

SPECTROSCOPIC ANALYSIS OF THE INTERFACE FOR WHEAT STRAW SPECIMEN GLUED WITH PMDI

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ABSTRACT

In order to obtain information about chemical characteristics on the interaction between wheat straw and PMDI, the exterior and interior surfaces of wheat straw, and the interface of wheat straw specimen glued by polymeric diphenylmethane diisocyanate (PMDI) resin were scanned by micro-Fourier Transform Infrared Spectroscopy (micro-FTIR) and Electron Spectroscopy for Chemical Analysis (ESCA), respectively. The specimens of pure cellulose and the reacted mixture of cellulose with PMDI resin were analyzed by FTIR and cross polarization/magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS C-13 NMR). Scanning by micro-FTIR showed that the major differences in functional groups between exterior and interior surfaces for the same section of wheat straw appeared in the fingerprint region (400 cm^{-1} to 1500 cm^{-1}). There were a few differentiated peaks in the region of $1174\sim 1000\text{ cm}^{-1}$ for the interior surface, whereas there was greater absorption in the exterior surface than in the interior surface, especially at 987 cm^{-1} . Generally, there were reaction functional groups ($-\text{OH}$) on exterior and interior surfaces for wheat straw. ESCA scanning and curve-fitting of the $\text{C}_{1\text{S}}$ peaks showed that the relative content of the functional group on the exterior surface differed from that of the interior surface. Results of ESCA scanning of the interface for wheat straw specimen glued with PMDI indicated that the glued interface chemically adsorbed PMDI resin. Furthermore, the contents of functional groups of the interface specimen glued with PMDI differed from those of the specimen without PMDI. Using FTIR and CP/MAS C-13 NMR, the results imply that $\text{N}=\text{C}=\text{O}$ functional group for PMDI could react with cellulose.

Keywords: CP/MAS C-13 NMR, ESCA (XPS), functional group, interface, micro-FTIR, PMDI resin, wheat straw.

INTRODUCTION

Since the 1940s, the chemistry and applications of polyisocyanates have been discussed

(De Bruyne 1965). The term polyisocyanate can be defined as an aliphatic or aromatic isocyanate containing two or more isocyanate groups ($\text{N}=\text{C}=\text{O}$). Isocyanate-based resins have been used for wood binding applications since the early 1970s. While many such resins are com-

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mercially available for bonding wood composites, the most commonly used resin is based on polymeric diphenylmethane diisocyanate or PMDI. PMDI and its modifications have a strong influence on the final properties of bonding materials and coatings. Crosslinkage properties, viscosity, and miscibility depend directly on the polymer PMDI version used (Gurke 2002).

PMDI binders are currently used worldwide in the wood industry because of their fast curing rate, improved moisture resistance, tolerance to high furnish moisture, and lack of formaldehyde emissions (Moriarty 1999). Small quantities of PMDI resin can result in excellent adhesion in wood composites and provide composites with desirable properties. This kind of adhesive and its modifications offer wood composite manufacturers a broad range of conditions under which to optimize their processing conditions, such as high moisture contents, low dryer temperatures, and low pressing temperatures.

The basic adhesion mechanism of PMDI is better suited to high moisture content pressing than that of conventional formaldehyde-based resins. In contrast to the conventional resins, PMDI not only creates a mechanical adhesion, but also forms strong chemical and physical bonds. PMDI reacts with both wood and water present in the wood. Many studies have shown that urea and urethane linkages are present after the reaction of PMDI with wood (Gaboriaud and Vantelon 1982; Chelak and Newman 1991; Jung et al. 2000; Harper et al. 2001).

Wheat (*Triticum aestivum* L.) straw is an annual herbage plant with a structure that differs from that of wood. The fissile and vegetal tissues of herbage plants are chiefly distributed in twigs and joints. There is no fissile or vegetal tissue at the hypodermis. When wheat grows, the stem of wheat straw does not become very thick across the grain direction, but extends along the grain direction. Wheat straw consists of the spike, stem, leaf, and root—all distinguishable with the naked eye (Paper and Pulp Manual 1987).

The chemical components of wheat straw are similar to those of wood. The major chemical components of wood are cellulose, hemicellu-

lose, lignin, and some extractives. The main difference between wheat straw and wood is wheat straw's high silica and wax content, concentrated primarily on the surface.

Different spectroscopic analyses have been used to study cellulosic materials. Some researchers employed cross polarization/magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS C-13 NMR) and wide-angle X-ray spectroscopy (WAXS) to assess the influence of starting cellulose materials on the transition between cellulose polymorphs (Takahashi and Ookubo 1994). Hirai et al. (1985) studied the differences in fiber structure between cotton and cuprammonium rayon by using proton NMR analysis. Kazayawoko et al. (1999) characterized maleated polypropylene-treated wood fibers in a high-intensity thermokinetic mixer using X-ray Photoelectron Spectroscopy (XPS). Matuana et al. (2001) studied the surface characterization of esterified cellulosic fibers using XPS and FTIR spectroscopy.

