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Vibrational spectroscopy and X-ray diffraction methods to establish the differences between hardwood and softwood

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ABSTRACT

FT-IR spectrometry and X-ray diffraction were applied to probe the differences between pulp fibers from Eucalyptus wood (hardwood) and Norway spruce wood (softwood). Wood processing was found to induce certain structural alterations within its components depending on the type of wood and the applied procedure. These differences were established by using techniques such as; spectral comparison of wood samples with those of individual component fractions, derivative spectroscopy, bands deconvolution, etc. FT-IR spectroscopy was shown to be an important tool that provided details about the structural characteristics of hardwood and softwood samples. Using second-derivative spectra and deconvolution processes small differences between spectra became apparent that allowed correlations to be made related to wood composition. In addition a correlation was established between the integral absorptions for the various bands and lignin content as well as the lignin/carbohydrate content. Relations between various spectral characteristics and the degree of crystallinity and sample composition were established.

1. Introduction

Wood consists of an orderly arrangement of cells with cell walls composed of varying amounts of cellulose, hemicelluloses, and lignin. The great diversity of woody plants is reflected in their varied morphology and chemical composition. Typically, two general groups, hardwoods (angiosperms) and softwoods (gymnosperms) can be easily distinguished. Hardwoods have pores or vessel elements that occur among fiber and parenchyma cells. It is well-known that the cellulose content ranges from 40 to 50 wt% and the lignin content is comprised between 15 and 25 wt%, while that of the hemicelluloses varies from 15 to 25 wt%. Softwoods are composed of overlapping tracheids, connected by bordered pit apertures, and parenchyma cells and, in some cases, resin canals. Greater concentrations of lignin, about 5–10% more than in hardwoods, are found in softwoods, and about the same amount of cellulose 40–50%. Less hemicelluloses may be found in softwoods than hardwoods. The chemical composition of softwoods is also different from hardwoods with different types of lignin (primarily guaiacyl propane units), hemicelluloses (mannose is the most common constituent) and wood extractives (different terpenes, fatty acids, etc.). Differences in composition are also common between temperate and tropical hardwoods. Woods such as teak, mahogany and ebony have greater concentrations of lignin and wood extractives than many temperate hardwoods such as maple, birch, and aspen (Blanchette, Haight, Koestler, Hatcheld, & Arnold, 1994).

Cellulose is the dominant polymer in the biosphere. It is an optically anisotropic system being made up of poly-(1 → 4)-β-D-glucose chains (Atalla, 1999; O'Sullivan, 1997).

The numerous polar groups make cellulose molecules predestined for building up hydrogen bonds within the molecule and between the different molecules. In the generally accepted structure of cellulose I, intramolecular hydrogen bonds of types 3-OH···O-5 and 2-OH···O-6 are present for both sides of the chain. As a result of hydroxyl groups showing different polarities, cellulose has different crystalline structures, ranging from cellulose I (native cellulose) to cellulose IV. Moreover, cellulose I is itself composed of two different crystalline forms: cellulose Iα and Iβ. Two chains, which take an almost fully extended conformation, are contained in the unit cell of cellulose I. It is generally known and accepted that the hydrogen bonds play an important role in the conformational and mechanical properties of cellulosic materials (O'Sullivan, 1997).

Besides its complex crystalline structure, native cellulose also has a complex arrangement within the wood fiber wall. In the

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secondary wall, the cellulose chains are grouped into fibrils by hydrogen bonds. These fibrils are aligned in different directions in the different secondary wall layers.

Infrared spectroscopy, which is known to be sensitive to structural features, has had a long tradition in wood research. Since the very first use of infrared spectroscopy to elucidate molecular structures, much effort has been devoted to separating the overlapping bands deriving, for example, from hydrogen bonds (Fengel & Ludwig, 1991; Nishiyama, Isogai, Okano, Müller, & Chanzy, 1999; Sugiyama, Persson, & Chanzy, 1991; Tashiro & Kobayashi, 1991).

General difficulties in wood and pulp analyses principally arise from the numerous components with different chemical character. The extractives of wood and pulp cover a wide range of low-molar-mass compounds, which may be isolated for a detailed chemical examination by means of different solvent extractions. The isolation of lignin from wood and pulp samples in its unaltered form at an acceptable and representative yield is currently a major problem, despite a variety of versatile extraction schemes that have been proposed. However, recently a new method of lignin isolation termed enzymatic mild acidolysis lignin (EMAL) promises to alleviate these problems, This method has actually been applied to the samples examined in this work (Guerra, Filpponen, Lucia, & Argyropoulos, 2006b; Guerra et al., 2006a; Popescu et al., 2006; Wu & Argyropoulos, 2003). Determination of the carbohydrate composition of wood and pulp samples is vital for many applications and is one of the most frequently performed chemical analyses for almost all biomass-derived materials. Elaboration of a procedure to analyse direct the differences between various kinds of wood samples is necessary.

The aim of this paper is to establish the main structural and morphological differences between hardwood and softwood samples. FT-IR spectrometry and X-ray diffraction have been used. Optimum experimental conditions were initially established for each method and differences between the various samples were assessed by assignment of the characteristic bands, evaluation integral absorption or carbohydrate/lignin ratio, etc., from FT-IR spectra and percentage of crystalline fraction by X-ray diffraction. The accumulated data were finally discussed in terms of sample composition.

