http://dx.doi.org/10.5935/0103-5053.20130038

J. Braz. Chem. Soc., Vol. 24, No. 2, 295-303, 2013.
Printed in Brazil - ©2013 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Cellulose Dissolution in an Alkali Based Solvent: Influence of Additives and Pretreatments

Martin Kihlman,[a] Bruno F. Medronho,[,b] Anabela L. Romano,[b] Ulf Germgård[a] and Bjorn Lindman[c,d]*

[a]*Department of Chemical Engineering, Karlstad University, Universitetsgatan 2, SE-651 88 Karlstad, Sweden*

[b]*Institute for Biotechnology and Bioengineering, Centre of Genomics and Biotechnology (IBB/CGB), Faculty of Sciences and Technology, University of Algarve, Campus de Gambelas, Ed. 8, 8005-139 Faro, Portugal*

[c]*University of Coimbra, Department of Chemistry, 3004-535 Coimbra, Portugal*

[d]*Division of Physical Chemistry, Center of Chemistry and Chemical Engineering, S-221 00 Lund University, Sweden*

A distinção entre termodinâmica e cinética de dissolução da celulose raramente tem sido considerada na literatura. Neste trabalho, discutimos este tema e fundamentamos as nossas hipóteses recorrendo a experiências simples. É do conhecimento geral que a celulose pode ser dissolvida no solvente aquoso de hidróxido de sódio ($NaOH/H_2O$) a baixa temperatura. Neste trabalho, demonstramos que este solvente alcalino pode ser consideravelmente melhorado em relação à sua estabilidade, solubilidade e propriedades reológicas se forem usados diferentes aditivos (sais e moléculas anfifílicas) na fase de dissolução. Este trabalho indica novos caminhos relativamente à dissolução da celulose em solventes aquosos, de uma forma mais econômica e ambientalmente amigável, aumentando o seu potencial comercial.

The distinction between thermodynamic and kinetics in cellulose dissolution is seldom considered in the literature. Therefore, herein an attempt to discuss this topic and illustrate our hypotheses on the basis of simple experiments was made. It is well-known that cellulose can be dissolved in a aqueous sodium hydroxide ($NaOH/H_2O$) solvent at low temperature but it is here shown that such an alkaline solvent can be considerably improved regarding solubility, stability and rheological properties as a whole if different additives (salts and amphiphilic molecules) are used in the dissolution stage. This work probes new aqueous routes to dissolve cellulose, thereby improving the potential to commercially dissolve cellulose in an inexpensive and environmentally friendly manner.

Keywords: cellulose dissolution, hydrophobic effect, sodium hydroxide, pretreatment amphiphiles

Introduction

Being the world's most abundant and renewable natural biopolymer and one of the most studied, cellulose is still challenging researchers. Cellulose is biodegradable and biocompatible, so that, it is seen as one of the main chemical resources in the future. Its uses range from, for instance, paints and paper industry to biofuel production including also areas related to pharmacological and medical applications. In addition, cellulose can be regenerated in several less conventional morphologies such as fibers, membranes, sponges, non-woven materials, nanoparticles, aerogels or even new blend compounds with biological activity.[1,2] In many applications, cellulose dissolution is a crucial step; often, the most challenging part in dissolving cellulose is to find a non-derivatizing solvent that does not reduce the degree of polymerization or reacts with the cellulose.[3] Thus, it

*e-mail: bfmedronho@portugalmail.pt

is understandable that the full potential of applications are still far from being reached because cellulose cannot be melted or easily dissolved in common cheap solvents as other raw materials. The most widely used industrial procedure for dissolving cellulose is the viscose process.[4] However, the traditional viscose route is generally a slow and environmentally problematic process.

Many solvents for cellulose, with striking unrelated properties, have been developed, such as aqueous inorganic complexes (cuoxam, cadoxen, cuen),[5] zinc chloride aqueous solutions,[6-8] ammonium, calcium and sodium thiocyanate solutions,[8-10] lithium chloride/N,N-dimethylacetamide,[11,12] ammonia/ammonium salt,[13-14] etc. However, most of these solvents are limited to a laboratory scale due to issues such as toxicity and environmental hazard, limited solvency, problems arising in developing closed processes and high power consumption in solvent recycle.

Recently, "greener" solvent systems have been developed such as the N-methylmorpholine-N-oxide (NMMO), which dissolves cellulose at elevated temperatures (ca. 90 ºC).[15,16] Nevertheless, this system is restricted to a small operating window in which the parameters are optimal and this constitutes a major limitation. Ionic liquids (ILs) have been found to be capable of dissolving cellulose and other carbohydrates to a large extent. The potential of ILs is huge, for example, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) can dissolve considerable amounts of cellulosic materials and lignin from different wood samples.[17] However, there are some important limiting factors which have been delaying large-scale applications of ionic liquids such as their typical high cost of production, viscosity, sensitivity to moisture content and poorly developed appropriate purification processes.[18-19]

Dissolution of cellulose in NaOH/H_2O can be achieved to a certain extent depending on factors such as the molecular weight and crystalline form.[20,21] Strikingly, within a certain concentration range (7-10%), NaOH/H_2O can be a direct solvent for cellulose provided the temperature is low enough (below 0 ºC). This unusual thermal behavior of cellulose is obviously not expected from either standard kinetic or thermodynamic points of view.