Liu et al. (2002) and Su et al. (2002) analyzed the elements of carbon (C), oxygen (O), nitrogen (N), and silicon (Si) on the wheat straw surface with Electron Spectroscopy for Chemical Analysis (ESCA). In the different sections of wheat straw, C content decreased from the exterior surface to the interior surface, but O and N contents increased; Si content was greatest in the middle section (the interface between exterior surface and interior surface along the same stem). In addition, Liu et al. (2004) carried out a study on the surface structure and dynamic adhesive wettability of wheat straw with SEM and a contact angle instrument. The objectives of this current study is to focus on the chemical characterization of the surface and interface between wheat straw and the PMDI resin using micro-Fourier Transform Infrared Spectroscopy (micro-FTIR), ESCA, and CP/MAS C-13 NMR. In order to characterize the reaction between wheat straw and PMDI, pure cellulose instead of wheat straw was used in this experiment. FTIR and CP/MAS C-13 NMR were also used to characterize cellulose and the reacted cellulose with PMDI resin obtained by hot-pressing in a miniature press. The specific spectroanalysis included:

1. Scanning and analyzing the functional groups on the exterior and interior surfaces of wheat straw specimen using micro-FTIR and ESCA;
2. Analyzing the interfacial chemical characterization of wheat straw specimen glued with PMDI resin using ESCA and micro-FTIR;
3. Assigning peaks and chemical shifts of the cellulose and analyzing the reacted mixture of cellulose and PMDI resin by hot-pressing in a miniature press using FTIR and CP/MAS C-13 NMR.

MATERIALS AND METHODS

Materials

Wheat straw was obtained from outside Zhengzhou City, He-Nan Province, P.R. China. After harvesting, the material was air-dried in airing shelves for several months. The moisture content of the wheat straw used in the experiment was 7.7%.

The PMDI resin was prepared in the adhesives laboratory of Northeast Forestry University. Resin color was dark brown to black; pH value was 6.3; nonvolatile content was 71.5%; and viscosity at 20°C was 260 cps. The density of the PMDI was $1.29 \text{ g} \cdot \text{cm}^{-3}$. The free -NCO was 14.5%. The crystalline cellulose was purchased from a chemical company in Harbin, P.R. China. Its purity was above 98%.

Methods

FTIR Analysis for wheat straw specimen.—The exterior and interior surfaces of wheat straw, and the interface of wheat straw specimen

glued with PMDI resin were scanned and analyzed using micro-FTIR (MAGNA IR560, Nicolet, USA). In order to simulate the interface of wheat straw/PMDI formed during hot-pressing wheat straw-based particleboard, specimens with exterior-to-exterior surfaces or interior-to-interior surfaces of wheat straw were glued together with PMDI and then hot-pressed in a miniature press (REGER Ltd., Shenzhen, P.R. China). The procedure for preparing the interface of wheat straw/PMDI specimen is illustrated in Fig. 1. The experimental conditions used in the wheat straw gluing were given as follows:

Materials: the natural wheat straw was divided into two parts with a knife and then cold-pressed in the miniature press

Specimen dimensions: 5 mm wide by 80 mm long

PMDI resin loading: about 6% based on dry straw weight

Pressure: 2 MPa

Hot-pressing temperature: $165 \pm 3^\circ\text{C}$

Hot-pressing time: 6 min

The adhesive loading was controlled by a precise balance after coating on relevant surface of wheat straw. The glued specimens were then stored in a conditioning room (20°C, 60% RH) for two days. The specimens were peeled off along the glued interface and separated into two pieces. The separated interface was then scanned from 4000 cm^{-1} to 400 cm^{-1} by micro-FTIR. Meanwhile, the control sample (corresponding to the straw surface without coating PMDI) was also scanned by micro-FTIR.

ESCA analysis for wheat straw specimens.—ESCA (ESCA750, made in Japan), also known as X-ray Photoelectron Spectroscopy (XPS),

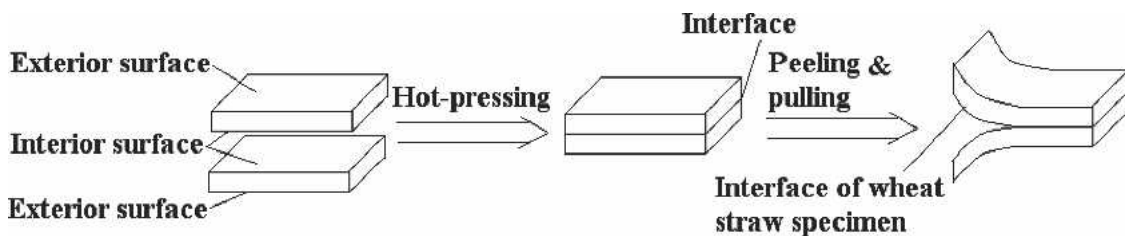


FIG. 1. The scheme of preparation of interface for wheat straw specimen glued with PMDI resin

