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Solid-state properties of softwood lignin and cellulose isolated by a new acid precipitation method

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ABSTRACT

Solid-state and powder properties of softwood lignin and cellulose prepared by a new catalytic oxidation and acid precipitation method were characterized and compared with the commercial softwood and hardwood lignin and cellulose products. Catalytic pre-treated softwood lignin (CPSL) and cellulose (CPSC) were isolated from pine wood (*Pinus sylvestris*). CPSL with nearly micronized-scale particle size showed excellent powder flow and densification behavior due to the round shape and electrically minimum charged surface characteristics of particles. CPSL and the reference lignin studied were amorphous solids while CPSC exhibited a typical crystal lattice for cellulose I. In conclusion, physicochemical material properties of lignin and cellulose can be modified for biomedical and pharmaceutical applications with the present catalytic oxidation and acid precipitation method.

1. Introduction

In recent years, the design and synthesis of new biomaterials for pharmaceutical and biomedical applications have created much interest [1–3]. Lignin and lignocellulose are by-products of the pulping or bio-ethanol industries, and they are readily available and cheap but have not been investigated very much in fabrication of biomedical or pharmaceutical systems. It is evident that application of these biomaterials as such, or in engineering other polymers could lead to new manufacturing opportunities for a wide range of pharmaceutical and biomedical systems intended for human and/or veterinary medicine applications (including controlled drug delivery). Recently, nanoscale lignin with significantly improved water-solubility was prepared with a supercritical antisolvent method [4].

Past twenty years, a number of physical and chemical pretreatment technologies for cellulose and isolation of lignin have been reported [5–11]. Microfibers of natural cellulose are typically sealed by lignin, which accounts for up to 31% of the biomass of woody tissues [12]. The goal of cellulose pretreatments is to increase the accessible surface area of cellulose and enhance conversion of the cellulose to glucose by removing the lignin seal, solubilizing hemicellulose disrupting cellulose crystallinity and/or increasing pore volume [6,7]. Recently, Hakola et al. [13] presented a new catalytic pretreatment method for the separation of cellulose and lignin from lignocellulosic biomass for enzymatic hydrolysis. The present technology has significant advantages compared to other established pretreatment methods (1) making cellulose that can easily undergo hydrolysis, (2) avoiding the loss of hydrolyzable carbohydrates, and (3) avoiding the formation of toxic compounds. It can be considered also as an environmentally benign concept based on in situ catalysts and pressurized air or oxygen as the oxidant. The hydrolysis is faster and the degree of hydrolysis notably higher for catalytically pretreated material than for steam-exploded spruce, which represents a state-of-the-art technique for the cellulosic ethanol production [13].

The aim of the present study was to investigate solid-state and bulk powder properties of catalytic pretreated softwood lignin (CPSL) and cellulose (CPSC) relevance to manufacturing and performance of pharmaceutical dosage forms and biomedical systems for human and/or veterinary medicine applications. The physicochemical material characterization included chemical structure analysis, solid-state properties, particle and powder properties (particle size, size distribution and shape, morphology, and flowing) and densification characteristics. The biomaterials studied were isolated from the pine wood (*Pinus sylvestris*) with a catalytic pretreatment

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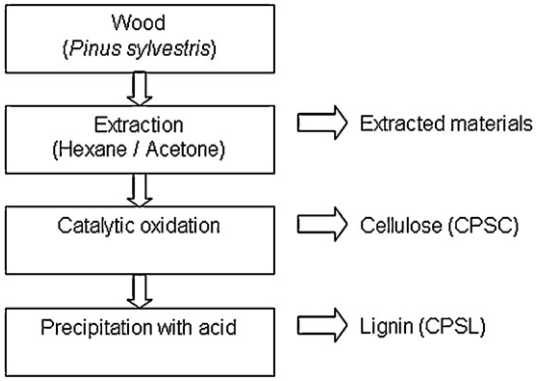

Fig. 1. Schematic diagram of the isolation of lignin and lignocelluloses from pine soft wood (*Pinus sylvestris*).

procedure described by Hakola et al. [13] with some modification. Using the present technique and by varying conditions of isolation process, chemical purity, physical material and powder properties as well as solubility of lignin and lignocellulose can be modified.

2. Materials and methods

2.1. Materials

Lignin and cellulose (carbohydrate fraction) were isolated from pine soft wood (*Pinus sylvestris*) by using a catalytic oxidation and subsequent acid precipitation pretreatments. Industrial softwood kraft lignin (Indulin AT), hardwood lignin (PC-1369) and commercial microcrystalline cellulose, MCC (Avicel® PH 101, FMC Biopolymer, USA) were used as reference materials.

