6 Physico-chemical Characterisation of Cellulose from the *Broussonetia papyrifera* Bark and Stem, and *Eucommia ulmoides* Oliver Stem

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6.1 Introduction

*Broussonetia papyrifera* (BP), known as paper mulberry, is a dioecious, deciduous and perennial tree or shrub occurring naturally in Asia and Pacific countries such as China, Thailand and USA [1, 2], which is characterised by a higher growth rate and a greater adaptability to adverse environments [3]. It has been cultivated extensively in East, Central and South Asia for papermaking, silk and timber production, and medicinal materials [4, 5]. *Eucommia ulmoides* Oliver, a unique type of plant in China, mainly spreads in the Shanxi, Hunan, Hubei, Sichuan and Yunnan provinces. It has various pharmacological properties including: strengthening tendons and bones, reinforcing muscle, benefiting the liver and kidney, preventing miscarriage, increasing longevity and lowering blood hypertension [6−8]. The leaf and bark of *Eucommia ulmoides* Oliver have been widely used in traditional Chinese medicine for the treatment of hypertension [8, 9], but the remaining stems of *Eucommia ulmoides* Oliver are often burnt as firewood in China. There has been a considerable amount of research based on the traditional medicinal utilisation however, very few investigations report the potential application of the major components of the cell wall.

Cellulose is a linear homopolysaccharide composed of D-glucopyranose units linked together by β-1,4-glycosidic bonds. The β-D-glucopyranose chain units are arranged in a chair conformation, and the secondary OH at the C-2 and C-3, and primary OH at the C-6 position are oriented equatorially. The molecules form microfibrils with partly highly ordered (crystalline) regions and partly less ordered regions (amorphous) by the formation of various strong intermolecular and intramolecular hydrogen bonds [10]. Microfibrils in turn build up into fibrils and finally, into cellulose fibres. The fibrous structure and strong hydrogen bonds give cellulose a high tensile strength and make the fibres insoluble in most solvents [11]. That is, in wood and other higher plants, cellulose is organised mainly into long, thin fibres of the cellulose I allomorph, surrounded by a sheet of hemicelluloses and lignin [12]. Cellulose I consists of two
forms: Iα (triclinic) and Iβ (monoclinic). Both are frequently found to coexist in cell wall structures together with amorphous cellulose [13]. There is little consensus regarding the ratio of cellulose Iα to Iβ in wood. In general, cellulose Iβ is the more abundant form and occurs in an almost pure form in the microfibrils of a wide range of species, from higher plants such as wood, to green algae, to tunicates [14]. In addition, within the fibril, the cellulose chains exist in regions of various degrees of order. Noncrystalline cellulose may be present as distortions in the cellulose lattice and the cellulose chains, located on the fibril surface, are not locked in a three-dimensional structure [15]. It is now well established that when subjected to strong alkali solutions, crystalline native cellulose or cellulose I becomes swollen and upon washing shrinks back to yield a new allomorph, cellulose II [16]. At present, cellulose is the most abundant polymer available worldwide with an estimated annual natural production of $1.5 \times 10^{12}$ tons and is considered as an almost inexhaustible source of raw materials [17]. As a raw material of an enormously underutilised energy resource for the production of paper, panel products, chemicals and other industrial products, cellulose has received much attention all over the world [18]. Within the lignocellulosic materials, cellulose is embedded in a matrix composed of hemicelluloses, lignin and other components [19]. Due to the recalcitrance of the cell wall, the isolation of highly pure cellulose has been the subject of extensive studies for many years [20]. A combination of chemical and mechanical treatments is necessary for the dissolution of lignin, hemicelluloses and other noncellulosic substances [21]. A protocol based on acidified sodium chlorite is frequently applied to delignify woody materials as an initial step in the isolation of cellulose [22]. Alkali extraction, before or after delignification, is the common method to dissolve hemicelluloses. In this work, α-cellulose was isolated from BP bark and stem, and Eucommia ulmoides Oliver stem. The isolated cellulosic preparations were characterised by their yield, content of hemicelluloses, viscosity, molecular weight and thermal stability. In addition, Fourier transform-infrared (FT-IR) and cross polarisation/magic angle spinning (CP/MAS) $^{13}$C solid-state nuclear magnetic resonance ($^{13}$C-NMR) were used to investigate the structural characterisation of cellulosic polymers.