was used to obtain information about chemical characterization of the surface and interface of the wheat straw specimens. ESCA allows one to quantitatively detect an elemental composition, which can suggest functional groups in the surface to a depth of about 0.1–1 nm (Andrade 1985; Briggs and Seah 1985). In the experiment, the exterior and interior surfaces of wheat straw as well as the interface of the wheat straw after PMDI gluing, all of which were prepared in the same way as for FTIR analysis, were detected by ESCA with a magnesium $K\alpha$ source (1253.6 eV). The magnesium $K\alpha$ source was operated at 8 kV and 30 mA. The straw specimen was mounted on a holder with double-sided adhesive tape and placed in a vacuum with pressure below 5×10^{-5} Pa. The analyzed sample area was about 4 mm \times 7 mm. The spectra were deconvoluted using curve-fitting software. In general, different oxidation states of carbon atoms characterize different binding energies. The binding energy of 285.0 ± 0.4 eV is the result of the bonding of C–C (C–H), the binding energy of 286.5 ± 0.4 eV results from the bonding of C–O; 288.0 ± 0.4 eV is related to the bonding of C=O (O–C–O); and 289.5 ± 0.4 eV is the result of the bonding of O=C–O (Wang et al. 1992; Kazayawoko et al. 1999).

NMR and FTIR analyses for cellulose and PMDI.—Cellulose and the reacted mixture of cellulose with PMDI were tested with the CP/MAS C-13 NMR (INOVA 500 NMR, Varian, USA). The cellulose was mixed with PMDI resin (cellulose: PMDI \approx 100:6(w/w)) and then hot-pressed at $165^\circ\text{C} \pm 3^\circ\text{C}$ and 2.0 MPa for 6 minutes in the miniature press. A solid slice was transferred to a carnelian mortar and ground completely in preparation for the FTIR and CP/MAS C-13 NMR analyses. For NMR study, the sample was put in a 5-mm TLT probe and tested under the control of the magnetic field intensity of 500 MHz at a rotation speed of 3000 r/sec. For FTIR analysis, part of the slice was weighed and transferred to the carnelian mortar and blended with potassium bromide (KBr); it was then ground completely and made into FTIR samples. The FTIR scanning of cellulose, PMDI

resin, and their reaction mixture was conducted respectively.

RESULTS AND DISCUSSION

Functional groups on the surface of wheat straw

The exterior and interior surfaces sampled from the same section of wheat straw were scanned by micro-FTIR (Fig. 2). The peaks at 3444 cm^{-1} and 3419 cm^{-1} resulted from the O–H stretching vibration, while the peaks at 2901 cm^{-1} and 2894 cm^{-1} from the C–H stretching vibration. The peak at 1636 cm^{-1} was due to the absorbed H_2O . The peak at 1433 cm^{-1} was associated with the deformation (bending) vibration of $-\text{CH}_2$. In the region of 1175 cm^{-1} to 1000 cm^{-1} , the peaks were thought to be the result of C–O–H or C–O–C deformed vibration. As shown in Fig. 2, the main differences in the two FTIR curves were in the fingerprint region below 1500 cm^{-1} . The significant differences between the interior surface (Curve 2) and the exterior surface (Curve 1) were the peaks at 1175 cm^{-1} , 1132 cm^{-1} , and 1082 cm^{-1} . The three peaks were assigned to C–O–H or C–O–C deformation vibration peaks (Browning 1963). In general, these results indicate the C–O–H or C–O–C functional groups on the interior surface were greater in number than on the exterior surface.

FTIR analysis of interface for wheat straw specimen glued by PMDI

By comparing curve gj (exterior surface glued with PMDI) with curve gb (exterior surface before gluing), and curve cj (interior surface glued with PMDI) with curve cb (interior surface before gluing), it was found that one weak absorbed peak appeared at 2276 cm^{-1} (Fig. 3). For the cj and gj curves, the peaks at 2276 cm^{-1} and 1700 cm^{-1} were assigned to $\text{N}=\text{C}=\text{O}$ and $\text{C}=\text{O}$ stretching vibrations, respectively. The two peaks at 1602 cm^{-1} and 1500 cm^{-1} were assigned to $\text{C}=\text{C}$ skeletal in-plane vibration in the benzene ring. The peak at 2276 cm^{-1} in the

