# Composition of the Cell Wall in the Stem and Leaf Sheath of Wheat Straw

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**ABSTRACT:** The composition of the cell wall of the stem and leaf sheath of extracted wheat straw was studied with X-ray photoelectron spectroscopy and with a field emission scanning electron microscope equipped with an energy-dispersive microanalysis system. The outer side (epidermal side) had more lignin, and the inner side (lumen side) of the stem was rich in cellulose. The compositions of the two sides of the leaf sheath were a little different. The chemical components for the same tissue at different growth stages were essentially constant, and this indicated that cellulose, lignin, and hemicelluloses deposited in constant proportions in the cell wall of the same tissue during growth. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1236–1240, 2007

**Key words:** cellulose; lignin; ESCA/XPS; biopolymers; electron microscopy

## INTRODUCTION

Agricultural residues such as cereal straw, which represents an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass, have drawn increasing attention in science and applications.[1–6] Straw consists primarily of cell walls that are mainly composed of cellulose, hemicelluloses, lignin, and some other compounds known as extractives that can be extracted by organic solvents, such as ethanol, acetone, chloroform, and toluene.[7,8] Plant cell walls may be considered perfect composite materials on both nanometer and micrometer scales. The investigation of the components of plant cell walls may provide useful information for guiding the preparation of manmade structural composites. Moreover, it may give some direct information on improving the properties of lignocellulosic fiber/thermoplastic polymer composites.[9–12]

Cell walls vary widely with the cell origins and cell types, in both the composition and composition distribution, and this leads to different performances and properties. For example, the epidermal side of the stem is denser and more resistant to water absorption than the lumen side. The surface properties are strongly influenced by the ratios of the cellulose, hemicelluloses, and lignin in the cell walls on the surface of the stem. In the case of wheat-straw tissue, the variations of the cell-wall component ratios on the outer side (epidermal side) and the inner side (lumen side) dominate the properties of the cells. Therefore, it is useful to investigate the composition and composition distribution in wheat-straw tissues.

X-ray photoelectron spectroscopy (XPS) is a widely used surface analysis technique because one can determine the surface composition as well as the electronic environment nondestructively (in many cases), and it is invaluable in many fields of science.[13,14] XPS was first used by Dorris and Gray in their studies of pulp fibers in 1978,[15–17] and then it was used to study the components of extractives and/or lignin on the surface of cellulosic materials, such as pulp samples, fibers, wood surfaces, fiber surfaces in papermaking processes, and even living trees,[18–25] with oxygen-to-carbon atomic ratio (O/C) analysis and the details of the deconvoluted bonding states of the C1s emission line.

In this study, the composition of the cell wall on the outer side and inner side of the wheat-straw stem at different growth stages was investigated with XPS and an energy-dispersive microanalysis system (EDS) on a field emission scanning electron

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microscope. The cell-wall components of the straw leaf sheath were also examined.

## EXPERIMENTAL

The samples were kindly provided by the Agriculture University of China and harvested in the jointing period and heading period, respectively.

The preparation of the sample for XPS and scanning electron microscopy (SEM) was conducted according to the following procedure. Each sample of wheat straw was separated by hand into the stem and leaf sheath carefully and cut into small pieces (ca. 8 mm long), washed several times with distilled water, and then dried at room temperature. The dried wheat straw was packed into extraction thimbles and extracted for 24 h with refluxing anhydrous ethanol/chloroform (1 : 1 v/v) in Soxhlet extractors. Then, the samples were subjected to water extraction at 50°C for 12 h to remove water-soluble substances and then dried at room temperature.[26] After these treatments, contamination on the sample surface and extractives were removed.

The extracted samples were cut into approximately $0.5 \times 0.5$ cm$^2$ pieces with clean tools and then dried in a vacuum desiccator at 40°C for a week. Before the XPS experiment, the samples were allowed to outgas overnight in the turbo-pumped entry chamber.

XPS measurements were carried out with a VG Escalab 220i-XL X-ray electron spectrometer (VG Scientific Ltd., East Grinstead, UK). An Al Kα X-ray source (1486.6 eV) was used as the anode and operated at 15 kV and 18 mA. The pass energy of the analyzer was fixed at 40 eV. The binding energy (BE) scales for these samples were referenced by BE of alkyl C1s being set to 284.6 eV. The standard takeoff angle used for the analysis was 90° from sample areas less than 1 mm in diameter, producing a maximum analysis depth in the range of 6–10 nm.

