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Effect of sonochemical treatments on the integrity and oxidation state of cellulose

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ABSTRACT

The sonochemical degradation of cellulose by a 24-kHz ultrasound probe system and the oxidative modification of cellulose upon sonication were studied. Both aqueous cellulose suspension (heterogeneous system) as well as cellulose solutions in *N*,*N*-dimethylacetamide/LiCl (homogeneous system) were used. In both cases, a significant reduction in the degree of polymerization was observed. The rate of the degradation process was dependent on the degree of polymerization of the starting material, temperature, cellulose amount in suspension, cellulose concentration in solution, and the pH value of the aqueous suspension. In solution, the degradation process was accompanied by cellulose oxidation as seen in the introduction of carbonyl groups. The introduction of carbonyl groups could be shown to occur close to chain ends. Sonochemical degradation of cellulose is a very efficient non-classical method in accordance with "green chemistry" concepts.

1. Introduction

Cellulose – the most abundant organic compound on earth – is a linear, stereo- and regioregular polysaccharide consisting of β-(1 → 4) linked D-glucopyranose units. It is insoluble in water and common organic solvents because of a complex network of intra- and inter-chain hydrogen bonds. For millennia, plant-derived cellulose has been utilized extensively for example as the major component of paper and as a textile fibre. Today, the pulp and paper and textile industries are very important for many national economies.

For several applications, cellulose depolymerization is required. In some cases, this depolymerization still stops at the polymeric state, e.g. in the adjustment of cellulose molecular weight (Mw) during rayon production to achieve pliable spinning dopes or in the production of micro-crystalline cellulose. In other cases, cellulose degradation is required to go down to cellulose oligosaccharides or even glucose, as in biorefinery applications that use these intermediates for fermentation. Cellulose degradation is one of the most important steps in cellulose processing. The methods available for the preparation of celluloses – and polysaccharides in general – of lower Mw can be chemical, enzymatic, or physical (Liu, Bao, Du, Zhou, & Kennedy, 2006; Xiuyuan, Yuefang, Bailin, & Xi, 2001). Regarding chemical cellulose degradation, acidic hydrolysis or oxidative degradation are the most common methods and are quite efficient (Kim, Lee, & Torget, 2001; Lenihan et al., 2010; Mosier et al., 2005; Qin, Du, & Xiao, 2002; Torget, Kim, & Lee, 2000). However, some disadvantages might be noticed, such as the use of chemicals and the resulting waste discharge problems, high costs, and lower yields. Some of the drawbacks related to the use of chemicals are eliminated by enzymatic methods using cellulases, but the high costs remain. The degradation of celluloses by means of ultrasound has many advantages. This type of cellulose depolymerization is both less used and less studied, yet it can be very attractive for the degradation of high-Mw polysaccharides (Kardos & Luche, 2001). The little attention sonochemical degradation has received in comparison with its chemical or enzymatic counterparts is supposed to be because ultrasound is still not fully accepted as a chemical instrument: sonochemically supported water baths for the cleaning of glassware are nearly ubiquitous in scientific labs, and sonochemical dispersion is an accepted means of promoting the dissolution of reagents; however, the use of ultrasound to "do chemistry" is very little developed in comparison, and sonochemistry even nowadays has a slightly exotic touch. Ultrasound, when going to be applied as a quasi chemical reagent, is provided in different frequencies and introduced into the chemical system by sonotrodes of different sizes and geometries.

Ultrasound has a frequency beyond the human range of hearing, usually ranging between 20 kHz and 100 MHz. Frequencies common for laboratory use are between 20 kHz and 40 kHz. High-frequency ultrasound of around 5 MHz and above is used in medical imaging (Mason, 1997). Ultrasonication generates high- and low-pressure waves in an exposed liquid. During the low-pressure cycle, ultrasonic waves create small bubbles in exposed liquid, which collapse violently during the high-pressure cycle. This process, called cavitation, is the driving force for sonochemically induced chemical processes. It is a rather complex phenomenon that involves

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nucleation, growth, and collapse of the micro-bubbles in solution (Czechowska-Biskup, Rokita, Lotfy, Ulanski, & Rosiak, 2005; Kardos & Luche, 2001; Striegel, 2007; Wong, Kasapis, & Tan, 2009; Wong, Kasapis, & Huang, 2012). Through the cavitation effect, the acoustic energy of the ultrasound is transformed into a chemically usable form that can be absorbed by molecules. Each cavitation bubble acts as a strongly localized micro-reactor that can generate a temperature of several thousand degrees and a pressure in excess of one thousand atmospheres (Mason, 1997). Implosion of the cavitation bubbles causes strong hydrodynamic shear and/or extensional forces. The degradation of polymers, including cellulose, can be understood on the basis of this stress: cellulose chain segments in the field near those strong forces move at a higher velocity than the chain segments farther away. This difference in velocity imposes elongation and shear stress to the cellulose chain and finally causes chain scission (Buchholz, Zahn, Kenward, Slater, & Barron, 2004).

