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

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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

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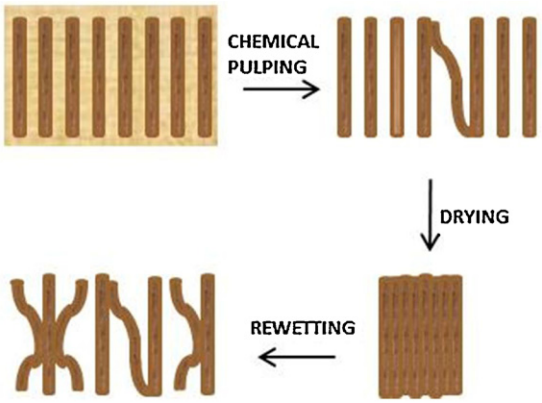
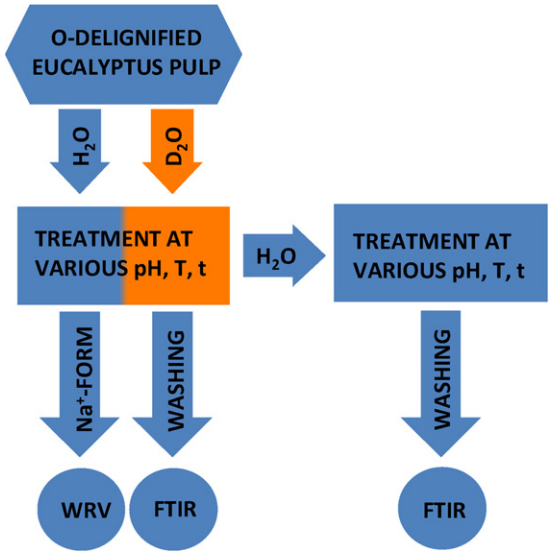


Scheme 1. Schematics of cellulose microfibril behavior during different processing steps.

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.

After the treatment the pulps were washed with an excess of water, namely 100 ml of water per 1 g of dry pulp, at room temperature by an identical period of time as the deuteration (2× 20 min). The slurry in an erlenmayer flask was mixed twice during the 20 min by shaking. The water was removed from the sample by filtration in a Büchner funnel.

2.3. WRV analysis

Prior to the WRV analysis the samples were washed to their Na^+-form. All of the following treatments were done 1% consistency and the change of solution was invariably done after a filtration in a Büchner funnel. First, the samples were washed to their protonated form in 0.01 M HCl for 1 h. Then the samples were washed twice with water. Washing to Na^+-form wash done in 0.001 M $NaHCO_3$ for 2 h with the pH adjusted to 9.5–10 with NaOH. Then, the samples were washed with water until the conductivity of the slurry was less than 5 μS/cm. The WRV analysis was done according to the standard SCAN-C 102 XE with a Jouan GR 4.22 centrifuge. Standard deviation was determined for the reference pulp. The other samples were measured predominantly once.

2.4. FT-IR spectroscopy

Prior to the FT-IR spectroscopic measurement, the samples were dried in 40 °C. The spectra were collected using a Bio-Rad FTS 6000 spectrometer (Cambridge, MA, USA) with a Gasera PA301 photoacoustic cell (Turku, Finland) at a constant mirror velocity of 5 kHz, 1.2 kHz filter, and 8 cm^{-1} resolution. In the beginning of each set of measurements, a background spectrum was collected using a standard carbon black. The samples were purged in the photoacoustic cell with helium gas for 30 s prior to each measurement including the duplicate measurements.

A minimum of 200 scans per spectrum were collected using the Win-IR Pro 3.4 software (Digilab (Holliston, MA, USA)). Every sample was measured as duplicate and averaged spectra were processed with Grams/AI 9.00 software (Thermo Fischer Scientific Inc. (Waltham, MA, USA)). The average spectra were baseline corrected and normalized to have the value of 1 at 1200 cm^{-1} (Hofstetter, Hinterstoisser, & Salmén, 2006).

The spectral interpretation is based on the detection of the protonation resistant OD groups after the treatment and following washing by the OD stretch band at around 2500 cm^{-1} in the FT-IR spectrum (Suchy, Virtanen, et al., 2010). This band does not overlap with any other band in the original pulp FT-IR spectrum and, thus, is reliable for the detection of the deuteration. The sufficiency of the deuteration period to convert all the free OH groups to OD groups has been discussed in an earlier paper (Suchy, Virtanen, et al., 2010). The complete reversibility of the deuteration during washing was proven by deuteration of the sample followed immediately by a washing phase. This treatment showed no increase in the OD stretch band in the FT-IR spectrum. Thus, the area of the OD stretch band at around 2500 cm^{-1} in the FT-IR spectrum can be considered a measure of the irreversible deuteration of the sample during the studied treatment. The area of the OD stretch band at around 2500 cm^{-1} in the FT-IR spectrum was integrated using Grams/AI 9.00 software (Thermo Fischer Scientific, Inc. (Waltham, MA, USA)).