There seems to be a consensus among leaders in the field that the insolubility of cellulose is due to its ability to form intra- and intermolecular hydrogen bonds.[22] Therefore, solvents such as the NaOH/H_2O are suggested to be able to break these hydrogen bonds.[23] This common notion that cellulose-cellulose hydrogen-bonding is the main obstacle to dissolution and the driving force of aggregation has been recently questioned and, instead, it was suggested that hydrophobic interactions play a very important role in cellulose (in)solubility.[24,25]

Various starting points have encouraged and triggered the development of new interesting, relatively inexpensive and environmentally friendly aqueous/alkali-based alternatives.[26-33] Nevertheless, the majority of these alkali-water based systems only allow the dissolution of cellulose with relatively low degree of polymerization, DP (typically, less than 300). In order to dissolve higher cellulose amounts with higher DP, it becomes important to improve cellulose accessibility. Therefore, several chemical, enzymatic and mechanic pretreatments have been investigated.[34-38] The so-called ethanolysis process has been widely used to pretreat cellulose based biomass, especially for biofuel production.[39] In some cases, this procedure is used to extract lignin from wood by degrading the cellulose and hemicelluloses.[40,41] This process is typically performed at high temperatures and pressures. Recently, Trygg *et al.*[42] developed a one-step chemical pretreatment method using a mixture of ethanol and hydrochloric acid (EtOH/HCl) using less harsh conditions than the typical ethanolysis procedure. The authors claim that the use of such pretreatment degrades the remnant primary cellulose fiber wall layer allowing a more efficient solvent accessibility to the inner core of the fiber thus resulting in complete cellulose dissolution in a NaOH/urea/H_2O solvent.

The work presented here attempts to contribute to the understanding of both kinetic and thermodynamic effects of cellulose dissolution. Therefore, the influence of the hydrothermal and the EtOH/HCl pretreatments (individually or combined) on the solubility of cellulose is evaluated and, additionally, the role of additives such as zinc oxide (ZnO) and amphiphilic molecules is discussed. Amphiphilic additives are particularly significant in the context of the controversy regarding hydrogen bonding *vs.* hydrophobic interactions.[43]

Experimental

Materials

Buckeye V67 dissolving pulp (prehydrolyzed kraft southern pine) was supplied by Buckeye Co. (USA) in the form of dried pulp sheets. This dissolving pulp has a cellulose content of 95.9%, 3.5% hemicellulose and 0.6% lignin. The measured water retention value is 0.69 and the polydispersity index is 5. Ethanol, hydrochloric acid and zinc oxide powder (micron-size particles) of 99.9% purity were supplied by Sigma-Aldrich (St. Louis, USA) while sodium hydroxide pellets, with purity higher than 97%, were supplied by Merck (Darmstadt, Germany). A zwitterionic surfactant solution (a derivative of trimethylglycine) was

used. All chemicals were used as received and all solutions were prepared with distilled water.

Cellulose pretreatments

Different pulps were used in this work, namely: untreated Buckeye dissolving pulp (BP), hydrothermally treated Buckeye pulp (HT-BP), ethanol-acid treated Buckeye pulp (EA-BP) and Buckeye pulp submitted both to ethanol-acid and hydrothermal treatments (EA/HT-BP). The pulp specification and calculated DP are summarized in Table 1.

HT-BP was prepared according to the procedure developed by Struszczyk *et al.*[44] Briefly, a cellulose suspension in water and a small amount of ascorbic acid were mixed and the mixture placed in a pressure reactor. The reactor was heated to 173 ºC for 40 min, after which the HT-BP pulp was extensively washed with cold water and pressed, reaching a moisture content of about 70%.

For EA-BP, the procedure used was as follows: 400 cm^3 of ethanol were pre-heated in a water bath to 60 ºC. After thermal equilibration, 16 cm^3 of hydrochloric acid (37 wt.%) were added. 16 g of cellulose pulp (BP or HT-BP) were carefully added under stirring to ensure a homogenous dispersion of the cellulose in the ethanol-acidic medium. After 30 min, the reaction was stopped by adding several liters of cold distilled water. EA-BP was then filtered and extensively washed with distilled water to remove any residuals of ethanol and HCl.

Preparation of solutions

The freshly prepared solvent system ($NaOH/H_2O$) was pre-cooled to −1 ºC, while the cellulose was kept in a freezer at 0 ºC. Afterwards, the cellulose was added to the solvent in a cooled container refrigerated via circulation of a water-polyethylene glycol solution. A robust stirrer with two counter-wise propellers was then immersed in the cellulose-solvent mixture. Each solution was stirred for 20 min at 500 rpm. The temperature was kept at −1 ºC during the first couple of minutes and then increased to +4 ºC. In the majority of the cases, a clear transparent solution was obtained after mixing. It should be noted that additives were added either before mixing of the solution (e.g., ZnO), or after dissolution (e.g., surfactant additive). In the latter case, since the additive is a surfactant-like molecule, its addition after mixing avoids extensive formation of foam. The solvent was composed of 8.5% NaOH in water while the amounts (based on a dry content) of cellulose, ZnO and surfactant additive were 6.0, 0.8 and 0.6 wt.%, respectively.

Methods

Polarized optical microscopy

An Olympus BX51 microscope equipped with a ColorView software system was used to evaluate the quality (transparency, birefringence and fraction of undissolved fragments) of the dissolution. A small aliquot of the cellulose solution was transferred to a microscopic glass slide, covered with a cover glass and viewed in the microscope between crossed polarizers. A magnification of 200 × was used in each trial.

