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Improvement mechanism of bondability in UF-bonded reed and wheat straw boards by silane coupling agent and extraction treatments

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Abstract The effects of silane coupling agents and extractives on the wettability of reed and wheat straws were investigated. The inherent wettability of these materials was low but could be significantly improved by treating with silane coupling agents. The degree of improvement achieved by each silane coupling agent was different: Vinyl silane had almost no effect on wettability, epoxide silane was found to be more effective for reed straw, and amino silane was better for wheat straw. The wettability of these materials could also be improved by ethanol-benzene extraction, which resulted in more improvement in wheat straw than reed straw. The analyses of untreated reed and wheat straws by electron spectroscopy for chemical analysis (ESCA) revealed that there was much silicon on both the outer and inner surfaces of the former but only on the outer surface of the latter. The influence of hot-water extractives and silane coupling agents on the gelation time and pH of urea formaldehyde (UF) resin was also examined. The addition of extractives was found to increase the gelation time. Amino silane greatly retarded the gelation of UF resin, whereas epoxide and vinyl silanes had no influence on resin gelation. This retardation was found to be due to an increase in the pH of the resin.

Key words Reed straw · Wheat straw · Urea formaldehyde resin · Bondability · Silane coupling agent

Introduction

Reed (*Phragmites communis Trin.*) and wheat (*Triticum aestivum L.*) straws have been considered as raw materials for the production of composite board. However, the natural characteristics of these materials make them difficult to bond with urea-formaldehyde (UF) resin, an adhesive popularly used in particleboard manufacture.[1–3]

A number of potential causes for the inferior properties of the composite boards manufactured from these materials have been reported. Loxton and Hague attributed these inferior properties to the presence of a wax-like substance that may result in a weak bond between particles, as well as extractives which may influence the curing behavior of UF resin.[4] Sauter concluded that the largest reduction in internal bond strength was due to the inability of UF resin to penetrate the wax layer of the straw to bond with the active hydroxy sites of the cellulose.[1] Hse and Choong suggested that the high silica content may influence the bonding properties of adhesives in rice-husk board manufacturing.[5]

Our previous paper reported the improvement of bondability of reed and wheat straw particleboards bonded with a UF resin using silane coupling agents.[3] This study deals with the effects of silane coupling agents and ethanol-benzene extraction on improving the wettability of straw surfaces. The distribution of silicon along the thickness of straws was analyzed by electron spectroscopy for chemical analysis (ESCA). The effects of hot-water extractives and silane coupling agents on the gelation time of UF resin were examined as well, in an attempt to clarify the causes of the inferior board properties and the improvement mechanism of bondability.

Materials and method

Materials

Reed and wheat straws, with 9.5% moisture content, were obtained from Heilongjiang Province, China. The straws were ground into powder for the extraction test and cut into 50-mm lengths for the wettability measurement. The ethanol-benzene solution was prepared by mixing one vol-

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ume of 95% ethanol with two volumes of benzene. Three silane coupling agents (SCAs)—epoxide silane (SiEP), amino silane (SiNH), and vinyl silane (SiVN)—were supplied by Shin-Etsu Chemical, Japan. Detailed information about SCAs, including their chemical structures and properties, was reported in our previous paper.[3] A UF resin (Oshika Resin KU-20, Japan) with a solid content of 64.9% and a UF molar ratio of 1.0:1.2 was used in this study. NH_4Cl (20% solution) was used as the hardener.

Extraction test

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

SCA Treatment

Reed and wheat samples were kept in a desiccator and then weighed and soaked in SCAs of various concentrations from 0.1% to 100% for 30s. 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:

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

where W_1 is the weight of treated sample after drying and reconditioning, and W_0 is the weight before treatment. Ethanol/benzene-extracted straws were treated with SCAs using the same procedure.

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 (6μl) of distilled water was dropped onto the surface with a micropipette. A photograph was taken 10s 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.