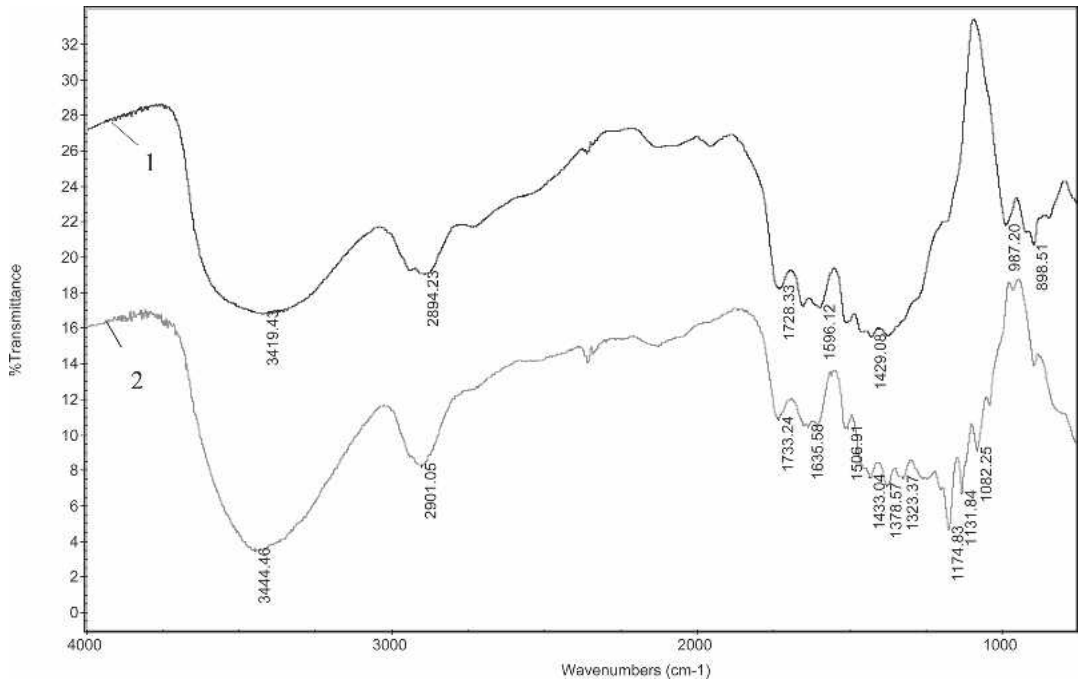


FIG. 2. FTIR spectra of interior and exterior surfaces in the same section for wheat straw; 1. Exterior surface; 2. Interior surface.

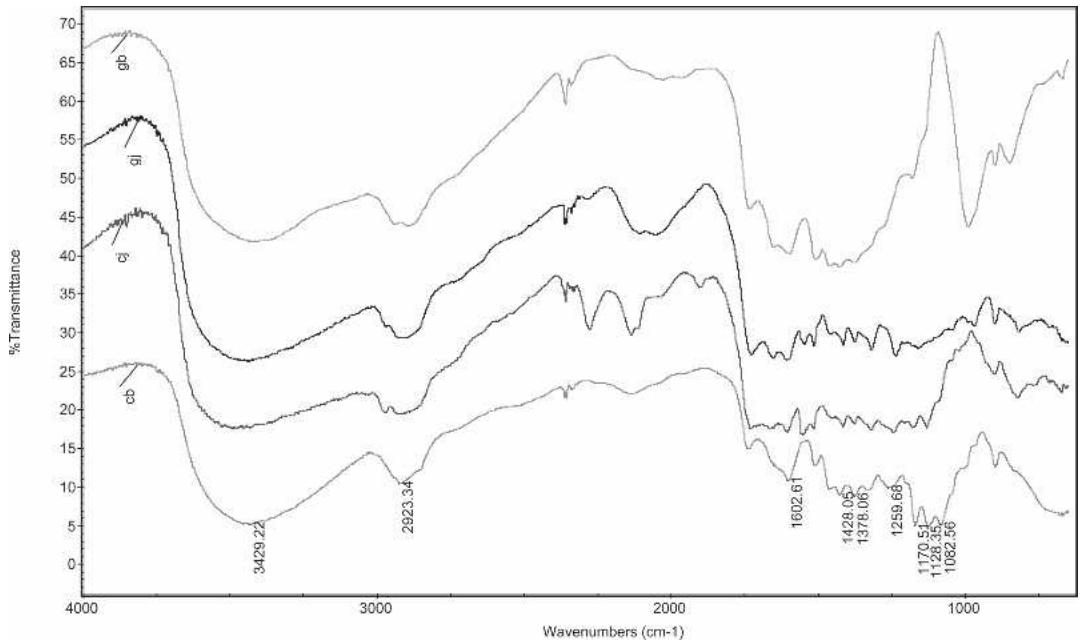


FIG. 3. FTIR spectra of interior and exterior surface for wheat straw with and without PMDI resin; gj—Spectrum of the exterior surface after gluing; gb—Spectrum of the exterior surface before gluing; cj—Spectrum of the interior surface after gluing; cb—Spectrum of the interior surface before gluing.

