

Investigation of the Structural Characteristics of Corn Stalk during Hot-Pressing

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Corn stalk is one of the most abundant agricultural residues in China. In this experiment, corn stalks were hot-pressed to prepare formalin-free particleboard. Milled wood lignin (MWL) samples were isolated from original and hot-pressed corn stalks. To illuminate the self-bonding mechanism of binderless particleboard, the structural characteristics of original corn stalk, hot-pressed corn stalk, and MWL samples were thoroughly investigated by Fourier transform infrared spectroscopy (FT-IR), solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance spectroscopy (CP-MAS ¹³C-NMR), X-ray diffraction (XRD), carbon-13 nuclear magnetic resonance spectroscopy (¹³C-NMR) and gel permeation chromatography (GPC). The degradation of hemicellulose and a portion of amorphous cellulose occurred during hot-pressing. Hot-pressing increased the crystallinity and crystallite size of cellulose in treated corn stalk. The analysis of MWL showed that hot-pressing resulted in corn stalk lignin depolymerization through cleavage of a substantial portion of the β -O-4 linkages in lignin, as well as the decrease of molecular weight of lignin in corn stalk. In addition, acid-catalyzed condensation occurred between lignin and xylose when liberated from hemicellulose. These results demonstrated that condensation between lignin and xylose may contribute to the self-bonding mechanism and improve board properties.

Keywords: Corn stalk; Hot-pressing; Crystallinity; Degradation; Condensation

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INTRODUCTION

Lignocellulose boards, such as fiberboard and particleboard, are widely used in the construction and furniture industries (Reddy and Yang 2005). Currently, these boards are produced with formaldehyde-based adhesives, such as urea-formaldehyde (UF), urea-melamine-formaldehyde (UMF), and phenol-formaldehyde (PF), regardless of the fiber source (Halvarsson *et al.* 2009). However, formaldehyde emissions during the production and end-use of the boards are a concern for manufacturers and consumers (Sellers 2001). To eliminate these concerns, the use of replacement adhesives from isocyanate resin (Umemura *et al.* 1999; Tohmura *et al.* 2005), epoxyresins (Kishi *et al.* 2006), and natural sources, including soy protein, lignin, starch, and tannin, have been extensively researched (Sowunmi *et al.* 1996; Xu *et al.* 2011; Wang *et al.* 2012; Zhou *et al.* 2013). However, higher costs and relatively poor performance limit their application in the industry.

Another way to reduce formaldehyde emissions from lignocellulosic boards is the production of boards without adhesives by the activation of the biomaterial's self-bonding ability, *i.e.*, binderless boards. Various methods can be applied to improve the self-bonding properties (Zhang *et al.* 2015). Generally, steam/heat treatment is an effective method (Suzuki *et al.* 1998; Sekino *et al.* 1999; Xu *et al.* 2003; Xu *et al.* 2004; Widyorini *et al.* 2005a; Quintana *et al.* 2009; Zhang *et al.* 2015). Steam/heat could lead to the degradation of hemicellulose, lignin, and amorphous cellulose. Degradation reactions of hemicellulose produce furfural products, which are believed to play an important role in the self-bonding mechanism of binderless boards (Mobarak *et al.* 1982; Suzuki *et al.* 1998; Widyorini *et al.* 2005b). Because these treatments require specialized equipment, high water consumption, and relatively long pressing times (Sellers 2001; Okuda and Sato 2004), this method is not practical for application.

However, Okuda *et al.* (2006a; 2006b) and Nonaka *et al.* (2013) successfully produced binderless boards with non-woody powder, without steam treatment, using only hot pressing. The authors suggested that condensation reactions in lignin, thermal softening of lignin, and chemical reactions from conjugated carbonyl compounds played an important role in self-bonding. However, the self-bonding mechanism during heat treatment has not been completely elucidated.

