

Enhancement of cellulose dissolution in water-based solvent via ethanol–hydrochloric acid pretreatment

Jani Trygg · Pedro Fardim

Received: 22 December 2010 / Accepted: 16 April 2011 / Published online: 30 April 2011
© Springer Science+Business Media B.V. 2011

Abstract Cellulose dissolution in water-based solvents is essential for processing of regenerated cellulose products such as fibres, films and particles. Cellulose dissolution in NaOH–urea aqueous solution has emerged as a simple and attractive alternative for processing cellulose solutions. However, this solvent requires energy intensive pretreatments such as milling or refining. In this paper we investigate a one step chemical pretreatment method using ethanol–hydrochloric acid prior to the dissolution of cellulose in NaOH–urea–water. The dissolution mechanism of the pretreated sample was initially examined in diluted cupri-ethylenediamine and 7% NaOH–12% urea–water solvent using optical microscopy methods and field emission scanning electron microscopy. The apparent energy of activation for the viscous flow of ethanol–acid pretreated pulp in NaOH–urea–water was calculated using rheological methods. Our results showed that the dissolution of pretreated pulp was achieved up to 4% cellulose concentration. We suggest that the enhancement of dissolution was due to a combination of degradation of remnant primary fibre wall layer and reduction of degree of polymerization of cellulose.

Keywords Cellulose · Acid treatment · Pretreatment · Intrinsic viscosity · Levelling-off degree of polymerization · Dissolution · Activation energy

Introduction

Dissolution of cellulose plays an essential role in the production of cellulose derivatives and blended materials. Cellulose solutions allow homogeneous chemical modifications while in solid state the solid–liquid heterogeneous reaction conditions causes uneven functionalization and low degree of substitution (Moigne et al. 2010). The dissolution of natural cellulosic fibre takes place in two steps; first the solvent penetrates into the fibre structure and then separates the polymer chains from each other. Dissolution mechanism depends on fibre type and mostly on the solvent system (Cuissinat and Navard 2006a, b, 2008; Le Moigne et al. 2010). Derivatizing solvents react chemically with hydroxyl groups and reduce hydrogen-bond network which makes it possible to dissolve cellulose. Derivatization prolongs the dissolution procedure and in the case of viscose, for example, regeneration of cellulose releases toxic CS₂ gas. Non-derivatizing solvents disrupt intramolecular hydrogen-bonding and dissolve cellulose directly without chemical reactions (Swatloski et al. 2002).

Solvent quality has a great effect on the mechanism of how a fibre dissolves. Good non-derivatizing

J. Trygg (✉) · P. Fardim
Laboratory of Fibre and Cellulose Technology,
Åbo Akademi, Porthansgatan 3, 20500 Turku, Finland
e-mail: jani.trygg@abo.fi

solvents break down the fibre structure by fragmenting whereas moderate and poor solvents first dissolve the inner parts of the fibre with less hemicelluloses (Freese et al. 2006). This causes swelling and ballooning of the outer layers. They are also unable to dissolve cellulose in greater extent so the dissolution of the fibre is often partial. Many good solvents, e.g. ionic liquids are able to dissolve even 25% of cellulose directly without any pretreatment (Swatloski et al. 2002). However, they are still debatable because of their water sensitivity and difficult purification (Spiess et al. 2009; Mazza et al. 2009).

NaOH–water with or without additives has got more attention as a water-based, cheap and environmentally friendly solvent (Jin et al. 2007; Qi et al. 2008; Isogai and Atalla 1998). It has been shown, however, that cellulose molecules are not completely dissolved in NaOH–water solvent but form aggregates (Roy et al. 2003). Also dependence of solubility on the degree of polymerization has been studied in NaOH–urea–water systems and concluded that only low DP cellulose can be dissolved (Qi et al. 2008). This means that native cellulose has to be pretreated in order to reduce the polymer chain length.

Acid hydrolysis has been applied usually as a pretreatment to make cellulose molecules shorter and more accessible for chemicals or complete hydrolysis to produce glucose. This is beneficial when aim is to produce, e.g. biofuels (Saha et al. 2005; Kumar et al. 2009). Traditionally hydrolysis has been carried out at high temperature and low acid concentration or vice versa (Adel et al. 2010). However, this can be very energy demanding and causes degradation of sugar producing unwanted byproducts, such as furfural, (hydroxymethyl)-furfural and formic and acetic acid (Lee et al. 1999).

