

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

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Contents

Introduction

Chapter 1 Manufacture of reed and wheat straw particleboards

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

1.1.1 Materials and methods

1.1.2 Results and discussion

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

1.2.1 Materials and methods

1.2.2 Results and discussion

1.3 Effects of ethanol/benzene extraction treatment on board properties and comparison with SCA addition

1.3.1 Materials and methods

1.3.2 Results and discussion

1.4 Summary

Chapter 2 Improvement mechanism of bondability by physical and chemical treatments

2.1 Materials and methods

2.1.1 Extraction test

2.1.2 Silane coupling agent treatment

2.1.3 Measurement of wettability

2.1.4 Electron spectroscopy for chemical analysis (ESCA)

2.1.5 Measurement of gel time and pH of UF resin

2.2 Results and discussion

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

2.2.2 Effects of ethanol/benzene extraction on the wettability of straw surfaces

2.2.3 Analysis of silicon distribution in straws by ESCA

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

2.3 Summary

Chapter 3 Manufacture of reed and wheat straw medium density fiberboards

3.1 Materials and methods

3.1.1 Preliminary experiment

3.1.2 Manufacture of MDF

3.1.3 Evaluation of panel properties

3.2 Results and discussion

3.2.1 Effects of steam cooking on wettability and weight losses of straws

3.2.2 Properties of MDF under various refining conditions

3.2.3 Comparison between MDF and particleboard

3.3 Summary

Conclusions

Acknowledgements

References

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 processing^{9,10)}. The excessive extractives may influence the curing behavior of UF resin⁵⁾. Higher pH and buffering capacity of some straws result in longer gel time of UF resin³⁾. 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 bonding¹¹⁻¹⁶⁾. 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

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Table 1.1. Some basic properties of silane coupling agents.

Coupling agent	Molecular weight	Specific gravity at 25°C	Boiling point (°C)
Vinyltriethoxysilane (SiVN1)	190.3	0.90	161
Vinyltris(β -methoxyethoxy)silane (SiVN2)	280.4	1.04	285
γ -Aminopropyltriethoxysilane (SiNH)	221.4	0.94	217
γ -Glycidoxypropyltrimethoxy (SiEP)	236.3	1.07	290

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 components¹⁷⁾. 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 it¹⁸⁾. 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/cm³, 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. The chemical structures of these compounds are as follows¹⁸⁾:

Vinyl silane (SiVN):

Vinyltriethoxysilane (SiVN1): $\text{CH}_2=\text{CH}-\text{Si}(\text{OC}_2\text{H}_5)_3$

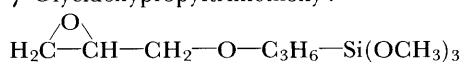
Vinyltris(β -methoxyethoxy)silane (SiVN2): $\text{CH}_2=\text{CH}-\text{Si}(\text{OC}_2\text{H}_4\text{OCH}_3)_3$

Amino silane (SiNH):

γ -Aminopropyltriethoxysilane: $\text{NH}_2-\text{C}_3\text{H}_6-\text{Si}(\text{OC}_2\text{H}_5)_3$

Epoxide silane (SiEP):

γ -Glycidoxypropyltrimethoxy:



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

(2) Method

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

Mesh size (mm)	Reed particles		Wheat particles	
	Fine	Coarse	Fine	Coarse
≥ 4.76	0	0.65	0	0.19
4.76–2.00	0.50	31.61	—	—
2.00–1.00	20.84	54.76	35.30	60.75
1.00–0.25	68.53	12.90	62.80	37.01
0.25–0.125	8.17	0.07	1.90	2.05
≤ 0.125	1.94	0	0	0

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 blender 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_4Cl , 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. During the first step the mat was pressed under a pressure of 3 MPa for 1 minute, during the second and third steps the mats were pressed at 2 MPa for 3 minutes and 1 MPa for 3 minutes, respectively. The dimension of boards was 450×430×8 mm with targeted densities ranging from 0.55 to 0.90 g/cm³. Two boards were made in the same condition; altogether 52 boards were manufactured. The densities of the boards manufactured are shown in Table 1.3.

Board evaluation

Specimens were cut from the boards after conditioning and tested according to GB/T 4897-92 (Particleboard Standard of China). The specimen size for bending test was 27×5 cm with an effective span of 15 cm. The sample sizes for internal bond (IB) and thickness swelling (TS) test were 5×5 cm and 2.5×2.5 cm, respectively.

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.

Particle size	Without coupling agent (g/cm ³)							With coupling agent (g/cm ³)			
								SiVN1	SiVN2	SiNH	SiEP
Reed board											
Fine	0.55	0.60	0.65	0.70	0.75	0.80	0.85				
Coarse	0.68	0.90						0.70	0.70	0.73	0.66
Wheat board											
Fine	0.55	0.60	0.65	0.70	0.75	0.80	0.85				
Coarse	0.66	0.75						0.72	0.72	0.76	0.68

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/cm³. 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 properties¹⁹. Generally, small particles result in low MOR and high IB of particleboards. The results of this experiment may be attributed to the

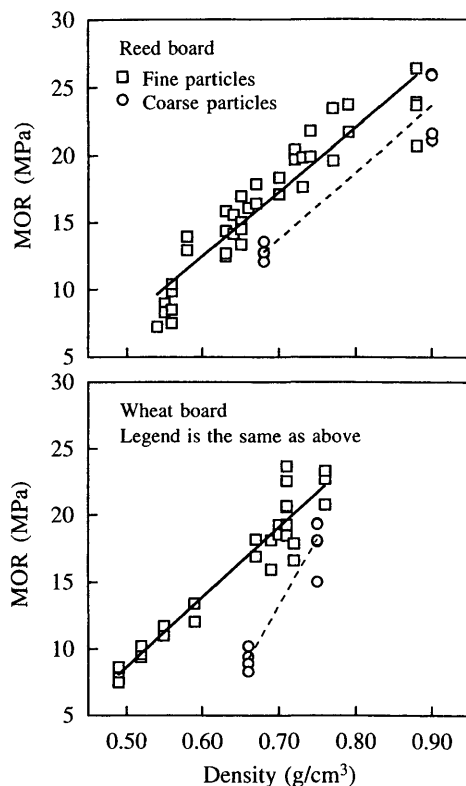


Fig. 1.1. Moduli of rupture (MOR) of reed and wheat particleboards made from fine and coarse particles at different densities.