Electron spectroscopy for chemical analysis

Samples of 7 × 7 × 0.2–0.3mm were cut by a microtome from three positions along the thickness of the 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 10mA and a voltage of 15kV.

Measurement of gelation time and pH of UF resin

Hot-water extractives and SCA were added to 10g of the UF resin at 1, 2, and 3 wt% and at 2, 4, 6, and 10 wt% based on its resin solid, respectively. After adding 1ml NH_4Cl solution, the gelation 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 using a pH meter immediately after adding extractives and SCA. Two replicates were used for each condition.

Results and discussion

Effects of SCAs on the wettability of straw outer surfaces

Based on our previous study, the inferior properties of reed and wheat straw boards were improved using SCAs; epoxide silane was more effective for reed board, and amino silane was better for wheat board.[3] To confirm the effects of SCAs on the straw materials, reed straw was treated with SCAs at 100% concentration. Figure 1 shows the effects of SCAs on the contact angle of the reed straw outer surface. The untreated specimen (control) had a large contact angle, indicating relatively low surface wettability. 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 SCAs, the contact angles were reduced by about 66% and 36% for epoxide silane and amino silane, respectively. Vinyl silane

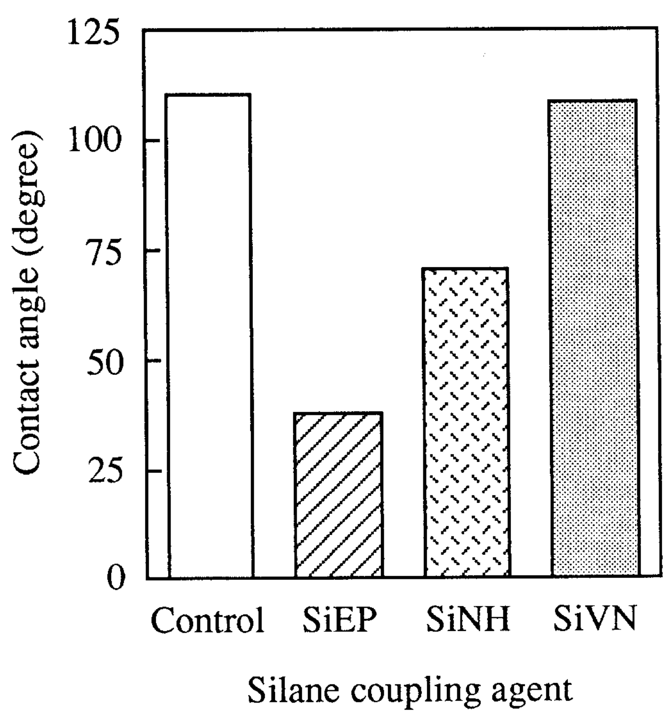

Fig. 1. Effects of silane coupling agents on the contact angles of reed straw outer surface. *SiEP*, epoxide silane; *SiNH*, amino silane; *SiVN*, vinyl silane