The relative amounts of different bonded carbons were determined from high-resolution C1s spectra with symmetric Gaussians. Neither the relative peak position nor the relative peak width was fixed in the curve-fitting process. The quantification of the elemental components of wheat straw was based on both C—C (C1 carbon) percentages and the O/C ratios.

A Hitachi S-4300 field emission scanning electron microscope (Hitachi High-Technologies Co., Tokyo, Japan) equipped with a Phoenix energy-dispersive microanalytical system (EDAS) was operated at 15 kV to analyze the bulk elements of the cross section of the wheat straw. The samples for SEM were not coated with gold.

## RESULTS AND DISCUSSION

Although C—C is extremely sensitive to all kinds of hydrocarbons during the preparation and handling of samples, reproducible results are attainable under critical and standardized experimental conditions.[27] Normally, the C1s spectra in XPS can be divided into three peaks: C1, C2, and C3. C1 corresponds to alkyl carbon; that is, the carbon atoms are bonded only to carbon or hydrogen (C—H and C—C bonds) and mainly come from lignin.[17] C2 represents carbon atoms that are singly bonded to a non-ketonic oxygen atom (—C—O—). The theoretical calculation of the relative C1–C3 peak areas of the deconvoluted C1s emission line from the chemical compositions of cellulose and hemicelluloses indicates that there is no difference between them.[19] Therefore, C2 should be attributed to both cellulose and hemicelluloses.[17,28] C3 represents carbon atoms that are doubly bonded to an oxygen atom, that is, bonded to a single ketonic oxygen atom or bonded to two nonketonic oxygen atoms (C=O or O—C—O).[16] The origin of C3 is much more complex than those of C1 and C2, which may come from cellulose, hemicellulose, and lignin and even from extractives from cellulose materials. Moreover, cellulose is theoretically devoid of C1 carbons because of its polysaccharide structure. Pure cellulose and hydrocarbon impurities also have a slight C—C contribution in XPS.[29,30] The latter can be eliminated by a minimum of contact with tools and complete coverage of the tape by the sample. Meanwhile, the contamination from pump oil can get to samples only through a very tortuous path; contamination spread by diffusion is eliminated in the substance.[31] Despite the influences of the impurities mentioned previously, C1 is mainly attributed to the lignin and/or extractives.

The XPS spectra of the samples are shown in Figures 1 and 2, and the deconvoluted data are summarized in Table I. The shapes of the XPS spectra for the outer and inner sides are tremendously different for both the jointing period [Fig. 1(a)] and the heading period [Fig. 1(b)]. The contributions of C1, C2, and C3 to the C1s emission line on the XPS spectra are 77–79, 14–16, and 6–7%, respectively, for the outer side and 43–45, 43–45, and 11–12%, respectively, for the inner side (Table I). The results indicate that there are obvious differences in the compositions of the outer and inner sides of the straw stem in both the jointing and heading periods. The results further indicate that the inner part of wheat straw is richer in cellulose and hemicelluloses than the outer part (and vice versa for lignin). Meanwhile, the contributions of C1, C2, and C3 to the C1s emission line on the XPS spectra of the outer side and inner side are similar to each other for the jointing and heading periods (Table I), and this indicates that there is no obvious difference in the compositions in the jointing and heading periods.

Figure 2 shows the deconvoluted XPS spectra of the C1s emission line for the cell wall of the straw leaf sheath on the outer side and inner side in the