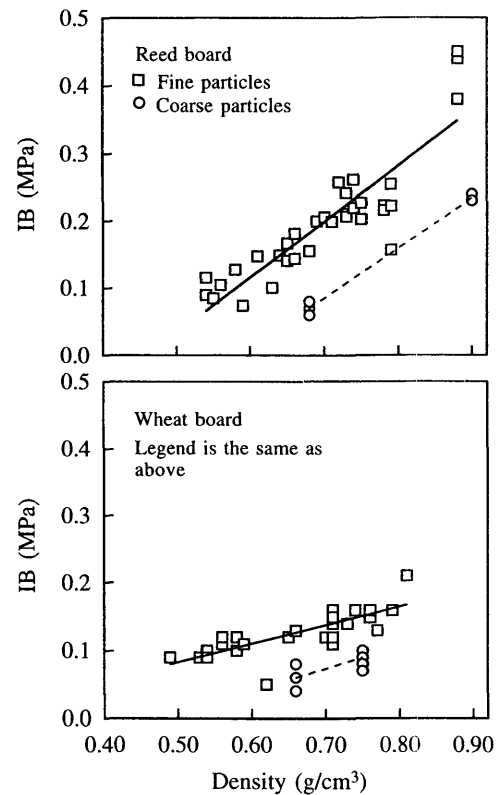


Fig. 1.2. Internal bond (IB) of reed and wheat particleboards made from fine and coarse particles at different densities.

inherent characteristics of the raw materials. Like other non-wood lignocellulosics, 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 density²¹. 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

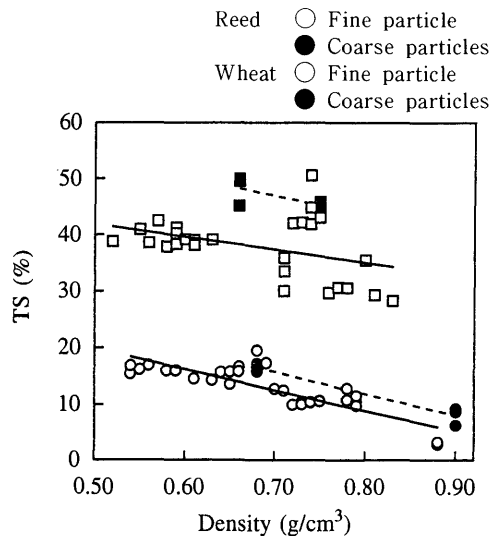


Fig. 1.3. Thickness swelling (TS) of reed and wheat particleboards made from fine and coarse particles at different densities.

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/cm^3 , based on the linear equations obtained from the correlation between board density and properties.

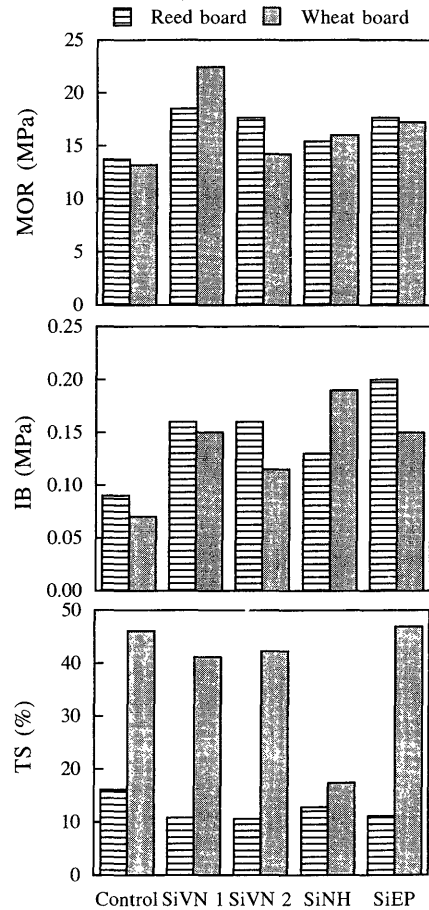


Fig. 1.4. Effects of various silane coupling agents on the properties of reed and wheat particleboards. Refer to Table 1.1. for explanation of various silane coupling agents.

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

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

Properties	Wheat board				Reed board			
	SiVN 1	SiVN 2	SiNH	SiEP	SiVN 1	SiVN 2	SiNH	SiEP
MOR	1.70	1.08	1.21	1.30	1.35	1.28	1.12	1.28
IB	2.14	1.92	2.71	2.00	1.78	1.78	1.44	2.22
TS	0.89	0.92	0.38	1.02	0.67	0.66	0.80	0.69

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 amide 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 2–3% 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 SCA⁶⁾, 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 350×400×9 mm, at a targeted density of 0.7 g/cm³. 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)²²⁾.

The static bending test in the dry condition was conducted for four specimens of 50×200 mm from each board, using a three-point bending test over an effective span of 150 mm at a loading speed of 10 mm/min. Five 50×50 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 50×200 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 MgCl₂, NaNO₂ and CaSO₄, 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	
	Coarse	Fine	Coarse	Fine
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.

Code	Particle types ^a	SCA addition levels (%) ^b
Control	C	—
SCA/2	C	2
SCA/5	C	5
SCA/7	C	7
Control-F	F	—
SCA/2-F	F	2

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

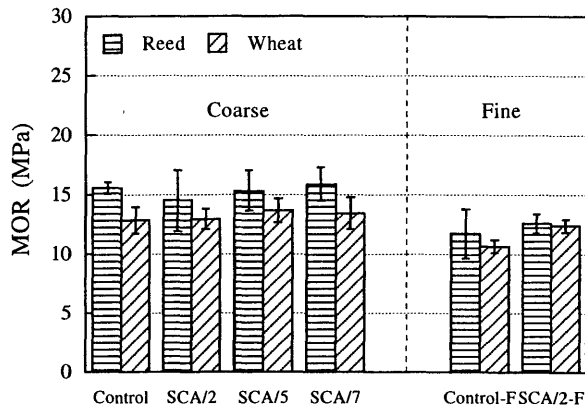


Fig. 1.5. Effects of silane coupling agent (SCA) addition level on moduli of rupture (MOR) of reed and wheat particleboards. Refer to Table 1.6. for the explanation of legend. Vertical lines through the bars represent the standard deviation from the mean value.