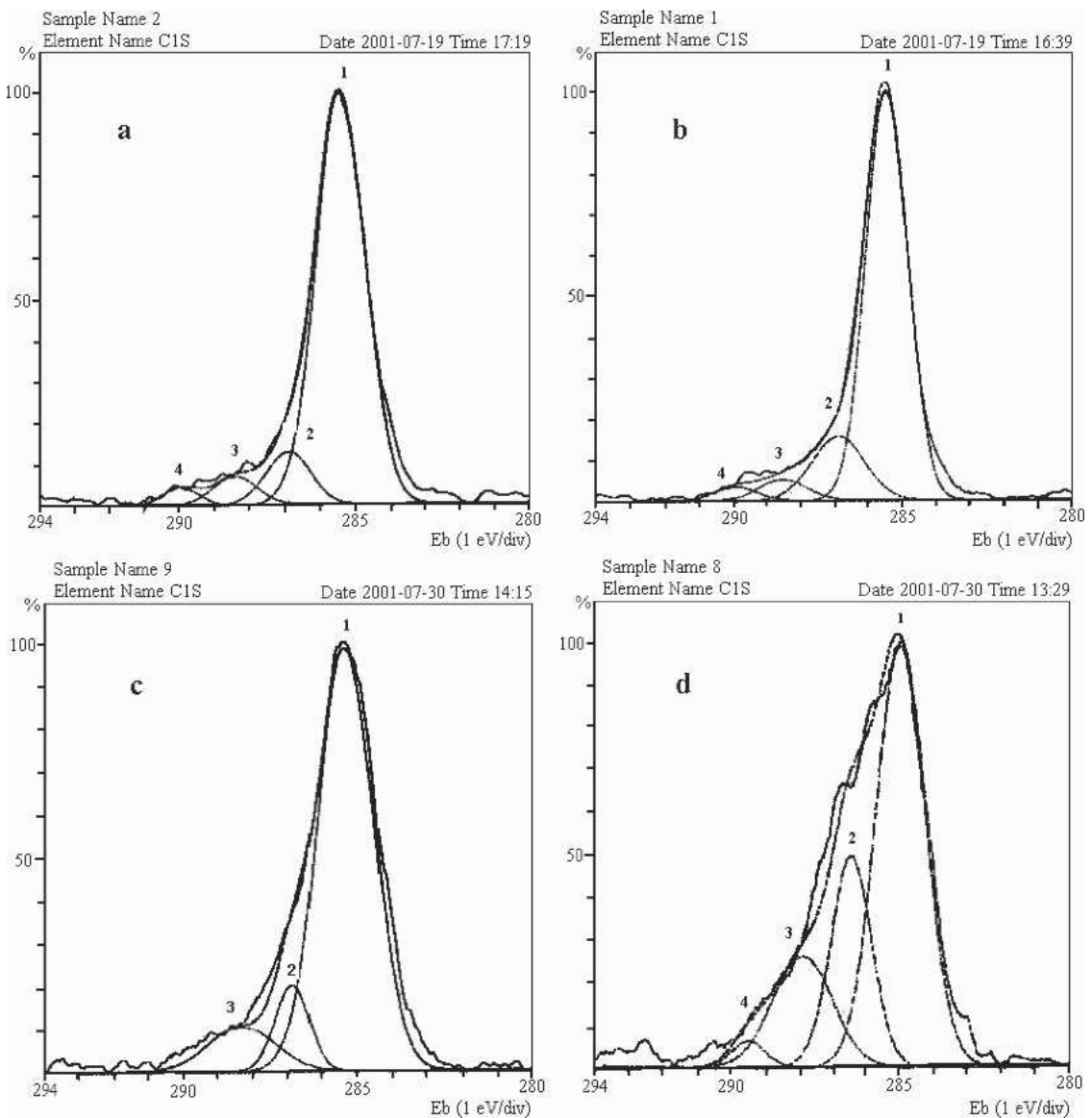


FIG. 4. C_{1s} Curve for different samples: a—Exterior surface of wheat straw; b—Interior surface of wheat straw; c—Exterior surface of wheat straw glued by PMDI resin; d—Interior surface of wheat straw glued by PMDI resin.

cj and gj curves showed that there was a small quantity of N=C=O functional group. Moreover, the peaks at 1602 cm^{-1} and 1500 cm^{-1} also indicated there were aromatic compounds on the interface of the specimen. These peaks in cj and gj curves proved that PMDI was cured on the interface of the glued wheat straw specimen. These results implied that PMDI could be cured

and reacted on the exterior and interior surfaces of wheat straw.

ESCA analysis of interface for wheat straw specimen glued by PMDI

Interface of the wheat straw specimen glued by PMDI, the exterior surface, and the interior

surface of wheat straw were scanned by ESCA. The curves for 1S electron of carbon (C_{1s}) for different samples are shown in Fig. 4, and the curve-fitting results are summarized in Table 1.

There were obvious differences in functional group contents between exterior and interior surfaces for wheat straw without PMDI resin (a vs. b in Table 1). The exterior surface contained a high quantity of C–C (C–H) (82.8%), but the quantity of the oxygenated functional groups was small: C–O (9.5%), C=O (5.1%), and –COO (2.5%). The very high quantity of C–C (C–H) functional group is interpreted as indicating that there was a much higher quantity of fat and wax on the exterior surfaces. On the other hand, the interior surface of wheat straw, compared with the exterior surface, contained more C–O functional group (15.6%). This indicates that chemical reaction with the interior surface could be more likely than with the exterior surface of wheat straw.

After PMDI gluing of the interior and exterior surfaces, ESCA scans showed that the content of functional groups (C=O and C–O) on the exterior surface after gluing was higher than before gluing (C=O: 10.5% vs. 5.1%; C–O: 10.2% vs. 9.5%, respectively). The same trend was observed for the interior surface (C=O: 17.7% vs. 4.7%; C–O: 23.6% vs. 15.6%, respectively). These results imply that the chemical character-

ization of the glued interface changed after PMDI gluing. This change could be attributed to the chemical reaction between most of PMDI and the interior and exterior surfaces.