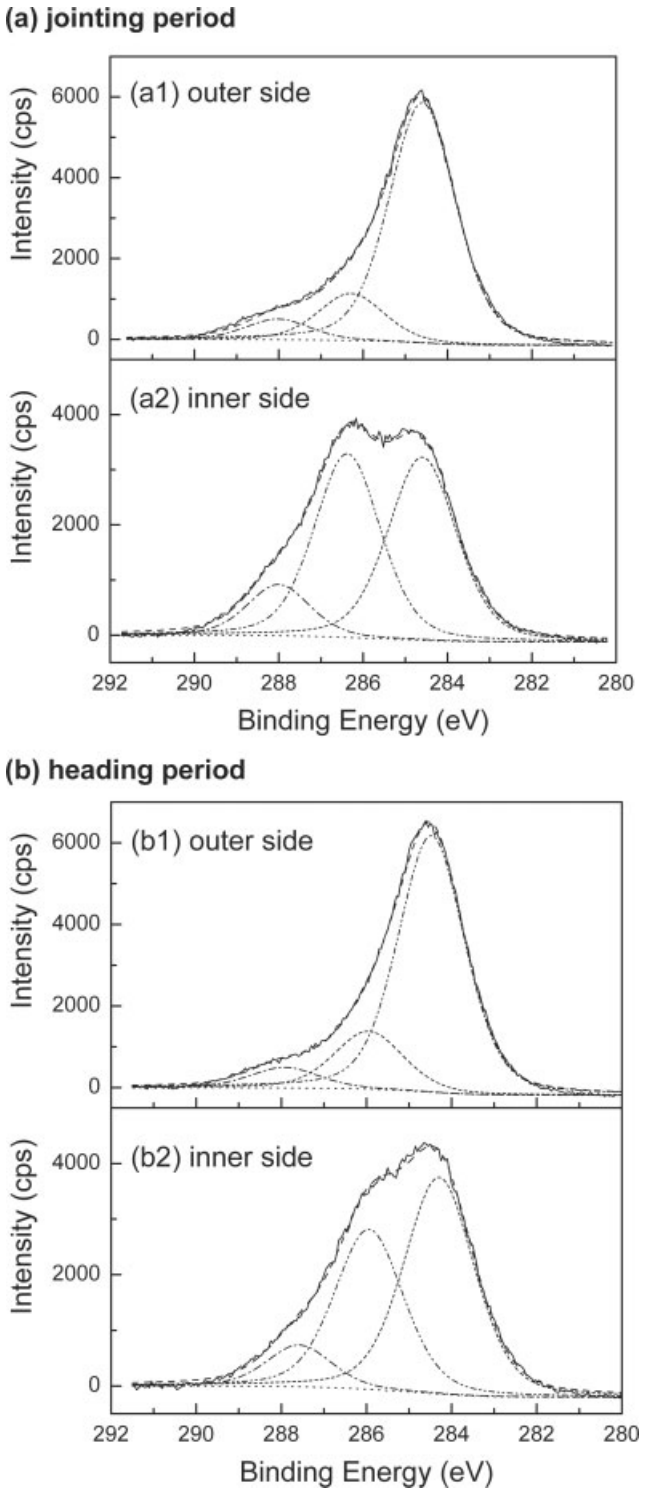


**Figure 1** Deconvoluted XPS spectra of C1s for the stem in (a) the jointing period and (b) the heading period: (a1,b1) the outer side and (a2,b2) the inner side.

jointing period and heading period. The contributions of C1 and C2 to the C1s emission line on the XPS spectra are similar to each other. The concentration of C1 carbon atoms is 82.6% in the outer side and 81.1% in the inner side of the leaf sheath in the jointing period and almost equals the concentration in the heading period within experimental error (78.2 and 80.0%, respectively). The results indicate that the contents of cellulose and hemicelluloses in the inner side are similar to those of the outer side of the leaf sheath and are independent on the growth stages.