Acid treatment on cellulose is performed in aqueous environment almost without exceptions. It has been shown that acid hydrolysis in alcohol improves the degradation of starch (Small 1919; Lin et al. 2003) and cellulose (Lin et al. 2009). This might be due to higher activity coefficient of hydrogen ions in alcohol (Harned and Fleyscher 1925).

Differences in acid hydrolysis of cellulose in water and in ethanol have rarely been studied (Lin et al. 2009) and it is concluded that degradation rate of cellulose has a dependence on the media favouring ethanol environment. However, connection of the acid hydrolysis in ethanol environment to the

solubility and dissolution mechanism of cellulose has not been studied before. The objective of this paper is to study the effect of the ethanol–acid pretreatment on the solubility of cellulose using microscopical and rheological methods.

Materials and methods

Materials

Dissolving pulp (Cellulose plus) was purchased from Domsjö Fabriker, Sweden. Pulp is a mixture of spruce and pine (60%/40%) with 93%–cellulose content and 0.6% of lignin (Domsjö 2007). Intrinsic viscosity of the delivered pulp was reported to be $530 \pm 30 \text{ cm}^3 \text{ g}^{-1}$ according to SCAN-CM 15:99 standard (complies with ISO 5351 standard) after two stage sodium based cooking. Pulp is Total Chlorine Free (TCF)-bleached. All reagents were obtained from commercial sources, analytical grade and used without further purification unless otherwise mentioned.

Methods

Ethanol–acid pretreatment of pulp

Ethanol (100 cm^3 , 92.5 w%) was pre-heated in water bath to the reaction temperature (25–75 °C) and 4 cm^3 of hydrochloric acid (37 w%) was added. After temperature had stabilized, 4.0 g of dry-weighed fibrillated dissolving pulp was added. Stirring was applied in the beginning to make sure that pulp was evenly distributed in the reaction vessel. Treatment time was varied from 15 min to 5 h. Reaction was stopped by adding cold distilled water (900 cm^3) and the mixture of ethanol, acid and water was filtered off instantly on a glass filter (porosity 1). Pulp was washed with distilled water until the pH of the filtrate was neutral and left in $1,000 \text{ cm}^3$ of distilled water overnight to ensure solvent exchange from ethanol–acid to water. On the next day pulp was filtered, suction dried and kept in an oven at 60 °C overnight.

Optical microscopy

Dissolution mechanisms and visual transparency of cellulose solutions were studied with a Wild M20 optical microscope attached to a Nikon Coolpix 990

digital camera. Dissolution steps were recorded when ethanol–acid treated (5 h at 75 °C, see above) and untreated pulp were introduced to a 0.2 M cupriethylene-diamine (CED) solution.

Undissolved fragments were examined after dissolving 0.2% of pretreated cellulose from total weight in 7% NaOH–12% urea–water solution (see *Dissolution of cellulose*). Cellulose was treated in ethanol–acid solution for 2 h at 25, 45, 55 and 65 °C like described above.

Surface morphology using FE-SEM

The morphology of the untreated pulp and samples treated in ethanol–acid solution for 2 h at 25 and 75 °C was examined by a Leo Gemini 1530 field emission scanning electron microscope with a In-Lens detector. Samples were coated with carbon in Temcarb TB500 sputter coater (Emscope Laboratories, Ashford, UK). An optimum accelerating voltage was 2.70 kV and magnifications were 5,000 and 50,000 \times .

Residual hemicelluloses in pulp by acid methanolysis-GC

8–10 mg of pulp treated in ethanol–acid for 2 h at 25, 45, 75 °C and one untreated sample were accurately weighed in pear-shaped flasks. Samples were subjected to acid methanolysis (Sundberg et al. 1996) by adding 2 cm³ of 2 M HCl in dry methanol and kept in an oven at 100 °C for 5 h. After methanolysis, the resulting solution was neutralized with pyridine and 4 cm³ of sorbitol standard in methanol (0.1 mg cm⁻³) was added. 1 cm³ of clear solution from each sample was transferred into another pear-shaped flask and dried first under nitrogen flow and then in a vacuum oven. Samples were dissolved in pyridine and silylated with 150 mm³ of hexamethyldisilazane and 70 mm³ of trimethylchlorosilane overnight. About 1 mm³ of silylated sample was injected via a split injector (250 °C, split ratio 25:1) into column coated with dimethyl polysiloxane (HP-1, Hewlett Packard), the film thickness being 0.17 μ m. Column temperature was first stabilized 1 min at 100 °C, then heated 4 °C min⁻¹ to 170 °C and followed by 12 °C min⁻¹ to 300 °C where temperature was kept stable for 7 min. The flame ionization detector (FID) temperature was 310 °C and carrier

gas was hydrogen. Peak positions were recognized comparing peaks to the prepared reference solution containing exact amounts of arabinose, xylose, galactose, glucose, mannose, rhamnose, glucuronic acid and galacturonic acid. Concentrations were calculated from peak areas using calibration factors determined from internal sorbitol standard. Two parallel measurements were analysed from each sample and an average value was calculated. Changes in the amount of cellulose were studied by measuring the yield of samples treated for 2 h at 25 and 75 °C.

