W</td>
<td>6</td>
<td>10</td>
</tr>
</tbody>
</table>

* R, Reed; W, Wheat.

Table 3.2. The dimensions of fibers under various refining processes.

<table>
<thead>
<tr>
<th>Fiber types</th>
<th>Length (mm)</th>
<th>Diameter (μm)</th>
<th>L/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>R 4/10</td>
<td>3.00 (1.32)</td>
<td>246.25 (127.99)</td>
<td>16.28 (12.49)</td>
</tr>
<tr>
<td>R 6/ 3</td>
<td>3.46 (1.75)</td>
<td>118.17 (72.26)</td>
<td>39.83 (31.22)</td>
</tr>
<tr>
<td>R 6/10</td>
<td>3.57 (1.68)</td>
<td>109.80 (56.56)</td>
<td>40.74 (26.30)</td>
</tr>
<tr>
<td>W 4/ 5</td>
<td>5.32 (2.63)</td>
<td>106.94 (117.56)</td>
<td>38.54 (26.71)</td>
</tr>
<tr>
<td>W 6/ 3</td>
<td>5.17 (2.60)</td>
<td>101.00 (57.79)</td>
<td>65.47 (48.83)</td>
</tr>
<tr>
<td>W 6/10</td>
<td>5.12 (3.19)</td>
<td>109.39 (76.02)</td>
<td>66.42 (50.01)</td>
</tr>
</tbody>
</table>

* Refer to Table 3.1 for the explanation of fiber types. L/D is the ratio of length to diameter of each fiber sample. The values above and in the parentheses were the averages and the standard deviations from the mean values of 200 randomly chosen fiber samples, respectively.

3.1.2 Manufacture of MDF

Fibers were made from reed and wheat straws of about 5-cm length by using a pressurized single disc refiner with the refiner plate diameter of 305-mm (BRP45-300SS, Kumagai Riki Kogyo). The straws were placed into a 6-liter pressure vessel where they had been steamed, and then passed through the refiner plates (plate gap: 0.37 mm). A certain pressure was maintained in the system by a constant supply of steam. Based on the results of the preliminary experiment, three different cooking conditions, as shown in Table 3.1, were used. Refined fibers were vented from the refiner housing into a blowline connected to a continuous flash dryer. The moisture content (MC) of the obtained fibers was about 12-15%. The lengths and diameters of 200 randomly chosen fiber samples were measured after the photographs of the fibers were taken at 25X magnification, and the length/diameter ratio of each fiber sample was calculated. The dimensions of the fibers are shown in Table 3.2.

The fibers were dried at 60°C to the target MC of 2-3% before blended with adhesive. The UF resin was added to the fibers in an air-cyclic pipeline by using a spray gun. The resin addition level was 15% based on the oven-dried weight of the fibers. Mat forming was done by passing the blended fibers through another pipeline which was ended in a forming box. A total of 12 mats were platen pressed at 130°C for 5 min. A three-phase pressing schedule was used to avoid blowing. The board dimension was 370×355×6 mm with target densities of 0.50 g/cm³ and 0.70 g/cm³ for each condition.

3.1.3 Evaluation of panel properties

For conventional evaluation of mechanical properties and dimensional stability, the test boards were conditioned for 2 weeks under 20°C and 65±5% relative humidity (RH). The unsanded boards were then evaluated according to Japanese Industrial Standard for fiberboard (JIS A 5905, 1994) 38).

The static bending test in dry condition was conducted on three specimens of 50×200 mm from each board, using a 3-point bending test over an effective span of 150 mm at a loading speed of 10 mm/min. Five specimens with dimensions of 50×50 mm from each board were tested for internal bond (IB) and thickness swelling (TS) tests, respectively.

