Effects of internal factors on surface wettability of corn stalk rind

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Abstract: Corn stalk is one of heterogeneous materials with anisotropy and variability. As the rind of corn stalk consists of rich lignin and cellulose similar to wood properties, and possessing high mechanical strength, then can be used as raw material of stalk artificial board and paper. The corn stalk rind has significant differences in fiber morphology, chemical composition and mechanical properties at different heights. Nano-SiO_2 composite material contained in the epidermis of corn stalk rind is not conducive to exert adhesive into a board. To study board-making technology by intact corn stalk rind, the wettability of corn stalk rind at different sampling heights is necessary to be analyzed by keeping or removing the epidermis. To analyze the surface wettability difference, the contact angle with water, element compositions and the chemical compositions of corn stalk rind at different sampling heights were studied before and after removal of epidermis. A Fourier transform infrared (FTIR) analysis was performed. The results showed that the removal of the epidermis could significantly improve the hydrophilicity of corn stalk rind. Before removal of the epidermis, the varying contents of elements including C and Si dominate the surface wettability differences at different sampling heights of corn stalk. With an increase in the sampling height, the mass fraction of C increases while that of Si decreases, which result in increasing hydrophilicity. After removal of the epidermis, the surface wettability of corn stalk rind is mainly determined by the mass fraction of hemicellulose, and the higher the sampling height, the larger the mass fraction of hemicellulose resulting in the increase of hydrophilicity.

Keywords: corn stalk rind, wettability, surface contact angle, element analysis, chemical compositions, mechanism
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1 Introduction

The development of straw board industry is beneficial to rural economies, the protection of forest and the development of ecological agriculture[1-3]. Corn stalk rind, the major component of corn stalk (comprising more than 30% of the mass of stalk), is the raw material for producing straw board[4,5]. Similar to the stalks of other crops, surface modification or direct grinding are commonly performed in the production of corn stalk board to reduce influence of the epidermis on scuffing[6-9]. By regulating rice straw using cold plasma technology, Yang et al.[10] modified the surface wettability of the straw in terms of the variation of surface chemical functional group and elements. Zhou et al.[11] studied variation in the surface properties of rice straw caused by the change of surface radical concentration and chemical compositions before and after microwave treatment. By analyzing the variation of surface contact angle, Zhang et al.[12] discussed the wettability of rice straw epidermis before and after treatment by using NaOH solution. In addition, they evaluated the physical and mechanical properties of the formed board made from the mixture of treated rice straw and coir. In addition, Shen et al.[13] treated wheat straw using lipase and tested the wettability changes of the wheat straw treated by different methods.

The above studies mainly investigated the surface wettability of straw based on the variation of chemical

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compositions and polar functional groups caused by external factors[14,15], while surface wettability of corn stalk rind is rarely studied in terms of the internal factors which include physiological characteristics and the basic tissue structure. Corn is a tall plant of gramineae that has multiple stem nodes and its stalk epidermis is a heterogeneous material with apparent anisotropy and variability. There are large differences considering the mechanical property[16], fiber morphology and chemical compositions[17] in different stem nodes of corn stalk rind. To utilize intact corn stalk rind in the board-making production and modify the surface wettability, at different sampling heights and before and after removal of epidermis, the contact angle with water was measured and the element compositions detected by using the scanning electron microscopy (SEM) and the energy dispersive spectrometer (EDS). The chemical composition variation of cellulose, hemicellulose and lignin were analyzed by using the Fourier transform infrared spectroscopy (FTIR). Therefore, the initial objective of this study was to reveal the mechanics of differences in the surface wettability of corn stalk rind at different sampling heights and before and after removal of the epidermis, and provide a theoretical basis and technological support for the technology of intact corn stalk rind board production and the improvement of physical and mechanical properties of the board.

2 Materials and methods

2.1 Materials

Xianyu 335-variety corn stalk rind was used in this study. The corn stalk was harvested in Maozhuang Farm of Henan Agricultural University of China, and the main physical dimension was as follows: 25-30 mm in diameter at the root, more than 2000 mm in length. The microstructure of the corn stalk rind measured by the slicing method was shown in Figure 1. The corn stalk rind consists of epidermis and sarciniform tissue, the sarciniform tissue is made of fibrocytes and vascular bundles, and the epidermis was around 0.04 mm in thickness and mainly consisted of nano-SiO_2[18]. Rind at root, lower, middle and higher part (the 2nd, 4th, 6th, and 8th stem nodes along the growth direction) of the corn stalk were cut. Each of these rinds was divided into two groups in the axial direction. In one of the groups, the epidermis of corn stalk rind was removed and sanding treatment was performed. The two groups were dried naturally and reserved, as shown in Figure 2.