NMR and FTIR analyses of cellulose and PMDI

The FTIR spectra of non-hot-pressed cellulose, liquid PMDI resin, and their hot-pressed mixture are illustrated in Figs. 5a, 5b, and 5c. In Fig. 5a, the peak at wavenumber 3415 cm^{-1} was assigned to O–H stretching. The peak at 2902 cm^{-1} was assigned to C–H stretching, while the peak at 1644 cm^{-1} to the absorbed H_2O . The peaks at 1370 cm^{-1} and 1282 cm^{-1} were associated with C–H deformation (bending) vibration. However, the peaks at 1164 cm^{-1} , 1115 cm^{-1} , and 1060 cm^{-1} were related to C–O and C–C stretching and CH_2 swing vibrations (Nikitin 1966). Among the peaks in Fig. 5b, the peak at 3335 cm^{-1} was assigned to N–H stretching, and 2978 cm^{-1} to C–H stretching. The peak at 2277 cm^{-1} was assigned to N=C=O stretching. C=O stretching vibration appeared at 1738 cm^{-1} , and the skeletal vibration of benzene ring appeared at 1609 , 1558 , 1526 and 1446 cm^{-1} . The assignment of Fig. 5c is summarized in Table 2. Figure 5c indicates that part of the cellulose and PMDI reacted because of the change

TABLE 1. The results of curve fitting for wheat straw glued by PMDI and wheat straw not glued.

Sample	Peak no.	Binding energy (eV)	Functional group	Relative content of functional group (%)
Exterior surface of wheat straw (a)	1	285.40	C–C (C–H)	82.84
	2	286.90	C–O	9.53
	3	288.40	C=O (O–C–O)	5.13
	4	289.95	–COO	2.50
Interior surface of wheat straw (b)	1	285.45	C–C (C–H)	77.07
	2	286.90	C–O	15.64
	3	288.55	C=O (O–C–O)	4.65
	4	289.95	–COO	2.64
Exterior surface glued by PMDI (c)	1	285.30	C–C (C–H)	79.34
	2	286.85	C–O	10.20
	3	288.30	C=O (O–C–O)	10.46
	4	289.80	–COO	0.00
Interior surface glued by PMDI (d)	1	285.25	C–C (C–H)	56.54
	2	286.75	C–O	23.55
	3	288.20	C=O (O–C–O)	17.65
	4	289.80	–COO	2.26

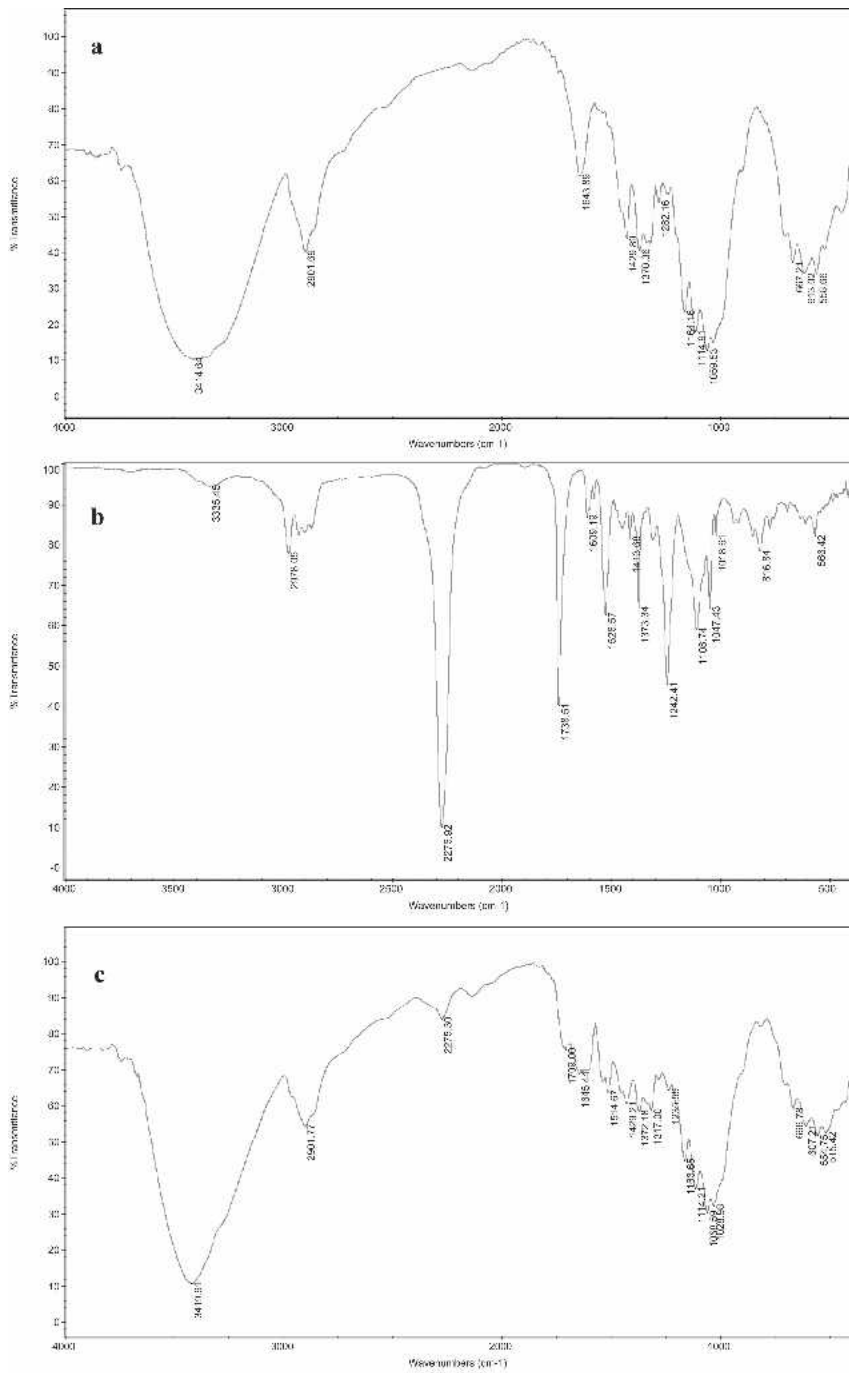


FIG. 5. FTIR spectra for different substances: a—Non-hot-pressed cellulose; b—Liquid PMDI resin; c—Reacted mixture of cellulose and PMDI resin.