Rheometry

The rheology experiments were performed on a Physica UDS 200 rheometer using a cone-and-plate measuring geometry (1º, 50 mm diameter). The instrument is equipped with an automatic gap setting. A temperature control unit ensures a temperature variation in the sample chamber not larger than 0.1 ºC of the set value. The shear viscosity (η) of the samples was determined in nonlinear rotational measurements. On the other hand, the small-amplitude dynamic tests provide information on the linear viscoelastic behavior of materials through the determination of the complex shear modulus, G*(ω), according to equation 1.[45]

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (1)$$

where G'(ω) is a measure of the reversible elastic energy, while G''(ω) represents the irreversible viscous dissipation of the mechanical energy as a function of frequency, ω. The gelation kinetics were monitored by recording the time evolution of G' and G'' over a fixed period, at a constant frequency of 1 Hz and constant

Table 1. Specification and calculated DPs of the different pulps used in this work

Pulp sample	Specification	DP
BP	original Buckeye pulp	637
HT-BP	hydrothermally treated Buckeye pulp	263
EA-BP	ethanol-acid treated Buckeye pulp	393
EA/HT-BP	ethanol-acid and hydrothermally treated Buckeye pulp	234

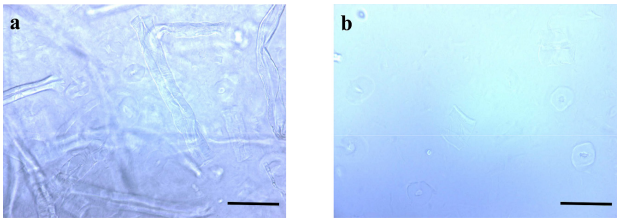

Figure 1. Optical micrographs of 6% HT-BP dissolved in an 8.5% $NaOH/H_2O$ solution without (a) and with (b) 0.8% ZnO. The scale bar represents 200 μm.

shear stress of 1 Pa. The shear stress used was found to be within the linear viscoelastic regime. ISO Standard 5351:2010, Determination of Limiting viscosity number in cupri-ethylenediamin (CED) solution.

Determination of the degree of polymerization

Viscosity measurements were done according to the ISO5351 standard norm in which, essentially, cellulose pulp is dissolved in a cupriethylenediamine (CED) solution and the flow rate is measured in a capillary viscometer. DP is then calculated through its correlation with the pulp intrinsic viscosity as shown in equation 2.[46]

$$DP^{0.905} = 0.75[\eta] \quad (2)$$

Results and Discussion

Influence of additives on the thermodynamics of dissolution of hydrothermally-treated Buckeye pulp

Hydrogen bonding *vs.* Charging up a neutral polymer

HT-BP with an average DP of 263 was dissolved in an 8.5% $NaOH/H_2O$ solution (with and without ZnO) following the procedure described above. In Figure 1a, it can be seen that a high density of swollen undissolved fibers still presents in the solution if ZnO is not used. However, the addition of a small amount of ZnO is crucial to promote full cellulose dissolution (Figure 1b).

Figure 2 demonstrates that the shear viscosity is considerably decreased when ZnO is added. This is of interest because it makes possible the dissolution of higher amounts of cellulose while maintaining a lower viscosity.

The enhancement of cellulose dissolution by adding relatively small amounts of ZnO to concentrated NaOH solutions has already been known for several years.[47-51] However, the mechanism is still not understood.[52] Recently, the role of the sodium zincate ion ($Zn(OH)_4^{2-}$, a possible reaction product of ZnO with NaOH) was analyzed by Yang *et al.*[53] It is claimed that $Zn(OH)_4^{2-}$ can form stronger hydrogen bonds with cellulose than hydrated NaOH. Additionally, and somewhat contradictory, the authors

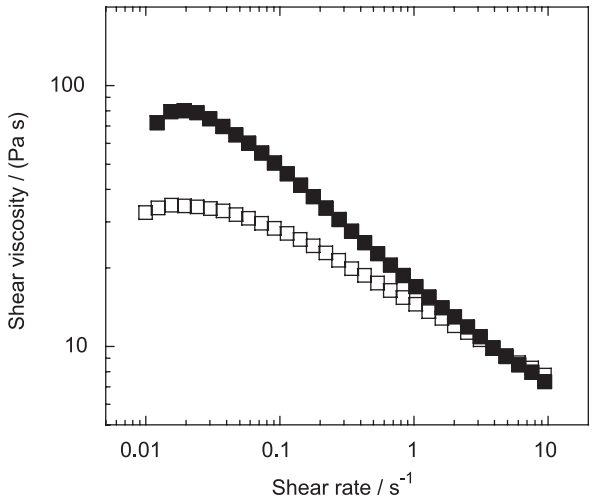

Figure 2. Shear viscosity of 6% HT-BP dissolved in an 8.5% $NaOH/H_2O$ solution with (open squares) and without (filled squares) 0.8% ZnO.

also consider that $Zn(OH)_4^{2-}$ plays an important role in breaking the intermolecular hydrogen bonds of cellulose, leading to an enhancement of the dissolution capability. Regarding a simple hydrogen-bonding mechanism, it is clear that all hydrogen-bond interactions involved (i.e., cellulose-cellulose, cellulose-water and water-water) are comparable in magnitude, ca. 20 kJ mol^{-1}. This has been demonstrated by quantum chemical calculations, which is a method that provides a rigorous way of determining the strength of hydrogen bonds.[54,55] It is not clear why the $Zn(OH)_4^{2-}$ anion would form stronger hydrogen bonds with cellulose than with water and, at the same time, be capable of selectively breaking cellulose intermolecular hydrogen bonds.

Recently, fundamental polymer physicochemical aspects with special focus on cellulose have been reviewed.[24,25] From this analysis, it becomes clear that polyelectrolytes are much more soluble than nonionic polymers due to the entropy of the small counterions. Therefore, charging up a polymer is always expected to be helpful for solubility. Clearly, this is the reason why cellulose tends to be more soluble in water at either high or low pH. However, the pK values are such that rather extreme conditions are needed for either deprotonation of the hydroxyls or protonation. In combination with the above described effect of an extreme pH, it is suggested that the $Zn(OH)_4^{2-}$ anion is simply charging up cellulose by associating to it. In fact, this charging up principle is widely used in the chemical modification of cellulose (e.g., carboxymethyl cellulose). It is foreseen the same effect by the association of cellulose with some ionic cosolutes, such as the $Zn(OH)_4^{2-}$ anion. Thus, as a consequence of the formation of a cellulose-zincate charged complex, the solubility of cellulose is enhanced. On the other hand, the viscosity of the polyelectrolyte solution (as a result of the interaction of

$[Zn(OH)_4]^{2-}$ with the chains of cellulose) should, in principle, increase due to the chain stretching (charge repulsion). Therefore, the observed viscosity drop is probably associated with some alignment of cellulose fibers under the shear field and the high ionic strength of the aqueous solution due to 8.5% of NaOH that screen the charges.