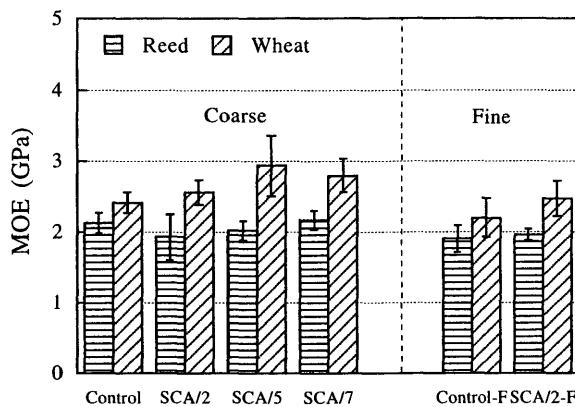


Fig. 1.6. Effects of SCA addition level on moduli of elasticity (MOE) of reed and wheat particleboards. Refer to Fig. 1.5. for other explanations.

relatively 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

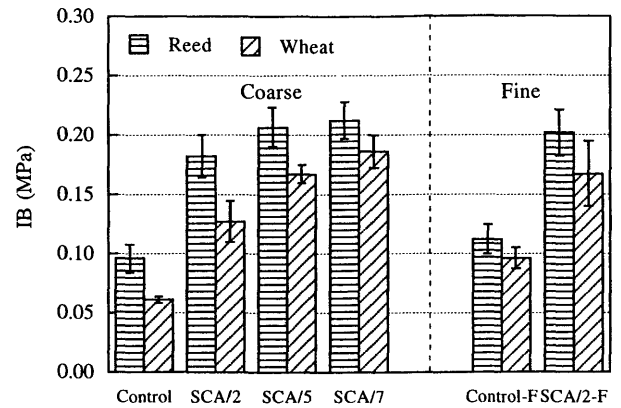


Fig. 1.7. Effects of SCA addition level on the IB of reed and wheat particleboards. Refer to Fig. 1.5. for other explanations.

treatment kept constant at above 5%. Similar to the earlier study¹⁵⁾, 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 straw¹⁶⁾. 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

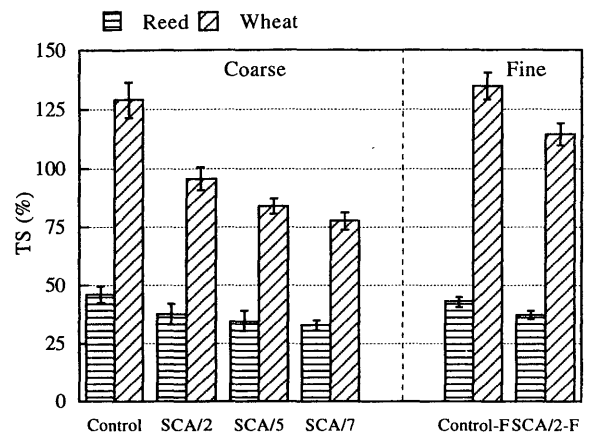


Fig. 1.8. Effects of SCA addition level on the TS of reed and wheat particleboards. Refer to Fig. 1.5. for other explanations.

board TS.

(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

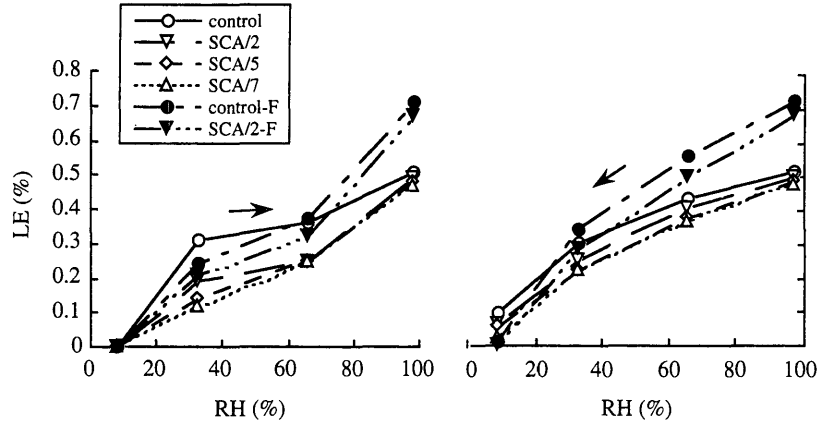


Fig. 1.9. Linear expansion (LE) of reed particleboard under different relative humidity (RH) during moisture absorption (left) and desorption (right) processes. Refer to Table 1.6. for the explanation of legend.

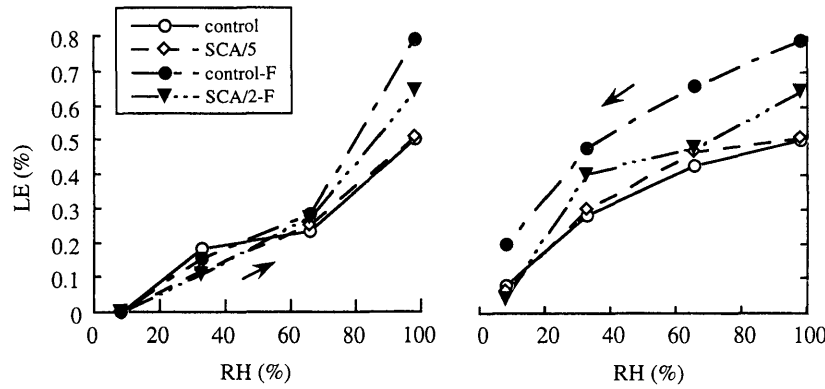


Fig. 1.10. Linear expansion (LE) of wheat particleboard under different relative humidity (RH) during moisture absorption (left) and desorption (right) processes. Refer to Table 1.6. for the explanation of legend.

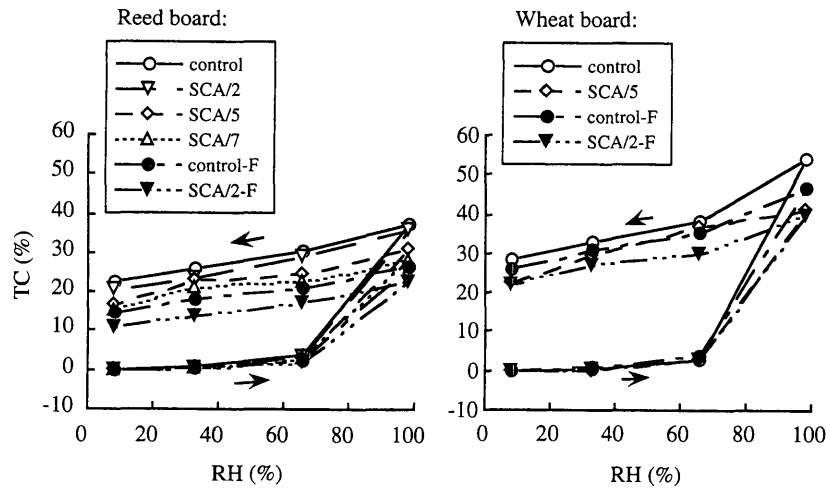


Fig. 1.11. Thickness changes (TC) of reed and wheat particleboards under different RH during moisture absorption and desorption processes. Refer to Table 1.6. for explanation of legend.