Degree of polymerization of cellulose

Intrinsic viscosities of ethanol–acid treated samples were measured according to standard ISO/FDIS 5351:2009 and average degrees of polymerization were calculated from intrinsic viscosity values (Immergut et al. 1953) to observe changes in cellulose chain length as a function of treatment time and temperature. One untreated sample and one treated for 5 h at 65 °C in ethanol without hydrochloric acid were used as references. Oven-dry samples were freeze-dried before dissolution into 1.0 M CED solution. Capillary temperature was 26.0 \pm 0.1 °C.

Results were used in evaluating recyclability of ethanol–acid solution. Pretreatment was carried out with 10 times higher volumes and masses than described earlier for 5 h at 65 °C and then treating new pulp using same solution without concentrating it between treatments. Intrinsic viscosity was measured and degree of polymerization was calculated like described above and values were compared with previous results.

Dissolution of cellulose

Cellulose solutions were prepared by using dissolving pulp which was treated in ethanol–acid for 2 h at 75 °C (see *Ethanol–acid pretreatment of pulp*). Humidity of the oven-dry pulp was measured and calculated amount of pulp was activated in 6% NaOH aqueous solution at room temperature through mechanical stirring. After fibres swelled and mixture became homogeneous it was enriched with NaOH and urea. Final concentrations were 7% NaOH and 12% urea from the solvent weight and 0.2–5% cellulose from total weight of the final solution. Vigorous stirring was applied with magnetic stirrer to

obtain a homogeneous mixture and then cooled down to -10°C . Mixing was continued until clear transparent solution was obtained, usually less than 20 min.

Rheological measurements

Rheological measurements of 0–5% cellulose in 7% NaOH–12% urea–water solutions were carried out using an Anton Paar Physica MCR 300 rotational rheometer with DG 26.7 double-gap cylinder. Temperature was controlled with a TEZ 150P thermostat with an external water cycle. Approximately 4 cm^3 of sample was pipetted into the cylinder and temperature was stabilized at 10, 15, 20 and 25°C with accuracy of 0.01°C . Apparent activation energies E_a of the viscous flow were calculated according to Arrhenius law from extrapolated zero-shear rate (Roy et al. 2003) and viscosity values from constant shear rates 10, 100 and $1,000\text{ s}^{-1}$. Cellulose solutions were stored at -5 to 0°C between measurements.

Results and discussion

Effect of ethanol–acid pretreatments on pulp investigated by dissolution in CED and NaOH–urea–water and optical microscopy analysis

Dissolution mechanism was studied with CED solution since it is known to dissolve cellulosic fibres directly at high concentrations (ISO/FDIS 5351:2009). When solvent is diluted, the dissolution of fibres proceeds via ballooning phase and not by fragmenting (Cuissinat and Navard 2006). Swelling and ballooning were observed when untreated pulp was added into a 0.2 M CED solution (Fig. 1A). Ballooning was rapid and usually began from the tip of the fibre but balloons were seen also in the middle of the fibres. Balloons continued to swell until they dissolved completely, but leaving rings (knots between balloons) undissolved. Ethanol–acid treated pulp did not show any ballooning (Fig. 1B). Fibres were dissolved directly through fragmenting and only arbitrary undissolved fragments were left behind.

