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Accessibility of cellulose: Structural changes and their reversibility in aqueous media

Raili Pönni, Eero Kontturi*, Tapani Vuorinen

Aalto University, School of Chemical Technology, Department of Forest Products Technology, P.O. Box 16300, 00076 Aalto, Finland

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ABSTRACT

During various processing treatments, the accessibility of cellulose in cellulosic fibers reduces, which is often interpreted as cellulose microfibril aggregation. This affects the reactivity of cellulose in further processing to novel cellulosic products such as nanocellulose. In this study, the effect of aqueous treatments at elevated temperatures and various pH on accessibility of an oxygen delignified eucalyptus kraft pulp was evaluated by using deuteration combined with Fourier-transform infrared (FT-IR) spectroscopy and water retention value (WRV) test. Acidic treatments reduced WRV and caused irreversible deuteration of the pulp. However, alkaline treatments increased WRV and caused reversible deuteration of the pulp. Both deuteration and reprotonation of the deuterated pulp followed the same slow, first-order dynamics. This led us to propose that incubation of alkaline cellulosic pulp suspensions at elevated temperatures does not only lead to reduction in accessibility but also to a dynamic interconversion between accessible and inaccessible regions.

1. Introduction

The plant cell wall can be viewed as a hydrogel: a network of intertwined polymers swollen by water. In conventional synthetic hydrogels, individual polymers are usually cross-linked by covalent bonds or specific supramolecular interactions, yielding water uptake values of easily more than 99% in weight (Oh, Drumright, Siegwart, & Matyjaszewski, 2008). In the plant cell wall, semi-crystalline cellulose microfibrils (nanometers in width, microns in length) are interspersed in a matrix of hemicellulose and lignin. The interior of microfibrils is largely impenetrable by water whereas the lignin–hemicellulose matrix is water-swollen. However, the swelling of the whole cell wall is not determined by cross-linking; it is restricted by the hierarchical structure of the cell wall. Therefore, the water uptake of the cell wall is governed by the conventional laws on osmotic pressure, including the hydration of the polysaccharide hydroxyl groups and the availability of charged groups, but the opposing force to swelling is a geometrical constraint. The complex hierarchy of the cell wall renders the interpretation of different structural factors influencing swelling often ambiguous.

Most plant cells can also be called fibers and they possess a vast industrial significance, particularly in the case of wood and cotton. The water uptake of fibers determines their accessibility in aqueous environment. In essence, accessibility technically refers to how well the surface hydroxyl groups in a cellulose microfibril (Scheme 1) can be reached by water. It is an important quality, largely responsible for, e.g., the success rate in heterogeneous chemical modifications of native cellulose. In this respect, the heterogeneous reactivity of cellulosic fibers is a decisive factor in novel applications of biomass such as hydrolyzing cellulose for biofuel production (Liu et al., 2011; Zhang & Lynd, 2004) or manufacture of nanosized cellulose (Henriksson, Henriksson, Berglund, & Lindström, 2007; Isogai, Saito, & Fukuzumi, 2011; Pääkko et al., 2007; Spence, Venditti, Habibi, Rojas, & Pawlak, 2010). The purpose of this paper is to unravel the influence of simple external conditions – pH and temperature – on the accessibility of native cellulosic fibers in aqueous media and to address the reversibility of the accessibility change.

Because the semi-crystalline cellulose microfibrils are not swollen by water and only their surface is attained, the reduction in accessibility during industrial processing is often interpreted to be due to cellulose microfibril aggregation, i.e., the formation of irreversible bonds between cellulose microfibrils (Scheme 1) (Back, 1967; Higgins & McKenzie, 1963; Newman, 2004). The reporting of this phenomenon has been extensive in the technical research concerning chemical pulping of wood fibers and their subsequent drying (Fahlén & Salmén, 2003; Hult, Larsson, & Iversen, 2001; Jayme, 1944; Lyne & Gallay, 1950; Maloney & Paulapuro, 1999). Although the phenomenon previously raised scientific and economic interest due to its effect on the paper strength properties (Lyne & Gallay, 1950; Maloney & Paulapuro, 2000), currently

* Corresponding author. Tel.: +358 503442978; fax: +358 947024259.
E-mail addresses: raili.ponni@aalto.fi (R. Pönni), eero.kontturi@aalto.fi (E. Kontturi), tapani.vuorinen@aalto.fi (T. Vuorinen).

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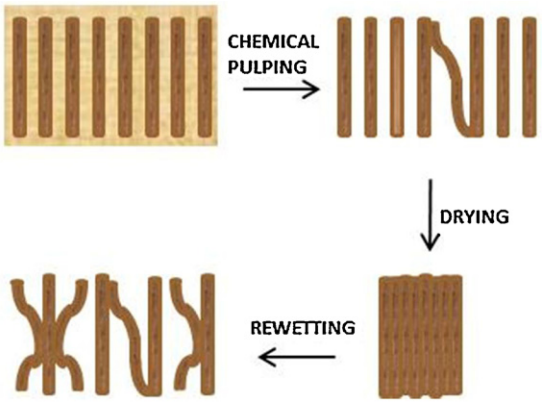
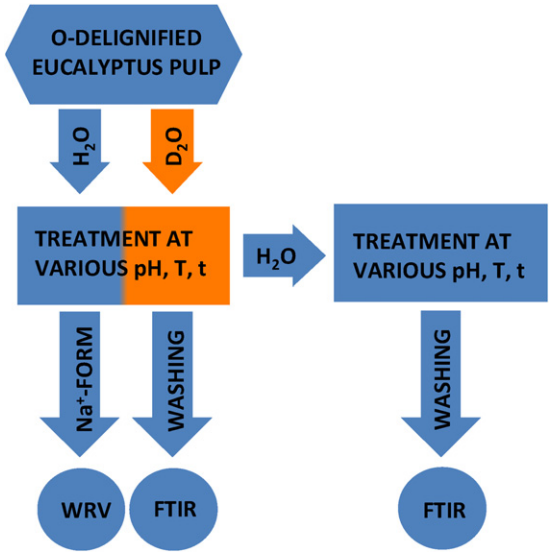