The shortage of wood and forestry regulations has led to a continuous effort to find new alternatives to wood (Halvarsson *et al.* 2009). Corn is one of the largest production crops in China; annual corn production comprises 1.22 to 1.27 million tons of corn stalk (Yang *et al.* 2009). Most of the corn is burned after harvest, contributing to environmental problems. However, the low cost and rich hemicellulose content of corn stalk makes it an attractive potential substrate for binderless board production (Okuda and Sato 2004). In the present work, corn stalk was treated through hot-pressing. Milled wood lignin (MWL) samples from the original corn stalk and hot-pressed corn stalk were isolated. The structural characteristics of the original corn stalk, hot-pressed corn stalk, and MWL samples were investigated by Fourier transform infrared spectroscopy (FT-IR), solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance spectroscopy (CP-MAS ¹³C-NMR), X-ray diffraction (XRD), carbon-13 nuclear magnetic resonance spectroscopy (¹³C-NMR), and gel permeation chromatography (GPC) to reveal the self-bonding mechanism of binderless particleboard manufactured from the corn stalk.

EXPERIMENTAL

Materials

The corn stalks were collected from a suburb of Mianyang City, China. The corn stalks were washed with deionized water and oven-dried at 50 °C to reduce the moisture content to approximately 10% to 12%. The dried corn stalks were ground separately in a vegetation disintegrator and sieved through a 120-mesh screen. The ground samples were used as the starting material.

Methods

Treatment of corn stalk by hot-pressing

The ground samples were handformed into a 220 mm × 220 mm × 6 mm homogeneous, single-layer mats in a forming box. The mat was then pressed with a hot-

press machine (BY302X2/15, Xinxieli Group Co., Ltd, Suzhou, China) under the following conditions: pressing temperature of 170 °C, pressing pressure of 5 MPa, and pressing time of 10 min. The target density for the mat was 1.1 g/cm³.

Preparation of MWL from original and hot-pressed corn stalks

Original and treated corn stalks were milled to the size of 60- to 80-mesh using a vegetation disintegrator. The powders were subsequently extracted with ethanol-benzene (1:2, v/v) and hot water, successively. The extractive-free corn stalk meal was ground in a vibratory ball mill for 72 h, and the powders were used to prepare milled wood lignin (MWL) according to the procedure outlined in Björkman (1956).

Determination of infrared spectra

Approximately 1.3 mg of sample was mixed with 180 mg of KBr. The mixed powder was pressed to obtain completely transparent tablets. Infrared spectra of the samples were obtained using a Nicolet 380 FT-IR spectrophotometer (ThermoFisher Scientific Inc., Waltham, MA, USA).

Determination of crystallinity and crystallite size of original and hot-pressing treated corn stalks

The crystallinities of original and treated corn stalks were measured using an X-ray diffractometer (AXS D8 Advance, Bruker Corp., Karlsruhe, Germany) with a Cu anode as the primary x-ray beam source, operating at 40 kV and 40 mA. The specimens were scanned at 1° per min from $2\theta = 10^\circ$ to 50° , with a step size of 0.04° . The crystallinity index (CrI, %) was calculated according to Segal's equation (Segal *et al.* 1959),

$$\text{CrI} = (I_{002} - I_{\text{am}}) / I_{002} \times 100 \quad (1)$$

where I_{002} is the intensity of the diffraction from the 002 plane at $2\theta = 22.5^\circ$, which represents both the crystalline and amorphous regions of cellulose, and I_{am} is the intensity from the amorphous regions of cellulose measured at $2\theta = 18^\circ$.

The crystallite size of the direction perpendicular to 002 lattice plane was calculated according to Scherrer's equation (Ju *et al.* 2015),

$$L_{002} = k\lambda / \beta \cos \theta \quad (2)$$

where L_{002} is the size of crystallite, k is a constant of value 0.9, λ is the X-ray wavelength, β is the full width half maximum of 002 reflection in radian and θ is the corresponding Bragg angle (reflection angle).