2. Experimental

2.1. Materials

The unfractioned samples of unbleached Kraft pulp brown stock (BSP) of *Eucalyptus globulus* (sampled after washing stages) and unbleached Norway spruce TMP (sampled in a Swedish mill, ca. 38% dryness, 85 ml CSF, standard newspaper quality, the mill has one-stage refining and a subsequent reject refining (ca. 20%) stage) were provided by Åbo Akademi University, Laboratory of Wood and Paper Chemistry, Turku, Finland. The samples were part of the COST Action E41 joint analytical effort on wood and its components.

Different working groups (WG1, WG2 and WG3 constituted of different laboratories partners) of COST Action E41 Project, determined the composition of the wood components following different separation procedures. The results were summarized at Grenoble Meeting (April 12–13, 2006). The average content of the various components are shown in Table 1.

The selected samples for study have very different contents in extractives, carbohydrates and lignins. Eucalyptus BSP has ~20 wt% more carbohydrates that Norway spruce, while lignin content is very small of 1–1.7 wt% and very high of 27–29 wt% in Norway spruce pulp. Unbleached pulps were studied.

Isolation of enzymatic mild acidolysis ligins (EMALs): These were isolated form Eucalyptus chips (*Eucalyptus globulus*) and from Norway spruce TMP. The wood chips, or TMP fibers, were ground to pass a 20-mesh screen in a Wiley mill and Soxhlet extracted with acetone for 48 h. The resulting Wiley-milled wood powder was air-dried and stored in a desiccator under vacuum. The *E. globulus* wood powder was submitted to an alkaline extraction with 0.3% (0.075 mol L^{-1}) NaOH for 1 h to remove tannins before use (Evtuguin et al., 2001).

Table 1
Average contents of total extractives, carbohydrates and lignin in *Eucalyptus globulus* and Norway spruce pulps.

Samples	Extractives[a] (wt%)	Carbohydrates[b] (wt%)	Lignin[c] (wt%)
Eucalyptus BSP	0.2	88.7–99.2	1.0–1.7
Norway spruce TMP	1.0	60.6–69.0	27.6–29.4

[a] Total average amounts determined by acetone extraction [15] (Willför, Hemming, & Leppänen, 2006).
[b] Total amounts determined by HPAEC-PAD [16] (Puls, 2006).
[c] Total amounts (ASL + AIL) [17] (de Jong, 2006).

Rotary ball milling was performed in a 5.5 L porcelain jar in the presence of 474 porcelain balls (9.4 mm of diameter), which occupied 18% of the active jar volume. One hundred grams of extractive-free wood powder was loaded into the jar, creating a porcelain ball/wood weight ratio of 16.6. The milling process was conducted at room temperature for up to 28 days with a rotation speed of 60 rpm (Guerra et al., 2006a). EMALs were isolated from ball milled wood according to the procedure described by Wu and Argyropoulos (2003). Some cautions to avoid contamination in the final product were taken into account, as previously reported (Guerra et al., 2006a).

2.2. Characterisation methods

The methods of investigation in this work were FT-IR spectroscopy and X-ray diffraction.

FT-IR spectra were recorded on solid samples in KBr pellets by means of an FT-IR Bomem MB-104 spectrometer (Canada) with a resolution of 4 cm^{-1}. The concentration of the samples in the pellets was constant of 5 mg/500 mg KBr. Samples were sieved and fractionated. The fraction with grains having diameter less than 0.2 mm was retained for analysis. Five recordings were performed for each sample after successive milling and the evaluations were made on the average spectrum obtained from these five recordings. Processing of the spectra was done by means of Grams/32 program (Galactic Industry Corp.). Each method yielded several components. For a better understanding of the structure of the samples, deconvolution of the spectra was carried out with Gaussian profiles. The number and the maximum of the deconvoluted peaks were taken from second-derivative spectra. The reduced chi-squared value for all the deconvoluted curves was $\chi^2 \leqslant 0.1$; therefore, the use of this function is a good approach.

The X-ray diffractograms were recorded on XRD equipment Rigaku RINT 2500/32 by Rigaku Co. Japan. The measurements were carried out in point focus geometry using CuKα radiation $\lambda = 0.1524$ nm. Experimental conditions: sequence scan mode; measuring axis: 2θ; voltage: 40 kV; current: 20 mA; start angle: 10°; stop angle: 80°; sampling angle: 0.021°; scan rate of goniometer: 2°/min; divergent slit width: 1°; receiving slit width: 1°; scattering slit width: 0.60 mm; monochromator receiving slit width: 0.80 mm. All the measurements were conducted in the diffraction mode at atmospheric pressure.

The diffractograms were deconvoluted using Gaussian and mixed Gaussian–Lorentzian profiles. The reduced chi-squared value for all the deconvoluted curves was $\chi^2 \leqslant 0.1$; therefore, the use of this function is a good approach. The fitting curve matches the experimental curve very well. After deconvolution, the several parameters can be calculated and compared (He, Tang, & Wang,