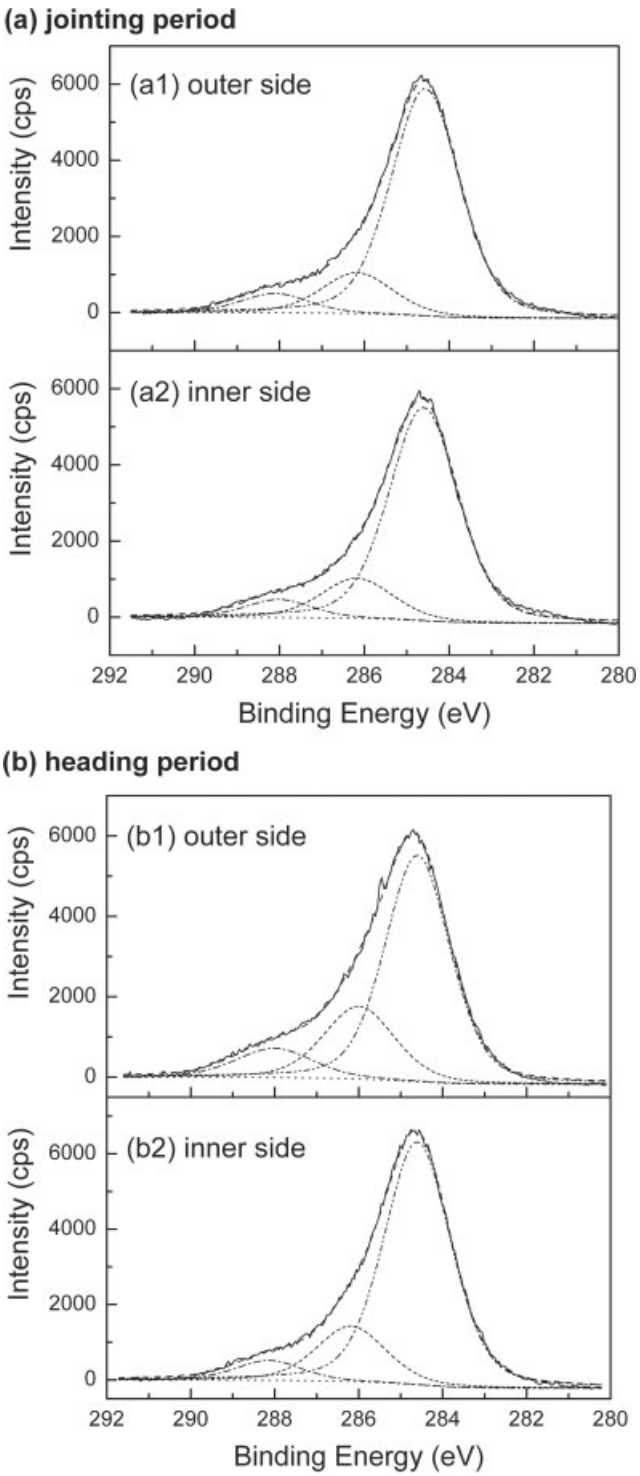


**Figure 2** Deconvoluted XPS spectra of C1s for the leaf sheath in (a) the jointing period and (b) the heading period: (a1,b1) the outer side and (a2,b2) the inner side.

**TABLE I**
**XPS Spectral Parameters of the Samples**

| | C1 | | | C2 | | | C3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample[a] | BE (eV) | fwhm[b] | Atomic ratio (%) | BE (eV) | fwhm | Atomic ratio (%) | BE (eV) | fwhm[b] | Atomic ratio (%) | O/C |
| 1 | 284.60 | 1.85 | 77.3 | 286.30 | 1.89 | 16.0 | 288.10 | 1.80 | 6.7 | 0.2632 |
| 2 | 284.59 | 1.90 | 44.8 | 286.36 | 1.84 | 43.2 | 287.97 | 1.78 | 12.0 | 0.4584 |
| 3 | 284.60 | 1.86 | 78.9 | 286.21 | 1.86 | 14.6 | 288.20 | 1.86 | 6.5 | 0.2230 |
| 4 | 284.61 | 1.99 | 43.6 | 286.21 | 1.98 | 45.2 | 288.01 | 1.97 | 11.2 | 0.4456 |
| 5 | 284.60 | 2.18 | 81.1 | 286.50 | 1.93 | 11.6 | 288.08 | 1.93 | 7.3 | 0.2140 |
| 6 | 284.59 | 1.96 | 82.6 | 286.30 | 1.88 | 11.9 | 288.20 | 1.92 | 5.5 | 0.2689 |
| 7 | 284.61 | 1.88 | 78.2 | 286.30 | 1.88 | 16.1 | 288.15 | 1.88 | 5.7 | 0.2654 |
| 8 | 284.60 | 1.89 | 80.0 | 286.30 | 1.88 | 13.7 | 288.20 | 1.87 | 6.3 | 0.2256 |

[a] 1 = outer side of the stem in the jointing period; 2 = inner side of the stem in the jointing period; 3 = outer side of the stem in the heading period; 4 = inner side of the stem in the heading period; 5 = outer side of the sheath in the jointing period; 6 = inner side of the sheath in the jointing period; 7 = outer side of the sheath in the heading period; 8 = inner side of the sheath in the heading period.
[b] Full wave at half-maximum.

The summarization of the deconvoluted XPS spectra data also shows that a higher content of C2 always corresponds to a higher content of C3 (Table I), and this indicates that the C3 content is related to the cellulose content in the samples. However, the origin of C3 is very complex, as discussed in the beginning of this section; no direct relationship has been found between the content of C3 and the compositions of the samples studied.