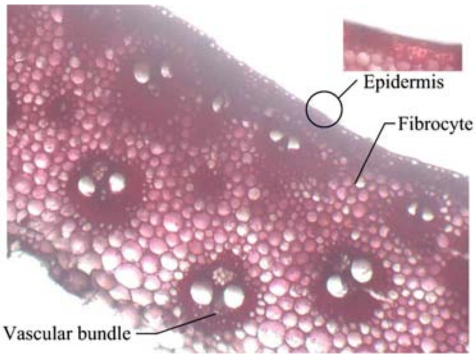


Figure 1 Microstructure of the corn stalk rind (×100)

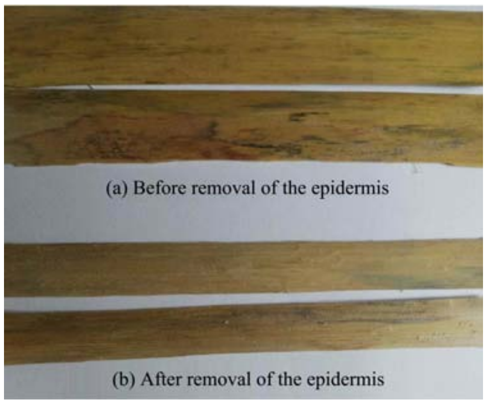


Figure 2 Experimental materials

2.2 Experimental methods

2.2.1 Measurement of surface contact angle

The experimental materials were prepared to standard samples of 40 mm×15 mm×1.5 mm (in the axial, chordwise and radial directions respectively) with a moisture content of 12%. The surface contact angles of corn stalk rinds at different sampling heights and before and after removal of the epidermis were measured by using a JC-2000C1 contact angle measurement at 25°C. In the measurement, distilled water was used and the droplet amount was set to be 5 μL. Then the contact angle of the sample surface with the distilled water for 5 s was detected off-line by transmitting images through an image sensor. The protractor used showed an accuracy of ±0.25°. For each sample, 10 points were selected randomly to test their chordwise and axial contact angles and an average value was calculated from 5 parallel samples.

2.2.2 Element contents

Qualitative and semi-quantitative analysis was carried out by a JSM-6490LV scanning electron microscope (SEM) and an INCA-EDS7573 energy dispersive x-ray detector for 10 areas of each sample. Then the average values were calculated from 5 parallel samples.

2.2.3 Detection for chemical compositions

The contents of lignin, cellulose, and hemicellulose were tested by using the Van Soest method[19]. The contents of extracts were measured according to Fibrous Raw Material-Determination of Water Solubility (GB/T2677.4-93), Fibrous Raw Material-Determination of One Percent sodium Hydroxide Solubility (GB/T2677.7-81), and Fibrous Raw Material-Determination of Benzene-alcohol (GB/T2677.7-81).

2.2.4 FTIR

According to General Rules for Infrared Analysis (GB/T6040-2002), the infrared spectra of the samples were scanned for 15 times using a Nicolet 6700 FTIR spectrometer (Thermo Fisher scientific, America) through KBr squash method. The infrared spectra were in the middle region of 4000-400 cm^{-1} with a spectral resolution of 4 cm^{-1}. The obtained spectra were processed using OMNIC software.