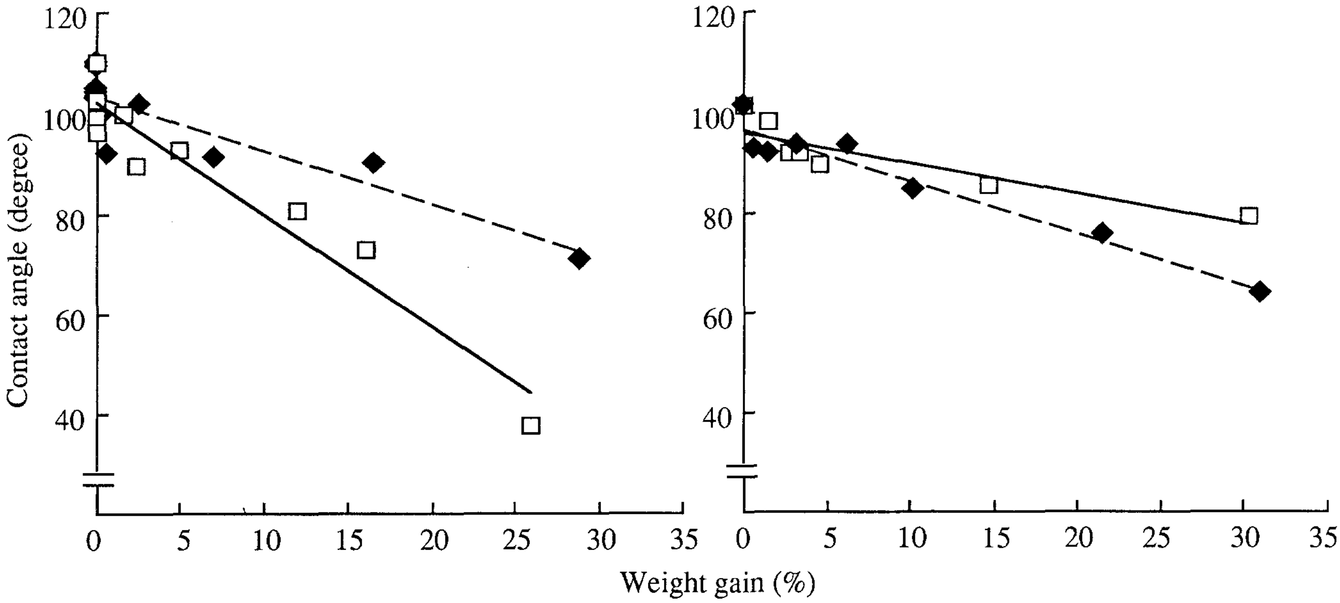

Fig. 2. Relation between the contact angles of straw outer surfaces and the weight gains of treated samples. *SiEP*, epoxide silane (*open squares*); *SiNH*, amino silane (*filled diamonds*). **Left** Reed. **Right** Wheat

had almost no effect on the contact angles, which could be due to the insoluble characteristic of vinyl silane.

Considering the fact that only a low content of SCAs was used for board manufacture in our earlier study, the SCAs were diluted to various concentrations in 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 vinyl silane, only epoxide silane and amino silane were used in this experiment. Figure 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. Epoxide silane was more effective in reducing the contact angles for reed straw, and amino silane was better for wheat straw. It was found that SCAs reduced the contact angles to a greater extent in reed straw than wheat straw. This improvement could be attributed to some hydrophilic components exposed on the straw surfaces, which might have resulted from some reaction between the SCA and the straw surfaces.

The results of this experiment indicate that the wettability of straw outer surfaces was improved by treating with SCAs, which may be one of the reasons the board properties were improved by the SCA additions. The reduction of contact angle achieved by each SCA shows good correlation with the improved board properties reported in the previous paper.[3]

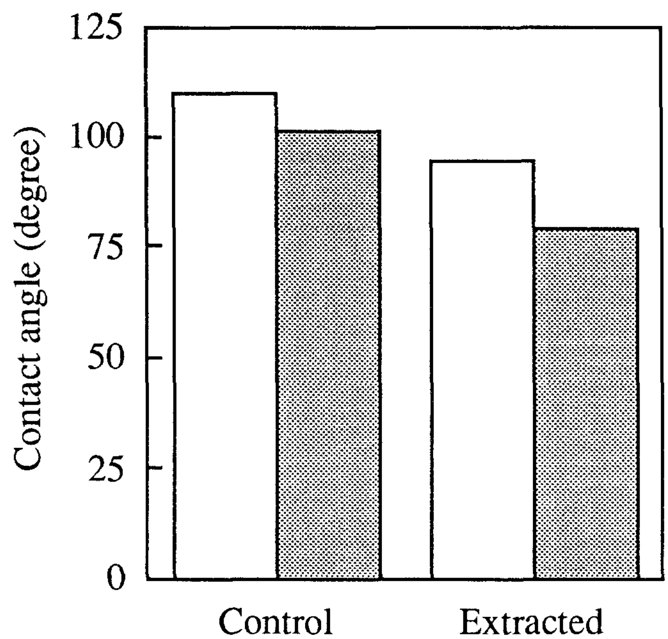

Fig. 3. Effects of ethanol-benzene extraction on the contact angles of reed (*open bars*) and wheat (*shaded bars*) straw outer surfaces