Sonochemical degradation of polysaccharides is dependent on many factors, including intensity of the ultrasound; duration of the treatment (Wong et al., 2009, 2012); temperature (Chen, Chang, & Shyur, 1997; Price & Smith, 1993; Trzcinski & Staszewska, 2004; Vijayalakshmi & Madras, 2004; Wu, Zivanovic, Hayes, & Weiss, 2008); concentration (Grönross, Pirkonen, & Ruppert, 2004); type of solvent (Vijayalakshmi & Madras, 2006); type of polymer; and chemical structure, including branching (Kulicke & Schittenhelm, 2000). A recent study (Striegel, 2007) demonstrated that sonochemical degradation of polysaccharides is dependent on the anomeric configuration of the monosaccharide units (β-configuration in cellulose vs. α-configuration in amylose). Sonication of cellulose in cuprammonium hydroxide (cuam) solution results in degradation to a limiting molecular weight (M_{lim}) of about 46 kDa after 60 min, whereas sonication in 0.5% DMAc/LiCl did not reach such a limit even after prolonged sonication times (Wong et al., 2012). Czechowska-Biskup (2005) demonstrated that yield of degradation of polysaccharides in aqueous solution is dependent on polymer concentration, ultrasound power, and the gas used to saturate the solution.

The aim of this work was to clarify whether ultrasonic degradation of cellulose is purely hydrolytic, i.e. similar to an acidic or enzymatic process just causing cleavage of glycosidic bonds, or whether cellulose is simultaneously oxidized. In addition, ultrasound-induced degradation of cellulose in solution and in suspension is compared, i.e. in a homogeneous vs. a heterogeneous system, and the effect of pH and temperature studied. Cellulose oxidation was monitored as the increase of carbonyl groups relative to the molecular weight distribution (MWD) according to the carbazole-9-carbonyl-oxy-amine (CCOA) method (Röhrling et al., 2002a, 2002b). Beta-elimination reactions were used as an additional diagnostic tool (Potthast, Schiehser, Rosenau, & Kostic, 2009).

2. Experimental

2.1. Materials

Chemicals were obtained from commercial sources and were of the highest purity available. Cellulose was a Whatman filter paper with an Mw of 323.1 kg mol^{-1} and a polydispersity index of 1.87 (determined by GPC, according to Potthast, Kostic, Schiehser, Kosma, and Rosenau (2006), Potthast et al. (2009) and Röhrling et al. (2002a, 2002b)).

2.2. Methods

2.2.1. Activation procedure and dissolution

The activation procedure consisted of mixing dry cellulose pulp, 3 × 10 s, in a mixer with 100 ml of water. After mixing, all samples were filtered, washed with 96% ethanol, and left overnight in DMAc. In the case of sonochemical degradation in suspension, DMAc was filtered and 100 ml of prepared suspension was added. In the case of sonochemical degradation in solution, DMAc was filtered and samples were dissolved in 100 ml of DMAc/LiCl 9% (v/w).

2.2.2. Ultrasonic treatment

The treatment was performed with the Hielscher UIS 250 ultrasonic probe system (24 kHz, 250 W) in a 100-ml beaker for different times (0–120 min). A cellulose suspension of 25 mg of dry cellulose pulp in 100 ml of distilled water was used. A homogeneous solution was prepared dissolving 50 mg, 500 mg, and 1000 mg of dry cellulose pulp in 100 ml of DMAc/LiCl 9% (v/w). The sonotrode was an LS24d10 type made of titanium with a tip diameter of 10 mm and a length of 100 mm.

After sonication in aqueous suspension, pulp was activated and dissolved in 3 ml of DMAc/LiCl 9% (v/w). Samples were then diluted (0.3 ml of sample solution: 0.9 ml of DMAc), filtered through a 0.45-μm filter, and analyzed in the GPC system. In the case of sonication in solution, prior to sonication and at each specified time, 3 ml was taken directly from the vessel and diluted (0.3 ml of sample solution: 0.9 ml of DMAc) and analyzed in the GPC system after filtration through a 0.45-μm filter.

2.2.3. GPC analytics

GPC measurements used the following components: online degasser, Dionex DG-2410; Kontron 420 pump; pulse damper; auto sampler, HP1100; column oven, Gynkotek STH 585; refractive index (RI) detector, Shodex RI-71; fluorescence detector, TSP FL2000; and multi-angle laser light scattering (MALLS) detector. Data evaluation was performed with standard ASTRA and GRAMS/32 software.