3 Results and analysis

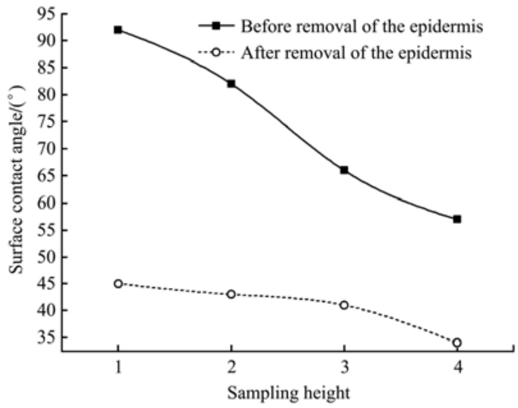
3.1 Wettability of corn stalk rind at different sampling heights

The variation reflects the difference in wettability of corn stalk rind. If the contact angle is larger than 90°, the corn stalk rind shows hydrophobicity; while a contact angle less than 90° results in the hydrophilic state of corn stalk rind[20]. As seen in Table 1, the One-way ANVOA results show that the contact angles of corn stalk rind at different sampling heights before and after removal of the epidermis are highly significant difference ($p < 0.01$). As shown in Figure 3, the contact angle of corn stalk rind at the root is larger than 90°, which indicated that corn stalk rind at root is hydrophobic; with the increase of the sampling height, the contact angle with water decreases and consequently hydrophilcity increases; After removal of the epidermis, as the sampling height increases, the contact angle reduces slightly. Compared with that prior to removing the epidermis, the corn stalk rind is coarser (shown in Figure 4) and the contact angle variation increases (shown in Figure 5).

Table 1 ANOVA of contact angle of corn stalk rind with water before and after removal of the epidermis at different sampling heights

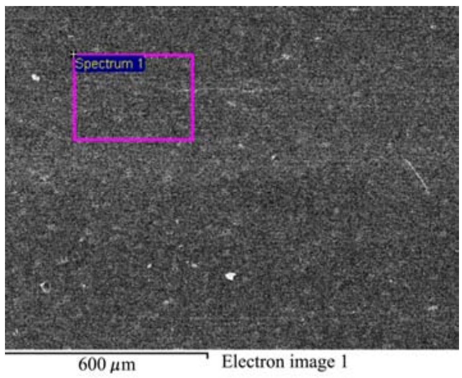
Origin	Source of variations	Sum of square	Degree of freedom	Mean square	*F* value	Sig.
Sampling height	Between groups	10036.224	1	10036.224	4865.117	**
	Within groups	78.390	38	2.063		
	Total	10114.614	39			
Sampling group	Between groups	7997.018	1	7997.018	636.899	**
	Within groups	477.135	38	12.556		
	Total	8474.153	39			

Note: Sampling group means the corn stalk rind divided into two groups, one is expressed before the removal of the epidermis, and the is expressed after the removal of the epidermis. ** means significant difference at the 0.01 level.

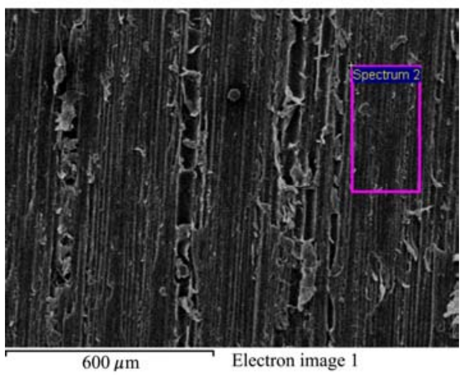


Note: 1, 2, 3, and 4 stand for the 2nd, 4th, 6th, and 8th stem nodes along the growth direction, respectively, the same as below.

Figure 3 Variation of surface contact angle between corn stalk rind and water at different sampling heights

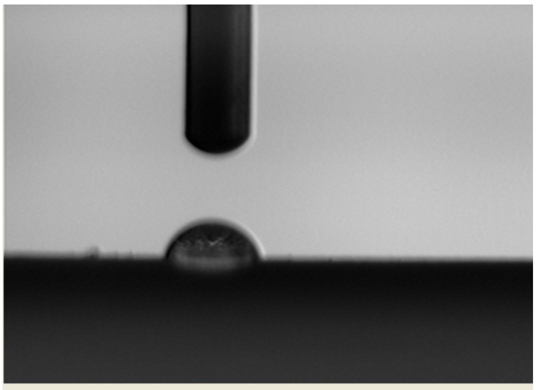


a. Before removal of the epidermis

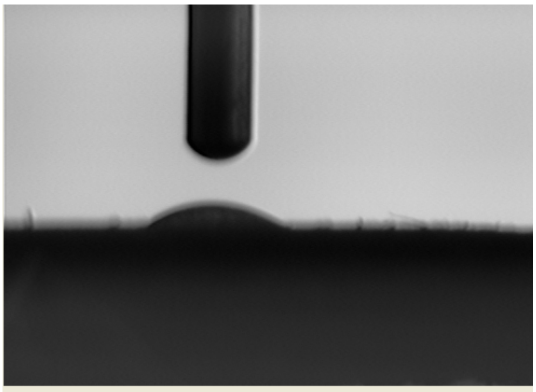


b. After removal of the epidermis

Figure 4 Microstructure observed before and after removal of epidermis of corn stalk rind