Effects of ethanol-benzene extraction on the wettability of straw surfaces

The presence of extractives can also influence the wettability of materials.[6] It has been reported that low wettability is related to the existence of nonpolar extractives.[7]

Figure 3 shows the effect of ethanol-benzene extraction on the contact angles of reed and wheat straw surfaces. The contact angles of the outer surfaces of both reed and wheat straws were reduced after ethanol-benzene extraction. The contact angles decreased by about 14% for reed straw and 22% for wheat straw compared to the control. Because the extractive contents are negligible for reed straw and about

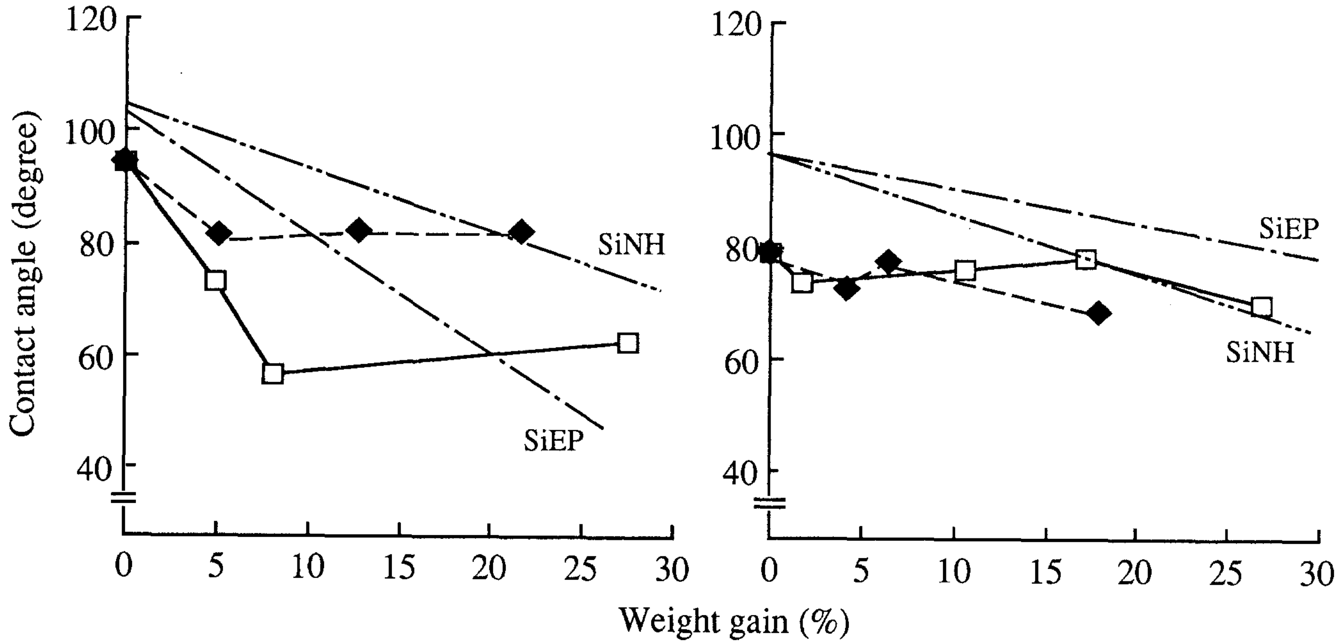

Fig. 4. Effects of silane coupling agents on the contact angles of reed (**left**) and wheat (**right**) straw outer surfaces before and after ethanol-benzene extraction. *Open squares*, SiEP, *filled diamonds*, SiNH. Effects of SiEP and SiNH on contact angles before extraction

17% for wheat straw, this might be related to the different effects of the extraction on these two materials. The wettability of straw surfaces was therefore improved by ethanol-benzene extraction. Wax can usually be extracted by ethanol-benzene,[8] so this improvement could be attributed to the removal of wax-like substances from straw surfaces.