Why is a low temperature favorable for the dissolution of cellulose in this alkali solvent? According to Lue *et al.*,[56] the underlying mechanism should be that the stability of the complexes formed between the cellulose and NaOH is promoted at low temperatures. These authors proposed that the complex induces the formation of new hydrogen bonds between the cellulose molecules and the solvent, hence enhancing the water solubility of cellulose. However, strong arguments can be raised against both a hydrogen-bonding mechanism and a complex formation between cellulose and NaOH. Regarding the striking temperature effect observed in the literature,[55] it is fruitful to consider other systems displaying such an inverse temperature effect. Lindman and Karlström[57] have reviewed and analyzed the analogous thermal behavior observed for ethyleneoxide-based nonionic polymers and surfactants and also for nonionic cellulose derivatives, such as methylcellulose and ethylhydroxyethylcellulose. A temperature-induced conformational change in which the $O–CH_2–CH_2–O$ segments with conformational freedom around the C–C bond can change their conformation as a function of temperature from a less polar state around the C–C bond (higher temperatures) to more polar states at lower temperatures is found to account for observations made and also agree with direct measurements of conformational changes.[24,25] Thus, as the temperature is decreased and more polar states are being populated, more favorable attractive interactions with the polar solvent are established, thus facilitating cellulose dissolution.

Hydrophobic effects in cellulose re-association: enhancing the stability of a cellulose solution

The stability of the cellulose solution is a very important parameter for the evaluation of a solvent system. Typically, cellulose dopes are unstable with the self-association of cellulose chains resulting in gelation of the system. It is expected that the electrostatic repulsion between the now charged polymer backbones (i.e., cellulose-zincate charged complexes) contributes to the stability of the solution by preventing cellulose re-association. In Figure 3, freshly prepared samples (with and without ZnO) are compared, which were allowed to rest at +4 ºC while the viscoelastic parameters G' and G'' were measured over time. Indeed, the sample with ZnO has a more pronounced liquid-like behavior (grey curves) indicating that gelation is not occurring. On the other hand, the cellulose dope without ZnO shows a higher elastic modulus (G'). Moreover, the progressive increase of G' during the first hour indicates that the solution is becoming more elastic and gelation is occurring much faster than in the case of the cellulose dope with ZnO, in which both moduli are far apart after 1 h. A similar effect was observed when the surfactant additive was used. It was observed that the solution, which did not contain ZnO, gelled after 3 h, while the one containing ZnO stayed liquid-like for several days.

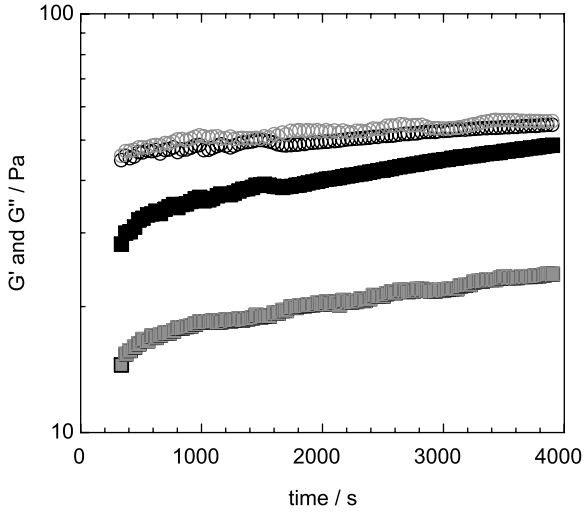

Figure 3. G'(squares) and G''(circles) as a function of time. Gelation of 6% HT-BP dissolved in an 8.5% $NaOH/H_2O$ solution with (grey symbols) and without (black symbols) 0.8% ZnO.

Other additives of intermediate polarity, such as poly(ethylene glycol), PEG, have also been found to enhance the solution stability by preventing it to form a gel.[26] Urea[28,30] and thiourea[23] also prevent, to some extent, gelation. How can this be understood? On a molecular level, the equatorial direction of a glucopyranose ring has a hydrophilic character (three hydroxyl groups are located on the equatorial positions of the ring) while the axial direction of the ring is hydrophobic (the hydrogen atoms of C–H bonds are located on the axial positions of the ring). Thus, cellulose molecules have intrinsically a structural anisotropy with sides of striking difference in polarity. Thus, cellulose is an amphiphilic molecule, the stability of which is mostly governed by hydrophobic interactions.[24,25,58-60] Cellulose amphiphilic nature and the different sites of polarity are clearly exemplified, for instance, in reference 59 (e.g., see Figure 4 therein). Gelation is then a phenomenon that results from the self-aggregation of the cellulose chains in the solution with time (or temperature). The progressively increased number of more hydrophobic junction zones between the cellulose chains in the solution is prevented by its association with

a surfactant. Therefore, it is argued that cosolutes which decrease the tendency of hydrophobic association between aqueous cosolutes (i.e., urea, PEG or surfactants such as the one used in this work), not only facilitate the aqueous dissolution of cellulose, thus increasing the amount of cellulose in the dope, but also increase the stability of the solution against aggregation (decrease of the viscoelastic properties and kinetics of gelation); these compounds would thus weaken hydrophobic interactions responsible for aggregation rather than breaking hydrogen bonds.