2.2. Preparation of softwood lignin and cellulose

Isolation of lignin and lignocelluloses from pine soft wood (*Pinus sylvestris*) was carried out according to the method described by Hakola et al. [13] with some modification. Schematic diagram of the isolation process is shown in Fig. 1. For the pretreatment, the pine chips were first extracted with hexane for 2 days and with acetone for one day to remove the extractives. The alkaline water solution was prepared by mixing 5.2 g (49.0 mmol) Na_2CO_3 to 200 ml of water, and it was added together with 10 g of extractive free pine chips (dry weight) to a preheated autoclave equipped with magnetic stirrer and oil bath heating. The reaction was carried out for 20 h at elevated temperature (120 °C) and with oxygen pressure (10 bar). After pretreatment, the solution was filtered. The solid cellulose fraction (CPSC) was dried in room temperature and subjected to size reduction (ball milling) using a Planetary Mono Mill pulverisette 6 (Fritsch GmbH, Germany) at 400 rpm for 3 min. The filtrate, which contained the solubilized lignin was acidified with HCl and the precipitated lignin (CPSL) was collected with additional filtration. The obtained solid lignin was vacuum dried and used without further size reduction.

2.3. Physicochemical material characterization

2.3.1. Particle size, shape and surface morphology

Particle size, shape, surface morphology and microstructure were studied by using a high-resolution scanning electron microscope, SEM (Helios NanoLab 600, FEI Company, USA). Particle size distribution was determined with a Malvern laser diffractometer (Malvern 2600c, Malvern, England) in an ethanol suspension. A focal length of 100 mm and beam length of 14.3 mm were used to determine the intensity of laser light and calculate the volume diameters d_{10}, d_{50} and d_{90} of the particle distribution. Three parallel measurements were preformed for each sample.

2.3.2. Water content and water activity

Moisture content of biomaterials was determined by using a Sartorius MA 100 moisture analyzer (Sartorius AG, Germany). The water-activity measurements were carried out with an AquaLab (Series 3TE, Sweden) water-activity meter. The measurements were carried out in triplicate.

2.3.3. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of powdered solids were obtained using a IRPrestige-21 Spectrophotometer (Shimadzu Corp., Japan) and Specac Golden Gate Single Reflection ATR crystal (Specac Ltd., U.K.). Spectra were collected from 4000 to 600 cm^{-1}.

2.3.4. X-ray powder diffraction

X-ray powder diffraction (XRPD) patterns on CPSL and CPSC powders were obtained by using a X-ray diffractometer (D8 Advance Bruker AXS GmbH, Germany). The XRPD experiments were carried out in symmetrical reflection mode (Bragg-Brentano geometry) with CuK_α radiation (1.54 Å).

2.3.5. Differential scanning calorimetry

The glass transition temperature range (T_g) was investigated using differential scanning calorimetry, DSC (DSC 4000, Perkin Elmer Ltd., Shelton, CT, USA). Samples of 2–3 mg were sealed in an aluminum pan with 2 pinholes in a lid. A nitrogen purge with a flow rate of 20 ml/min was used in the furnace. The scans were obtained by heating from 30 °C to 220 °C at a rate of 20 °C/min. Each run was performed in triplicate.

2.3.6. Physical powder and consolidation properties

Bulk, tapped and true (absolute) densities of the powders were determined by the standard method described in the European Pharmacopoeia [14]. A standardized tapped density tester (Erweka SVM1, Erweka GmbH, Heusenstamm, Germany) was employed. Each sample was measured in triplicate. The true (absolute) density of materials was measured using a helium pycnometer (Micromeritics, Model 1305, Norcross, GA, USA). Each sample was measured in triplicate. The Carr's index and Hausner ratio were calculated from the bulk, tapped and true densities [15]

Flow rate of powders was measured by using a laboratory FlowPro flow meter (SAY Group, Helsinki, Finland). This flow meter measures the mass of a powder that flows through a hopper assisted by vertical oscillations, which break the cohesive forces [16]. Five parallel measurements were performed under controlled room conditions (21 ± 2 °C/50% RH).

2.4. Data analysis

The experimental data was analyzed in accordance with the analysis of variance (ANOVA). The spectra analyses were performed using Matlab 7.10.0 software.

3. Results and discussion

3.1. Particle size, shape and surface morphology

Particle size, particle size distribution, shape, and surface morphology are fundamental properties of pharmaceutical powders defining, for example, powder texture, and affecting physical and bulk powder properties. The pre-milled CPSL powder consisted of particles with a relatively round but irregular shape, and particle size ranged from 20 μm to 70 μm (Fig. 2). Despite of relatively small particle size, the CPSL powder was freely flowing obviously