Generally, there is a waxy layer on the cereal straw surface.[1,2,4] The wax on the straws is probably one of the main factors responsible for the reduction of bond quality. Further studies should be conducted to investigate whether the board properties can be improved by a pretreatment for wax removal. It has been reported that a pressure-refining process can be used to remove the wax on wheat straw surfaces.[1]

Figure 4 shows the effect of SCAs on the contact angles of straw surfaces extracted with ethanol-benzene. For reed straw, at a weight gain of less than 8% there was a great reduction in the contact angles of straw surface after treatment with epoxide silane, whereas at more than 8% weight gain only a slight change was observed in the contact angles. In the case of amino silane treatment, there was a clear decrease in contact angles when the weight gain was less than 5%. SCA had no effect on the contact angle when the weight gain exceeded 5%. For wheat straw, the contact angle of the ethanol/benzene-extracted specimens remained almost constant despite a hike in the weight gain.

It can be concluded that SCAs were more effective in reducing the contact angle of reed straw both before and after extraction. However, ethanol-benzene extraction had a greater effect than SCAs on improving the wettability of wheat straw.

Analyses of reed and wheat straws by ESCA

To further elucidate 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. 5. The silicon peaks are shown at a binding energy of 100–102eV. 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 SCAs, UF resin, and the particles,[3] 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 ethanol-benzene extraction method may be more effective for improving the bondability of wheat straw considering the relatively greater improvement in wettability after extraction compared to reed straw.

Our previous study concluded that the properties of reed and wheat boards manufactured from fine particles are better than those made of coarse particles.[3] 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 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 by the milling process.[9] The presence of silicon was reported to affect tool wear during board cutting.[1]