Determination of CP/MAS ¹³C-NMR spectra

The powders of original and treated corn stalks were filled with dense, 4-mm ZrO₂ balls and analyzed using CP/MAS for ¹³C-NMR analysis. The ¹³C NMR spectra were recorded on an AV-III 400M spectrometer (Bruker Corp., Karlsruhe, Germany) at 100.6 MHz. The spectra were acquired with an acquisition time of 0.02 sec and a relaxation delay of 0.5 sec. The number of scans was 3500.

Determination of ¹³C-NMR spectra

The MWL samples were dissolved in DMSO-d₆ (0.5 mL in a 5 mm tube). The ¹³C-NMR spectra were obtained on an Agilent 400 MR DD2 superconducting Fourier-transform NMR spectrometer (400MHz, Agilent Corp., Palo Alto, CA, USA), which was

equipped with a 5 mm broad-band probe tuned to 150.9 MHz at 50 °C, with a scanning width of 0 to 220 ppm. An acquisition time of 0.9 sec and a relaxation delay of 1.75 sec were used. A total of 20000 scans were accumulated.

Determination of gel permeation chromatography(GPC)

The MWL samples were dissolved in N,N-dimethylformamide (DMF, 1 mg/mL) followed by filtration using a 0.45 μm polytetrafluoroethylene (PTFE) filter to remove undissolved solid prior to GPC analysis. The molecular weight distributions of the MWL samples were analyzed by a GPC instrument (LC-20AD, Shimadzu Corp., Kyoto, Japanese) equipped with Styragel HR 4E column (300 \times 7.8 mm, Waters Inc., Massachusetts, USA) and a refractive index (RI) detector(RID-10A, Shimadzu Corp., Kyoto, Japanese). DMF was the mobile phase (1.0 mL/min) with injection volumes of 20 μL at 40 °C. A calibration curve was constructed based on polystyrene standards. Molecular weights (M_n and M_w) of MWL samples were calculated through polystyrene calibration curve

RESULTS AND DISCUSSION

FT-IR Analysis

Figure 1 shows the FT-IR spectra of the original and treated corn stalks. The absorbance in the vicinity of 1730 cm^{-1} in the spectrum of the original corn stalk disappeared from the spectrum of the treated corn stalk. The 1730 cm^{-1} band belongs to C=O of the acetyl groups and other carbonyl groups of carboxylic acids in hemicelluloses (Delmotte *et al.* 2008). This indicated that hemicelluloses were degraded during the hot-pressing of corn stalk.

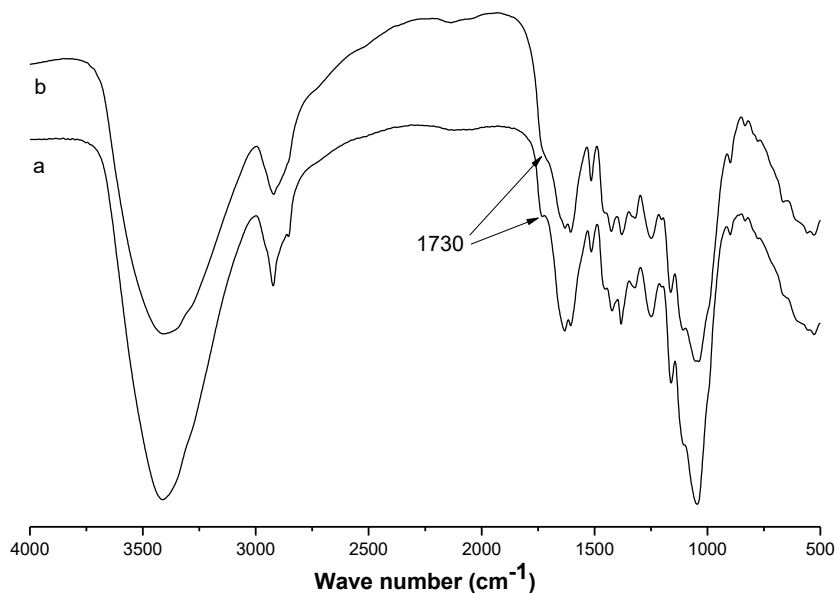


Fig. 1. FT-IR spectra of a) original corn stalk and b) hot-pressed corn stalk

The spectra of MWL from original and treated corn stalks are shown in Fig. 2. The spectrum of MWL shows bands at 1603, 1514, and 1422 cm^{-1} , characteristic of the

aromatic skeleton of the lignin macromolecule (Hoareau *et al.* 2004; Delmotte *et al.* 2008). This observation confirmed that the lignin polymer was not appreciably modified during the hot-pressing of corn stalk. Overall, the differences among the spectra of MWL were small. However, one small difference was observed in Fig. 2.