The following parameters were used in the GPC measurements: eluent flow = 1.00 ml min^{-1}; columns = four PL mixed A LS, 20 μm, 7.5 × 300 mm; fluorescence detection λ_{ex} = 290 nm, λ_{em} = 340 nm (CCOA); injection volume = 100 μl; run time = 45 min; DMAc/LiCl 0.9% (v/w), filtered through a 0.02-μm filter, used as a mobile phase.

2.2.4. CCOA method

The labeling of carbonyl groups and analysis of carbonyl profiles were performed as described (Röhrling, 2002a, 2002b).

2.2.5. Beta-elimination reaction

Beta-elimination as a diagnostic tool to analyze the distribution of carbonyl groups along the cellulose chain was performed as described earlier (Potthast, 2009).

3. Results and discussion

3.1. Sonication in suspension

When cellulose was subject to sonochemical treatment in distilled water, a fast reduction of the Mw was observed. Fig. 1 compares the weighted-average Mw of the cellulosic starting material with that of the cellulose after different sonication times. Interestingly, sonication caused a fairly rapid degradation during the first 2 min, which slowly levelled off until 30 min and showed no further effect after that time. The weighted-average molecular mass decreased from about 320 kg mol^{-1} to 270 kg mol^{-1} within the first 2 min, reached approximately 250 kg mol^{-1} at 30 min, and remained constant even if sonication was continued to 120 min (Fig. 1).

Thus, sonication of cellulose in aqueous suspension causes cellulose degradation, but the depolymerisation effect is not very pronounced and stops at about 80% of the starting Mw. The major effect on the Mw is seen within the first few minutes of sonication,

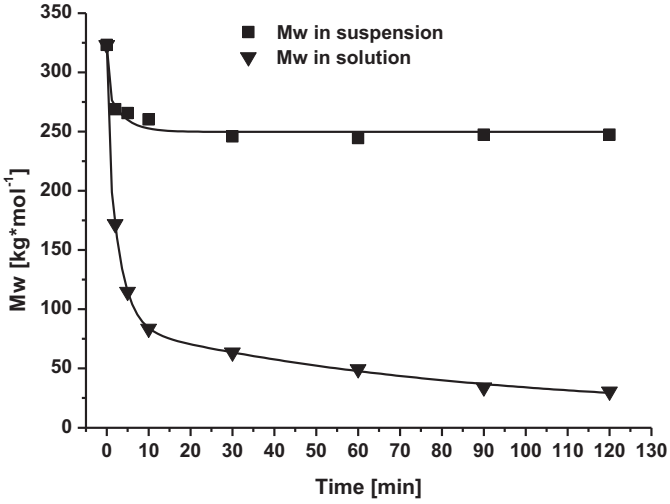


Fig. 1. Course of the cellulose degradation based on Mw over sonication time.

which is an important result regarding the reaction setup: sonication of cellulose in aqueous suspension for prolonged times beyond approximately 20–30 min does not change the cellulose further and can be avoided to save the energy for ultrasound generation.

The influence of the pH value on the sonochemical degradation of polymers has been studied (Vijayalakshmi and Madras, 2006) with the conclusion that significantly more pronounced degradation was obtained at pH extremes. Fig. 2 compares the sonochemical degradation of cellulose after 30 min in aqueous media of pH 2.2, 7.0 (distilled water), and 11.6.

The shift of the MWD curves for all three treated celluloses relative to that of the starting material was evident. The differences between the three graphs of the treated celluloses were rather minor. Considering that the medium itself already had a minor effect on the cellulose integrity by simple hydrolytic effects (data not shown here), it can be concluded that both acidic and alkaline aqueous media promote sonochemical degradation of the cellulose, albeit to a rather limited degree only. It cannot be derived from the experimental results whether this minor additional effect is caused by some synergism with the input of acoustic energy or just due to conventional hydrolytic effects. For cellulose in aqueous suspension, the influence of the pH was much smaller than described

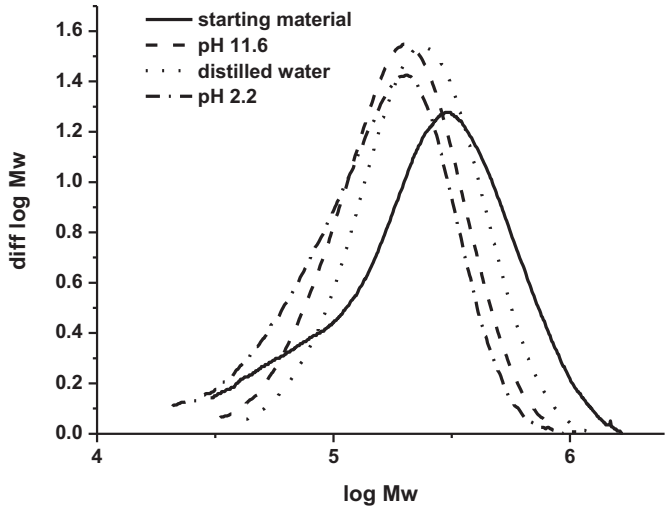


Fig. 2. Influence of pH on the sonochemical degradation of cellulose in aqueous suspension (30 min).

for other polymers, such as poly(vinyl alcohol) (Vijayalakshmi and Madras, 2006).