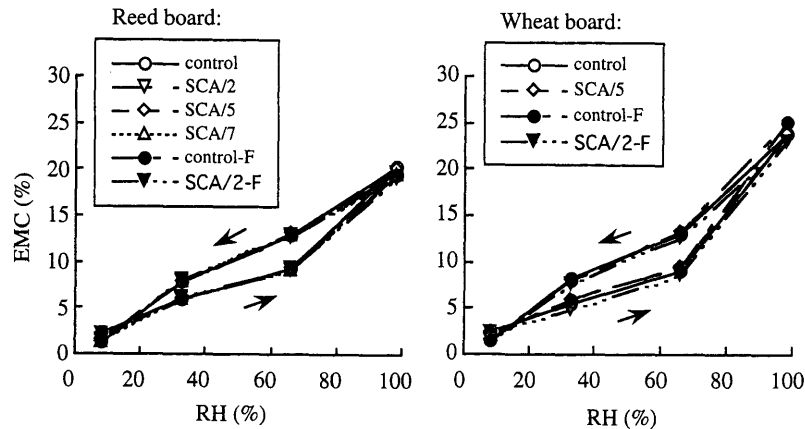


Fig. 1.12. Equilibrium moisture content (EMC) of reed and wheat particleboards under different RH during moisture absorption and desorption processes. Refer to Table 1.6. for explanation of legend.

wheat control boards, the thickness increased about 2 mm and 2.5 mm after redrying at the end of RH cycle, respectively, resulting the residual TC to be 22% and 28%, respectively. The LE of both reed and wheat boards produced from fine particles registered higher values compared to those from coarse particles, but a reversed trend was observed in TC. This may be due to a higher proportion of vertically oriented elements in boards composed of fine particles compared to coarse particles, hence an improved dimensional stability in the thickness direction, but reduced longitudinal stability.

Similar to conventional particleboard, the degree of springback in both reed and wheat boards was highly dependent on the EMC, as shown in Figs. 1.11 and 1.12, where wheat board recorded higher TC and EMC than reed board when subjected to 98% RH. The higher TC of wheat board may be caused by a greater expansion due to higher moisture absorption, in addition to the recovery of a greater compressive set resulted from higher compaction ratio (about 2.26)¹⁵⁾.

1.3 Effects of ethanol/benzene extraction treatment on board properties and comparison with SCA addition

1.3.1 Materials and methods

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

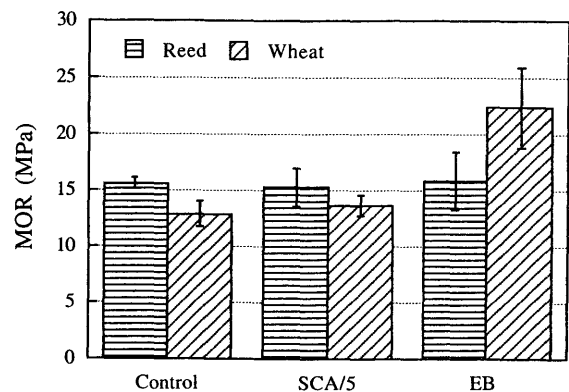


Fig. 1.13. Effects of ethanol/benzene (EB) treatment on the MOR of reed and wheat particleboards and the comparison with SCA addition. Refer to Fig. 1.5. for other explanations.

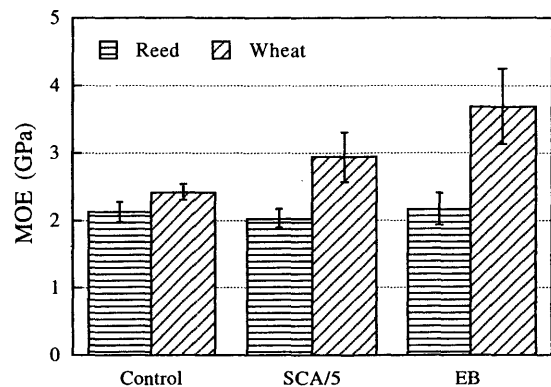


Fig. 1.14. Effects of EB treatment on the MOE of reed and wheat particleboards and the comparison with SCA addition. Refer to Fig. 1.5 for other explanations.

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 surface²³⁾, hence facilitating the adherence of UF resin to the active hydroxyl sites of the cellulose.

Comparing the effectiveness of SCA and EB treatment,

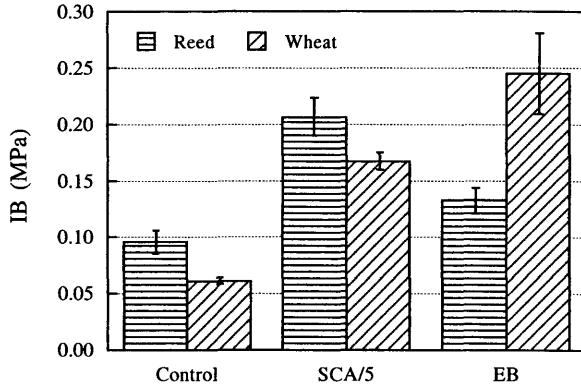


Fig. 1.15. Effects of EB treatment on the IB of reed and wheat particleboards and the comparison with SCA addition. Refer to Fig. 1.5. for other explanations.

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.

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

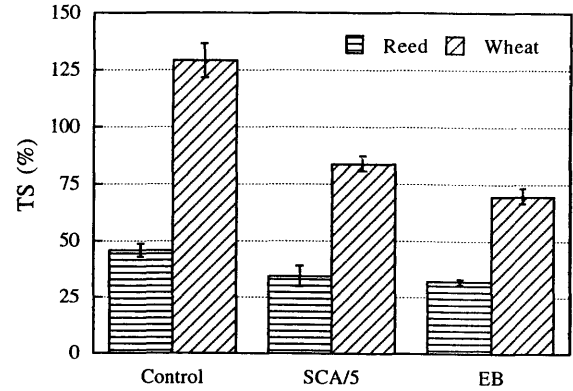


Fig. 1.16. Effects of EB treatment on the TS of reed and wheat particleboards and the comparison with SCA addition. Refer to Fig. 1.5 for other explanations.