6.2 Experimental

6.2.1 Materials

BP bark and stem (3 and 12 years old) and Eucommia ulmoides Oliver stem (3 years old) were obtained from the experimental farm of North-Western University of Agriculture and Forestry, Yangling, China. The air-dried barks and stems of BP and stems of Eucommia ulmoides Oliver were cut into small pieces, then ground.
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and sieved to obtain a 40–60 mesh powder. The powder was dewaxed with toluene-ethanol 2:1 (v/v) in a Soxhlet apparatus for 6 h to remove fats, waxes and oils, and then air dried. All chemicals used in the experiments were of analytical reagent grade and purchased from the Beijing Chemical Reagent Company, China.

6.2.2 Isolation of Cellulose

Figure 6.1 shows the scheme for the isolation of cellulose from the BP bark and stem (3 and 12 years old), and Eucommia ulmoides Oliver stem. The dewaxed samples were sequentially subjected to extraction with 70% ethanol for 3 h and water at 80 °C for 3 h in a solid-to-liquor ratio of 1:25 (g/mL), in order to isolate 70% ethanol-soluble materials and water-soluble hemicelluloses, and with acidified water at pH 2.0 (adjusted with HCl) at 80 °C for 3 h to isolate pectin substances. The remaining residues were delignified with 6% sodium chlorite at pH 3.6–3.8 (adjusted with 10% acetic acid) at 75 °C for 2 h [23]. The residue, holocellulose, was subsequently washed with distilled water and ethanol, and dried at 60 °C for 16 h. Then the holocellulose was separately extracted at 25 °C with aqueous potassium hydroxide or sodium hydroxide under different conditions. At the end of the extraction, the insoluble residue (cellulose) was collected by filtration, washed thoroughly with distilled water and 95% ethanol until the filtrate was neutral, and then dried in an oven at 60 °C for 16 h. Note that cellulose preparations from the BP bark (3 years old) isolated at 25 °C with 10% KOH for 15 h, 8% NaOH for 15 h and 10% KOH for 18 h were labelled as cellulose preparations C₁, C₂ and C₃, respectively. The cellulose preparation from the Eucommia ulmoides Oliver stem (3 years old) was isolated at 25 °C with 10% KOH for 15 h and labelled as cellulose preparation C₄. The cellulose preparations from the BP stem (3 years old) and bark (12 years old) isolated with 10% KOH for 15 h at 25 °C were labelled as cellulose preparations C₅ and C₆, respectively.
6.2.3 Structural Characterisation of Cellulose

The average degrees of polymerisation (DP) and molecular weight of the cellulotic preparations were determined using the British Standard Methods for the determination of limiting viscosity number of cellulose in dilute solutions, Part 1: cupriethylenediamine (CED) method (BS 6306: Part 1: 1982). The viscosity-average DP \( (P) \) of the samples was calculated by their intrinsic viscosity \([\eta]\) in a cupriethylenediamine hydroxide (cuene) solution using Equation 6.1:

\[
P^0s (mL g^{-1}) = 1.65[\eta] \tag{6.1}
\]
where P is an indeterminate average of DP. The molecular weight of the preparations was then calculated from their P value using a multiplication factor of 162.

The composition of neutral sugars and uronic acids in the cellulosic fractions was determined by high performance anion exchange chromatography (HPAEC). The neutral sugars and uronic acids in the cellulosic preparations were liberated by hydrolysis with 72% H₂SO₄ for 45 min at 25 °C, followed by a high temperature hydrolysis at 105 °C for 2.5 h after dilution to 1.0 M H₂SO₄. After hydrolysis, the samples were diluted 50-fold, filtered and injected into the HPAEC system (Dionex ISC 3000, USA) with an amperometric detector, AS50 autosampler, a CarbopacTM PA-20 column (4 x 250 mm, Dionex) and a guard PA-20 column (3 x 30 mm, Dionex). Neutral sugars and uronic acids were separated in a 5 mM NaOH isocratic (carbonate free and purged with nitrogen) for 20 min, followed by a 0−75 mM NaAc gradient in 5 mM NaOH for 15 min. Then the columns were washed with 200 mM NaOH for 10 min to remove carbonate, followed by a 5 min elution with 5 mM NaOH to reequilibrate the column before the next injection. The total analysis time was 50 min and the flow rate was 0.4 mL/min. Calibration was performed with standard solutions of L-arabinose, L-rhamnose, D-xylose, D-glucose, D-mannose, D-galactose, glucuronic acid and galacturonic acids.