The oxidation state (carbonyl content) of the sonochemically treated celluloses is as follows: after 2 min: 5.1 μmol g^{-1}; 60 min: 7.1 μmol g^{-1} and after 120 min: 7.9 μmol g^{-1} measured by selective fluorescence labeling and GPC measurement (CCOA method). The total amount of carbonyl groups monitored is the sum of reducing end groups (REGs) and carbonyl groups along the chain. It should be noted that all carbonyl values measured are rather small, ranging well below 10 μmol g^{-1}. Cellulose sonicated for 2 min showed a carbonyl content of about 5 μmol g^{-1}, which corresponds nearly to the theoretical content of reducing ends, indicating no significant oxidation along the chain. The carbonyl content increased only insignificantly to about 8 μmol g^{-1} after 120 min of sonication. This minor change corresponds to the small chain degradation seen in this time period (cf. Fig. 1). Additional chain oxidation, i.e. introduction of carbonyl groups along the chain, is very minor, if occurring at all. The likely reason for the very minor degradation in the heterogeneous sonication treatment is the low potential of cavity formation within the solid matrix of the non-dissolved polymer: cavities are formed in the surrounding liquid only and thus do not – or only to a negligibly small extent – effect the solid celluloses suspended therein.

3.2. Sonication in solution

For sonication in solution, the solvent system *N*,*N*-dimethylacetamide/LiCl (v/v = 9%) was used because it is well characterized and best suited for the subsequent structural investigations. Sonication was performed over the same time period as for cellulose suspensions, until 120 min. The ultrasonic treatment caused a drastic loss in Mw. After 120 min of sonication, a stable value was reached at an Mw of approximately 26 kg mol^{-1}, which is about 8% of the starting Mw. Already within the first 2 min, the Mw dropped to 50%, and within 30 min it dropped to about 20%. After 90 min, the changes were only marginal, and the Mw was not further influenced beyond 120 min of sonication.

The final value of 26 kg mol^{-1} was evidently the limiting molar mass, M_{lim}, which could not be further decreased by sonication. The rate of sonochemical degradation decreased with decreasing Mw of the cellulose, eventually approaching M_{lim}. This value was reproducibly reached when the sonication conditions (cellulose concentration, temperature) were the same. It is apparently defined by the size (hydrodynamic volume) of the cellulose in solution. When this size becomes so small that it is no longer affected by cavitation collapse, i.e. the shear force between wave-low and wave-high, the molecule is not further degraded by ultrasound, even at prolonged sonication times. This outcome is somehow comparable to the case of dry ball milling of cellulose. Several studies addressed the reaching of a limiting degree of polymerization (DP) below which no further decrease in DP is possible (Schwanninger, Rodrigues, Pereira & Hinterstoisser, 2004). Even after several hours of continuous milling, no further decrease in DP was observed. No evidence of oxidation phenomena has been reported to occur as a consequence of the ball milling treatment (Avolio et al., 2012). The sonication results, as the weighted-average Mw at different sonication times, are displayed in Fig. 1.

Several studies have addressed the effect of concentration on polymer degradation by ultrasound (Caruso et al., 2009; Grönross et al., 2004). In the case of sonication of carboxymethylcellulose with 23-kHz ultrasound (Grönross et al., 2004), degradation efficiency increased with concentration. For chlorinated polyphenols, the opposite behavior – a faster degradation at lower concentration – was observed (Uraki, Chen, Gratzl, 1997). In our case, behavior similar to the latter example was observed: the extent of sonochemical degradation of the dissolved cellulose was higher when its