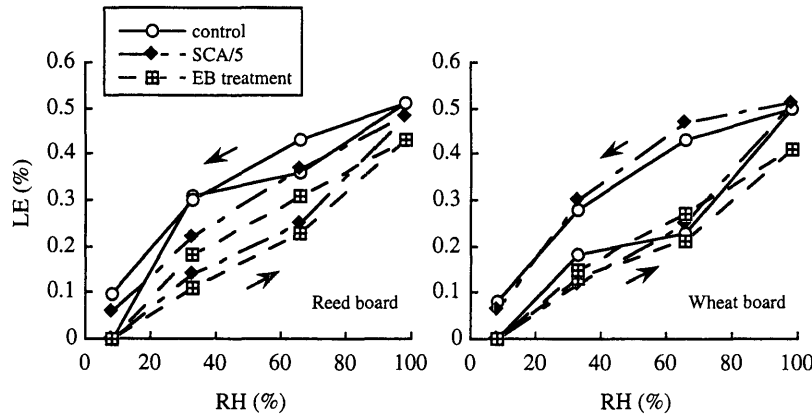


Fig. 1.17. Linear expansion (LE) of reed and wheat particleboards after EB treatment under different RH, and comparison with the effect of SCA addition. Refer to Table 1.6 for other explanations.

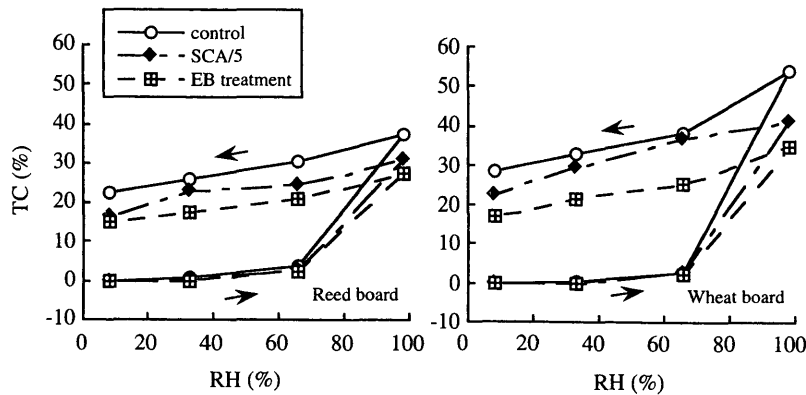


Fig. 1.18. Thickness changes (TC) of reed and wheat particleboards after EB treatment under different RH, and comparison with the effect of SCA addition. Refer to Table 1.6 for other explanations.

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 in 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 method¹⁾. 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 *W*₁ is the weight of treated sample after drying and reconditioning, and *W*₀ is the

$$WG = \frac{W_1 - W_0}{W_0}$$

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 straw²⁴⁾. 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 measured²⁵⁾. 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 6801²⁶⁾. 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

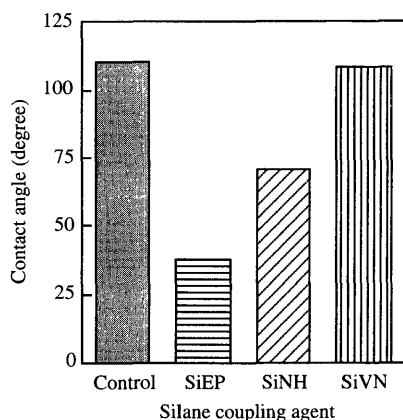


Fig. 2.1. Effects of silane coupling agents on the contact angles of reed straw outer surface. SiEP, epoxide silane; SiNH, amino silane; SiVN, vinyl silane.

used for each condition.

2.2 Results and discussion

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^{27,28}. 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 wood²⁴. 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 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

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 study¹⁶.

2.2.2 Effects of ethanol/benzene extraction on the wettability of straw surfaces

The presence of extractives can also influence the wettability of materials^{29,30}. It has been reported that low wettability is related to the existence of nonpolar extractives³¹.

Figure 2.3 shows the effect of EB extraction on the contact angles of reed and wheat straw surfaces. The

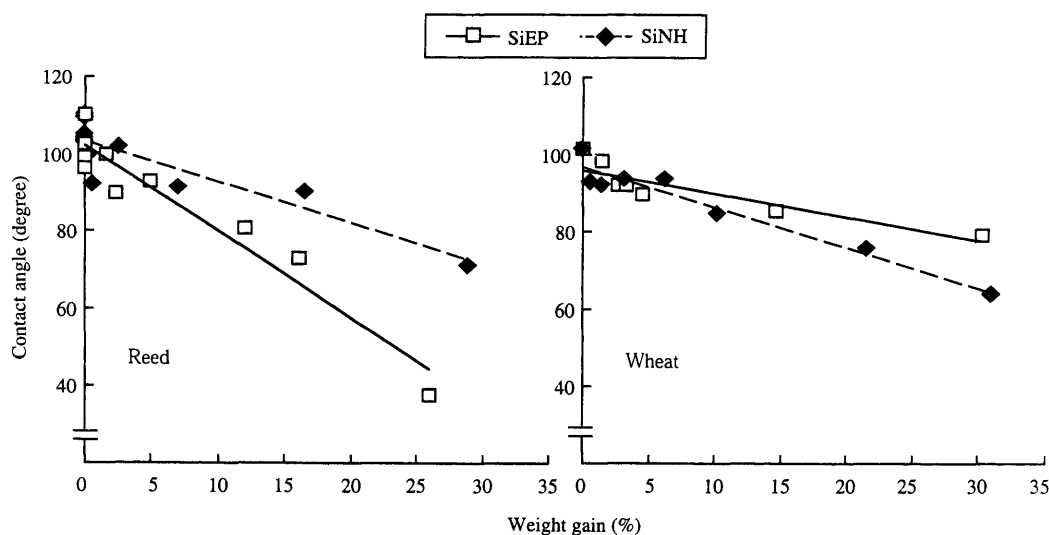


Fig. 2.2. Relation between the contact angles of the straw outer surfaces and the weight gains of treated samples. Refer to Fig. 2.1 for the explanation of legends.

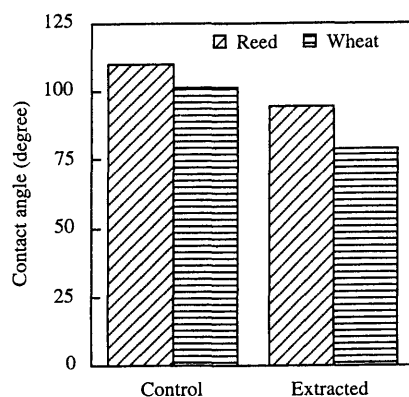


Fig. 2.3. Effects of ethanol/benzene extraction on the contact angles of reed and wheat straw outer surfaces.

contact angles of the outer surfaces of both reed and wheat straws were reduced after EB extraction. The contact angles decreased by about 14% for reed straw and 22% for wheat straw compared to the control. Since the extractive contents are negligible for reed straw and about 17% for wheat straw, this might be related to the different effects of the extraction on these two materials. The wettability of wheat straw surfaces was therefore improved by EB extraction. Wax can usually be extracted by the organic solvents like EB^{23,32)}, so this improvement could be attributed to the removal of wax-like substances from the straw surfaces.