FT-IR spectra of hemicellulosic samples were obtained on an FT-IR spectrophotometer (Nicolet 510) using a KBr disc containing 1% finely ground samples. Thirty-two scans were taken of each sample recorded from 4,000 to 400 cm⁻¹ at a resolution of 2 cm⁻¹ using the transmission mode. CP/MAS ¹³C-NMR spectra were recorded on a Bruker AV-III 400M spectrometer (100 MHz) at 25 °C with a 4 mm MAS probe. About 250 mg of sample was packed into zirconia rotors for MAS. The measurement was performed using a CP pulse program with an acquisition time of 0.034 s, delay time 2 s and with an accumulation of 5,000 scans.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were performed on a simultaneous thermal analyser (SDT Q600, TA Instrument, Selb, Germany) under a nitrogen atmosphere. Samples weighing between 8 and 12 mg were heated from room temperature to 600 °C at a rate of 10 °C/min.

6.3 Results and Discussion

6.3.1 Yield of Cellulose

Alkali extraction is the most efficient method for isolating cellulose from delignified materials by releasing large amounts of hemicellulosic polysaccharides into the
alkaline solution [24]. In particular, a delignification step using chlorite prior to isolating cellulose from holocellulose can significantly facilitate the extraction of hemicelluloses, and thus results in high purity residues of the cellulosic polymers. The yield of six cellulosic preparations, obtained using the alkali treatment on the delignified BP bark and stem, and Eucommia ulmoides Oliver stem is listed in Table 6.1. As can be seen from the table, altering the treatment conditions from 10% KOH to 8% NaOH, resulted in a decrease in the cellulose yield from the delignified BP bark from 50.9% (C₁) to 37.5% (C₂), indicating that the alkali strength played an important role in dissolving the hemicelluloses from the holocellulose of the BP bark, and 8% NaOH was more powerful than 10% KOH for dissolving hemicelluloses. It should be noted that the treatment with 8% NaOH under the given conditions may degrade a small amount of cellulose, giving a lower yield of cellulose. In addition, increasing the treatment time from 15 h to 18 h led to a decrease in cellulose yield from 50.9% (C₁) to 43.9% (C₃), obtained from the delignified BP bark. These results indicate that the relatively higher alkali strength and longer treatment time lead to an increased solubility of the hemicelluloses. The reason for this higher solubility is probably due to the fact that hemicelluloses are mainly present on the outer surface of cellulose, from which they dissolve easily in the alkaline solution. On the other hand, the long cellulose chains are located on the inner parts of the fibres and therefore, are not easily dissolved. Similar results were observed in our previous studies which investigated obtaining cellulose from sugarcane bagasse [25]. Under the same treatment conditions, 10% KOH at 25 °C for 15 h, the yields of cellulose from the delignified BP bark and stem (3 years old), and Eucommia ulmoides Oliver stem (3 years old) are 43.9% (C₂), 42.5% (C₅) and 42.4% (C₆), respectively. In addition, the yield of cellulose obtained from the delignified BP bark (12 years old) is 51.8%, which is higher than the yield (43.9%) of cellulose obtained from the delignified BP bark (3 years old), suggesting that the older BP bark (12 years old) probably had a higher cellulose content or greater number of hydrogen bonds between the hemicelluloses and cellulose than that of the younger BP bark.

