CELLULOSE CHEMISTRY AND TECHNOLOGY

CONTROLLED DEPOLYMERISATION OF CELLULOSE TO A GIVEN DEGREE OF POLYMERISATION

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Cellulose Chemistry and Technology

The degree of polymerization of cellulose is very relevant for physical and chemical properties of highly engineered biomaterials. The ability to control the level of depolymerisation to a final specific value opens new opportunities to design cellulose-based nanostructured materials. In this paper, the controlled hydrolysis of cellulose in 0-96% ethanol environment and with nine chosen acids (pK*a* -10-4.7) was studied in order to tailor the pretreatment of dissolving and kraft pulps for various applications. The acid hydrolysis of cellulose in aqueous environment decreased the viscosity-averaged degree of polymerisation (DPv) and relative cellulose content. However, the addition of small amounts of ethanol preserved the cellulose content nearly at the original level, while decreasing the DPv. Furthermore, when the ethanol concentration increased, the DPv decreased manifoldly. The treatment with strong mineral acids in ethanol environment decreased the DPv by 75-80%, regardless of the initial DPv of the pulps. The correlation between the pK*a* of the acid and the final DPv was notable, and organic acids yielded a much higher DPv. Also, the electron microscopy study revealed that the outer cell wall layers were intact after the treatment with weak acids, whereas mineral acids in ethanol environment weakened the outer cell wall layers. This caused the dissolution mechanism to change when fibres were immersed in 0.2 M cupriethylenediamine. Fibres with intact outer cell wall layers dissolved via the ballooning mechanism, whereas fibres with ruptured outer cell wall dissolved via either fragmenting or uniform swelling.

Keywords: cellulose, hemicellulose, hydrolysis, ethanol, degradation, fibre composition, morphology, cell wall layers

INTRODUCTION

Cellulose is a starting material for several products, such as textiles, films and cellulose derivatives, which are further used in countless applications. The main source of this biopolymer is wood material, which is usually chemically treated to a more usable cellulosic pulp with lower contents of hemicelluloses and lignin. Depending on the application, sometimes the pulp is pretreated to reduce the consumption of energy and reagents in the manufacturing process. These pretreatments can roughly be categorized in three classes: physical, chemical and biological. Often the pretreatment stage is a combination of several methods, to be applied either simultaneously or sequentially.

Physical pretreatments, such as milling, grinding and refining, use mechanical forces to reduce the particle size and crystallinity of the pulp and open up the fibre wall. Chemical pretreatments, on the other hand, are targeting some of the components in pulp. Typical chemical treatments are, for example, ozonolysis,[1] mild and strong acid hydrolysis, organosolv processes[2] and alkaline hydrolysis.[3] Since the chemical treatments are not specific, side-reactions are common and they might produce byproducts that inhibit further treatments with biological reagents, such as enzymes. Enzymes can be very specific on certain components in pulp, but they require controlled reaction conditions, especially pH and temperature. In practice, combinations of physical and chemical or physical and biological methods are used, for example, steam explosion can be used prior to the BioCellSolv treatments. The HyCellSolv-treatment, which is an ethanol-hydrochloric treatment, has been shown to be an effective method to reduce the viscosity-averaged degree of polymerisation (DPv) of cotton cellulose.[4] Also, besides the DPv, it ruptures the primary cell wall and provides better accessibility for the solvents to penetrate into the fibre.[5] Ruptured and opened fibre cell wall is beneficial when aiming at homogeneous modification of the cellulose and even distribution and higher degrees of substitution (DS) of desired active groups.[6] Cellulose with a lowered degree of polymerisation can be used to form novel cellulosic shapes where the parallel alignment of this structural polymer does not play a crucial role, as it would do in high tensile strength yarns.[7,8] These novel shapes with randomly aligned cellulose molecules would be, for example, spheres, sponges and films.[9,10]

Usually, such pretreatment processes are done at high temperatures and pressures, causing the breakage of intermolecular bonds between cellulose, lignin and hemicelluloses.[2] Often, the aim of hydrolysis is to produce sugar units smaller than oligomers for the biofuel production.[11] Generally, in acid hydrolysis, control over the parameters of different hydrolysis steps is required in order to avoid the formation of undesired byproducts, such as levulinic and formic acids.[12] Acetyl groups on the xylopyranose backbone are the main source of acetic acid in an acid hydrolysis.[13] Due to these competing reactions during the hydrolysis, the effectiveness of the pretreatment method is dependent on the hemicellulose content. Luckily, these side-reactions do not occur at lower temperatures and the degradation of non-cellulosic components is prevented.

With well-controlled reaction conditions, only cellulose is degraded, but only to certain level, the so-called leveling-off DP (LODP).[14] This would not be the optimal end product in biofuel production, but when aiming at low-DP products, as mentioned above, LODP and its stability can be used to gain the optimal length for the weak water-based solvents, which cannot dissolve high-DP cellulose.[15,16] The values of LODP are related with the size of the crystallites and it is specific for each raw material, but independent of the initial viscosity of the pulp and the pulping method.[17] The LODP is, however, highly dependent on the acid used and its concentration.