a. Before removal of the epidermis

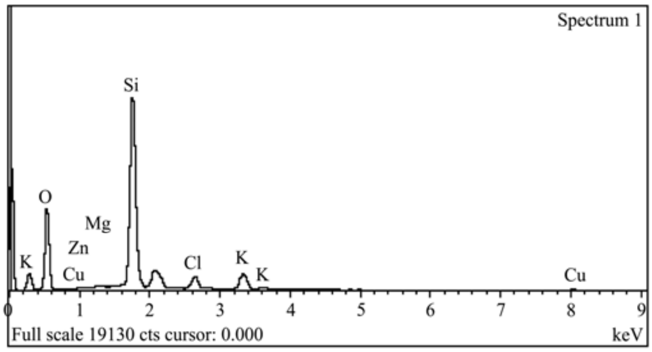


b. After removal of the epidermis

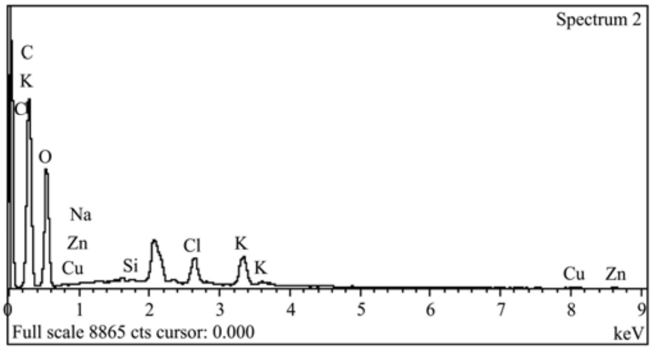
Figure 5 Images of sessile drop of before and after removal of epidermis of corn stalk rind

Figure 6 demonstrates the corn stalk rind EDS curves of the marked areas in Figure 4. By Figure 6, it can be seen that corn stalk rind mainly contains C, O, Si, and K, as well as small amounts of other elements including Cu, Zn and Mg. Among these, the absorption peaks of C and Si show obvious differences between before and after removal of the epidermis.

Figure 7 shows the different mass fractions of C and Si at different sampling heights of corn stalk rind before and after removal of epidermis. The *t*-test results show that the variation of C, Si mass fraction are highly significant difference (p<0.01, shown in Table 2) before and after removal of epidermis of corn stalk rind at different sampling heights. Before removing the epidermis, the mass fraction of Si is in the range of 34.22%-21.74%. With an increase of the sampling height, the mass fraction decrease gradually. The mass fraction of C is in the range of 21.02%-24.76% and decreases with the increase of the sampling height. After removing the epidermis, the mass fraction of Si is around 0.1%, which is significantly (p<0.01) less than that before removal, and shows not significant difference (p=0.186 > 0.05) at different sampling heights. The mass fraction of C varies from 53.27% to 56.12%, and similar to that before the removal of the epidermis, the mass fraction also increases as the sampling height increases.



a. Before removal of the epidermis



b. After removal of the epidermis

Figure 6 Corn stalk rind EDS curves of the marked areas in Figure 4

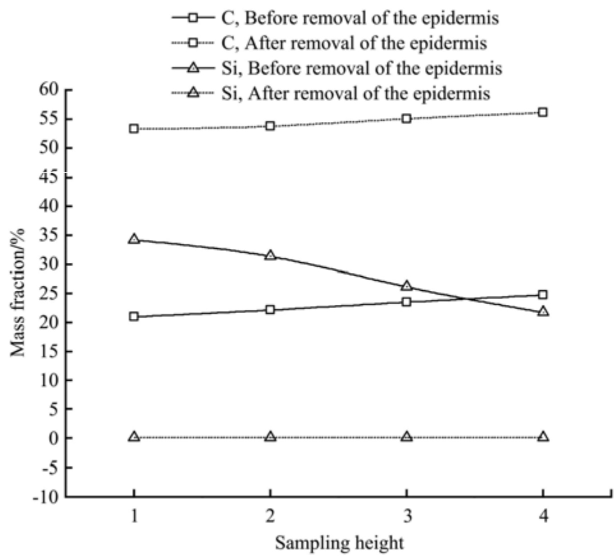


Figure 7 Variation of C, Si mass fraction before/after removal of the epidermis of corn stalk rind at different sampling heights