### 6.3.2 Sugar Component Analysis

It is well known that cellulose and hemicelluloses are the major components of the secondary layers of the cell wall in lignocellulosic materials. Hemicelluloses interact with cellulose presumably through hydrogen bonds [26]. The sugar components of the cellulosic preparations are presented in Table 6.2. As can be seen, glucose was the predominant sugar component in the six cellulosic preparations, comprising 71.8 to 83.8% of the total sugars, the higher values indicating a higher content of cellulose. While the appearance of a noticeable amount of xylose (5.1–16.9%), and minor amounts of arabinose, rhamnose, galactose and mannose suggest that the cellulosic samples contained noticeable amounts of associated hemicelluloses. The remaining
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Hemicelluloses, which were inaccessible to the alkali solution, suggest that the hemicelluloses in the cell wall of the BP bark and stem, and Eucommia ulmoides Oliver stem are tightly associated with cellulose, probably by hydrogen bonds, coaggregation or chemical linkage [27, 28]. Interestingly, a change in alkali concentration from 10% KOH to 8% NaOH resulted in a distinct enhancement of the glucose content from 71.8 (C1) to 83.8% (C2), indicating again that treatment with 8% NaOH was more powerful than with 10% KOH for releasing hemicelluloses from the holocellulose. In addition, a noticeable increase in glucose content from 71.8% (C1) to 80.1% (C3), upon increasing the extraction time from 15 h to 18 h during the alkali treatments, corresponded to the higher cellulose content and lower residual hemicelluloses in the cellulosic preparations, which reversed the yield of cellulose. The reason for the increase is obviously due to the significant solubilisation or degradation of the macromolecular hemicellulosic polymers during the alkali treatment. As shown in Table 6.2, the cellulosic preparations C4 and C5, obtained by extraction with 10% KOH at 25 °C for 15 h from the delignified Eucommia ulmoides Oliver and BP stem, contained a relatively high amount of glucose, 73.4 and 77.5%, respectively. In addition, the content of glucose (73.7%) in C6 obtained from the delignified BP bark (12 years old) was higher than that (71.8%) in C1 obtained from the delignified BP bark (3 years old). This result showed that the older BP bark (12 years old) probably had a higher content of cellulose, which was in good agreement with the result for cellulose yield.

Table 6.1 Yields and isolating conditions of cellulosic preparations obtained from BP and EU

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Material</th>
<th>Isolating conditions</th>
<th>Yield (% dry matter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>BP bark, 3 years old</td>
<td>10% KOH, 25 °C, 15 h</td>
<td>50.9</td>
</tr>
<tr>
<td>C2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>BP bark, 3 years old</td>
<td>8% NaOH, 25 °C, 15 h</td>
<td>37.5</td>
</tr>
<tr>
<td>C3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>BP bark, 3 years old</td>
<td>10% KOH, 25 °C, 18 h</td>
<td>43.9</td>
</tr>
<tr>
<td>C4&lt;sup&gt;c&lt;/sup&gt;</td>
<td>EU stem, 3 years old</td>
<td>10% KOH, 25 °C, 15 h</td>
<td>42.4</td>
</tr>
<tr>
<td>C5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>BP stem, 3 years old</td>
<td>10% KOH, 25 °C, 15 h</td>
<td>42.5</td>
</tr>
<tr>
<td>C6&lt;sup&gt;c&lt;/sup&gt;</td>
<td>BP bark, 12 years old</td>
<td>10% KOH, 25 °C, 15 h</td>
<td>51.8</td>
</tr>
</tbody>
</table>

<sup>a</sup>C1 and C3 represent the cellulosic preparations obtained by extraction with 10% KOH at 25 °C for 15 h and 18 h from the delignified BP bark (3 years old), respectively.
<sup>b</sup>C2 represents the cellulosic preparation obtained by extraction with 8% NaOH at 25 °C for 15 h from the delignified BP bark (3 years old).
<sup>c</sup>C4, C5 and C6 represent the cellulosic preparations obtained by extraction with 10% KOH at 25 °C for 15 h from the delignified BP and EU stem (3 years old), and BP bark (12 years old), respectively.
Table 6.2 The content of neutral sugars (relative % cellulosic sample, w/w) in the isolated cellulosic preparations

<table>
<thead>
<tr>
<th>Sugars (%)</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabinose</td>
<td>5.5</td>
<td>3.7</td>
<td>4.1</td>
<td>0.4</td>
<td>0.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Rhamnose</td>
<td>0.3</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Galactose</td>
<td>7.4</td>
<td>5.3</td>
<td>6.2</td>
<td>1.1</td>
<td>1.2</td>
<td>7.8</td>
</tr>
<tr>
<td>Glucose</td>
<td>71.8</td>
<td>83.8</td>
<td>80.1</td>
<td>73.4</td>
<td>77.5</td>
<td>73.7</td>
</tr>
<tr>
<td>Xylose</td>
<td>11.3</td>
<td>5.1</td>
<td>6.7</td>
<td>13.6</td>
<td>16.9</td>
<td>9.3</td>
</tr>
<tr>
<td>Mannose</td>
<td>3.7</td>
<td>1.9</td>
<td>2.4</td>
<td>11.3</td>
<td>3.8</td>
<td>2.6</td>
</tr>
</tbody>
</table>

*aCorresponding to the cellulose preparations in Table 6.1.