3. Results

3.1. Acidic treatment at elevated temperature

Our aim was to survey the occurrence and the extent of accessibility alterations in mild acidic and alkaline conditions for an oxygen delignified eucalyptus kraft pulp. Fig. 1 shows that the acidic

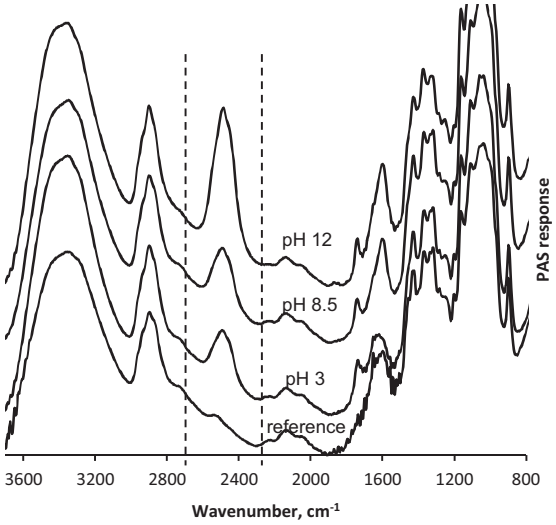


Fig. 1. FT-IR spectra of the deuterated eucalyptus pulp samples treated for 4 h in 90 °C at pH 12 (top), pH 8.5 (upper middle), pH 3 (lower middle), and the control reference (bottom).

treatment in pH 3 in deuterium oxide caused irreversible changes as seen in the retention of OD groups by FT-IR spectroscopy. The irreversible reduction in accessibility was demonstrated by the conversion of OD groups, formed during the pulp deuteration from free OH groups, into inaccessible, reprotonation-resistant OD groups in the acidic/alkaline treated and washed pulp. The inaccessible OD groups were detected by the OD stretch band at around 2500 cm^{-1} in the FT-IR spectrum. The irreversibility of the bonds was confirmed by effective washing that protonated all the free OD groups into OH groups.

The retention of deuterium in acidic conditions correlated with a decrease in WRV, a parameter that is commonly applied in evaluating hornification, i.e., the irreversible reduction in accessibility of cellulosic fibers during drying. Fig. 2 shows the integrated OD-band areas measured from the FT-IR spectra and the corresponding WRV values. It has been earlier concluded that hornification during drying is more pronounced for acidified pulps where carboxylic groups are in their protonated form and thus able to form additional bonds with hydroxyl groups (Lindström & Carlsson, 1982).

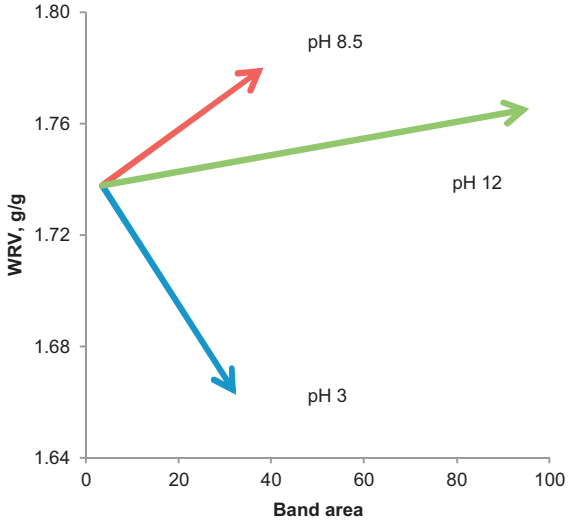


Fig. 2. Eucalyptus pulp samples treated at various pH for 4 h at 90 °C in D_2O (FT-IR) and H_2O (WRV). The arrows depict the change in OD-band areas at 2370–2610 cm^{-1} in normalized FT-IR spectra (*x*-axis) and WRV values (*y*-axis) during the treatments.