Table 2 *T*-test for independent samples

Origin		Levene's test for quality of variance		*T*-test for equality of means						
		F	Sig.	T	df	Sig. (2-tailed)	Mean difference	Std. error difference	99% confidence interval of the difference	
									Lower	Upper
C	Equal variance assumed	0.794	0.378	-69.750	38	0.000	-31.68000	0.45419	-32.91157	-30.44843
	Equal variance not assumed			-69.750	36.852	0.000	-31.68000	0.45419	-32.91358	-30.44642
Si	Equal variance assumed	84.714	0.000	25.236	38	0.000	28.27750	1.12054	25.23909	31.31591
	Equal variance not assumed			25.236	19.000	0.000	28.27750	1.12054	25.07171	31.48329

3.2 Variation of chemical compositions of corn stalk rind at different sampling heights

The infrared spectra of corn stalk rind at different sampling heights are illustrated in Figure 8. It can be seen that there is stretching vibration of the hemicellulose OH functional group at around 2350 cm^{-1} and the absorption peak intensifies with an increase of the sampling height. In addition, stretching vibration of the C=O functional group is found at 1734 cm^{-1} and the absorption peak also strengthens with the increase of the sampling height. These above findings indicated the increase of relative content of hemicellulose and the amounts of oxygen containing functional groups such as acetyl and carboxyl in the corn stalk rind. The absorption peak of C=O stretching vibration of acetyl and carboxyl at 1734 cm^{-1} displays the specific characteristic of hemicellulose[21]. C-O and C-C stretching vibration at 1240 cm^{-1} and the absorption peak reduce with the increase of the sampling height, suggesting the relative contents of lignin and xylan decrease. Aromatic framework vibration is observed at 1514 cm^{-1} and the absorption peak weakens as the sampling height increases, which indicates the decreases continuously of lignin content.

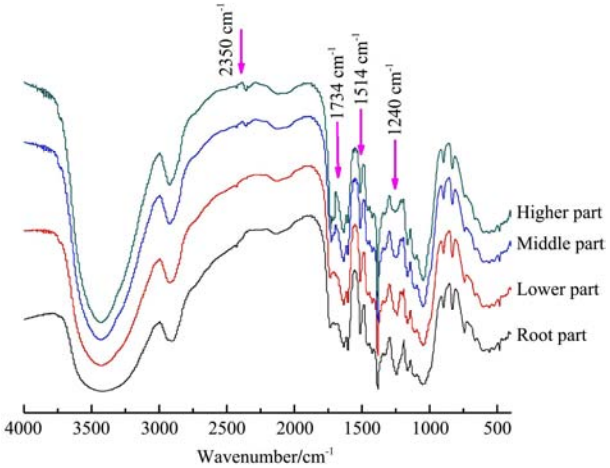
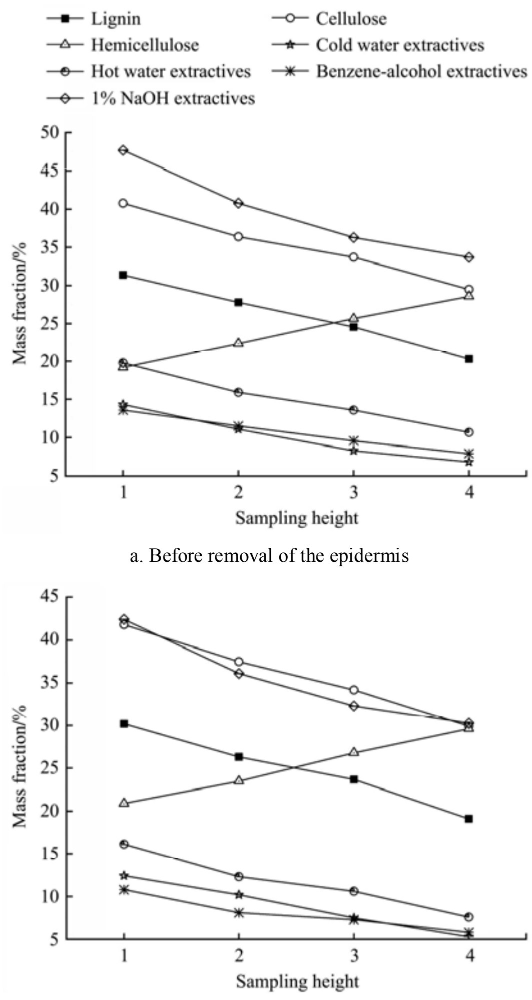