Ethanol–acid treated pulp was dissolved in 7% NaOH–12% urea–water and solution was studied for undissolved fragments. Undissolved fibres and ballooning was observed after dissolution procedure

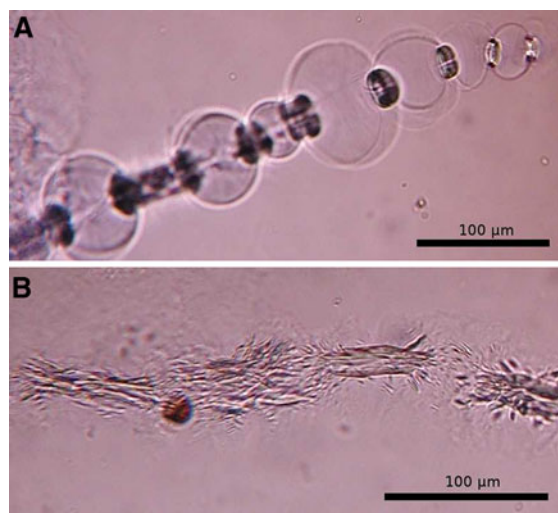


Fig. 1 **A** Untreated and **B** ethanol–acid treated pulp (5 h at 75°C) in 0.2 M CED solution

when pulp was treated in ethanol–acid for 2 h at 25 and 45°C (Fig. 2A, B). Swollen fibres or balloons were not observed when treatment temperature was 55°C (Fig. 2C). However, in solution, rings and fragments from ballooning could be seen, which indicated that dissolution proceeded through ballooning. When treatment temperature was 65°C or higher, fragments or rings could not be observed at all in NaOH–urea–water solution (Fig. 2D). This might be due to the weakened cell wall structure so that solvent can access throughout the fibre dissolving all the components without creating osmotic pressure inside and causing ballooning (Cuissinat and Navard 2006). This would lead to direct dissolution through fragmenting.

Effects of ethanol–acid pretreatment on the morphology of external fibre walls as analysed by FE-SEM

The effect of the ethanol–acid treatment on fibre wall was studied using FE-SEM. When pulp was treated for 2 h at 25°C fibre wall showed some minor changes compared to untreated pulp (Fig. 3A–D). Primary fibre wall or its remnants were present on both samples. In the sample treated at 75°C fibril bundles could be seen (Fig. 3E–F). Orientation of the fibrils in the bundles indicated that they are on the secondary fibre wall and primary wall was extensively removed.

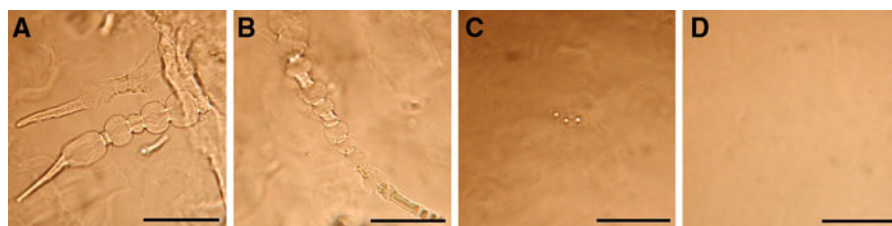


Fig. 2 Pulp treated in ethanol–acid for 2 h at **A** 25, **B** 45, **C** 55 and **D** 65 °C. Cellulose content was 0.2% from total weight and solvent was 7% NaOH–12% urea–water. Scale bars are 100 μ m

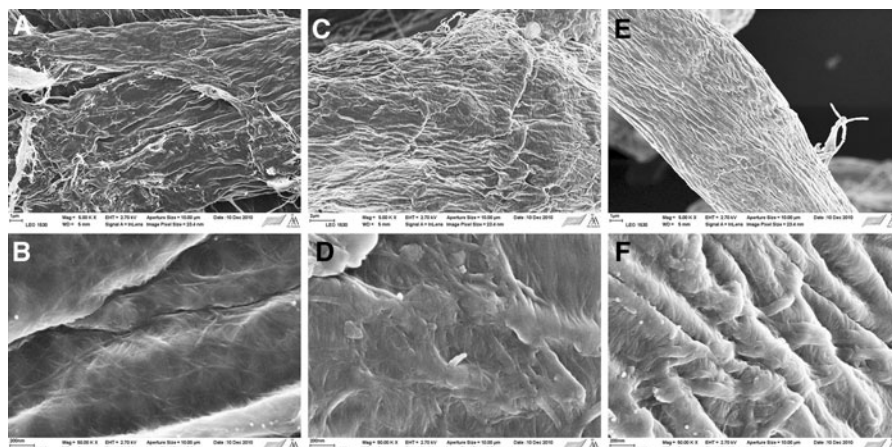


Fig. 3 SEM images of reference pulp **A**, **B** and pulp pretreated in ethanol–acid for 2 h at **C**, **D** 25 and **E**, **F** 75 °C. Magnifications are in top row 5,000 and in bottom 50,000 \times

Residual hemicelluloses and content of cellulose in ethanol–acid pretreated pulps