Kinetic barriers of dissolution

Combination of hydrothermal and ethanol-hydrochloric acid pretreatments

The presence of ZnO is thus observed to enhance solubility and stability of cellulose solutions. However, a ZnO-based process might not be easy to implement on an industrial scale. Therefore, an additional treatment of HT-BP to make it easier to dissolve, eventually without the need of ZnO, was considered. Regarding cellulose dissolution, it is often stated that it is dependent on the way of handling (pretreatments), temperature, time of heating or cooling, as well as its molecular weight. This indicates that kinetic rather than thermodynamic control is decisive. Given this, HT-BP was further treated with an ethanol-acidic solution. The resulting pulp (EA/HT-BP) had a slightly lower DP (234) than HT-BP. In Figure 4a, it can be seen that EA/HT-BP could be mostly dissolved in the NaOH-water system following the same procedure as described above. Although no ZnO was used in this case, no undissolved fibers or fragments are noticed. It should be noted in Figure 4b that the shear viscosity of the EA/HT-BP solution is lower than the HT-BP solution indicating a better and faster dissolution after the ethanol-acidic treatment.

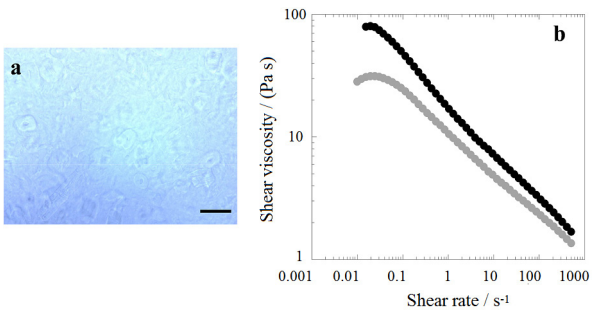

Figure 4. (a) Optical micrograph of 6% EA/HT-BP dissolved in an 8.5% $NaOH/H_2O$ solution. The scale bar represents 200 µm. (b) Shear viscosity of both HT-BP (black circles) and EA/HT-BP solutions (grey circles).

Very few studies have been performed regarding acid treatment of cellulose in ethanol. There are, at least, two effects that have to be considered here; the molecular weight reduction and the degradation of the cellulose fiber cell walls. The former effect has a direct consequence on the translational entropy of mixing of the system. In other words, the lower the molecular weight the stronger is the entropic driving force for dissolution; it is thus more difficult to dissolve high molecular weight macromolecules than low molecular weight ones. The latter is believed to be the main effect here, i.e., weakening of the cell wall structure allowing the solvent to penetrate throughout the fiber, thus dissolving it. Typically, if a polymer sample is placed in a solvent, solvent molecules will relatively fast contact the polymer and penetrate into the surface, often resulting in a gel-like consistency of the outermost part, thus retarding molecular transport and, consequently, dissolution. Polymer molecule diffusion is intrinsically much slower than solvent diffusion and for concentrated polymer solutions (as would apply for the surface layer) severely delayed by entanglement and association. Since the ethanol-acid treatment deteriorates the first barrier for fiber dissolution, solvent molecules will permeate and diffuse easily and faster into the internal parts of the cellulose fibers.[42] This has been observed to clearly increase the rate of dissolution. In addition, since the cell wall structure has been weakened, the osmotic pressure built up inside the fiber is not enough to create the normal "ballooning" phenomena typically found in different solvents and considered as part of the mechanism for cellulose dissolution.[61] In the present case, the "balloons" were not observed when EA/HT-BP was used. Instead, the result seems to be a direct dissolution through fragmentation and formation of small discs.

EA/HT-BP dissolved in $NaOH/H_2O$ presents a predominant liquid-like behavior with both viscoelastic parameters, G' and G'', being considerably lower when compared with the HT-BP system (Figure 5). No cross-over of moduli was observed after 1 h (black curves). On the other hand, the HT-BP sample essentially gelled after only 1 h (grey curves). This shows that the ethanol-acidic treatment efficiently increases both the solubility, kinetics of dissolution and the stability of the solution, thus resembling the ZnO effect.

The effect of ZnO and the surfactant additive on the physicochemical properties when added to the EA/HT-BP solutions was also investigated. In Figure 6a, the shear viscosities of different samples are compiled. For easier comparison, the data from Figure 4b is also included. The addition of ZnO to the EA/HT-BP system decreases considerably the viscosity and was observed to increase considerably the rate of dissolution. A slightly better rheological performance was observed when the surfactant additive was added to the ZnO-containing solution (see the discussion above). Again, this is important because it

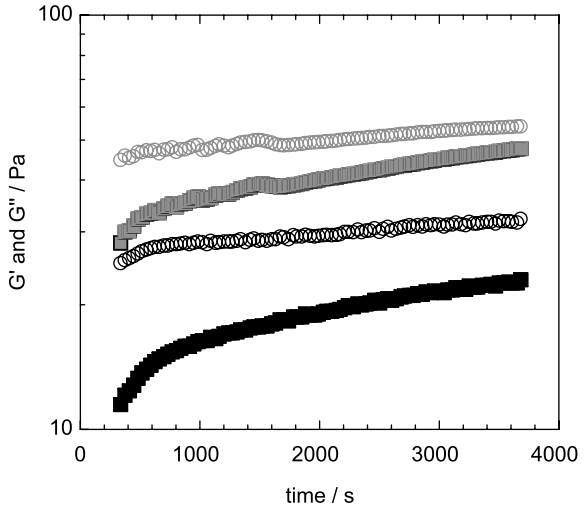

Figure 5. G'(squares) and G''(circles) as a function of time. Gelation of 6% HT-BP dissolved in an 8.5% NaOH/H_2O solution with (black symbols) and without (grey symbols) the ethanol-acid treatment.