Figure 8 FTIR spectra of corn stalk rind at different sampling heights

The chemical compositions of corn stalk rind at different sampling heights are demonstrated in Figure 9, in which the analysis of covariance results shows no significant difference (p>0.05) for the slope of linear models of lignin, cellulose, and four extracts, the variations of chemical compositions are consistent before and after removal of the epidermis. With the increase of the sampling height, the mass fractions of lignin, cellulose, and four extracts decrease while that of hemicellulose increases. Compared with observed pictures before removal of the epidermis, the mass fraction of lignin in the corn stalk rind after removal of the epidermis reduce slightly while those of cellulose and hemicellulose increase relatively, and those of the four extracts decrease.

Cellulose, hemicellulose, and lignin show strong hygroscopicity. The free hydroxyl in the upper molecular chain of the amorphous region of cellulose is a polar group which is likely to absorb polar water molecules to form hydrogen bond[22]. Hemicellulose is an amorphous material with a branching structure which is composed of two or more glycosyl groups with hydrophilic groups on both main chain and side chain. The extracts mainly contain materials including fat and silicide with strong hydrophobicity, which cause inhibition of the adsorption of cellulose and hemicellulose for water[23]. Although surface coarseness is a leading factor influencing the surface wettability of corn stalk rind, and the larger the coarseness of hydrophobic solid is, the larger the surface contact angle is, it shows a slight influence on the surface wettability of hydrophilic materials[24]. For corn stalk rind, the surface wettability differs significantly at different sampling heights and before and after removal of the epidermis. This is caused by variations in mass fractions of cellulose and hemicellulose which contain hydrophilic functional groups and hydrophobic extracts such as fat and silicide. Before removing the epidermis, the hydrophilic materials in the corn stalk rind, including fat and silicide, determine the variation of the wettability. In the root, large fat and silicide extracts attached to the surface impede the combination of water and hydrophilic groups resulting in hydrophobicity. As the sampling height increases, the mass fractions of fat and silicide decreases thereby the contact angle between the surface of corn stalk rind and water reduces. After removing the epidermis, the hydrophilic materials including fat and silicide are removed, so the mass fraction of hemicellulose is the leading factor determining the wettability of corn stalk rind. With the increase of the sampling height, the mass fraction of hemicellulose increases and the activities of polar group of free hydroxyl and other hydrophilic groups are enhanced. All these factors contribute to the increase of surface hydrophilicity of corn stalk rind.



a. Before removal of the epidermis

b. After removal of the epidermis

Figure 9 Variation of chemical composition of corn stalk rind at different sampling heights

4 Conclusions

Before and after removal of the epidermis, the surface wettability and chemical compositions of corn stalk rind differ greatly at different sampling heights. Before removing the epidermis, the contact angle of corn stalk rind with water and the mass fractions of lignin and cellulose reduce with the increase of the sampling height, while the mass fraction of hemicellulose increases. After removing the epidermis, as the sampling height increases, the contact angle of corn stalk rind with water increases, the mass fractions of lignin and cellulose decrease, and the mass fraction of hemicellulose increases.

Removing the epidermis may improve the surface wettability of corn stalk rind. Before removing the epidermis, the wettability is mainly influenced by the variation of mass fractions of C and Si, and the existence of hydrophobic materials including fat and silicide inhibits the hydrophilicity of corn stalk rind. After removing the epidermis, the mass fractions of Si and extracts reduce, and the mass fraction of hemicellulose is the dominant factor influencing the surface wettability of corn stalk rind.

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