The spectrum of MWL from original corn stalk exhibited a peak intensity of 1655 cm^{-1} , derived from C=O stretching vibration of aromatic carbonyl compounds, that was reduced after the heat treatment of corn stalks. This fact suggests that the lignin side chain, with conjugated carbonyl groups, underwent some chemical changes to form new chemical structures during the hot-pressing treatment of corn stalk (Okuda *et al.* 2006a; Nonaka *et al.* 2013).

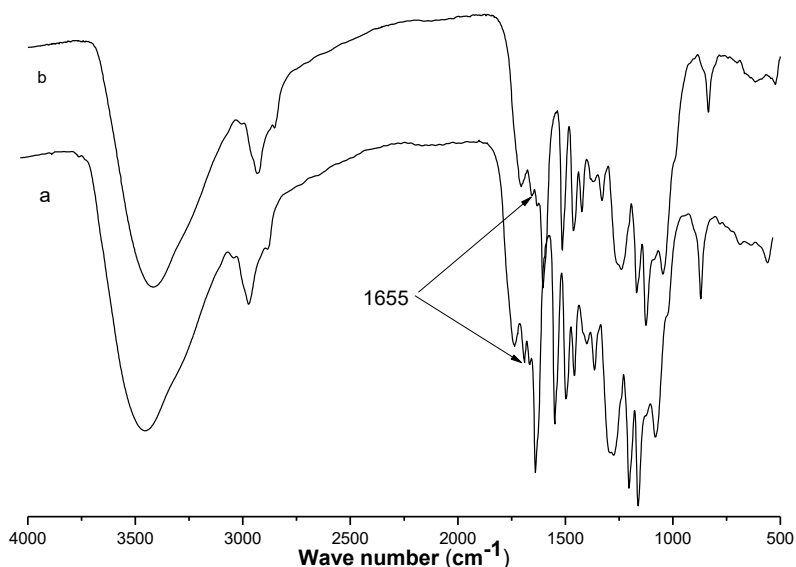


Fig. 2. FT-IR spectra of MWL samples from a) original corn stalk and b) hot-pressed corn stalk

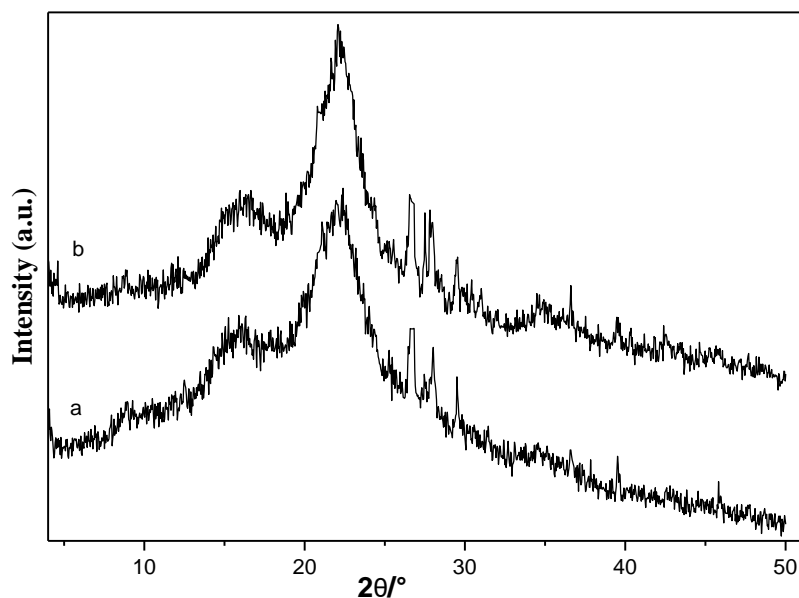


Fig. 3. X-ray diffraction patterns of a) original corn stalk and b) hot-pressed corn stalk