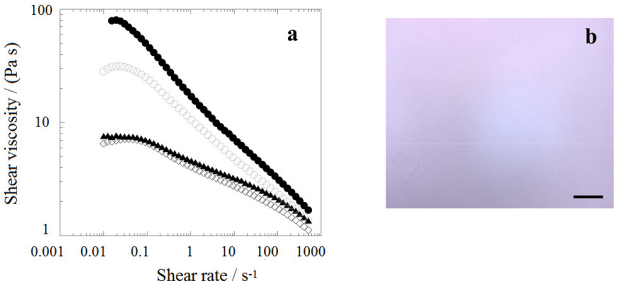

Figure 6. (a) Shear viscosities of HT-BP without ZnO (filled black circles), EA/HT-BP without ZnO (open grey circles), EA/HT-BP with ZnO (filled black triangles) and EA/HT-BP with ZnO and surfactant additive (open diamonds). All samples were prepared in an 8.5% NaOH/H_2O solution with a cellulose content of 6%. The additives used were 0.8% ZnO and 0.6% surfactant. (b) Optical micrograph of 6% EA/HT-BP dissolved in an 8.5% NaOH/H_2O solution with 0.8% ZnO and 0.6% surfactant additive. The scale bar represents 200 µm.

opens the possibility of higher concentrations of cellulose being dissolved at a maintained viscosity. In this latter case (i.e., surfactant additive and ZnO present in the solution), Figure 6b shows a micrograph, in which no undissolved material is observed.

Ethanol-hydrochloric acid pretreatments of Buckeye pulp

As described above, the solubility and stability of HT-BP, when treated with the ethanol-acid mixture, was observed to be improved. Moreover, both ZnO and the surfactant additive were found to further improve the rheological properties. The next step was to use the ethanol-acid mixture directly on the BP without the HT treatment. BP has a reasonably high DP (637) and, without activation, it is insoluble in the NaOH/H_2O solvent system. After the ethanol-acid treatment of BP, the resulting material (EA-BP) had a DP of 393 as measured by viscosity. EA-BP was then dissolved in the NaOH/H_2O solvent (containing 0.8% ZnO) following the standard procedure. In Figure 7, it can be seen how the concentration of EA-BP influences the dissolution.

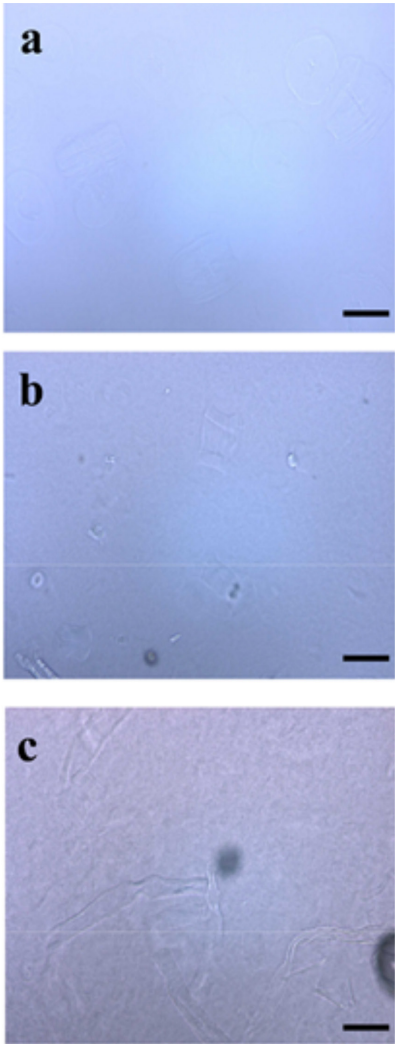

Figure 7. Optical micrographs of (a) 4%, (b) 6% and (c) 9% EA-BP dissolved in an 8.5% NaOH/H_2O solution containing 0.8% ZnO. The scale bar represents 200 µm.

With a pulp concentration of 4%, full dissolution was observed after 20 min of mixing. When the EA-BP concentration was further increased to 6%, a viscous, but transparent, solution was obtained. In this case, only a residual fraction of undissolved fragments could be observed. Finally, a high concentration of 9% EA-BP was tried and, despite a low fraction of undissolved material and fibers, as the micrograph shows, the sample gelled quite fast during the vigorous mixing. In any case, it should be emphasized that, at least, 6% EA-BP with an average DP of 393 could be dissolved in the NaOH/H_2O solvent. This demonstrates a considerable and remarkable improvement regarding most of the previous studies with this solvent system.

In figure 8, the shear viscosities of the EA-BP solutions (4 and 6%) with the viscosity of a 6% HT-BP sample treated and not treated with the ethanol-acid solution are compared. The shear viscosity of the 4% EA-BP is comparable to the one of the 6% EA/HT-BP solution. This is not surprising since EA-BP has a DP much higher than EA/HT-BP. Thus, the molecular weight difference balances the difference in pulp concentration.

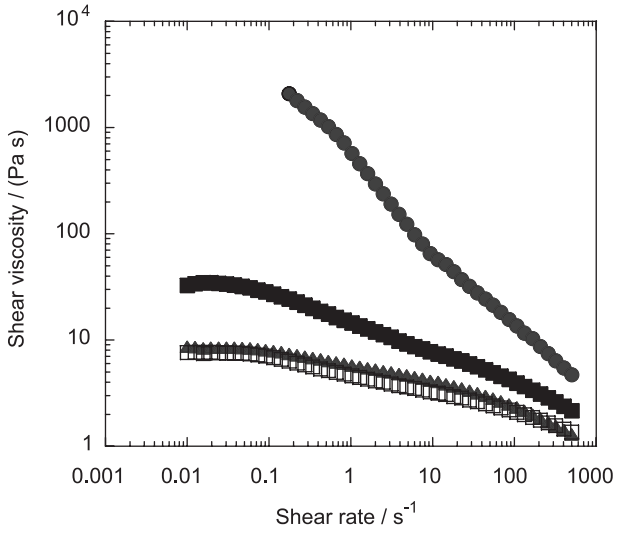

Figure 8. Shear viscosities of 6% EA/HT-BP (open black squares) and 6% HT-BP (filled black squares), 4% EA-BP (grey filled triangles) and 6% EA-BP (grey filled circles).