TABLE 2. The peaks assignments of FTIR spectra for the reacted mixture of cellulose and PMDI.

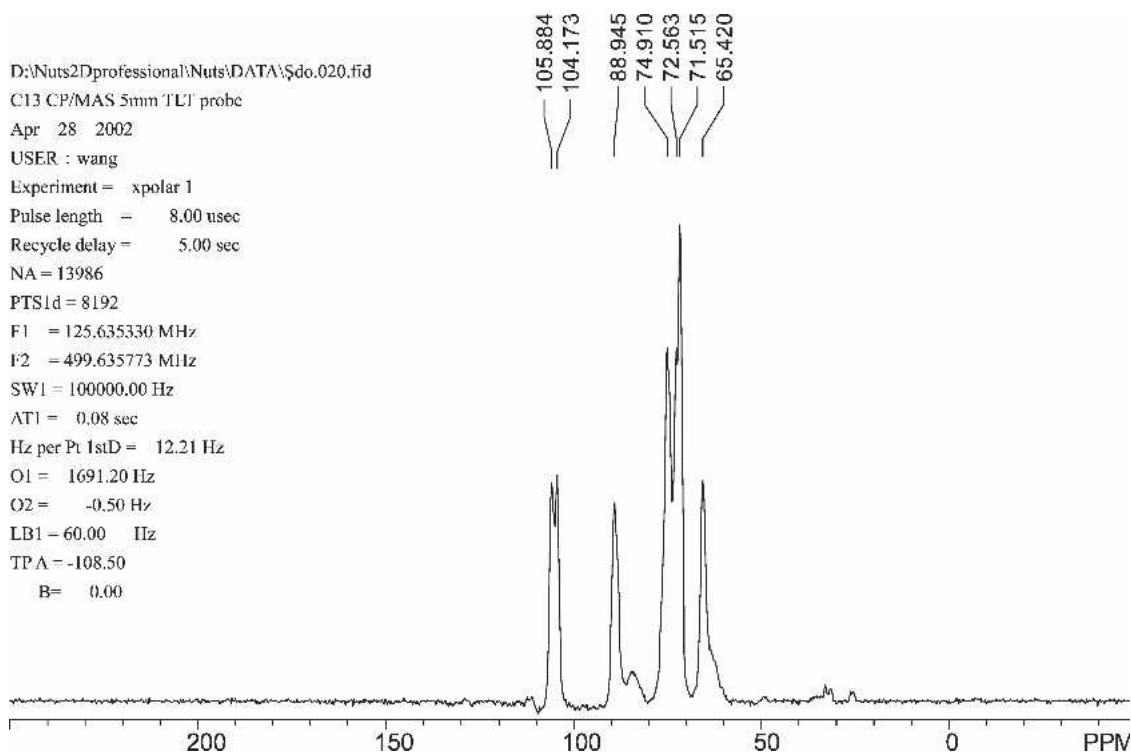
Wave-number/cm ⁻¹	Assignment	Wave-number/cm ⁻¹	Assignment
3420	OH or NH stretching	1600	Skeletal vibration of benzene ring
2902	CH stretching	1526	
2275	N=C=O stretching	1515	
1709	C=O stretching	1447	

of N=C=O peak intensity (2275 cm⁻¹) and the appearance of carbonyl group of a urethane (1709 cm⁻¹).

The non-hot-pressed cellulose was analyzed by CP/MAS C-13 NMR (Fig. 6). The chemical shifts of 71.5 ppm~74.9 ppm were assigned to C2, C3, and C5, 104.2 ppm and 105.9 ppm to C1; 88.9 ppm to C4, and 65.4 ppm to C6. The chemical shifts of cellulose from different materials are slightly different. For example, the C1

chemical shifts of cellulose from cotton are 107.0, 106.3, and 105.2 ppm; C6 is 66.3 and 66.2 ppm, C2, C3, and C5 are 76.2, 75.4, 73.5, and 72.5 ppm; and C4 is 89.9 and 89.4 ppm (Horii et al. 1984; Hirai et al. 1985).