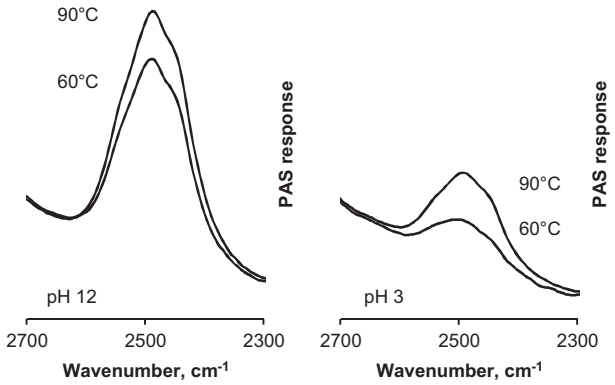


Fig. 3. FT-IR spectrum of the influence of temperature during the treatment of eucalyptus pulp for 4 h. pH 12 (left): temperature 90 °C (top), 60 °C (bottom). pH 3 (right): temperature 90 °C (top), 60 °C (bottom).

The magnitude of the OD-band area of the samples treated at pH 3 is comparable to softwood bleached kraft pulp samples dried at mild conditions (Suchy, Virtanen, et al., 2010). However, the change in WRV is somewhat smaller (around 5%) in the wet treatment compared to drying (around 10%). Drying at harsher conditions is often reported to cause an even more pronounced change in WRV, commonly around 30% (Kontturi & Vuorinen, 2009).

3.2. Neutral and alkaline treatment at elevated temperature

Neutral treatments of the pulp were done without any pH adjustment at pH 8.5 whereas alkaline treatments were done by adjusting the pH to 12. Both treatments caused the formation of protonation-resistant OD groups in the cellulosic material. The higher the pH, the more significant was the extent of deuteration (Fig. 1). The area of the OD stretch band was at the same level for the treatments at pH 3 and pH 8.5. Treatment at pH 12 caused a more significant band. The magnitude of the OD-band after treatment at pH 12 is at the same level with softwood bleached kraft pulp dried at elevated temperature (Suchy, Virtanen, et al., 2010). The same trend for alkalinity has also been reported for the growth of cellulose microfibril aggregates in the course of chemical pulping (Virtanen et al., 2008). In pulping, however, the conditions are much more severe and the removal of hemicelluloses plays some role contrary to this study where the hemicellulose content is already substantially lower. Distinct from the samples treated in acidic conditions, WRVs for the samples treated at neutral and alkaline conditions were not lower compared to the original oxygen delignified pulp (Fig. 2). Actually, the WRV increased during these treatments. In this respect, the treatment in pH 8.5 had a parallel effect with the treatment at pH 12.

3.3. Temperature dependence

Change in the accessibility of cellulose within fibers is known to be temperature dependent during drying (Kontturi & Vuorinen, 2009; Laine, Lindström, Bremberg, & Glad-Nordmark, 2003). It has been reported previously that the reduction in accessibility is more severe during drying at temperatures above 70 °C (Maloney & Paulapuro, 2000). Yet the critical temperature for proposed microfibril aggregation in a wet alkaline treatment, such as chemical pulping, has been suggested to be as high as 150 °C (Fahlén & Salmén, 2003; Virtanen et al., 2008). In our studies, however, the accessibility appears to decrease in the wet state already at much lower temperatures and the temperature dependence can be seen for both acidic and alkaline treatments already at temperatures below 100 °C, although the dependence is not radical (Fig. 3 and Table 1). The temperature dependence is clearly seen in both FT-IR spectroscopy as well as WRV measurements.

Table 1
WRV for samples treated at pH 3 and pH 12 for 4 h at various temperatures.

Treatment			WRV (g/g)
pH	T (°C)	t (h)	
3	60	4	1.67
3	90	4	1.64
12	60	4	1.70
12	90	4	1.77

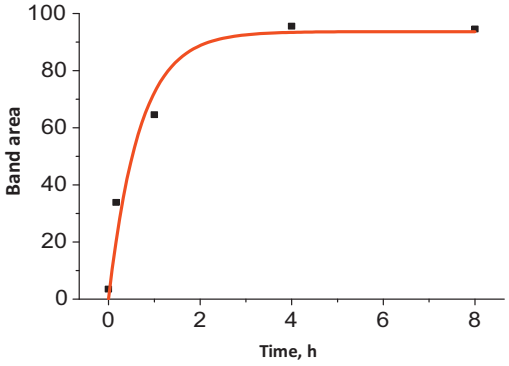


Fig. 4. OD-band areas in the FT-IR spectrum expressing the dynamics of the treatment of eucalyptus pulp at pH 12 at temperature 90 °C.