Besides the standard water soaking test, two specimens of 50×200 mm were prepared from each board for linear expansion (LE), thickness change (TC) and equilibrium moisture content (EMC) test under an RH conditioning cycle of 33, 66% and 98%. The initial and final dimensions and weights were measured after oven dried at 50°C under vacuum for 36 h, followed by at 105°C for 5 h. The corresponding changes in length, thickness and weight were examined after the test samples were conditioned to equilibrium at 33, 66% and 98% RH over saturated solutions of MgCl₂, NaNO₂ and CaSO₄, respectively, in airtight chambers at 20°C. The length was measured to the nearest 0.01 mm by means of a linear gauge sensor, which was fixed on a platform with the sensor parallel to the length direction of the specimen.

3.2 Results and discussion

3.2.1 Effects of steam cooking treatment on wet-tability and weight losses of straws

Figure 3.1 shows the contact angles and weight losses of reed and wheat straws under various steam cooking conditions. The contact angles of the straws were reduced after cooking treatment, and this reduction was greater for wheat straw. The wettability of the straws was therefore improved by cooking treatment. This improvement could be attributed to the removal of wax from the straws. The F-test statistical analysis revealed that the
effect of cooking time on wheat straw and the co-effect of steam pressure and time on reed straw exist at 95% significance level. This indicates that the steam cooking conditions in the studied range had a little effect on the wettability of both reed and wheat straw surfaces.

The effect of cooking conditions on the weight losses of the straws shows that the weight losses of both reed and wheat straws increased with increasing steam pressure and cooking time. When the pressure was under 6 atm, there was a relatively slow escalating trend of the weight loss, especially for reed straw. The weight loss increased significantly at above 6 atm of the pressure. The cooking time had much greater effect on the weight loss than the steam pressure. At the same steam pressure, longer cooking time resulted in higher weight loss; this is true especially as the steam pressure is above 6 atm. In addition, the weight loss in wheat straw shows a higher increasing extent than in reed straw. This means that much more extractives were removed from wheat straw. The study of J.M. Lawther et al. reported that steam treatment removed some portion of pectic substances and hemicellulose from wheat straw. Since the pectic substances and high content of hemicellulose in non-wood lignocellulosic materials usually result in a lower adhesion between resin adhesive and these materials, the extraction of these substances would certainly contribute to the improvement of board properties.

3.2.2 Properties of MDF under various refining conditions

Figures 3.2 to Fig. 3.4 show the properties of the straw MDF with the fibers under different refining conditions. Since the effect of densities on the board properties is a
due to a 98% RH. in boards at 0.7 higher 113 board elements 6/10 6/3 degree of its be 51x505 g/cm 3 and 0.69-0.72 major concern, the densities among the boards and within the board were investigated. The results show that the ranges of densities among the boards are 0.49-0.57 g/cm 3 and 0.70 g/cm 3 , respectively; the average and the range of coefficient variances for the densities within the board are 5.85% and 3.9-7.5%, respectively. It was found that the deviations of the board densities among the boards and within the board were rather small. But considering that density has usually significant effect on board property, all the property values in this study were corrected to the board target densities of 0.50 g/cm 3 and 0.70 g/cm 3 , respectively, based on the linear correlation between board densities and properties. Generally, the board properties on MOR, MOE and IB were improved with increasing steam pressure and cooking time during refining process. Both for reed and wheat boards, the MOR and MOE had a significant increase when the steam pressure was up to 6 atm. While there was a relatively little improvement on MOR but not on MOE as the cooking time increased from 3 to 10 min under the steam pressure of 6 atm.

For reed board, a greater upgrading of IB was observed when the steam pressure was increased to 6 atm, while for wheat board, this higher improvement happened as the cooking time was expanded from 3 to 10 min under 6atm. Based on the result of cooking treatment, the improvement of the mechanical properties could be attributed to the removal or extractives from the straw materials, this is true especially for wheat board. A range of factors, such as wettability, extractives and fiber dimensions have effects on the properties of MDF. For wheat board, the removal of extractives would play a more significant role in upgrading board performance under different cooking conditions. While for reed board, the improved properties may be highly due to the greater increase of the defibration degree under higher steam pressure, as reflected in Table 3.2 where the L/D of the fibers under 6atm was about 2.5 times that of fibers under 4atm. The higher degree of defibration causes the increase of the surface area of fibers and the formation of fibrill which makes the fibers felted together more readily and makes them in more intimate contact during pressing 40.