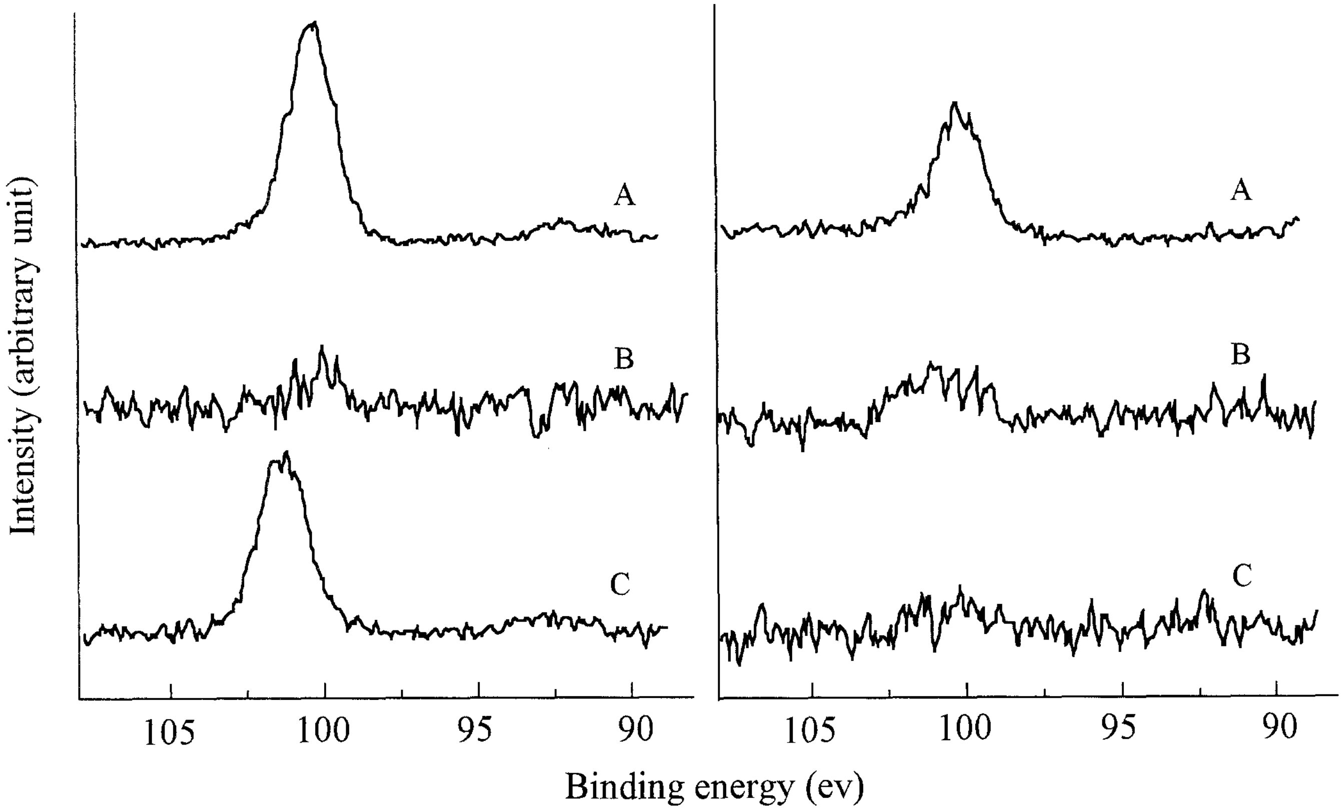

Fig. 5. X-ray photoelectron spectroscopy (XPS) of silicon (Si2p) on the outer (*A*), sectioned (*B*), and inner (*C*) surfaces of reed (**left**) and wheat (**right**) straws

Table 1. Gelation time and pH of UF resin added with hot-water extractives of reed straw

Extractives added (%)	Gelation 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

The amount of extractives added was based on the weight of UF resin solid
The values in parentheses are the relative gelation time based on the control value
UF, urea formaldehyde

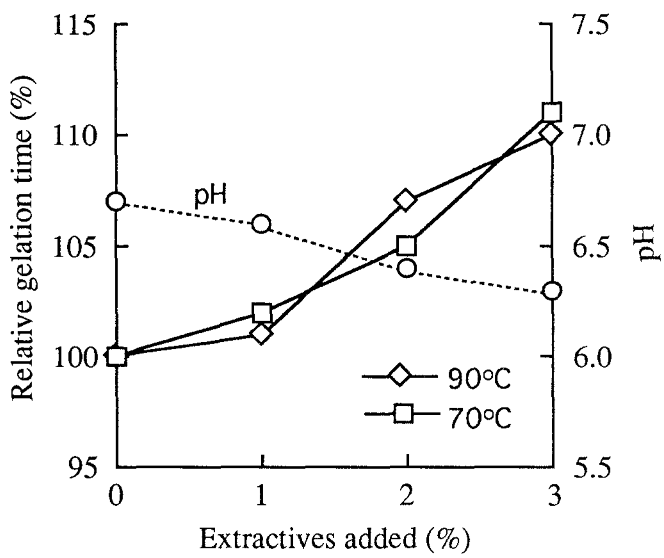

Fig. 6. Effects of hot-water extractives of reed straw on the gelation time of UF resin at 70°C (*squares*) and 90°C (*diamonds*); pH (*circles*) was measured at 25°C. The relative gelation time was based on that of the control (neat UF resin)