Hemicellulose content of the samples and reference pulp was analysed using acid methanolysis and gas chromatography. Glucose content in samples treated at 25, 45 and 75 °C was 8, 5 and 11% lower than in reference (Table 1). Glucose formed in acid methanolysis is mainly non-cellulosic (Sundberg et al. 1996). Amounts of galactose, mannose and xylose decreased the most during 75 °C pretreatment (14, 14

and 18%). Differences between reference and samples treated at 25 and 45 °C were too low to make any conclusions about the connection to the treatment temperature. Arabinose was present in such a low quantities in all samples that it was not possible to conclude any changes due to reaction temperature. Though relative changes in contents are notable, especially between reference and samples treated at 75 °C, the overall concentration of the hemicellulose constituents decreased only from 4.8 to 4.3%. It can be concluded that ethanol–acid treatment does not have an impact on the hemicellulose content of the pulp. Yields of samples treated at 25 and 75 °C were 98 and 97%.

Table 1 Sugar units from hemicelluloses as mg g^{−1} of pulp before and after ethanol–acid treatment for 2 h at 25, 45 and 75 °C

Temperature (°C)	Ara	Xyl	Gal	Glc	Man	Total
Reference	0.1	3.6	1.2	39.4	4.1	48.3
25	0.2	3.3	1.1	36.2	3.9	44.7
45	0.1	3.4	1.2	37.4	3.9	46.0
75	0.1	2.9	1.0	34.9	3.5	42.6

Degradation of the cellulose chains during the ethanol–acid pretreatment

Intrinsic viscosities of the samples were measured using capillary viscosimetry. Viscosity value of the pulp treated in ethanol (5 h at 65 °C) without

hydrochloric acid is only $1 \text{ cm}^3 \text{ g}^{-1}$ lower than that of untreated reference. Both values are in good agreement with the viscosity value of the starting material. This shows that ethanol treatment alone does not cause degradation of cellulose. When hydrochloric acid was added, degradation of cellulose chains took place even at low temperatures (Fig. 4). A study showed (Håkansson and Ahlgren 2005) that a similar treatment in water–hydrochloric acid mixture needed notably longer time and temperature to reach similar changes in intrinsic viscosity. Use of ethanol instead of water enhances the degradation kinetics drastically. This was due to higher mobility of the molecules close to the boiling point of ethanol and increased activity coefficients of hydrochloric acid in ethanol (Harned and Fleysher 1925).

Degree of polymerization descended more rapidly when reaction temperature increased (Fig. 4). Degradation of cellulose chains also reached the leveling-off degree of polymerization (LODP) faster at higher temperatures and degradation slowed down substantially after the first hour. At lower temperatures degradation seemed to continue even after five hours.

Ethanol–hydrochloric acid treatment was repeated at 65°C for 5 h with 10 times higher volumes and masses. Ethanol–acid solution from the first treatment was re-used and treatment was repeated with new pulp without concentrating the solution. Intrinsic viscosities were measured and degrees of polymerization were calculated. DP values were only slightly higher (198

and 203) than calculated on the first time (189) with lower volume and mass (Fig. 4). Similar DP values indicated that ethanol–acid solution was possible to use at least twice and gain practically same DP values. This indicated that the pretreatment process can be upscaled and the solution can be recycled by small supplemental additions of acid and ethanol (Fig. 5). After pretreatment ethanol–acid solution could be pressed out and enriched before re-use.

Dissolution of ethanol–HCl pretreated cellulose in NaOH–urea–water–solvent

Ethanol–acid treated (2 h at 75°C) cellulose was dissolved successfully in 7% NaOH–12% urea–water in various amounts (0.2–5% from total weight) and clear solutions were obtained. On shear rates below 10 s^{-1} at low cellulose concentrations viscosity was fluctuating and hence left out from calculations.

Solutions behaved like newtonian liquids on higher shear rates at low cellulose concentrations (Fig. 6). However, when cellulose concentration increased shear-thinning behaviour was observed uniformly on the whole shear rate range. At each cellulose concentration viscosity increased as temperature decreased. Time to stabilize the temperature and measure the viscosity was approximately 10 min for all the samples. This is notably shorter than gelation time for the temperature and cellulose concentration used here (Roy et al. 2003; Cai and Zhang 2006).