Based on F-test statistical analysis, the TS values of both reed and wheat boards were insignificant among different refining conditions. This could be related to that the water immersion time of 24 h might be too short to allow complete springback of the steadily compacted fibers. In addition, even though there was no much difference on MOR and MOE values, the IB and TS of reed board were better than those of wheat board. In the previous studies, it was found that there is much more silica and wax in reed and wheat straw materials, respectively. The higher upgrading of reed particleboard by silane coupling agent (SCA) was considered to be due to the improved wettability, which might be in part resulted from some reactions between the SCA and silica on the straw surfaces. The greater improvement of wheat particleboard by extraction could be caused by the removal of wax-like substances from wheat straw 15,16,41. Based on these conclusions, the superior IB of reed MDF in this study could be mostly attributed to the removal of silica in reed fibers during defibration process, and this effect may be greater than the effect of the extractives removal on wheat MDF. The excellent TS of reed board is because the inherent water resistance of reed straw 16, and its higher IB also contributes to the superior TS.

The dimensional stabilities of reed and wheat straw MDF at different relative humidities are shown in Fig. 3.5 to Fig. 3.7. The LE of both reed and wheat boards produced from fibers under 4 atm registered higher values than under 6 atm, but a reversed tendency was present in the TC especially at 98% RH. This may be due to a higher proportion of vertically oriented elements in boards composed of the fibers made under 4atm, which is related to their lower L/D (Table 3.2). The TC of the boards increased steadily when the RH was below 66%, but recorded high values as reaching equilibrium at 98% RH. In addition, wheat board represents a higher LE and TC than reed board. The residual TC of wheat board was about two times that of reed board. This greater irreversible swelling is caused by the release of higher compressive stresses imparted to the wheat board during pressing process. It was also found that the degree of springback in both reed and wheat boards was dependent on the EMC, where wheat board recorded a higher TC and EMC than reed board did when subjected to 98% RH.

3.2.3 Comparison between MDF and particleboard

Figure 3.8 shows the properties of the straw MDF and particleboard. The MDF is 0.7 g/cm 3 board with the fibers made under the refining condition of 4 atm/10 min. The particleboard is the board without SCA and EB treatment made from coarse particles at 0.7 g/cm 3 density level in the previous study 41. It was found that all the properties of both reed and wheat MDF were significantly higher than those of particleboard, especially the IB. The IB values of reed and wheat MDF were about 13 and 16 times that of particleboard, respectively. Based on the previous conclusions 15,41 and the result of cooking treatment, the greatly high performance of wheat MDF could be attributed to the improved wettability caused by wax removal and the removal of extractives from the straw material. The excellent properties of reed MDF may be partly due to the wettability improvement and extractives removal, and mostly because silica was removed in reed...
Fig. 3.5. Linear expansion (LE) of reed (a) and wheat (b) straw MDF under different relative humidities (RH). Refer to Table 3.1 for legend explanations.

Fig. 3.6. Thickness changes (TC) of reed (a) and wheat (b) straw MDF under different relative humidities (RH). Refer to Table 3.1 for legend explanations.

Fig. 3.7. Equilibrium moisture content (EMC) of reed (a) and wheat (b) straw MDF under different relative humidities (RH). Refer to Table 3.1 for legend explanations.
straw by refining process.

All the properties of straw MDF except for the TS of wheat board can meet the requirement of JIS fiberboard standard. Dimensional instability has been a big problem in non-wood lignocellulosic composites, and also is a major reason for their restricted use. Recently, it is reported that the dimensional stability of agro-based fiber composites was greatly improved by chemical modification of agricultural fibers\(^2\).