Generally, there is a waxy layer on the cereal straw surface^{3,5,6)}. 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.

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 particles¹⁵⁾, 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.

Our previous study concluded that the properties of reed and wheat boards manufactured from fine particles are better than those made of coarse particles¹⁴⁾. It seems that the presence of silicon and wax components on the straw surfaces results in the inferior properties of board made from coarse particles. With fine particles, the

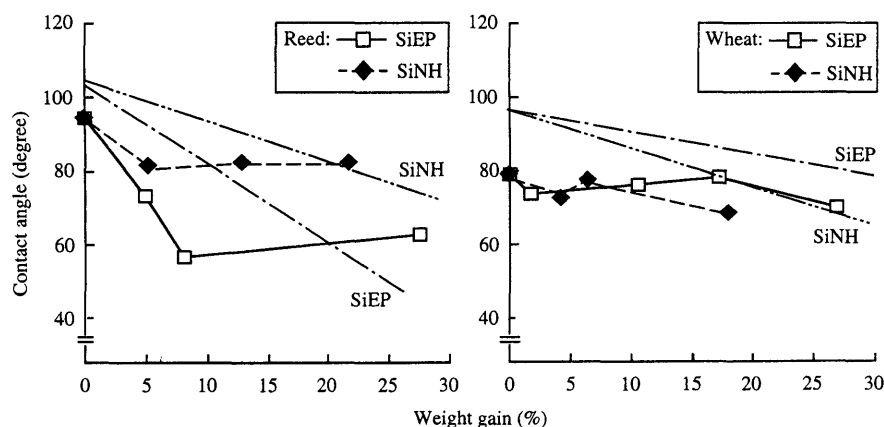


Fig. 2.4. Effects of silane coupling agents on the contact angles of reed and wheat straw outer surfaces before and after ethanol/benzene extraction. —, — — — Corresponding effects of epoxide silane (SiEP) and amino silane (SiNH) on contact angles before extraction.

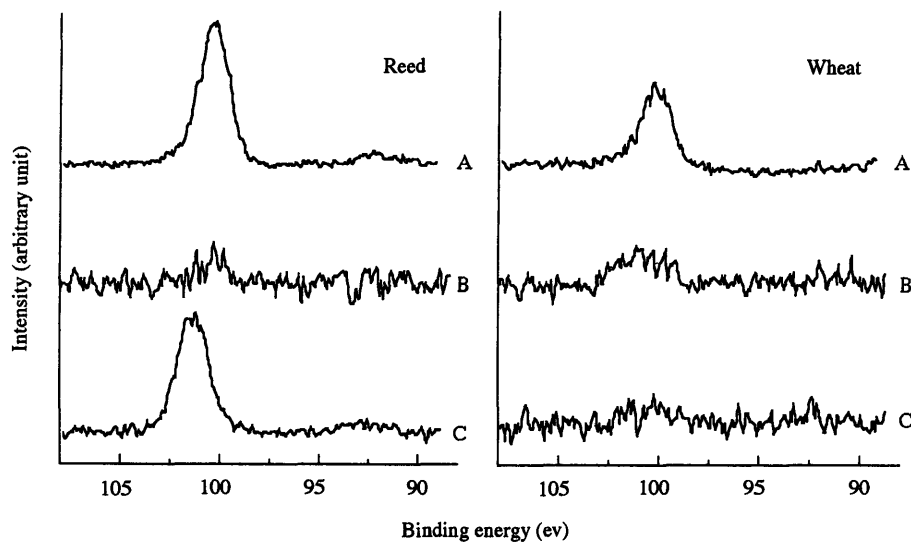


Fig. 2.5. X-ray photoelectron spectroscopy (XPS) of silicon (Si2p) on the outer (A), sectioned (B), and inner (C) surfaces of reed and wheat straws.

Table 2.1. Gel time and pH of UF resin added with hot-water extractives of reed straw.

Extractives added (%)	Gel time (min)		pH at 25°C
	70°C	90°C	
Control (neat UF resin)	4.87 (100)	1.40 (100)	6.7
Extractives 1	4.96 (102)	1.42 (101)	6.6
2	5.12 (105)	1.50 (107)	6.4
3	5.39 (111)	1.54 (110)	6.3

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 process¹⁴⁾.

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 resin³³⁻³⁵⁾. UF resin is known to be acid-catalyzed and cannot attain an optimum state of cure in a low acid environment³⁶⁾.

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

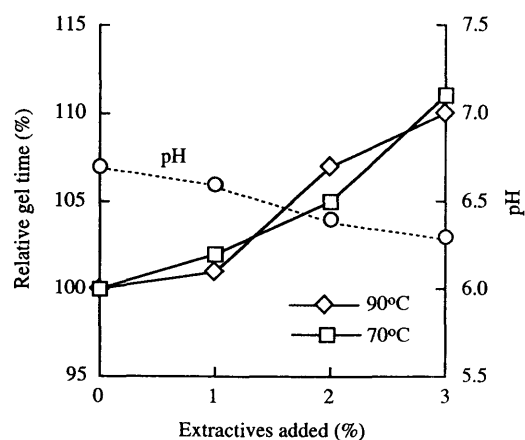


Fig. 2.6. Effects of hot-water extractives of reed straw on the gel time of UF resin at 70°C and 90°C; pH was measured at 25°C. The relative gel time was based on that of the control (neat UF resin).

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

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

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

SiNH, amino silane; SiEP, epoxide silane; SiVN, vinyl silane. ^aThe gel time was measured at 90°C; pH was measured at 25°C.

^bThe amount of silane coupling agent added was based on the weight of the resin solid.

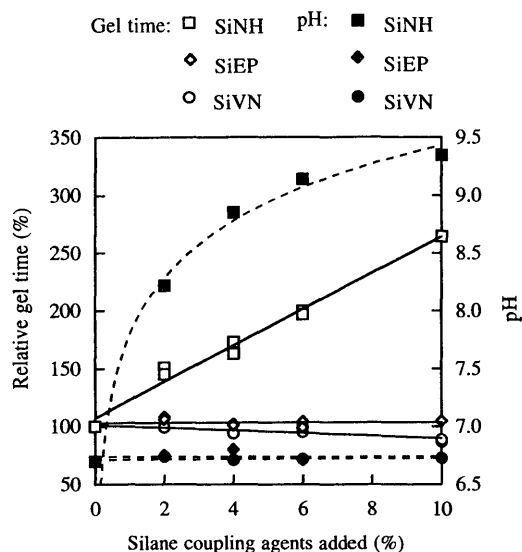


Fig. 2.7. Effects of silane coupling agents on the gel time and pH of UF resin at 90°C and 25°C, respectively. Relative gel time was based on the control (neat UF resin). Refer to Fig. 2.1 for the explanation of legends.

curing of UF resin, as indicated by a rapid increase in the resin pH following the addition of SiNH. This retardation of resin gelation could be due to the higher pH of the mixture caused by the hydrolysis reaction of SiNH in the resin.