Fig. 4 Viscosity average degree of polymerization (DP_v) of ethanol–acid treated dissolving pulp at various temperatures as a function of time

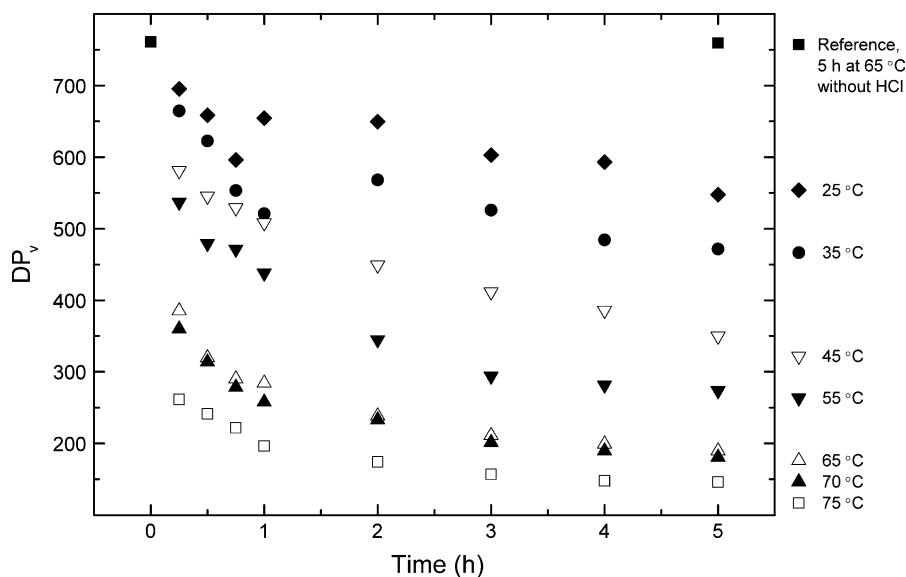


Fig. 5 A diagram of the pretreatment and dissolution steps

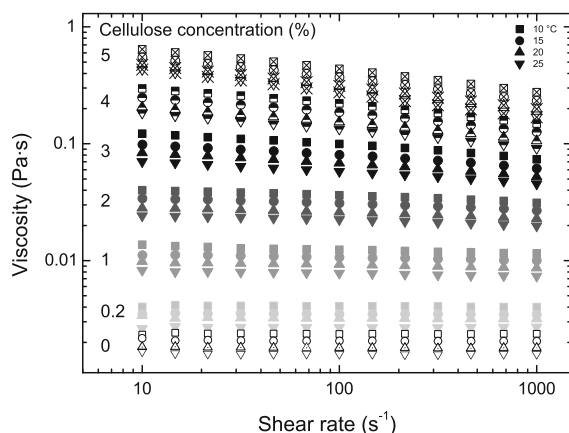
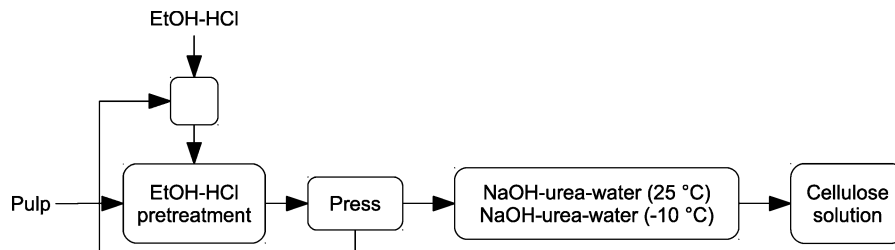


Fig. 6 Viscosity of 0–5% cellulose solutions in 7% NaOH–12% urea–water solvent system at temperatures 10–25 °C as a function of shear rate

Arrhenius plots could be fitted linearly at all cellulose concentrations and apparent activation energy of the viscous flow was calculated. Zero-shear-rate viscosities were extrapolated from viscosity-shear-rate curves. On shear rates up to 100 s⁻¹ activation energies were growing until cellulose concentration reached 3% (Fig. 7). When shear rate was 1,000 s⁻¹, the activation energy increased up to a concentration level of 4%. The increase of the activation energy as a function of cellulose concentration indicates that cellulose was dissolved completely. At higher concentrations and lower shear rates a decline was seen in the activation energy values. This indicates that addition of cellulose does not change the solution properties but cellulose forms aggregates and inclusion complexes (Roy et al. 2003).