Crystallinity and Crystallite Size Analysis

The XRD patterns of original and hot-pressed corn stalks are shown in Fig. 3. The cellulose from treated corn stalks formed a type-1 crystalline structure. This indicates that cellulose from corn stalk retained its basic crystalline structure after hot-pressing. However, the hot-pressing treatment increased the crystallinity and crystallite size of corn stalk, as shown in Table 1. The reasons will be discussed further below.

Table 1. Crystallinity and Crystallite Size of Corn Stalk by X-ray Diffraction

Sample	CrI (%)	Crystallite size (nm)
Original corn stalk	33.019±0.037	8.717±0.061
Hot-pressed corn stalk	38.428±0.262	11.543±0.681

CP/MAS ¹³C-NMR Analysis

The CP/MAS ¹³C-NMR analysis was performed to characterize corn stalk that was chemically modified after hot-pressing. The CP/MAS ¹³C-NMR spectra of original and treated corn stalks are shown in Fig. 4. The signals were assigned based on previous research (Xie and Terashima 1993; Wikberg and Maunu 2004; Trindade *et al.* 2005; Delmotte *et al.* 2008), as shown in Table 2. Strong signals were observed in the region between 60 ppm and 110 ppm. These signals were assigned to the different carbons of cellulose, namely C-1 (105 ppm), C-4 crystalline (88 ppm), C-4 amorphous (84 ppm), C-2/C-3/C-5 (72 ppm to 75 ppm), and C-6 (64 ppm). The signals from hemicelluloses and lignin were less obvious in this region because they overlapped with cellulose. The signals at 21 ppm and 173 ppm were assigned to methyl and carbonyl groups of acetoxy and other ester groups in hemicellulose. The signals at 56 ppm were attributed to methoxy groups of aromatic moieties and were assigned to lignin. The region between 110 ppm and 160 ppm was specific to the aromatic carbon of lignin.

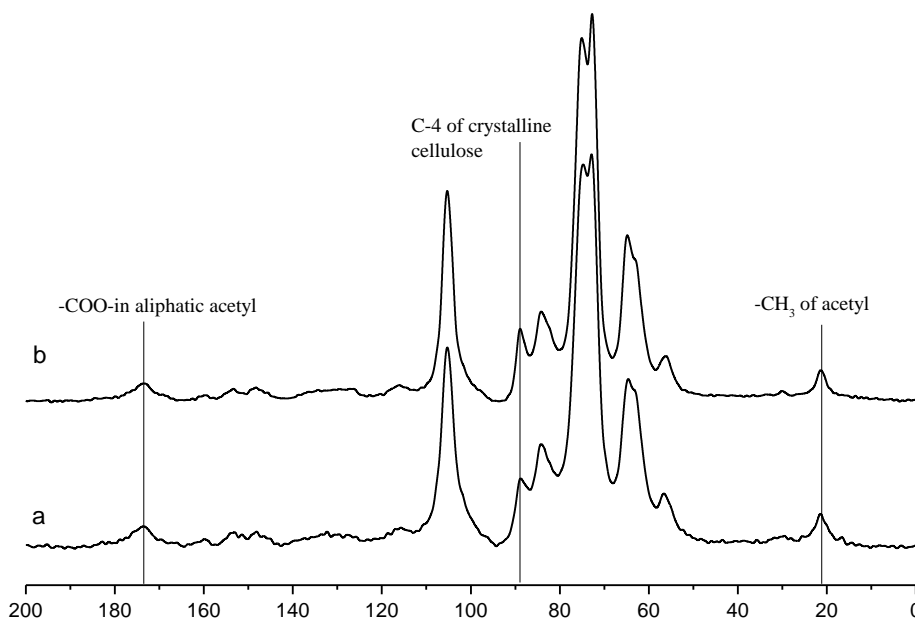


Fig. 4. CP/MAS ¹³C NMR spectra of a) original corn stalk and b) hot-pressed corn stalk