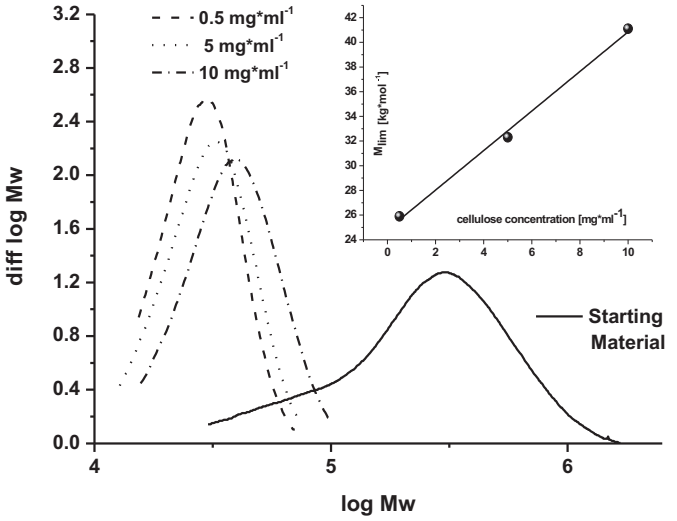


Fig. 3. Sonochemical degradation of cellulose in solution (DMAc/LiCl 9%) over 120 min. Linear influence of the cellulose concentration on the degradation process (M_{lim}).

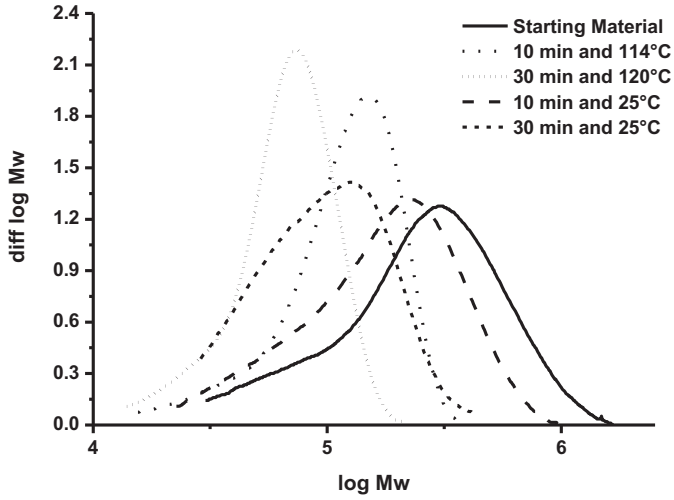


Fig. 4. Influence of temperature on the sonochemical degradation of cellulose (5 mg ml^{-1}) in solution (DMAc/LiCl 9%) for different times.

concentration was lower. In addition, there was also a dependence of M_{lim}, which was increasing with increasing cellulose concentration (Fig. 3).

Whereas M_{lim} was 26 kg mol^{-1} at a cellulose concentration of 0.5 mg mol^{-1}, it reached 32 kg mol^{-1} at a concentration of 5 mg ml^{-1} and 43 kg mol^{-1} at a concentration of 10 mg ml^{-1}. A linear relationship between cellulose concentration and M_{lim} could be demonstrated (see Fig. 3). The reason for this is the well-known dependence of sonochemical energy input on the solution viscosity: at higher viscosities, formation of cavitations is impeded, and formed cavitations are smaller compared with less viscous solutions. This translates into smaller hydrodynamic shear forces exerted on dissolved polymers.

Several studies have addressed the impact of temperature during ultrasound treatment on polymer degradation (Chen et al., 1997; Trzcinski and Staszewska, 2004; Vijayalakshmi and Madras, 2004; Wu et al., 2008). The majority of these studies conclude that sonochemical degradation of polysaccharides has a negative temperature coefficient, i.e. the rate of sonochemical degradation of polysaccharides accelerates by decreasing the temperature. Sonochemical degradation of cellulose in solution had a positive temperature coefficient, i.e. the increasing temperature strongly increased cellulose depolymerisation (Fig. 4). It should be noted that for exact measurements, the temperature of the sonication systems needed to be kept constant by a thermostat; otherwise, the energy intake would cause rapid heating of the solution. From these experiments on the factors influencing sonochemical degradation, it can be concluded that the degradation proceeds faster when the temperature is increased and the cellulose concentration is decreased. A decrease in cellulose concentration also causes a lower M_{lim} to be reached, whereas the reaction temperature has no effect on M_{lim}.

In order to detect possible oxidative changes during the sonication in solution, the CCOA method for carbonyl profiling in cellulosics was used (Röhrling et al., 2002a, 2002b). The total number of carbonyls is the sum of REG and aldehyde (C-6)/keto (C-2, C-3) groups along the chain. Whereas the reducing ends are present as hemiacetals, the carbonyl functionalities along the chain are present both in their double-bond form and as hydrates, and the amount of hemiacetals and hemiketals (which would mean inter- or intra-chain cross-linking) is negligible. The (theoretical) number of REGs can be directly calculated from the number-average Mw. When cellulose is hydrolyzed, the cellulose chain is cleaved and the REG content (in μmol g^{-1}) increases: in shorter chains, there are more REGs relative to non-reducing anhydroglucose units than in longer chains. The difference between total carbonyl content and (theoretical) amount of reducing ends is the amount of keto (aldehyde) groups along the chain. The course of the three carbonyl numbers – overall content, REGs, and keto/aldehyde groups along the chain – is shown in Fig. 5.