6.3.3 Intrinsic Viscosity, Viscosity Average Degrees of Polymerisation and Molecular Weight

In general, pulp viscosity is used to estimate cellulose degradation during delignification, although the data obtained using viscosity are relative values. Intrinsic viscosity is a characteristic of macromolecules which is directly related to their ability to disturb flow and indirectly to their size and shape [29]. For molecules that can exist with a variety of molecular weights, the relation between intrinsic viscosity and molecular weight ($M_w$) is one of the most important properties [30]. The viscosity average DP of a cellulose sample is conveniently estimated from the intrinsic viscosity of its solution in 0.5 M cupriethylenediamine hydroxide by applying the equation $\eta^0.9$ (mL g$^{-1}$) = 1.65 [\eta]. The molecular weight of the cellulose was estimated using a multiplication factor of 162, the molar mass of anhydroglucose. Table 6.3 lists the intrinsic viscosity ([\eta]), the viscosity average DP ($P$) and the $M_w$ of the six cellulosic preparations. Obviously, the intrinsic viscosity, the viscosity average and the molecular weight of the three cellulosic preparations (C1, C2 and C3) obtained from the delignified BP bark (3 years old) followed in this order: C2 (8% NaOH treatment for 15 h) > C3 (10% KOH treatment for 18 h) > C1 (10% KOH treatment for 15 h). The reason for this is presumably due to the removal of some low molecular weight hemicelluloses during the alkaline extraction from the holocellulose, thereby increasing the viscosity and molecular weight of the cellulose. As shown in Table 6.3, the C5 ($M_w$, 253,560 g/mol) obtained from the delignified BP stem (3 years old) and C6 ($M_w$, 273,470 g/mol) obtained from the delignified BP bark (12 years old) had higher molecular weights than that of C1 ($M_w$, 232,700 g/mol) obtained from the delignified BP bark (3 years old), under the same extraction conditions. This suggested that the cellulose in the BP stem and older bark had a higher molecular weight than that of cellulose in the younger BP bark (3 years old). In addition, as compared with the molecular weight of
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cellulose from the BP stem, the cellulosic preparation C₄ obtained from the Eucommia ulmoides Oliver stem had a relatively low molecular weight (244,720 g/mol).

### Table 6.3 The intrinsic (η), viscosity average DP (degree of polymerisation) (P) and Mₘ of the isolated cellulosic preparations

<table>
<thead>
<tr>
<th>Properties of cellulose</th>
<th>Cellulosic preparation⁵</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₁</td>
<td>C₂</td>
</tr>
<tr>
<td><strong>Intrinsic viscosity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(η, mL g⁻¹)⁶</td>
<td>420.8</td>
<td>615.6</td>
</tr>
<tr>
<td>**Viscosity average DP (P)**⁷</td>
<td>1,436.4</td>
<td>2,192.1</td>
</tr>
<tr>
<td><strong>Mₘ</strong>⁸</td>
<td>232,700</td>
<td>355,120</td>
</tr>
</tbody>
</table>

⁵Corresponding to the cellulose preparations in Table 6.1.  
⁶Determined by British Standard Methods for the determination of limiting viscosity number of cellulose in dilute solutions, Part 1. CED method.  
⁷Calculated using P⁰.⁹ = 1.65[η].  
⁸Calculated using P × 162.

