Impact of lignin on water sorption properties of bioinspired self-assemblies of lignocellulosic polymers

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ABSTRACT

The hygroscopic properties of lignocellulose-based films were investigated by designing bio-inspired nanostructured assemblies of increasing complexity. Binary and ternary films were prepared from three main secondary cell wall polymers, namely, cellulose, hemicellulose (xylan or glucomannan) and lignin. The effect of lignin was studied by varying the manner of lignin introduction as the dehydropolymer (DHP, model lignin). The infrared analysis and water-sorption properties of the films that resulted from mixing DHP and polysaccharides were compared with films obtained from the polymerisation of coniferyl alcohol (lignin monomer) in the presence of polysaccharides. Comparison of the film behaviours was achieved using the GAB and PARK models for the sorption isotherms and the PEK model for the sorption kinetics. Our data indicated that without chemical functionalization, the water-sorption properties of the hemicellulose films were enhanced after forming lignin under mild enzymatic conditions. Notably, the hydrophobic nature of lignin was not expressed in these films, in contrast to the systems that resulted from a simple mixing of lignin with hemicelluloses. The presence of cellulose also modified these sorption properties, most likely by altering the interactions between the polymers and/or the monolignol reactions.

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1. Introduction

Lignocellulosic biomass, the most abundant renewable resource on earth, is a subject of increasing interest as a sustainable source of biofuels [1], chemicals and biomaterials via the incorporation of natural fibres in the polymeric matrix [2,3]. Lignocelluloses are essentially cell walls that are composed of polysaccharides (cellulose and hemicelluloses) and lignin with a small amount of protein. Plant cell walls are highly hierarchised and multilayered structures that vary according to the plant species, growing conditions and maturation [4]. In the thick secondary cell walls, cellulose nanofibrils interact via hydrogen bonds to produce microfibrils, which are embedded in an amorphous matrix of hemicellulose–lignin, thus yielding a tightly interconnected polymer network consisting of numerous covalent and non-covalent bonds [5,6]. However, the use of lignocelluloses to produce biocomposites with certain desired physico-chemical properties remains challenging [3]. Among these properties, hygroscopic behaviour is a key characteristic [7]. Indeed, plant cell walls

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and lignocellulosic polymers are very sensitive to water [8], which may affect the performance of the biocomposites.

The water-sorption properties of lignocelluloses are studied by (1) the sorption isotherm, which is defined by the water content of the sample as a function of the relative humidity and (2) the sorption kinetics, which are defined by the weight of the sample during a humidity transition. The interactions between water and lignocellulosic polymers can be investigated using various mathematical models to determine certain physical parameters that describe the state of the water molecules inside the material. The Hailwood Horrobin [9] model has been extensively used to investigate the sorption behaviour of fibrous materials and wood [9,10] and to describe the formation of the water monolayer in polymers. The GAB (Guggenheim–Anderson–de Boer) and PARK models are commonly used to fit the water-sorption behaviour of food materials [11], of polysaccharides as pure films of arabinoxylans and glucans [12], of cellulose [13] and of composite films [14–16]. The PARK model has also been tested to fit water-sorption experimental data from isolated fibres [17] and composites [18]. Sorption kinetics can be modelled using Fick's law or the PEK model. Fick's law postulates the existence of two consecutive diffusion processes and involves the calculation of two diffusion coefficients [18], whereas the PEK model postulates the existence of two parallel and independent processes (fast and slow processes) and involves the calculation of the characteristic time for each process [19]. The primary disadvantage of Fick's law is that the thickness of the sample must be known during each transition to precisely calculate the diffusion coefficients. Moreover, several plant cell wall polymers do not respect Fick's law [20,21]. In contrast, the PEK model provides some clues regarding the mechanism for the adsorption of water in materials.