3.4. Kinetics of the deuteration

The kinetics of the deuteration at pH 12 and 90 °C is depicted in Fig. 4. These conditions were selected for the kinetic studies because they led to the highest response in FT-IR spectroscopy. The hypothesis was that the deuteration would follow first order dynamics. Thus, the following equation was fitted to these results:

$$X = A(1 - e^{-kt}) \quad (1)$$

where A in this fitting is 94 and k is 1.5 h^{-1} (Fig. 4). Subsequently, the formation of protonation resistant OD groups is faster in the beginning and then levels off.

3.5. Reversibility in aqueous media

The samples treated in alkaline conditions in D_2O were further exposed to both alkaline and acidic conditions in H_2O to evaluate the reversibility of the accessibility reduction that occurred during the first treatment in D_2O. Accordingly, the reduction in the OD-band in the second treatment in H_2O indicates that the decrease in accessibility during the first treatment is reversible. In dynamic equilibrium between accessible and inaccessible regions within the fiber, observing the formation of new inaccessible regions is not possible anymore at this analytical step which is able merely to assess the break-up of the formerly inaccessible areas. FT-IR spectroscopy clearly shows that most of the inaccessible OD groups formed during the first treatment were reversed in the alkaline high temperature treatment in pH 12 at 90 °C (Fig. 5). Treatment in pH 3 at 90 °C as well as the treatment in pH 12 at 60 °C reversed the inaccessibility only to a minor extent. Hence, temperature and pH have a significant effect on the reversion.

The kinetics of the reversibility is depicted in Fig. 6. The dynamics of the reversibility was estimated to follow the corresponding reaction rate to the initial formation of inaccessible regions. However, an additional constant B was added to the equation because of the assumption that part of the accessibility reduction is

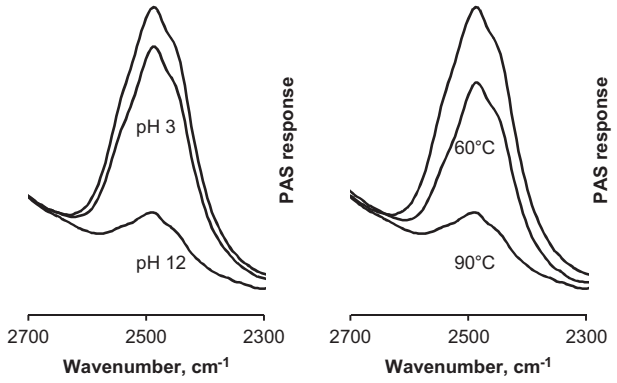


Fig. 5. FT-IR spectra of the deuterated eucalyptus pulps at 90 °C for 4 h at pH 12 (top ones). This sample has then been treated in water at 90 °C for 4 h at pH 3 (middle left) and pH 12 (bottom left). The same treatment has been done at pH 12 for 4 h at 60 °C (middle right) and 90 °C (bottom right).

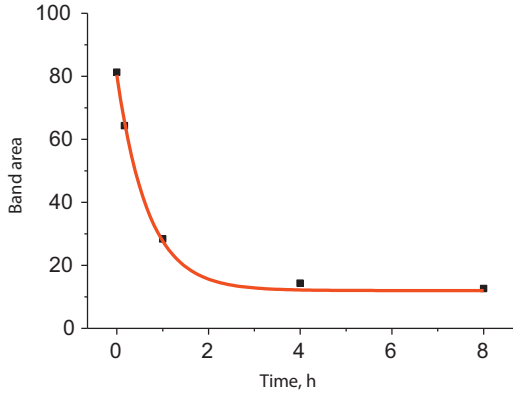


Fig. 6. OD-band areas in the FT-IR spectrum expressing the dynamics of the reversion of the phenomenon of eucalyptus pulp at a water treatment in pH 12 at temperature 90 °C. The time of zero represents a sample treated in pH 12 at temperature 90 °C for 4 h in D_2O.

completely irreversible. Thus the following equation was fitted to these results:

$$X = A \times e^{-kt} + B, \quad (2)$$

where A in this fitting is 68, k is 1.5 h^{-1}, and B is 12. The reversion, thus, follows very closely the corresponding reaction rate of the initial accessibility reduction, i.e., 1.5 h^{-1}. The level of irreversible changes, namely the constant B, was adjusted under the assumption that the reaction reaches plateau slightly after 4 h analogous to the dynamics in Fig. 6. Consequently, the reduction in accessibility seem not to be completely reversible, even though the majority of these changes appear to be in equilibrium and thus reversible at the chosen conditions.