### 6.3.4 Fourier Transform-infrared Spectra

Fourier Transform-infrared (FT-IR) is the most widely used method to identify chemical constituents and to elucidate their structures. The aim of using FT-IR in this work involved measuring the differences of the structure of the cellulose preparations obtained under various alkaline extraction conditions. Figure 6.2 illustrates the FT-IR spectra of cellulosic preparations C₁ (spectrum 1), C₂ (spectrum 2) and C₃ (spectrum 3). The absorption at 3,397 cm⁻¹ is attributed to O-H stretching, and those of 2,932 and 2,855 cm⁻¹ are due to C-H stretching. The absorbed water in the samples gives a signal at 1,628 cm⁻¹ [31]. The band at around 1,427 cm⁻¹ of all the spectra, indicated that all samples contain a mixture of crystallised cellulose I and amorphous cellulose [32]. The C-H asymmetric deformation occurs at 1,380 or 1,372 cm⁻¹. The peak at 1,325 or 1,316 cm⁻¹ is assigned to C-C and C-O skeletal vibrations. The absorption bands in the 1,200–1,000 cm⁻¹ region are dominated by ring vibration overlapped with stretching of the C-OH side groups. Two peaks at 1,163 and 902 cm⁻¹ arise from C-O-C stretching at the β-(1,4)-glycosidic linkages [33]. Two shoulder bands at 1,056 and 1,030 cm⁻¹ are indicative of C-O stretching at C-3, C-C and C-O stretching at C-6 [34]. In comparison, the spectral profiles and relative intensities of the signals in spectra 1 and 2 are rather similar, indicating the same structures. On the other hand,
it should be noted that the spectrum of cellulosic sample $C_3$ (spectrum 3) showed two carboxylic bands at $1,752 \text{ cm}^{-1}$ (C=O) and $1,568 \text{ cm}^{-1}$ (COO$^-$$^\text{ ).}$ These carboxylic groups are probably due to the oxidation of cellulose and hemicelluloses under the longer treatment time with 10% KOH at 25 °C for 18 h. In addition, all the extraction procedures removed most of the lignin polymers because of the disappearance of the lignin-associated signals at $1,600$ and $1,510 \text{ cm}^{-1}$. Similarly, the peaks at: $3,397; 2,919; 2,850; 1,611; 1,423; 1,376; 1,316; 1,167; 1,116; 1,056; 1,026$ and $902 \text{ cm}^{-1}$ in the spectra of cellulosic samples $C_4$, $C_5$, and $C_6$ (Figure 6.3) obtained from the delignified *Eucommia ulmoides* Oliver and BP stem, and BP bark (12 years old), respectively, are associated with the typical value of cellulose. Evidently, the bond intensity of the bands is very similar, indicating similar structures of the cellulosic preparations.

![FT-IR spectra of cellulosic preparations](image)

**Figure 6.2** FT-IR spectra of cellulosic preparations $C_1$ (spectrum 1), $C_2$ (spectrum 2) and $C_3$ (spectrum 3) isolated from the delignified BP bark (3 years old)
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Figure 6.3 FT-IR spectra of cellulose preparations C₄ (spectrum 1), C₅ (spectrum 2) and C₆ (spectrum 3) from the delignified Eucommia ulmoides Oliver stem, BP stem (3 years old) and bark (12 years old)

6.3.5 Cross Polarisation/Magic Angle Spinning ¹³C Solid-state Nuclear Magnetic Resonance Spectra

Figure 6.4 shows CP/MAS ¹³C-NMR spectra of cellulose preparations C₄ (spectrum a), C₅ (spectrum b) and C₆ (spectrum c). The analysis of the three spectra was carried out based on previous literature [35–37]. As can be seen from the spectra, the most intense signals are those from cellulose carbons that appear between 60 and 110 ppm. Starting from the upfield side of the spectra, the region from 60–70 ppm is attributed to C₆, the cluster of resonances from 70–80 ppm is assigned to C₂, C₃ and C₅, the next region from 80–90 ppm is due to C₄ and finally, the region from 100–110 ppm belongs to C₁ [35]. In more detail, the signals at 88.2, 88.4 or 88.5 ppm originate from the C-4 of the highly ordered cellulose of the crystallite interior, whereas the signals at 83.5, 83.2 or 83.7 ppm are attributed to the disordered cellulose. Similarly, the signals at 64.4, 64.6 or 64.7 ppm relate to C-6 in the crystalline cellulose, and at 62.3, 57.8 or 62.4 ppm correspond to crystal surfaces or disordered cellulose. The signals of xylan should be at 103 ppm (C-1), 82 ppm (C-4), 73–79 ppm (C-2, C-3) and 63 ppm (C-5), but the majority of the signals are overlapped by the cellulose...
signals [36]. Obviously, in the spectrum of $C_6$ (spectrum c), the signals at 103.4, 24.5 and 174.9 ppm are attributed to the C-1 of xylose, the carbon of the methyl group and the carbon of the carboxylic group of hemicelluloses, respectively, indicating that the cellulosic preparation $C_6$ contained a small amount of hemicelluloses. On the other hand, it also suggests that the bonds between hemicelluloses and cellulose in the delignified BP bark (12 years old) are relatively strong, as during the process of alkaline extraction the side chains of 4-O-methyl-glucuronic acid were not completely removed from the backbone of the xylans. In addition, the absence of the signals at 56 and 110−160 ppm, relating to methoxy and aromatic groups of lignin, revealed that the cellulosic preparations were free of the associated lignin, which was consistent with the absence of signal at 1,510 cm$^{-1}$ in the FT-IR spectra.