The composition of the cellulosic materials can be further characterized by the O/C ratio from the XPS spectra of the samples. The O/C ratio is proportional to the cellulose content in the sample (and vice versa for lignin).[16,17] The theoretical O/C values for pure cellulose/hemicelluloses, pure lignin, and extractives are 0.8–0.83, 0.25–0.33, and 0.04–0.11, respectively.[17,28] As the data in Table I show, the O/C atomic ratio of the stem inner side (samples 2 and 4) is between the theoretical values of the pure lignin and the pure cellulose/hemicelluloses. The O/C atomic ratio of the stem outer side (samples 1 and 3), however, is low, and this also suggests that the inner side of the stem is rich in cellulose and hemicelluloses compared with that of the outer side. Moreover, the O/C atomic ratio in the surface of the stem is higher than that of the leaf sheath, and this indicates that the content of cellulose and hemicelluloses in the surface of the stem is higher than that in the leaf sheath. The O/C ratio results confirm the deconvoluted data of C1s. The O/C ratio is slightly lower than that of pure lignin (0.25–0.33) in some samples but higher than that of extractives (0.04–0.11). This may be attributed to incomplete extraction of the extractable compounds.

For comparison with the results of XPS, three typical sites of the stem from the outer side to the inner side in the cross section of wheat straw were measured via bulk analysis with a field emission scanning electron microscope equipped with an EDS. Figure 3 shows a typical SEM micrograph of a cross section and a typical EDS spectrum of the straw stem in the heading period. The sample positions near the outer side, in the middle, and near the inner side in the cross section of the wheat straw are noted as positions 1, 2, and 3, respectively. The EDS spectrum shown in Figure 3(b) was recorded at position 1. The elemental analysis of the EDS spectra resulted in the O/C atomic ratios, and the corresponding data for positions 1, 2, and 3, are 0.336, 0.4089, and 0.4539, respectively. The results suggest that the content of cellulose and hemicelluloses increases from the outer side to the inner side in the stem, and this agrees with the results of XPS measurements. The value of the O/C atomic ratio at position 1 by EDS (0.336) is higher than that of XPS data at the outer surface of the stem (0.2230 or 0.2632). This is due to the fact that XPS can detect only to a depth of about 10 nm on the surface; the difference in the EDS data at position 1 and the XPS data at the surface of the stem is due to the different sample positions, whereas the content of cellulose and hemicelluloses at the outer

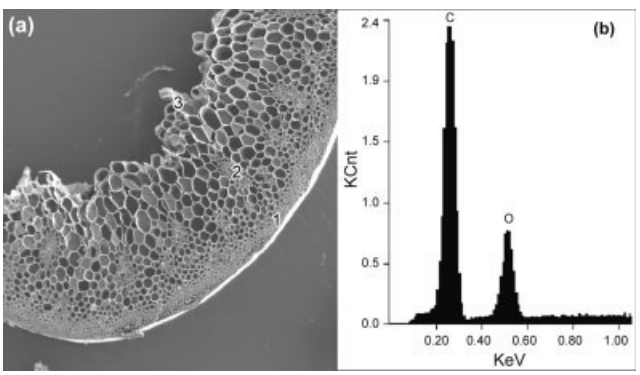


**Figure 3** (a) SEM micrograph of a cross section of the stem and (b) typical EDS spectrum recorded at position 1 on the SEM micrograph.

surface of the wheat-straw stem is lower than that of the inner part. Moreover, the EDS results for the sample in the jointing period are similar to those in the heading period, and this indicates that the composition in the wheat-straw stems is dependent on the growth stages.

It is known that different tissues of plants play different functions. In the case of wheat straw, the outer side of a stem is subjected to tensile and compressive stresses from wind and rain. Meanwhile, lignin plays a major role in mechanical support and stress protection, as well as water-transport regulation, in a plant cell wall.[2] The reduction of the C1 component from the outer side to the inner side of the stem means that the concentration of lignin on the inner surface decreases and the content of cellulose/hemicelluloses on the inner surface increases; this is related relates to its transportation function for nutrition and water on the lumen side of the straw. The compositions on both sides of the leaf sheath are similar and have a higher content of lignin in comparison with the surface of the stem because the leaf sheath acts to protect the wheat straw from any damage by the environment and attack by plant diseases and insect pests.

The chemical components for the same tissues at different growth stages are essentially constant, and this suggests that cellulose, lignin, and hemicelluloses deposit in constant proportions in the cell wall in the same tissue during growth. Meanwhile, the composition differs between tissues, even in the same growth period.

## CONCLUSIONS

The chemical components are significantly different between the outer side and inner side of the wheat-straw stem; the inner side of the stem is rich in cellulose, and the outer side has more lignin. The contents of cellulose for both sides of the leaf sheath are almost the same. The chemical components for the same tissues in different growth stages are essentially constant, and this suggests that cellulose, lignin, and hemicelluloses deposit in constant proportions in the cell wall of the same tissue during growth. The composition differs between tissues, even in the same growth period.

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