A comparison of the spectra of treated corn stalk and original corn stalk showed that the intensities of signals at 21 ppm and 173 ppm were lower. This signal was assigned to the carbons of hemicellulose. Hemicelluloses degrade during hot-pressing (Wikberg and Maunu 2004; Delmotte *et al.* 2008); however, the ratio of the relative intensities of the signals at 88 ppm of crystalline cellulose C-4 and at 84 ppm of C-4 of amorphous cellulose were notably increased (Wikberg and Maunu 2004). This indicated an increase in crystallinity of the hot-pressed corn stalk. This fact also agreed with the XRD determination of the original and treated corn stalks. There are two reasons for an increase in crystallinity. One reason is the degradation of a portion of amorphous cellulose during heat treatment of corn stalks. This is because a slight shoulder on the C-6 peak, associated with amorphous cellulose, decreased considerably, and the C-6 peak became more defined in Fig. 4 (Bhattacharya *et al.* 2008). The second reason could be that part of the amorphous region of cellulose from corn stalks transformed into crystalline region from elimination by the heat treatment, resulting in an increase in the amount of crystalline cellulose (Murate *et al.* 2008). In addition, no obvious change was observed in the aromatic carbon region of lignin from the CP/MAS ^{13}C -NMR spectra of original and treated corn stalks.

Table 2. Chemical Shifts and Assignments of Major Signals in the CP/MAS ^{13}C NMR Spectra of Original Corn Stalk (A) and Hot-pressed Corn Stalk (B)

Chemical Shifts (δ , ppm)		Assignments ^a
A	B	
173.5	173.5	-COO- in aliphatic acetyl
159.8	159.6	C-4 in FA and CA esters
153.8	153.3	C-3/C-4 in S etherified
148.1	148.3	C-3/C-4 in S, C-3/C-4 in G
127.7	126.3	C-1/C-4 in S, C-1/C-6 in G, C-1 in H, C-2/C-6 in FA and CA esters
115.7	116.1	C-3/C-5 in FA and CA esters, C-3/C-5 in H, C-5 in G
105.3	105.2	C-1 of cellulose
88.8	88.9	C-4 of crystalline cellulose
84.2	84.1	C-4 of amorphous cellulose
74.7 to 72.8	75.1 to 72.7	C-2/C-3/C-5 of cellulose
64.6	64.8	C-6 of cellulose
56.6	56.1	methoxyl groups in lignin
21.4	21.3	-CH ₃ of acetyl

^aAbbreviation: G: guaiacyl units; S: syringyl units; H: p-hydroxyphenyl units; FA: ferulic acid; CA: p-coumaric acid

^{13}C -NMR Analysis

MWL is known to represent the “true” lignin structure in wood (Hu *et al.* 2006). To gain an understanding of the variation among native lignin characteristics during heat treatment, MWL was isolated from original and treated corn stalks and analyzed by ^{13}C NMR (Fig. 5). The signals were assigned based on the reports of Lüdemann and Nimz (1973), Xie and Terashima (1993), and Sun *et al.* (2005). The presence of the absorption peaks at 166.7 ppm, 162.8 ppm, 160.2 ppm, 130.5 ppm, 125.4 ppm, and 111.6 ppm originated from ferulic acid (FA) and p-coumaric acid (CA), indicating that there were ferulic acid and p-coumaric acid substructures in the lignin samples of the corn stalk (Fig. 5).