As is evident also from Fig. 1, sonication in solution caused a rapid decrease in Mw, which corresponds to the increase in REGs. Compared with cellulose sonication in suspension, the rate of hydrolysis and thus also carbonyl (REG) generation in solution was about ten times faster, and the overall carbonyl contents for the solution-sonicated cellulose (Fig. 5) were about 10 times higher than those for the suspension-sonicated cellulose.

Also, while in suspension, only hydrolytic cleavage and no oxidative cellulose alteration was observed (formation of new reducing ends without the introduction of additional carbonyls along the chain); sonication in solution caused cellulose oxidation

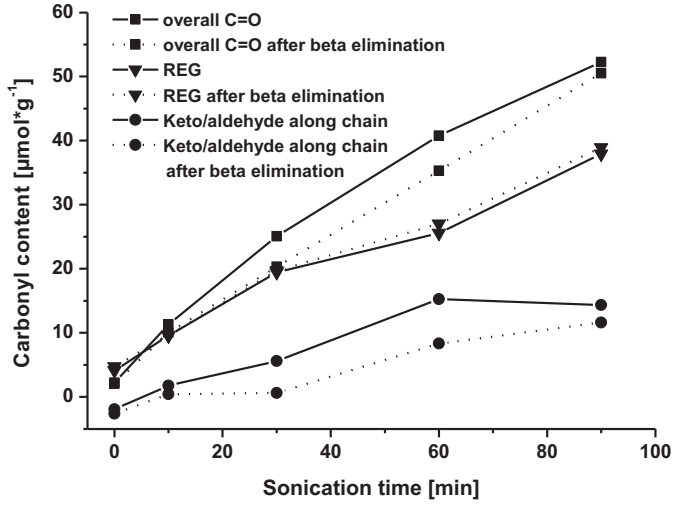
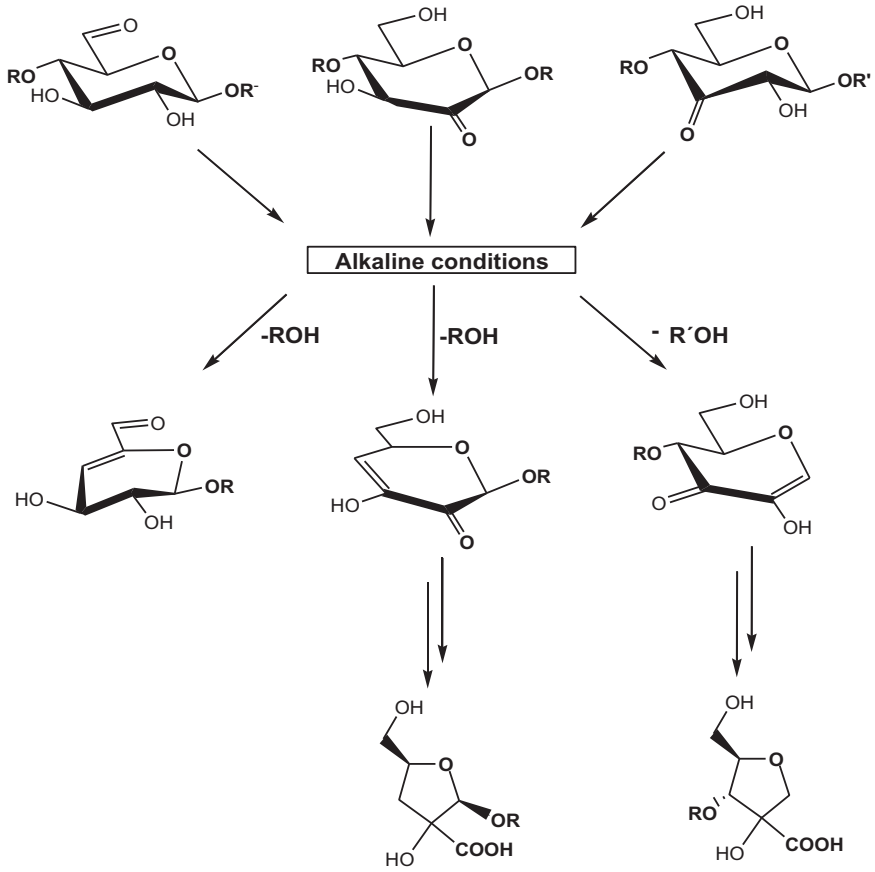


Fig. 5. Changes in the oxidation state (carbonyl content) of cellulose dissolved in DMAc/LiCl (9%) upon sonication over different times. Solid lines: overall carbonyl, REG, and keto/aldehyde content in the pulp after sonication. Dotted lines: overall carbonyl, REG, and keto/aldehyde content in the pulp after sonication and beta-elimination by strong alkaline treatment.