Scheme 1. Schematics of cellulose microfibril behavior during different processing steps.

the interest has shifted to accessibility during the chemical and enzymatic treatments in novel, sustainable processes involving cellulosic fibers such as preparation of nanocellulose (Liimatainen, Visanko, Sirviö, Hormi, & Niinimaki, 2012; Wu, Saito, Fujisawa, Fukuzumi, & Isogai, 2012). Accessibility of cellulose is known to be influenced by the raw material characteristics, e.g., hemicellulose and acid group content (Lindström & Carlsson, 1982; Oksanen, Buchert, & Viikari, 1997). In addition, process variables, such as, temperature, pH, and moisture content, have an influence on the phenomenon (Lindström & Carlsson, 1982; Maloney & Paulapuro, 2000). In chemical pulping, which targets at lignin removal from the cell wall, microfibril aggregation is reported to require the temperature of around 150 °C (Fahlén & Salmén, 2003; Virtanen, Maunu, Tamminen, Hortling, & Liitiä, 2008). Alkaline conditions influence accessibility also by improving the swelling properties of dried as well as never dried fibers. At sufficiently high alkaline concentration and suitable physical state of cellulose, cellulose can be even dissolved in alkali (Kontturi et al., 2011; Le Moigne & Navard, 2010).

Even though the technical swelling behavior of cellulosic fibers upon varying pH values has been studied widely, the explicit influence of a systematic acid/base treatment on accessibility has not been reported. One major drawback of the experimental work conducted in this field, is the lack of precise methods to characterize the alterations which cause changes in accessibility. Here, deuteration combined with FT-IR spectroscopy has been applied to detect the formation of inaccessible regions within the fiber cell wall (Suchy, Kontturi, & Vuorinen, 2010; Suchy, Virtanen, Kontturi, & Vuorinen, 2010). By directly addressing the ultrastructural changes inside the fiber, this method bears the advantage over several indirect techniques that characterize fiber swelling or pore size distribution (Berthold & Salmén, 1997; Maloney, Paulapuro, & Stenius, 1998; Östlund, Köhnke, Nordstierna, & Nydén, 2010). The method is simple and it is able to analyze fresh samples with minimal pretreatment. Nuclear magnetic resonance (NMR) spectroscopy has also been successfully applied to determine the changes in the lateral dimensions of fibrils and fibril aggregates (Hult et al., 2001; Virtanen et al., 2008). However, NMR spectroscopy generally requires the isolation of cellulose from the sample prior to the analysis. The effect of different treatments that decrease cellulose accessibility and thus its potential in further processing needs to be established in a more fundamental level in order to evaluate the applicability of various raw materials for novel and traditional cellulosic products. To address this, this study presents the changes in cellulose accessibility at various conditions covering a wide range of common conditions of fiber processing at temperatures below 100 °C. The raw material of choice was oxygen delignified eucalyptus kraft pulp whose accessibility has been vastly improved by chemical pulping while still retaining a sufficient amount of lignin



Scheme 2. Schematics of the experiments and analysis.

and hemicellulose in its structure. Deuterium exchange combined with FT-IR spectroscopy was implemented to study the changes in accessibility and the more traditional measure of water retention value (WRV) was carried out as a reference. The reversibility of the accessibility changes was also addressed by putting forward evidence that the accessibility is at dynamic equilibrium. Reversing the reduced accessibility is an intriguing feature when considering the tunability of properties in native cellulosic fibers. It is a contribution to the current technology which aims at tailoring the quality of biologically derived materials to fit their use in modern materials science.

2. Experimental

2.1. Materials

Oxygen delignified eucalyptus kraft pulp manufactured in Veracel pulp mill in Brazil with a kappa number of 11.4 and dry matter content of 31.3% was used as the raw material. Deuterium oxide (99.9 atom% D, Sigma–Aldrich (St. Louis, USA)) was used for deuteration. pH was adjusted in all the experiments with NaOH and HCl prepared from a 0.1 M stock solution (Merck (Darmstadt, Germany)). Water was purified in a Milli-Q system (Millipore Corporation, resistivity 18.2 M cm). For washing the pulp to Na^+-form for the WRV determination solution of $NaHCO_3$ was prepared from a solid 99.5% $NaHCO_3$ (Merck (Darmstadt, Germany)) in addition to the stock solutions of NaOH and HCl already mentioned.

2.2. Treatments

The deuteration combined with FT-IR method applied in this study has been meticulously discussed in an earlier paper (Suchy, Virtanen, et al., 2010). The pulp samples were deuterated in plastic bags for a period of 2 × 20 min with an excess of D_2O, namely 20 ml of D_2O per 1 g of dry pulp. The slurry was mixed twice during the 20 min by kneading. Between the deuteration treatments, the D_2O was squeezed out of the bag before fresh D_2O was added.

The treatments were done in plastic bags in a temperature controlled water bath at 10% consistency. The pH of the samples was measured by an Orion 720A pH-meter (Sigma–Aldrich (St. Louis, USA)). The solvent in the samples for the FT-IR spectroscopic analysis was D_2O, but the solvent in the samples for the WRV measurement was H_2O. Otherwise the conditions were identical. The schematic of the experiments is presented in Scheme 2.