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 than in wheat straw. The wettability improvements show good correlation with the upgraded board properties by various SCA and EB treatment in the previous studies.

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 greater improvement in the properties of reed board achieved by adding SCA might be related to the higher silicon content in reed straw.

The addition of hot-water extractives of reed straw

increased the gel time of UF resin. The gel time was considerably retarded with SiNH addition. SiEP and SiVN had no influence on the UF gel time.

The inferior properties of UF-bonded reed and wheat straw 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, 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 other³⁷.

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 weights 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. The

Table 3.1. Experimental variables of the cooking conditions in refining processes.

Code	Straw types*	Steam pressure (atm)	Steaming time (min)
4/ 5	W	4	5
4/10	R	4	10
6/ 3	R, W	6	3
6/10	R, W	6	10

* R, Reed; W, Wheat.

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

Fiber types ^a	Length (mm)	Diameter (μm)	L/D ^b
R 4/10	3.00 (1.32)	246.25 (127.99)	16.28 (12.49)
R 6/ 3	3.46 (1.75)	118.17 (72.26)	39.83 (31.22)
R 6/10	3.57 (1.68)	109.80 (56.56)	40.74 (26.30)
W 4/ 5	5.32 (2.63)	186.94 (117.56)	38.54 (26.71)
W 6/ 3	5.17 (2.60)	101.00 (57.79)	65.47 (48.83)
W 6/10	5.12 (3.19)	109.39 (76.02)	66.42 (50.01)

^a Refer to Table 3.1 for the explanation of fiber types. ^b 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.

measurement of contact angle was the same as in the previous study¹⁶⁾. Seven replicates were used for each condition.

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 25 $\times$ 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 $\times$ 355 $\times$ 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 $\pm$ 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 $\times$ 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 $\times$ 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 $\times$ 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 wettability 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

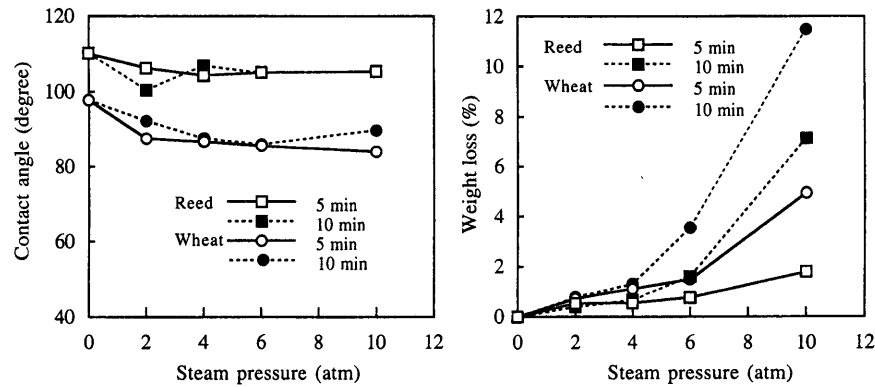


Fig. 3.1. Contact angles and weight losses of reed and wheat straws under various steam cooking conditions.

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 straw³⁹. 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

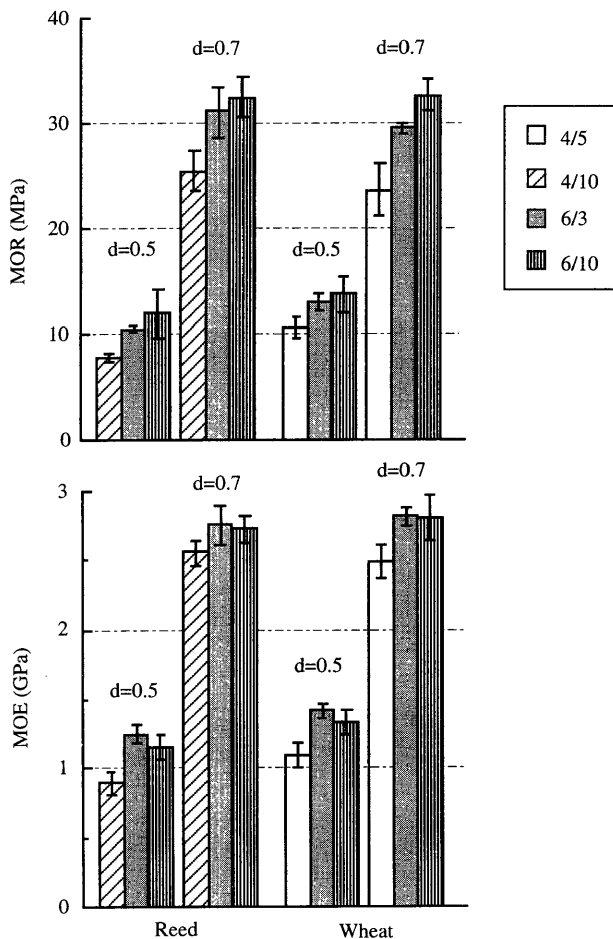


Fig. 3.2. Moduli of rupture (MOR) and elasticity (MOE) of reed and wheat straw MDF with the fibers under different refining conditions. Refer to Table 3.1 for legend explanations.

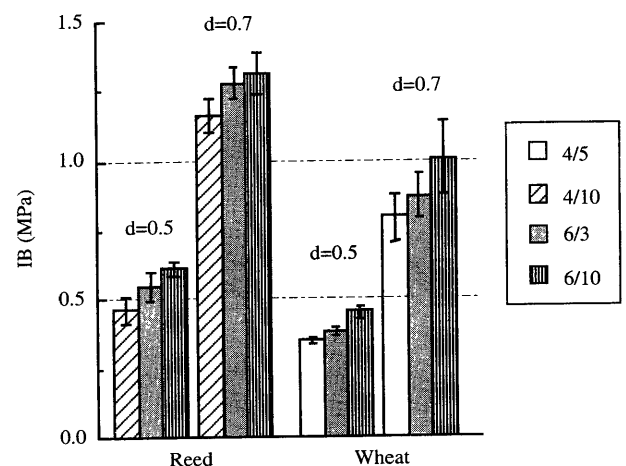


Fig. 3.3. Internal bond (IB) of reed and wheat straw MDF with the fibers under different refining conditions. Refer to Table 3.1 for legend explanations.