Scheme 1. Alkali-induced beta-elimination reaction starting from carbonyl functionalities at C-6 (formulae in left column), C-2 (formulae in middle column), and C-3 (formulae in right column), causing cleavage of the adjacent glycosidic bond and leaving behind two chain fragments, which can undergo further rearrangements to stable products.

in addition to the hydrolytic chain cleavage. This can be seen by the amount of non-REG carbonyl groups (Fig. 5). Where are these additional carbonyls introduced at the cellulose chain? The beta-elimination reaction is a powerful and versatile tool to address in more detail the nature of such along-chain carbonyls (Potthast et al., 2009). The reaction is induced by the action of alkali and causes cleavage of a glycosidic bond next to a carbonyl at C-2, C-3, or C-6. In all cases, the alkoxy substituent in beta-position relative to the carbonyl group, i.e. the residual cellulose chain, is cleaved off. The former keto-sugar unit, after elimination, might undergo subsequent reactions – mostly of the benzilic acid rearrangement type – to produce stable furanoid products. The outcome of the beta-elimination reaction in dependence on the carbonyl position in the anhydroglucose units is shown in Scheme 1.

The cleavage of the glycosidic bond next to a carbonyl function causes chain fragmentation in any case, and the length of the two resulting chain fragments depends on the position of the carbonyl group along the cellulose chain. If the carbonyl is situated in a more central section, the two fragments will be of comparable length; however, if it is positioned in outer regions, both a longer and a shorter fragment will result. All these fragments can be detected by GPC, and the MWD will display a significantly reduced Mw. The number of carbonyls will remain nearly constant because the "old" reducing end is not influenced, and a new reducing end (of the second fragment chain) is produced for the along-chain carbonyl. However, if the carbonyl is located very close to the reducing end – e.g. in the same, the neighboring, or the adjacent anhydroglucose units – the cleaved-off fragment will comprise only one, two, or very few anhydroglucose units. On the one hand, such low-Mw fragments will not be detectable by GPC; on the other hand, the minor loss in the Mw of the large fragment will be very hard to monitor, so that the apparent Mw of the cellulose stays the same within the error of measurement. The overall carbonyl content will decrease: a reducing end is present before and after the beta-elimination reaction, but the additional carbonyl function that was present before is lost upon the process. The dependence of the length of the chain fragments after beta-elimination on the position

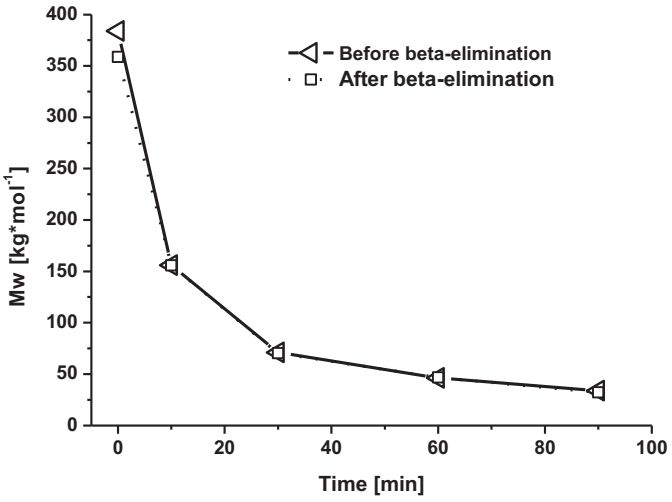
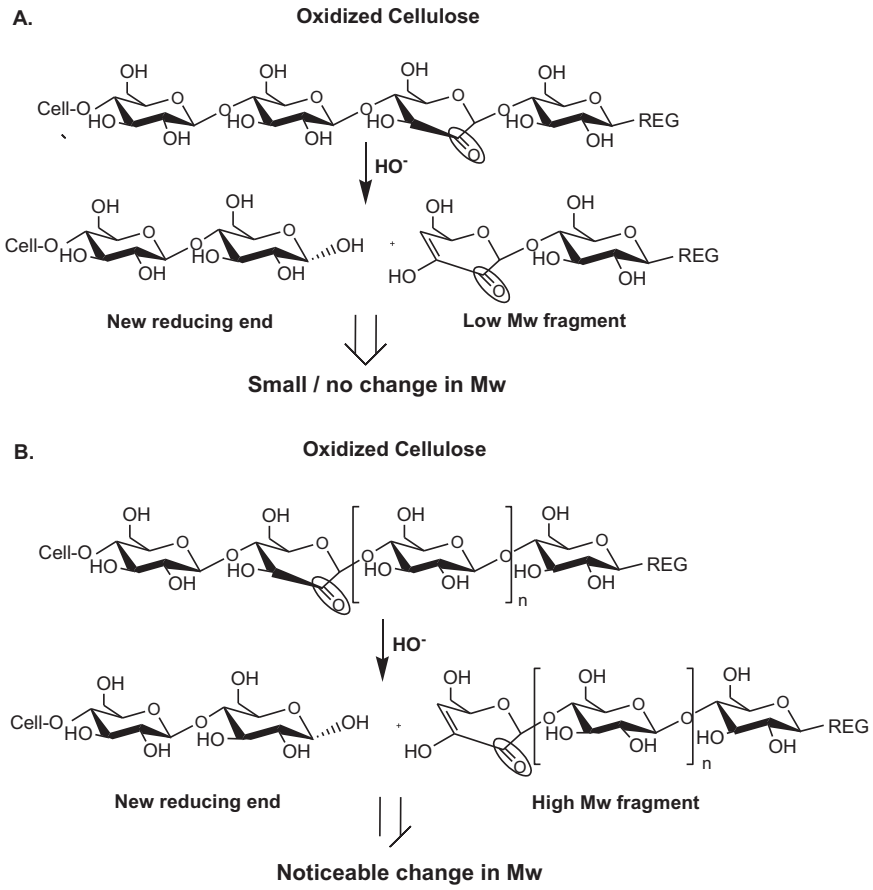