Conclusions

Treatment in ethanol–acid improves the dissolution of cellulose in 7% NaOH–12% urea–water solvent

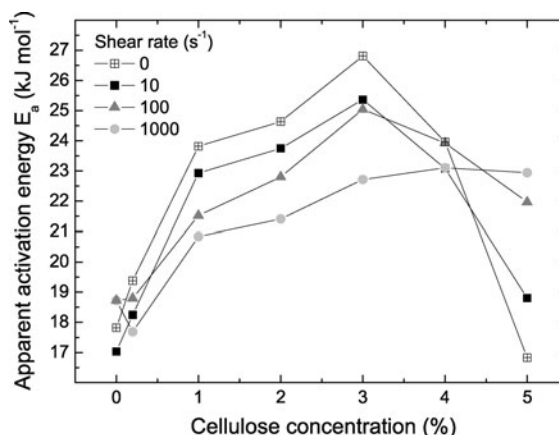


Fig. 7 Apparent activation energies of the viscous flow calculated on shear rates 0, 10, 100 and 1,000 s⁻¹ as a function of cellulose concentration. Lines are given to guide the eye

system by allowing complete dissolution without undissolved fragments. Without the pretreatment NaOH–urea–water solvent system is not efficient enough to break the fibre structure. Pretreatment at 65 °C or higher temperatures removes the primary cell wall and shortens cellulose chains. This weakens other cell wall layers and the fibre dissolves completely without ballooning phase even in NaOH–urea–water. How treatment affects the mechanical properties of the coagulation product is still unknown, and should be studied later.

Cellulose molecules can be fully dissolved up to 4% concentration when pulp has been treated for 2 h at 75 °C. With higher cellulose concentration, molecules will form aggregates but solution will remain visually transparent at least up to 5%. Since the hemicellulose content of pulp is not changed regardless of the pretreatment time and temperature, improved solubility in NaOH–urea–water is suggested to be due to the degradation of cellulose chains and removal of the primary cell wall layer.

Intrinsic viscosity values, and hence the cellulose chain length, could be easily controlled by these reaction conditions. Reduced strength of the cell wall structure causes the dissolution by fragmenting even in weaker solvents. Weakened cell wall is also more open for chemicals, e.g. enzymes and solvents. In heterogeneous reactions the accessibility of reagents into the fibres is in significant role and therefore opened structure after ethanol–acid pretreatment might improve reaction rate and yield. It is possible to re-use ethanol–acid solution at least twice without concentrating it. This makes it a considerable pretreatment method even at industrial scale.

Acknowledgments This work is part of Future Biorefinery (FuBio) funded by TEKES and coordinated by Forest Cluster Oy, Finland.