![Figure 6.4 CP/MAP $^{13}$C-NMR spectra of cellulosic preparations $C_4$ (spectrum a), $C_5$ (spectrum b) and $C_6$ (spectrum c)](image-url)
6.3.6 Thermal Analysis

Thermal analysis of polymers is an important study covering the field of application and method used for understanding the structure-property relation, and mastering the technology required for the industrial production of different polymeric materials [38]. Figure 6.5 illustrates TGA and DTG curves of cellulosic preparations C₄ (Curve 1), C₅ (Curve 2) and C₆ (Curve 3). In general, there are three stages of degradation in the TGA curves of the three samples. The initial low temperature mass loss (50–150 °C) corresponds to evaporation of the adsorbed moisture. This loss depends on the initial moisture content of the cellulosic samples. During the second stage, the cellulosic preparations readily start their decomposition, with the severe weight loss mainly occurring at 190–380 °C for C₄, 190–360 °C for C₅ and 180–340 °C for C₆, respectively, which was caused by concurrent cellulose degradation processes such as depolymerisation, dehydration and decomposition of glycosyl units followed by the formation of a charred residue. The third stage above 400 °C is due to the oxidation and breakdown of the charred residue into lower molecular weight gaseous products [39–41]. The three cellulosic preparations showed an earlier weight loss at 180 and 190 °C, which was due to the thermal decomposition of unstable hemicelluloses in the cellulosic samples. Hemicelluloses are easily degraded into volatiles at a relatively low temperature because of various saccharides, amorphous structures and branch characteristics [42]. In addition, the maximum weight loss rate reached 2.0 mg/min at 350 °C for C₄, 0.8 mg/min at 320 °C for C₅ and 1.4 mg/min at 350 °C for C₆, which were lower than those reported by Yang and co-workers [42]. As can be seen from the TGA curve, when the temperature reached 600 °C, the remaining solid residues are 17% for C₄, 23% for C₅ and 34% for C₆ of the initial weight. The higher amount of the remaining solid residues in C₆, are due to the higher content of ash in the BP bark (12 years old). On the basis of the above results, the thermal stability of cellulosic preparations followed this order: C₄ (Eucommia ulmoides Oliver stem) > C₅ (BP stem) > C₆ (BP bark). This indicated that the cellulose obtained from the BP stem had a higher thermal stability than that of the BP bark.
6.4 Conclusions

In summary, the BP bark and stem, and Eucommia ulmoides Oliver stem were subjected to delignification using chlorite and extraction with alkali, yielding cellulosic fractions of 37.5–51.8%. The results indicated that the relatively higher alkali strength (e.g., 8% NaOH) and longer time of treatment led to an increase of the solubility of the hemicelluloses, and increased the cellulose purity. In addition, the cellulosic polymers in BP stem (3 years old) and older bark (12 years old) had a higher \( M_w \) than that of the cellulosic preparation of the BP younger bark (3 years old). The TGA and DTG curves showed three stages of cellulose degradation behaviour. Additionally, the cellulose obtained from the BP stem had a higher thermal stability than that of the BP bark.

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References

Pulp Production and Processing: From Papermaking to High-Tech Products

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