Fig. 6. Mw of cellulose sonicated in solution, before and after beta-elimination by alkaline treatment. The differences are so small that they are difficult to display.



Scheme 2. Length of the two cellulose chain fragments produced upon a beta-elimination process in dependence of the position of the carbonyl functionality along the cellulose chain. Beta-elimination process: (A) oxidized position and cleavage close to reducing end, resulting in a long fragment with nearly unchanged Mw and a GPC-silent low-Mw fragment, with a decreasing overall carbonyl content; (B) oxidized position and cleavage far from the reducing end, resulting in two shortened cellulose fragments that are both detectable in GPC and result in a readily detectable decrease in Mw, while the overall carbonyl content stays nearly the same.

of the carbonyl function along the chain, and the resulting changes in Mw as observed by GPC, are displayed in Scheme 2.

When the sonicated, dissolved celluloses were subject to beta-elimination, the changes in the Mw were negligibly small (Fig. 6). At the same time, the number of carbonyl groups decreased noticeably (Fig. 5, dotted line). As discussed above, this allows only the conclusion that the along-chain carbonyl groups were introduced at or very close to the reducing end or to the opposite terminal chain end, so that the cleaved-off low-Mw fragments are very small and the decrease in the Mw of the long, major chain is so minute that it cannot be detected by GPC. This is a novel and quite surprising insight into the mechanism of cellulose sonication in solution: the chain cleavage leaves an oxidized spot at (or very close to) the terminal glucopyranose units, where the chain was cleaved by ultrasound. Subsequent beta-elimination has only a negligible effect on Mw, but the carbonyl content is reduced as the carbonyl-carrying unit is split off.

4. Summary and conclusion

Sonication of cellulose in aqueous suspension causes cellulose degradation that is not very pronounced, reaching about 80% of the Mw starting value. The largest part of the depolymerization occurs during the first 2 min of the treatment. Sonication beyond 30 min has no further effect on the MWD. Changes in the molecular structure of the cellulose are hydrolytic (chain cleavage); there were no indications for an additional oxidation (introduction of carbonyl groups) along the cellulose chain to any significant degree.

Ultrasonic treatment of cellulose in solution changed the Mw drastically. An M_{lim} at approximately 10% of the starting value is reached; the Mw is halved within the first 2 min of sonication. After 90 min, the changes become marginal, and no further changes occur beyond 120 min of sonication time. The sonochemical degradation is faster at higher temperatures and at lower cellulose concentrations. In addition to the hydrolytic cleavage, oxidation also occurred as seen by the introduction of carbonyl groups along the chain. These functionalities are introduced at or very close to the terminal glucopyranose units (the reducing end or the opposite glucopyranose with free 4-OH) as seen by an unchanged Mw with a simultaneous decrease in carbonyl content upon beta-elimination reactions. Sonochemical cellulose cleavage in DMAc/LiCl solution thus occurs according to a binary mechanism that is both hydrolytic and oxidative: the cellulose chain is split and at the same time oxidized at or close to the spot of cleavage.

In future studies, we will further examine the dependence of the M_{lim} on the starting cellulose and on the sonication frequency. We will also try to determine whether sonication in the presence of mild reductants will be able to avoid the additional oxidation upon sonication in solution so that the mechanism becomes similar to that for cellulose suspensions, which is purely hydrolytic lacking the oxidative aspect.

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