Effects of water extractives and SCAs on gelation time and pH of UF resin

It has been reported that hot-water extractives of wood have a significant effect on the gelation time of UF resin.[10,11] UF resin is known to be acid-catalyzed and cannot attain an optimum state of cure in a low acidic environment.[12]

In this study the hot-water extractives of reed straw and SCA were added to UF resin, and their effects on the gelation time and pH of the resin were examined. As seen in Table 1 and Fig. 6, a higher extractive addition resulted in longer gelation 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

Table 2. Gelation time and pH of UF resin with silane coupling agents[a]

Silane coupling agent added (%)[b]	SiNH + UF		SiEP + UF		SiVN + UF	
	Gelation time (min)	pH	Gelation time (min)	pH	Gelation 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 (2.88)	9.38	1.48 (105)	6.73	1.24 (88)	6.73

SiNH, amino silane; SiEP, epoxide silane; SiVN, vinyl silane
[a]The gelation time was measured at 90°C; pH was measured at 25°C
[b]The amount of silane coupling agent added was based on the weight of the UF resin solid

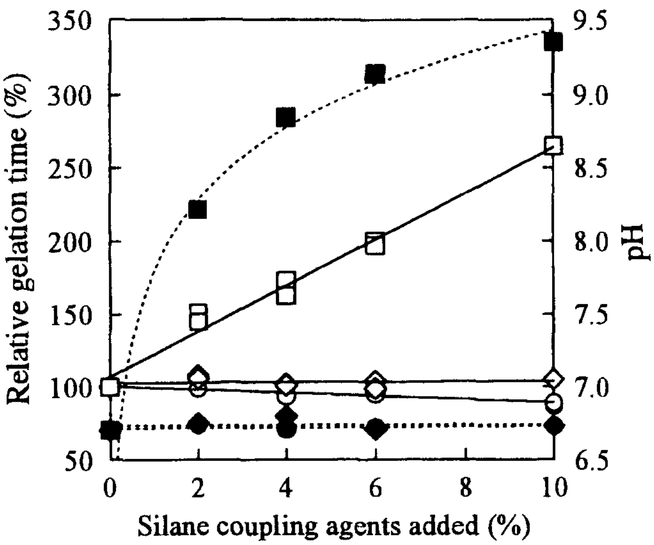

Fig. 7. Effects of silane coupling agents on the gelation time (*open symbols*) and pH (*filled symbols*) of UF resin at 90°C and 25°C, respectively. Relative gelation time was based on the control (neat UF resin). *Squares*, SiNH; *diamonds*, SiEP; *circles*, SiVN

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 gelation time. The pH descent was reported to be retarded by the addition of water extractives of wood in the UF resin.[10,11] 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 slowing of the pH decrease seemed to prolong the gelation time.

The effects of SCAs on the gelation time and pH of UF resin are shown in Table 2 and Fig. 7. The gelation 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 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.

However, the bond formation between the resin and straws may be more complicated and subject to the influence of many factors. As Freeman concluded, wettability, pH, and specific gravity of the materials are closely related to glue-bond quality.[13] All these factors will be taken into consideration in the upcoming board manufacture plan.

Conclusions

The poor wettability of reed and wheat straw surfaces was improved by SCA treatment and ethanol-benzene extraction. The improvement due to epoxide silane was more obvious in reed straw, whereas amino silane was more effective in wheat straw. Ethanol-benzene extraction resulted in a greater increase in the wettability of wheat straw than reed straw.

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 than 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. On the other hand, the ethanol-benzene extraction could be more effective for bondability improvement in wheat straw as revealed by the substantial increase in its wettability after extraction.

The addition of hot-water extractives of reed straw increased the gelation time of UF resin. The gelation time was considerably retarded with amino silane addition. Epoxide and vinyl silanes had no influence on the UF gelation time.

The inferior properties of 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. Addition of SCA could improve the wettability of straw surfaces, resulting in improved board properties.

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