Recently, several attempts have been made to study the hygroscopic properties of mixed systems of cellulose and hemicellulose [12–14], including plasticisers [15,22] or synthetic polymers [16] for designing biobased materials which may ensure different applications. Few studies have focused on the effect of lignin on the hygroscopic properties of polysaccharide assemblies [23–26]. In plant cell walls, lignin, which is mostly hydrophobic, is closely associated with hemicellulose through non-covalent and/or covalent bonds [6]. Some of the interactions that occur during the lignification of the secondary cell walls can be mimicked via *in vitro* monolignol polymerisation, thereby providing bio-inspired cell-wall systems for the investigation of the features involved in cell-wall lignification and deconstruction [27–29].

The objective of the present study is to evaluate the effect of lignin on the hygroscopic properties of a bio-inspired assembly constructed from lignocellulosic cell wall polymers. To this end, non-lignified and lignified systems were obtained using cellulose nanocrystals (CNs), hemicelluloses (xylan, XYL or glucomannan, GM) and lignin as single, binary and ternary nanocomposites, respectively. In particular, the polymer systems were lignified either by mixing model compound (dehydrogenation polymer, DHP) with polysaccharides or via monolignol polymerisation in the presence of polysaccharides prior to

film formation. Polymer ratios were first selected to mimic the large chemical variation of the plant secondary cell walls; for instance the stem of certain fibre plants (flax, hemp) contain bast fibres with highly cellulosic cell walls (∼60–80% cellulose) in addition to woody cells that are more lignified (∼25–30% lignin) [4]. In addition, smaller proportion of cellulose (∼20%) was also tested to identify the effect of cellulose on hygroscopic properties of lignocellulosic assemblies. The sorption isotherms and kinetics were evaluated using the GAB and PARK models and the PEK model, respectively.

2. Materials and methods

2.1. Polysaccharides and lignin polymers

2.1.1. Preparation of cellulose nanocrystals (CNs)
The CNs were prepared from bleached ramie (*Bohemia nivea*) fibres (Stucken Melchers, Germany) [30]. Small, cut pieces of the fibres were treated with 2% NaOH at 35 °C for 48 h to remove any residual proteins, hemicelluloses and traces of pectin. The homogeneous suspensions obtained from the pre-treated ramie fibres were subjected to overnight hydrolysis (∼16 h) with 65% (w/w) H_2SO_4 at 35 °C under stirring. The suspension was washed with water until neutrality was achieved and then dialysed with a regenerated cellulose membrane with a 6000 Mw (molecular weight) cut-off. The resulting colloidal cellulose nanocrystal suspension was stored at 4 °C and sonicated using a Sonics Vibra-Cell (750 W, Fisher-Bioblock) at an appropriate concentration (20 g L^{-1}) for a few minutes prior to use. The average crystal dimensions were measured based on an AFM image analysis performed using ImageJ; the CN was 99% pure glucose and 0.7% ± 0.1% sulphur, as estimated from the elementary analysis of the dry matter, corresponding to an average surface charge of 0.4 charges nm^{-2}. The average length of the CNs measured from the AFM images was 135 nm ± 5 nm, according to [31].

2.1.2. Hemicellulose solutions
Glucomannan (GM) and xylan (XYL) solutions were obtained from konjac glucomannan (low viscosity, Megazyme) and a water-soluble xylan isolated from oat spelt [32], respectively. The hemicelluloses were dissolved in a solution of water/ethanol (94/6, v/v). The hydroethanolic solutions were heated to boiling and then stirred as they cooled at room temperature. The solutions were then centrifuged at 12,000 g for 10 min, and the volume of the supernatant was adjusted with water to obtain stock solutions of 10 g L^{-1} (w/v).

The sugar-monomer composition was determined following acid hydrolysis using high-performance anion-exchange chromatography with pulsed amperometric detection (Dionex, Thermo Fisher) [33]. The molecular weights were determined as described by [28] using high-performance size-exclusion chromatography with online refractive index detection (Waters). Chromatography was performed using Shodex OH pack columns and an aqueous eluent (50 mM $NaNO_3$ containing 0.02%