The hot-pressed mixture of cellulose and liquid PMDI resin (cellulose: PMDI ≈ 100:6(w/w)) was analyzed by CP/MAS C-13 NMR (Fig. 7). In comparing Fig. 6 with Fig. 7, it is noted that new chemical shifts appeared at 180, 155, 130, 96, and 48 ppm (Fig. 7). The most obvious change was observed for the chemical shift at C6 (65.0 ppm) (Fig. 7). This implies that the free hydroxyl group (-OH) at C6 could react with N=C=O and generate urethane linkage. The chemical shift of 72.0 ppm in Fig. 7 resulted from the overlapped chemical shifts of C2, C3 and C5, suggesting that hydroxyl groups at C2 and C3 could also react with N=C=O to some extent. It was deduced that 180 ppm was the chemical shift of -CO-NH and that perhaps 155

FIG. 6. CP/MAS ¹³C-NMR of cellulose

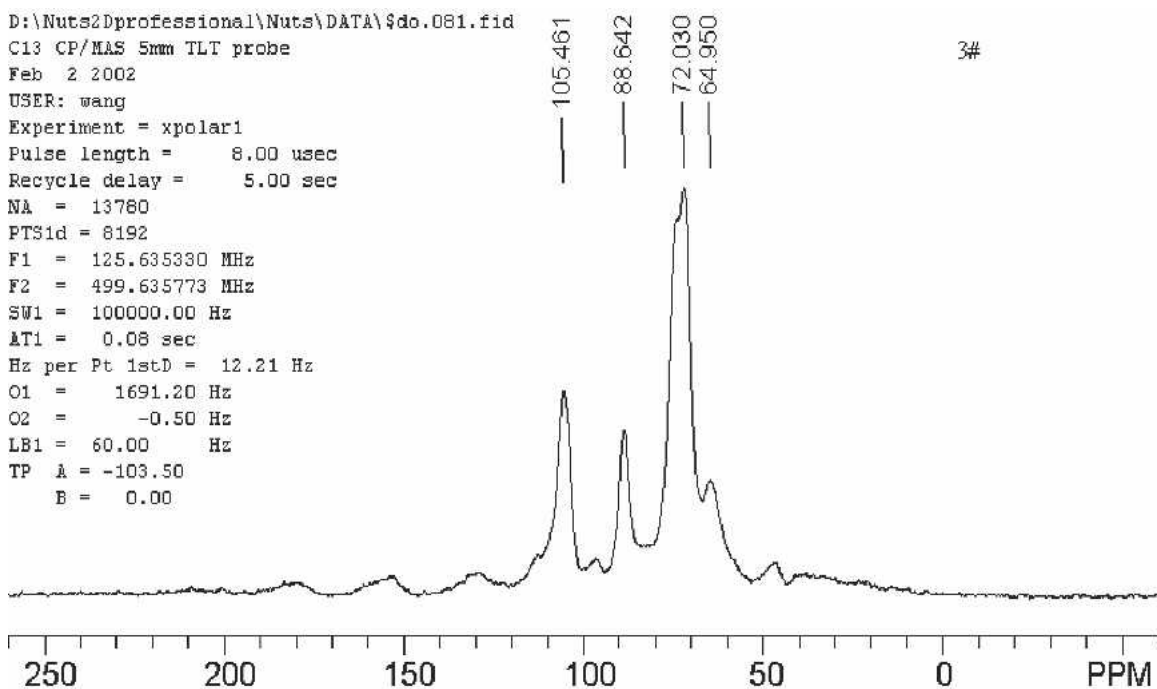


Fig. 7. CP/MAS ^{13}C -NMR for the reacted mixture of cellulose and PMDI resin

ppm was the chemical shift of $-\text{NHCOO}$ or $-\text{HNOC}-\text{NHCOO}$. The chemical shift of benzene ring is 130 ppm, and the chemical shift of $-\text{CH}_2-\text{N}$ is 49 ppm (Horii et al. 1984; Hirai et al. 1985).

CONCLUSIONS

The functional groups on exterior and interior surfaces of wheat straw samples were scanned and analyzed using micro-FTIR. The results showed that there were some differences in functional groups between the exterior and interior surfaces. The main differences in the exterior and interior surfaces for the same section of wheat straw were present in the fingerprint region (400 cm^{-1} to 1500 cm^{-1}). Although there were a few differentiated peaks in the region of $1174\text{--}1000\text{ cm}^{-1}$ for the interior surface, there were differentiated absorption peaks in this region for the exterior surface. These peaks were assigned to $\text{C}-\text{O}-\text{H}$ or $\text{C}-\text{O}$ deformation or bending vibration. This indicated that many

more functional groups ($\text{C}-\text{O}-\text{H}$ or $\text{C}-\text{O}$) existed in the interior surface compared to the exterior surface. In general, there were reactive functional groups ($-\text{OH}$) on exterior and interior surfaces for wheat straw.

The results of ESCA scanning of wheat straw surfaces showed that the relative contents of functional groups on the exterior surface differed from those of the interior surface. This study showed, with ESCA scanning of the interface of PMDI-bonded wheat straw specimen, that the glued interface adsorbed PMDI resin—especially chemical adsorption. Furthermore, the contents of functional groups on the interface of specimen glued by PMDI differed from those for the specimen without PMDI.

With CP/MAS C-13 NMR and FTIR analyses for the reacted mixture of cellulose and PMDI resin, it was observed that new chemical shifts appeared after hot-pressing of the mixture of cellulose and PMDI resin. Furthermore, the chemical shift of C6 changed most obviously compared to the pure non-hot-pressed cellulose and

the reacted mixture of cellulose with PMDI resin. The results imply that N=C=O functional group for PMDI could react with cellulose.

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