### 3.3 Summary

The wettability of the straws was improved by cooking treatment. The steam cooking conditions in the range of this study had a little effect on the wettability of the straw surfaces. The weight losses of the straws increased with increasing steam pressure and cooking time. Wheat straw shows a higher increasing extent of weight loss than reed, which means that much more extractives were removed from wheat straw.

The mechanical properties and LE of the straw MDF were improved with increasing steam cooking pressure and time during refining process. But the TS didn’t vary much among different refining conditions. The improved performance could be due to the removal of extractives and increased delamination degree. In addition, even though there was no big difference on MOR and MOE, the IB and TS of reed board were better than wheat board.

All the properties of both reed and wheat MDF were significantly higher than those of the particleboards. The greatly high performance of wheat MDF could be attributed to the improved wettability and removal of extractives from the straw material. The excellent properties of reed board may be partly due to the improved wettability and the removal of extractives, and mostly because silica was removed in reed straw during refining process. It is considered that MDF is one of the most feasible products for utilizing such straw materials.

### Conclusions

The fundamental performances of reed and wheat straw particleboards were first investigated. It was found that the properties of UF-bonded straw particleboards were rather lower compared to those of conventional wood particleboards.

To upgrade the board performances, silane coupling agents (SCA) (i.e., vinyl silane, amino silane, and epoxide silane) and ethanol/benzene (EB) extraction treatment were used. All the board properties were improved by the addition of SCA. The degree of improvement achieved from each coupling agent was different: epoxide silane was more effective for reed board, amino silane was better for wheat board, and vinyl silane was not so effective as epoxide and amino silanes. In addition, the properties of both reed and wheat boards increased significantly when up to 5% of SCA was incorporated, but the improvement did not vary much at above 5% SCA content. EB extraction treatment was found to improve the properties of wheat board significantly, whereas SCA incorporation was more effective for reed board.

To clarify the improvement mechanism of bondability between the straw materials and UF resin, the effects of SCA and EB treatments on the wettability of the straw surfaces were investigated. The distribution of silicon along the thickness of straws was analyzed by X-ray electron spectroscopy for chemical analysis (ESCA).

The inherent wettability of the straw materials was low but could be significantly improved by treating with SCA. The degree of improvement achieved by each SCA was different: Vinyl silane had almost no effect on the wettability, epoxide silane was more effective for reed straw, and amino silane was better for wheat straw. SCA improved the wettability to a greater extent in reed straw than in wheat straw. The wettability of the straws could also be improved by EB extraction treatment, which resulted in more improvement in wheat straw than in reed straw. This improvement could be attributed to the removal of wax-like substances from the straw surfaces. The wettability improvements show good correlation with the upgraded board properties discussed in the above study.

The analyses of straws by ESCA revealed that there was much silicon on the outer surfaces of reed and wheat straws and the inner surface of reed straw. Reed straw seems to contain more silicon compared to wheat straw.

The inferior properties of UF-bonded reed and wheat boards could be due to the poor wettability of these materials caused by the presence of wax-like substances and silicon on the surfaces. SCA addition and EB extraction can improve the wettability of the straw surfaces, therefore resulting in enhanced board performances.

Based on the above conclusions, it was considered that the wax layer would be destroyed by proper thermal-mechanical refining process. Therefore, the effects of various steam cooking treatments on the wettability and weight losses of the straws were investigated. The effects of steam cooking conditions in refining processes on the properties of MDF were examined. The wettability of the straws was improved by cooking treatment. The weight
losses of the straws increased with increasing steam pressure and cooking time. The properties of the straw MDF were improved with increasing steam cooking pressure and time during refining process. The improved performances could be due to the removal of extractives including wax and the increased delibration degree.

Comparing MDF with particleboard, it was found that all the properties of both reed and wheat MDF were significantly higher than those of the particleboards. All the properties of the straw MDF except for the thickness swelling of wheat board can meet the requirement of JIS fiberboard standard. It is considered that MDF is one of the most feasible products for utilizing such straw materials.

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