References

- Adel AM, El-Wahab ZHA, Ibrahim AA, Al-Shemy MT (2010) Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part I. Acid catalyzed hydrolysis. *Bioresour Technol* 101:4446–4455. doi:[10.1016/j.biortech.2010.01.047](https://doi.org/10.1016/j.biortech.2010.01.047)
- Cai J, Zhang L (2006) Unique gelation behavior of cellulose in naoh/urea aqueous solution. *Biomacromolecules* 7:183–189. doi:[10.1021/bm0505585](https://doi.org/10.1021/bm0505585)
- Cuissinat C, Navard P (2006a) Swelling and dissolution of cellulose part I: free floating cotton and wood fibres in *N*-methylmorpholine-*N*-oxide-water mixtures. *Macromol Symp* 244:1–18
- Cuissinat C, Navard P (2006b) Swelling and dissolution of cellulose part II: free floating cotton and wood fibres in NaOH–water–additives systems. *Macromol Symp* 244:19–30
- Cuissinat C, Navard P (2008) Swelling and dissolution of cellulose, part III: plant fibres in aqueous systems. *Cellul Chem Technol* 15:67–74
- Domsjö (2007) Specification Domsjö cellulose. Produkter—Specialcellulosa—Produktinformation Domsjö Cellulose. Accessed 10 Nov 2010. <http://www.domsjoe.com>
- Freese M, Schmidt I, Fischer K (2006) Hemicellulose composition in the outer cell wall layers of paper grade and dissolving pulp. *Macromol Symp* 232:13–18
- Håkansson H, Ahlgren P (2005) Acid hydrolysis of some industrial pulps: effect of hydrolysis conditions and raw material. *Cellul Chem Technol* 12:177–183
- Harned HS, Fleysher MH (1925) The activity coefficients of hydrochloric acid in solutions of ethyl alcohol. *J Am Chem Soc* 47:82–92. doi:[10.1021/ja01678a011](https://doi.org/10.1021/ja01678a011)
- Immergut E, Schurz J, Mark H (1953) Viskositätszahl-Molekulargewichts-Beziehung für Cellulose und Untersuchungen von Nitrocellulose in verschiedenen Lösungsmitteln. *Monatsh Chem* 84:219G249. doi:[10.1007/BF00899186](https://doi.org/10.1007/BF00899186)
- Isogai A, Atalla RH (1998) Dissolution of cellulose in aqueous NaOH solutions. *Cellul Chem Technol* 5:309–319
- Jin H, Zha C, Gu L (2007) Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution. *Carbohydr Res* 342:851G858. doi:[10.1016/j.carres.2006.12.023](https://doi.org/10.1016/j.carres.2006.12.023)
- Kumar P, Barrett DM, Delwiche MJ, Stroeve P (2009) Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Ind Eng Chem Res* 48:3713G3729. doi:[10.1021/ie801542g](https://doi.org/10.1021/ie801542g)
- Le Moigne N, Bikard J, Navard P (2010) Rotation and contraction of native and regenerated cellulose fibers upon swelling and dissolution: the role of morphological and stress unbalances. *Cellul Chem Technol* 17:507–519
- Lee Y, Iyer P, Torget R (1999) Dilute-acid hydrolysis of lignocellulosic biomass. In: Tsao G, Brainard A, Bungay H, Cao N, Cen P, Chen Z, Du J, Foody B, Gong C, Hall P, Ho N, Irwin D, Iyer P, Jeffries T, Ladisch C, Ladisch M, Lee Y, Mosier N, Mhlemann H, Sedlak M, Shi N, Tsao G, Tolan J, Torget R, Wilson D, Xia L (eds) Recent progress in bioconversion of lignocellulosics, advances in biochemical engineering/biotechnology, vol 65. Springer, Berlin, pp 93–115
- Lin JH, Lee SY, Chang YH (2003) Effect of acid–alcohol treatment on the molecular structure and physicochemical properties of maize and potato starches. *Carbohydr Polym* 53:475–482. doi:[10.1016/S0144-8617\(03\)00145-0](https://doi.org/10.1016/S0144-8617(03)00145-0)
- Lin JH, Chang YH, Hsu YH (2009) Degradation of cotton cellulose treated with hydrochloric acid either in water or in ethanol. *Food Hydrocoll* 23:1548–1553. doi:[10.1016/j.foodhyd.2008.10.005](https://doi.org/10.1016/j.foodhyd.2008.10.005)
- Mazza M, Catana DA, Vaca-Garcia C, Cecutti C (2009) Influence of water on the dissolution of cellulose in selected ionic liquids. *Cellul Chem Technol* 16:207–215. doi:[10.1007/s10570-008-9257-x](https://doi.org/10.1007/s10570-008-9257-x)
- Moigne NL, Spinu M, Heinze T, Navard P (2010) Restricted dissolution and derivatization capacities of cellulose fibres under uniaxial elongational stress. *Polym Adv Technol* 51:447–453. doi:[10.1016/j.polymer.2009.11.053](https://doi.org/10.1016/j.polymer.2009.11.053)
- Qi H, Chang C, Zhang L (2008) Effects of temperature and molecular weight on dissolution of cellulose in NaOH/urea aqueous solution. *Cellul Chem Technol* 15:779–787
- Roy C, Budtova T, Navard P (2003) Rheological properties and gelation of aqueous cellulose–NaOH solutions. *Biomacromolecules* 4:256–264
- Saha BC, Iten LB, Cotta MA, Wu YV (2005) Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol. *Process Biochem* 40:3693–3700. doi:[10.1016/j.procbio.2005.04.006](https://doi.org/10.1016/j.procbio.2005.04.006)
- Small JC (1919) A method for the preparation of soluble starch. *J Am Chem Soc* 41:113–120. doi:[10.1021/ja01458a012](https://doi.org/10.1021/ja01458a012)
- Spieß AC, Zavrel M, Bross D, Funke M, Bchs J (2009) High-throughput screening for ionic liquids dissolving (ligno-) cellulose. *Bioresour Technol* 100:2580–2587. doi:[10.1016/j.biortech.2008.11.052](https://doi.org/10.1016/j.biortech.2008.11.052)
- Sundberg A, Sundberg K, Lilland C, Holmbom B (1996) Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography. *Nordic Pulp Paper Res J* 11:216–219. doi:[10.3183/NPPRJ-1996-11-04-p216-219](https://doi.org/10.3183/NPPRJ-1996-11-04-p216-219)
- Swatloski RP, Spear SK, Holbrey JD, Rogers RD (2002) Dissolution of cellulose with ionic liquids. *J Am Chem Soc* 124:4974–4975. doi:[10.1021/ja025790m](https://doi.org/10.1021/ja025790m)