The region from 104 ppm to 160 ppm was assigned to the aromatic portion of the lignin molecule. Syringyl (S) units appeared at 152.7 ppm (C-3/C-5, etherified), 148 ppm (C-3/C-4), 135.7 ppm (C-4), 132.9 ppm (C-1), 106.8 ppm (C-2/C-6 with α -CO), and 104.8 ppm (C-2/C-6). The guaiacyl (G) units were detected by signals at 150.9 ppm (C-3, etherified), 148 ppm (C-3/C-4), 144.7 ppm (C-4), 135.7 ppm (C-1), 132.9 ppm (C-1), 121.1 ppm (C-6), 119.8 ppm (C-6), 116.2 ppm (C-5), and 111.8 ppm (C-2).

Excluding the signals appearing at 132.9 ppm, 128.4 ppm, and 111.6 ppm, all of the other signals originated from p-hydroxyphenyl (H) units. Therefore, the lignin of corn stalk contained three basic structural units: H, G, and S.

When the spectrum of the MWL sample from original corn stalk was compared with that of the treated sample, a reduction in the relative intensity of the signal at 152.7 ppm and an increase in the relative intensity of the signal at 148.1 ppm appeared (Fig. 5). This result indicated the cleavage of a substantial portion of the β -O-4 linkages in lignin (Wikberg and Maunu 2004).

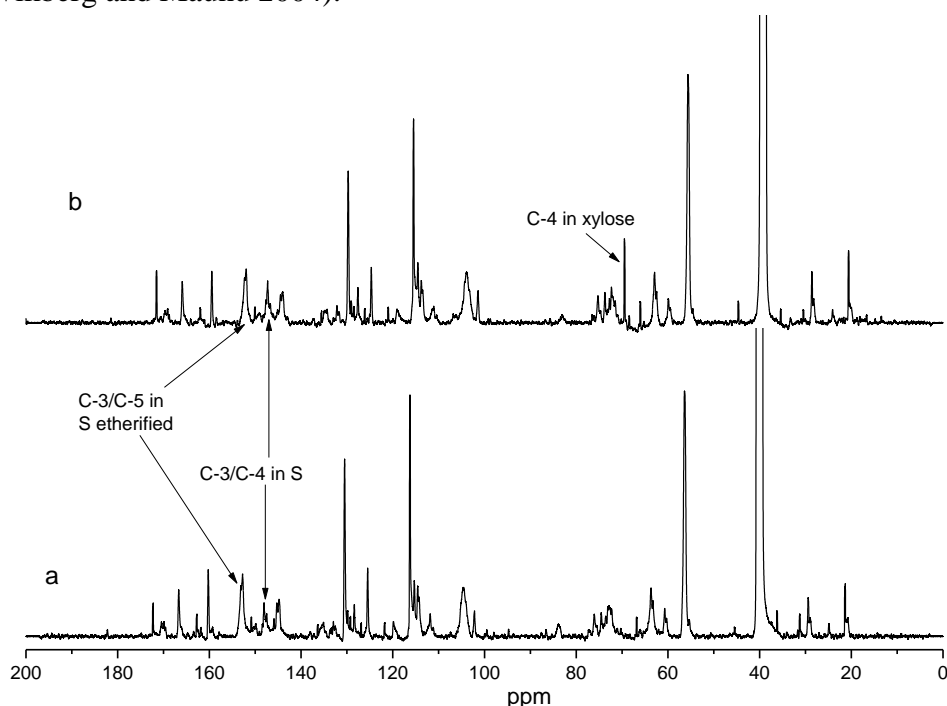


Fig. 5. ^{13}C NMR spectra of MWL samples from a) original corn stalk and b) hot-pressed corn stalk

A remarkable enhancement in ^{13}C resonance was noted at 70.2 ppm, which was assigned to the C-4 in xylose (non-reducing end unit; Fig. 5). Matsushita *et al.* (2004) reported the sulfuric acid-induced condensation between carbohydrates and the lignin model compounds.

According to results by Matsushita *et al.* (2004), it was concluded that acid-catalyzed condensation occurred between lignin and xylose from hemicellulose under acidic conditions. This resulted from the liberation of acetic acid from acetyl groups in hemicellulose. Degradation of hemicellulose and a portion of amorphous cellulose most likely contributed to a reduction in the self-bonding strength of board; hence, the condensation reaction between lignin and xylose (from hemicelluloses) might contribute to the self-bonding mechanism and the improvement in board properties (Nonaka *et al.* 2013).