Alkaline treatment is known to reverse some properties lost in cellulosic fibers during drying in mild acidic conditions at around pH 3 (Lindström & Carlsson, 1982; Lindström, 1992). Thus, pulps first treated in acidic conditions and then exposed to alkaline conditions should presumably gain an increase in WRV. In our experiments, this was not observed to a significant extent. For samples treated vice versa, i.e., first alkaline then acidic, the WRV dropped, probably due to the acidic conditions which induced the irreversible formation of inaccessible regions in fibers.

4. Discussion

Reduction in accessibility (hornification) is often deemed as an irreversible phenomenon, although the irreversible hydrogen bond formation related to hornification is always cited with little explicit experimental justification. In contrast, we have approached this from the point of view that the reduction in accessibility is at dynamic equilibrium, i.e., that it is a reversible phenomenon. We have two hypotheses for this equilibrium: (1) the equilibrium between the microfibrils and microfibril aggregates or (2) the equilibrium between amorphous and crystalline parts of cellulose. The latter is based on the assumption that microfibril aggregation is only able to occur in the amorphous regions, which are accessible to water (Aulin et al., 2009; Müller, Czihak, Schober, Nishiyama, & Vogl, 2000). Subsequently, the conceivable shift between the amorphous and crystalline forms of cellulose would have a considerable effect on the aggregation.

Fig. 5 puts forward strong evidence that the hypothetical microfibril aggregation upon alkaline and acidic treatments is at dynamic equilibrium and not an irreversible phenomenon. The reversibility is pronounced the higher the temperature and pH. First, in D_2O environment, the hypothetical aggregation is observed upon alkaline treatment but when the very same alkaline conditions are prolonged in an H_2O environment – which is able to detect disaggregation – the aggregates appear to disassemble. Our interpretation on these observations is that, if the aggregation hypothesis is valid, links between the microfibrils are broken and formed simultaneously: a dynamic equilibrium. The equilibrium state of the aggregation in alkaline conditions explains why the change in accessibility is not seen in WRV, even though the proposed aggregation is observed in deuteration combined with FT-IR spectroscopy. The reduction in WRV in acidic conditions, on the other hand, is due to the more irreversible nature of the aggregation in acidic conditions comparable to that occurring during, e.g., drying. The equilibrium state is further strengthened by the kinetic studies that show the reaction rate to be the same for the deuteration and its reversion. In conclusion, our results suggest that aggregation of microfibrils does occur while the cell wall swelling is increased and aggregation especially at alkaline high temperature conditions is at an equilibrium state.

5. Conclusions

This study clearly demonstrates the potential in using the deuteration combined with FT-IR spectroscopy in the analysis of cellulose accessibility in aqueous systems. We have demonstrated that this method has the potential to illuminate phenomena that would not have been observed by traditional WRV measurements. With this method we were able to detect the equilibrium state of accessibility reduction and the effect of pH and temperature on this equilibrium.

Acidic treatments (pH 3) in temperatures below 100 °C were illustrated to cause similar changes in the pulp as, e.g., drying. These include reduction in accessibility that is hypothesized to be due to cellulose microfibril aggregation. Alkaline treatments (pH 12) in temperatures below 100 °C, however, led to an equilibrium state of the proposed aggregation. We propose two hypotheses for this equilibrium: (1) the equilibrium between the microfibrils and microfibril aggregates or (2) the equilibrium between the amorphous and crystalline parts of cellulose. Thus, we suggest that the hypothetical aggregation in these conditions is not an irreversible phenomenon but an equilibrium state dependent on the conditions. The reversibility of the reduction in accessibility was the more pronounced, the higher the pH and the temperature. The treatment at very mild alkaline conditions (pH 8.5) led to increased swelling, as observed by WRV. However, the extent of deuteration was less extensive compared to the treatment at pH 12. Even though the level of deuteration was at the same level with the treatment at pH 3, we suggest that the treatment at very mild alkaline condition resembles the changes occurring in alkaline conditions, only to a

lesser extent. These findings are important in the view of changes occurring during, e.g., pulp bleaching, which is conducted at mild alkaline or acidic conditions at temperatures lower than 100 °C with the main aim of removing lignin from the pulp fibers.

The technological prospects of these findings include the possibility to tailor the cellulosic pulp accessibility properties. On one hand, accessibility is a key factor in determining the rate of the heterogeneous chemical modifications of cellulose, e.g., in the enzymatic saccharification of lignocelluloses to produce ethanol (Luo & Zhu, 2011), to name but one. On the other hand, inaccessibility as a property of a raw material can also have applications in the future cellulosic products.

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