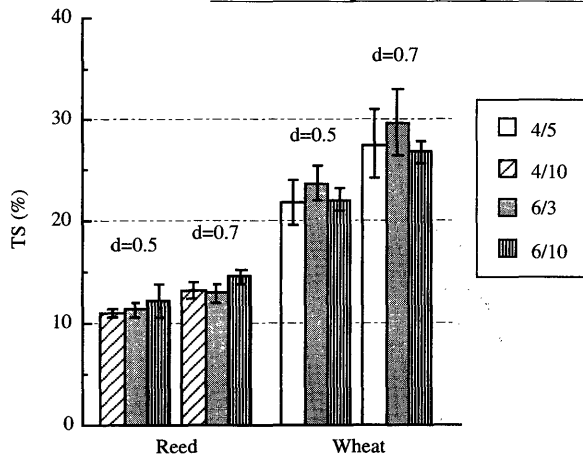


Fig. 3.4. Thickness swelling (TS) of reed and wheat straw MDF with the fibers under different refining conditions. Refer to Table 3.1 for legend explanations.

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 $0.49\text{--}0.57\text{ g/cm}^3$ and $0.69\text{--}0.72\text{ g/cm}^3$ for board target densities of 0.50 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 of 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 pressing⁴⁰⁾.

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 straw¹⁶⁾, 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 6 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 study⁴¹⁾. 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

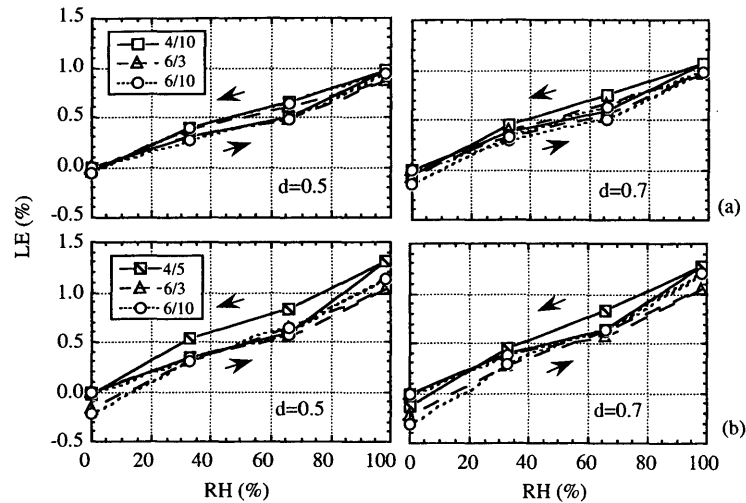


Fig. 3.5. Linear expansion (LE) of reed (a) and wheat (b) straw MDF under different relative humidities (RH). Refer to Table 3.1. for legend explanations.

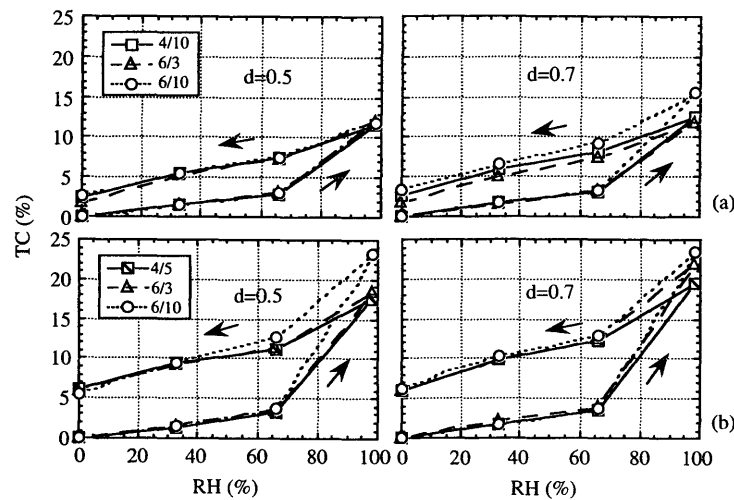


Fig. 3.6. Thickness changes (TC) of reed (a) and wheat (b) straw MDF under different relative humidities (RH). Refer to Table 3.1 for legend explanations.

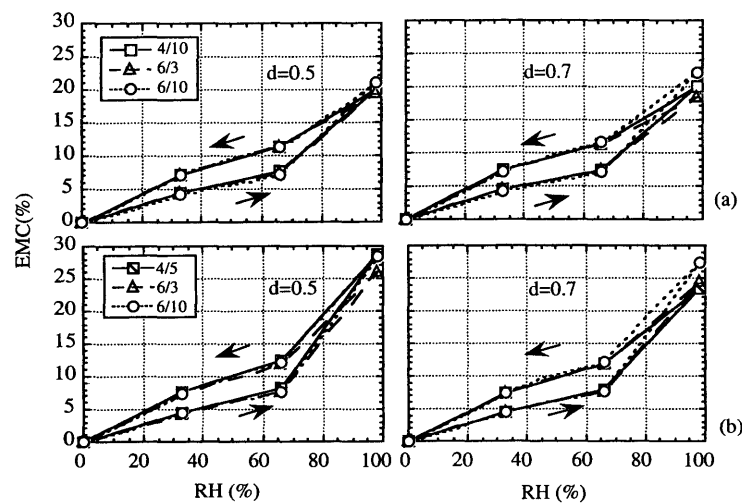


Fig. 3.7. Equilibrium moisture content (EMC) of reed (a) and wheat (b) straw MDF under different relative humidities (RH). Refer to Table 3.1 for legend explanations.

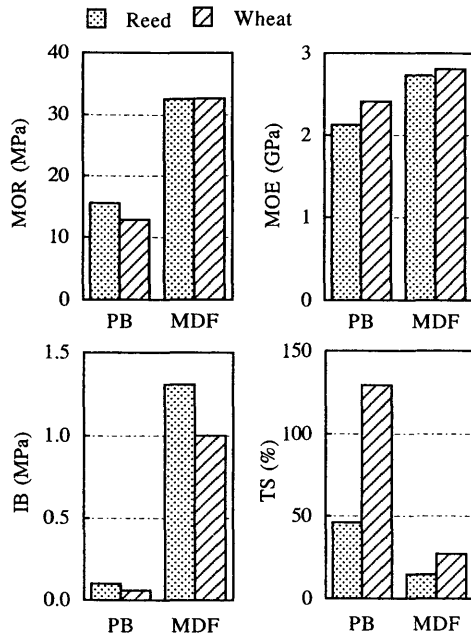


Fig. 3.8. Comparison between straw particleboard (PB) and MDF.

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 fibers⁴²⁾.

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 defibration 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 defiberation 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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