Table 3. Chemical Shifts and Assignments of Major Signals in ^{13}C NMR Spectra of MWL Samples from Original Corn Stalk (A) and Hot-Pressed Corn Stalk (B)

Chemical shifts (δ , ppm)		Assignments ^a
A	B	
172.3	172.2	-COO- in aliphatic acetyl
169.9	169.8	C=O in acetyl of second carbon
166.7	166.8	-COO- in FA and CA esters
162.8	162.7	C- γ in FA etherified
160.2	160.2	C-4 in FA and CA esters
152.7	152.7	C-3/C-5 in S etherified
150.9	150.7	C-3 in G etherified
148.0	148.1	C-3/C-4 in S, C-3/C-4 in G
144.7	144.8	C-4 in G
135.7	135.4	C-4 in S, C-1 in G
132.9	132.9	C-1 in G, S and H
130.5	130.5	C-2/C-6 in FA and CA esters
128.4	128.3	C-2/C-6 in H
126.8	126.9	C-6 in G
125.4	125.4	C-1 in FA and CA esters
121.1	121.7	C-6 in G
119.8	119.8	C-6 in G
116.2 to 114.5	116.2 to 114.2	C-3/C-5 in FA and CA esters, C-3/C-5 in H, C-6 in G
111.8	111.8	C-2 in G
106.8	106.0	C-2/C-6 in S with α -CO
104.8	104.4	C-2/C-6 in S
102.1	102.1	C-1 in xylans
83.8	83.9	C- β in β -O-4
76.0	76.0	C-3 in xylose non reducing end unit
74.5	74.5	C-3/C-4 in xylose internal unit
73.1	73.1	C- α in β -O-4
70.2	—	C-4 in xylose non reducing end unit
66.8	66.8	C-5 in xylose non reducing end unit
63.7	63.6	C- γ in β -1, C-5 in xylose internal unit
60.6	60.7	C- γ in β -O-4
56.4	56.3	-OCH ₃
45.4	45.3	unknown
36.2 to 24.8	36.2 to 24.9	-CH ₃ and CH ₂ in saturated aliphatic chain
21.4	21.3	-CH ₃ of acetyl

^aAbbreviations: G: guaiacyl units; S: syringyl units; H: p-hydroxyphenyl units; FA: ferulic acid; CA: p-coumaric acid

GPC Analysis

To investigate the effect of hot-pressing treatment process on the molecular weights of lignin in corn stalk, molecular weight of MWL samples was analysed through GPC. The results of molecular weights and polydispersity of MWL samples are shown in Table 4. It was observed that M_n and M_w of MWL sample hot-pressed corn stalk was slightly lower than that of MWL sample from original corn stalk. This observation confirmed that lignin depolymerization occurred during hot-pressing treatment.

Table 4. Weight-average (M_w), Number-average (M_n) molecular weights and Polydispersity Indexes (M_w/M_n) of MWL Samples from Original Corn Stalk and Hot-Pressed Corn Stalk

MWL sample	M_w	M_n	M_w/M_n
Original corn stalk	11671 ± 137	11127 ± 172	1.049 ± 0.004
Hot-pressed corn stalk	11520 ± 249	10913 ± 299	1.056 ± 0.006

CONCLUSIONS

1. Hot-pressing resulted in the degradation of hemicellulose and a small portion of amorphous cellulose. The crystallinity and crystallite size of cellulose increased after hot-pressing.
2. Hot-pressing partially depolymerized corn stalk lignin through the cleavage of a portion of the β -O-4 linkages.
3. Hot-pressing resulted in the decrease of molecular weight of lignin in corn stalk.
4. Lignin-to-xylose condensation reactions occurred during hot-pressing. These condensation reactions may contribute to the self-bonding mechanism and improvement of board properties.

ACKNOWLEDGMENTS

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