Conclusions

In this study, thermodynamic (hydrophobic interactions, hydrogen bonding, effect of charges) and kinetic aspects (effect of pretreatments) in cellulose dissolution were discussed. Cellulose was dissolved in an environmentally friendly aqueous solvent system after the application of hydrothermal and/or ethanol-acid pretreatments. The solutions are not thermodynamically stable but the addition of ZnO and amphiphilic molecules was observed to improve not only the rate of dissolution but also the stability of the cellulose dopes reducing, to some extent, the degree of gelation. While ZnO is suggested to "charge up" cellulose ("polyelectrolyte effect"), the surfactant is suggested to weaken the hydrophobic interactions in cellulose, rather than breaking hydrogen bonds. The application of an ethanol-acid treatment improves the rate of dissolution of previously hydrothermally treated dissolving pulp in a 8.5% $NaOH/H_2O$ solvent, thus allowing a faster and complete dissolution without remains of undissolved material. The application of an ethanol-acid treatment to the previously hydrothermally treated dissolving pulp increased significantly the rate of dissolution in a 8.5% $NaOH/H_2O$ solvent. The improvement of the dissolution ability when using the ethanol-acid treatment on the HT pulp was similar to the improvement obtained by the ZnO addition. The ethanol-acid treatment of the starting untreated dissolving pulp resulted in a pulp with an average DP of 393 and despite of the high DP clear cellulose solutions with vestiges of undissolved material were prepared with a concentration up to 6%. Higher pulp consistencies were also prepared (9%) but fast gelation was observed even if ZnO or the surfactant additive were present. The ethanol-acid pretreatment is believed to have a main effect in removing the primary cell wall and, to a less extent, decrease in the cellulose molecular weight. As a consequence, the cellulose fibers are more accessible for solvent penetration and complete dissolution, without the typical ballooning effect.

Acknowledgements

The authors would like to thank the CelluNova project, a part of the EcoBuild Excellence Centre, for its financial support. Dr. Wawro (Institute of Biopolymers and Chemical Fibers, Lodz, Poland) is acknowledged for the preparation of hydrothermally treated Buckeye dissolving pulp. Bruno Medronho acknowledges Fundação para a Ciência e a Tecnologia (FCT, SFRH/BPD/74540/2010) and the CelluNova I project for funding.

References

1. Wertz, J. L.; Mercier, J. P.; Bédué, O.; *Cellulose Science and Technology*, 1st ed.; EPFL Press: Boca Raton, 2010.
2. Liebert, T. In *Cellulose Solvents: For Analysis, Shaping and Chemical Modification*. vol. 1033, 1st ed.; ACS Symposium Series: Washington, USA, 2010.
3. Heinze, T.; Liebert, T.; *Prog. Polym. Sci.* **2001,** *26*, 1689.
4. Woodings, C.; *Regenerated Cellulose Fibres*; CRC Press LLC: Boca Raton, USA, 2001.
5. Kasaai, M. R.; *J. Appl. Polym. Sci.* **2002,** *86*, 2189.
6. Leipner, H.; Fischer, S.; Brendler, E.; Voigt, W.; *Macromol. Chem. Phys.* **2000**, *201*, 2041.
7. Grinshpan, D. D.; Lushchik, L. G. N.; Tsygankova, G.; Voronkov, V. G.; Irklei, V. M.; Chegolya, A. S.; *Fibre Chem.* **1988**, *20*, 365.
8. Fischer, S.; Leipner, H.; Thummler, K.; Brendler, E.; Peters, J.; *Cellulose* **2003**, *10*, 227.
9. Degroot, W.; Carroll, F. I.; Cuculo, J. A.; *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 673.
10. Hattori, M.; Koga, T.; Shimaya, Y.; Saito, M.; *Polym. J.* **1998**, *30*, 43.
11. Ramos, L. A.; Assaf, J. M.; El Seoud, O. A.; Frollini, E.; *Biomacromolecules* **2005**, *6*, 2638.

12. Mccormick, C. L.; Callais, P. A.; Hutchinson, B. H.; *Macromolecules* **1985**, *18*, 2394.
13. Liu, C. K.; Cuculo, J. A.; Allen, T. C.; Degroot, A. W.; *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 181.
14. Cuculo, J. A.; Smith, C. B.; Sangwatanaroj, U.; Stejskal, E. O.; Sankar, S. S.; *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 229.
15. Perepelkin, K. E.; *Fibre Chem.* **2007**, *39*, 163.
16. Schrempf, C.; Schild, G.; Ruf, H.; *Papier* **1995**, *49*, 748.
17. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D.; *J. Am. Chem. Soc.* **2002**, *124*, 4974.
18. Zavrel, M.; Bross, D.; Funke, M.; Buchs, J.; Spiess, A. C.; *Bioresour. Technol.* **2009**, *100*, 2580.
19. Mazza, M.; Catana, D. A.; Vaca-Garcia, C.; Cecutti, C.; *Cellulose* **2009**, *16*, 207.
20. Sobue, H.; Kiessig, H.; Hess, K.; *Z. Phys. Chem. (Muenchen, Ger.)* **1939**, *43*, 309.
21. Isogai, A.; Atalla, R. H.; *Cellulose* **1998**, *5*, 309.
22. Bodvik, R.; Dedinaite, A.; Karlson, L.; Bergstrom, M.; Baverback, P.; Pedersen, J. S.; Edwards, K.; Karlsson, G.; Varga, I.; Claesson, P. M.; *Colloids Surf., A* **2010**, *354*, 162.
23. Zhang, L. N.; Ruan, D.; Gao, S. J.; *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 1521.
24. Lindman, B.; Karlstrom, G.; Stigsson, L.; *J. Mol. Liq.* **2010**, *156*, 76.
25. Medronho, B.; Romano, A.; Miguel, M. G.; Stigsson, L.; Lindman, B.; *Cellulose* **2012**, *19*, 581.
26. Yan, L. F.; Gao, Z. J.; *Cellulose* **2008**, *15*, 789.
27. Cai, J.; Zhang, L. N.; Zhou, J. P.; Li, H.; Chen, H.; Jin, H. M.; *Macromol. Rapid Commun.* **2004**, *25*, 1558.
28. Cai, J.; Zhang, L.; *Macromol. Biosci.* **2005**, *5*, 539.
29. Cai, J.; Zhang, L.; Liu, S. L.; Liu, Y. T.; Xu, X. J.; Chen, X. M.; Chu, B.; Guo, X. L.; Xu, J.; Cheng, H.; Han, C. C.; Kuga, S.; *Macromolecules* **2008**, *41*, 9345.
30. Cai, J.; Zhang, L. N.; Zhou, J. P.; Qi, H. S.; Chen, H.; Kondo, T.; Chen, X. M.; Chu, B.; *Adv. Mater. (Weinheim, Ger.)* **2007**, *19*, 821.
31. Zhou, J. P.; Zhang, L. N.; Cai, J.; *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 347.
32. Chen, X. M.; Burger, C.; Wan, F.; Zhang, J.; Rong, L. X.; Hsiao, B. S.; Chu, B.; Cai, J.; Zhang, L.; *Biomacromolecules* **2007**, *8*, 1918.
33. Qi, H. S.; Cai, J.; Zhang, L. N.; Kuga, S.; *Biomacromolecules* **2009**, *10*, 1597.
34. Kihlman, M.; Wallberg, O.; Stigsson, L.; Germgard, U.; *Holzforschung* **2011**, *65*, 613.
35. Wawro, D.; Steplewski, W.; Bodek, A.; *Fibres Text. East. Eur.* **2009**, *17*, 18.
36. Kamide, K.; Okajima, K.; *US pat.* 4634470 **1987**.
37. Le Moigne, N.; Jardeby, K.; Navard, P.; *Carbohydr. Polym.* **2010**, *79*, 325.
38. Yamashiki, T.; Matsui, T.; Saitoh, M.; Okajima, K.; Kamide, K.; *Br. Polym. J.* **1990**, *22*, 73.
39. Hsu, T. A.; Ladisch, M. R.; Tsao, G. T.; *Chemtech* **1980**, *10*, 315.
40. Itoh, H.; Wada, M.; Honda, Y.; Kuwahara, M.; Watanabe, T.; *J. Biotechnol.* **2003**, *103*, 273.
41. Kumar, P.; Barrett, D. M.; Delwiche, M. J.; Stroeve, P.; *Ind. Eng. Chem. Res.* **2009**, *48*, 3713.
42. Trygg, J.; Fardim, P.; *Cellulose* **2011**, *18*, 987.
43. Glasser, W. G.; Atalla, R. H.; Blackwell, J.; Brown, R. M.; Burchard, W.; French, A. D.; Klemm, D. O.; Nishiyama, Y.; *Cellulose* **2012**, *19*, 589.
44. Struszczyk, H.; Wawro, D.; Urbanowski, A.; Mikolajczyk, W.; Starostka, P.; *WO pat. 2002022924* **2002**.
45. Larson, R. G.; *The Structure and Rheology of Complex Fluids*; Oxford University Press: New York, USA, 1999.
46. Immergut, E. H.; Ranby, B. G.; Mark, H. F.; *Ind. Eng. Chem.* **1953**, *45*, 2483.
47. Borgin, K.; Stamm, A. J.; *J. Phys. Colloid Chem.* **1950**, *54*, 772.
48. Davidson, G. F.; *J. Tex. Inst.* **1937**, *28*, T27.
49. Lang, H.; Laskowski, I.; *Cellul. Chem. Technol.* **1991**, *25*, 143.
50. Vehvilainen, M.; Kamppuri, T.; Rom, M.; Janicki, J.; Ciechanska, D.; Gronqvist, S.; Siika-Aho, M.; Christoffersson, K. E.; Nousiainen, P.; *Cellulose* **2008**, *15*, 671.
51. Zhang, L.; Qi, H.; Ang, Q.; *Chinese pat. ZL 00114486.3*, **2003**.
52. Lu, A.; Liu, Y. T.; Zhang, L. N.; Potthast, A.; *J. Phys. Chem. B* **2011**, *115*, 12801.
53. Yang, Q. L.; Qi, H. S.; Lue, A.; Hu, K.; Cheng, G. Z.; Zhang, L. N.; *Carbohydr. Polym.* **2011**, *83*, 1185.
54. Astrand, P. O.; Karlstrom, G.; Engdahl, A.; Nelander, B.; *J. Chem. Phys.* **1995**, *102*, 3534.
55. Canuto, S.; Fileti, E. E.; Chaudhuri, P.; *Chem. Phys. Lett.* **2004**, *400*, 494.
56. Lue, A.; Zhang, L.; Ruan, D.; *Macromol. Chem. Phys.* **2007**, *208*, 2359.
57. Lindman, B.; Karlström, G.; *C. R. Chim.* **2009**, *12*, 121.
58. Bergenstråhle-Wohlert, M.; Berglund, L. A.; Brady, J. W.; Larsson, P. T.; Westlund, P.-O.; Wohlert, J.; *Cellulose* **2012**, *19*, 1.
59. Yamane, C.; Aoyagi, T.; Ago, M.; Sato, K.; Okajima, K.; Takahashi, T.; *Polym. J.* **2006**, *38*, 819.
60. Miyamoto, H.; Umemura, M.; Aoyagi, T.; Yamane, C.; Ueda, K.; Takahashi, K.; *Carbohydr. Res.* **2009**, *344*, 1085.

Submitted: October 30, 2012
Published online: February 21, 2013