In our previous study, the HyCellSolv-treatment was used to hydrolyse cellulose to approximately DP 174, so the cellulosic pulp became more soluble in weak solvents.[5] In the HyCellSolv-treatment, hydrochloric acid and concentrated ethanol were used as medium and different physical parameters, such as temperature and time, were adjusted and their effect on the treatment was studied. It was shown that the composition of the softwood dissolving pulp did not notably change during the treatment at various temperatures. This paper demonstrates how the HyCellSolv-pretreatment can be tailored using various acids, ethanol concentrations and raw materials. It also elucidates the mechanism of hydrolysis in the ethanol environment.

EXPERIMENTAL

Materials

Five different bleached pulps were used in this study (Table 1). Domsjö softwood dissolving pulp was used as a reference pulp in all experiments. All reagents were of analytical grade unless otherwise mentioned. They were obtained from commercial sources and used without purification.

Methods

HyCellSolv-treatment

In a reference experiment, 100 cm^3 of ethanol (92.5 v-%) was preheated to 75±1 °C, then 4.0 cm^3 of 37% HCl (~48 mmol) was added into the reaction vessel. After temperature was stabilised, 10 g of pulp was immersed and treated for 2 h. After the treatment, the pulp (abbreviated as HCS-pulp) was filtered, washed with distilled water until the pH was neutral, and dried at maximum 60 °C.

Table 1
Properties of pulps

Pulp	Provider (country)	Notes*	Reference
Domsjö	Domsjö Fabriken(Sweden)	D, spruce/pine60/40	28
Enoalfa	Stora Enso(Finland)	D, birch/aspen	29
BNP	MetsäFibre(Finland)	K, pine	30
Euca	UPM-Kymmene(Finland)	K, eucalyptus	31
Birch	UPM-Kymmene(Finland)	K, birch	31

*D=dissolving pulp, K=kraft pulp

Table 2
Acids, formulae and pK*a* values

Acid	Formula	pKa	Reference
Acetic	CH_3COOH	4.76	32
Formic	$HCOOH$	3.75	32
Hydrofluoric	HF	3.20	32
Phosphoric	H_3PO_4	2.16	32
Trifluoro-acetic	CF_3COOH	0.52	32
Nitric	HNO_3	-1.4	33
Sulphuric	H_2SO_4	-2	34
Hydrochloric	HCl	-7	34
Perchloric	$HClO_4$	-10	32

The role of acid moiety was studied by using different acids in equal amounts (Table 2). The amounts of moles of the acids with different stock concentrations were equalized by adding a sufficient amount of water so that the concentrations were comparable.

The efficiency of the treatment in various ethanol concentrations was studied by diluting 92.5% ethanol with water so that the final concentration was 9-89%. Additionally, 99% ethanol was used to study the efficiency in highly concentrated environment. After adding 4 cm^3 of 37% HCl, the ethanol concentration was ~ 96%.

Also, hydrolysis in water without ethanol was carried out with the same and approximately 4.7 and 12.3 times higher HCl amounts, corresponding to increased activity coefficient of hydrochloric acid in 71% and 89% ethanol environments.[18]

Intrinsic viscosity

Intrinsic viscosities of the pulps and HCS-pulps were measured according to the standard ISO/FDIS5351:2009 and the viscosity averaged degrees of polymerisation DPv were computed from the values with a formula $(0.75\times\eta)^{1/0.905}$.[19] Briefly, samples were freeze-dried, weighed, dissolved in 0.5 M cupriethylenediamine (CED), and viscosities were measured with capillary viscosimeters. According to the procedure, the temperature of the capillary was 25.0±0.1 °C and the error of the limiting viscosity number did not exceed 2%.

SEC

Molar mass distributions of Domsjö and HCS-Domsjöpulps with treatment times of 0.5, 2 and 5 h, and withformic and nitric acids (2 h at 75 °C) were measured with a JASCO SEC system with a degasser DG 980-50, pump 980, UV detector 975 working at k=254 nm, refractive index detector 930, columns Suprema1000+ and Suprema 100 from Kromatek, Great Dunmow, Essex, UK, with eluent flow rate of 1.000 ml min^{-1}. Samples were dissolved in DMAc/LiCl and pullulan was used as a standard.

Carbohydrate analysis

Approximately 30 mg of freeze-dried samples were accurately weighed and hydrolysed with 300 µl of 72% sulphuric acid (prepared from 95-97% H2SO4) for 1 h at 30 °C. After the hydrolysis, 8.34 cm^3 of deionised water was added and samples were hydrolysed in an autoclave for 1 h at 125 °C. 500 µl of clear hydrolysates were neutralized with ~ 50 $mMBa(OH)_2$, so that the pH did not exceed 8.5. Sorbitol standard was injected and used as an internal reference. The concentrations of arabinose, galactose, glucose (Glu), rhamnose, xylose (Xyl), and mannose (Man) were analysed with a high-performance liquid chromatography (HPLC) Dionex ICS 5000 system with a pulsed amperometric detector (PAD), equipped with a single pump, dual piston and online degasser. Potassium hydroxide was used as an eluent. The analytical column was a CarboPac PA20 (3x150 mm) attached to a Carbo Pac PA20 guard column (3x50 mm) with a flow rate of 0.35 cm^3min^{-1}. Chromatograms were processed and analysed with Chromeleon 7.0 software, purchased from ThermoScientific.

Amount of anionic groups

The amount of anionic groups or charge of the pulps was determined by methylene blue (MB) adsorption isotherms.[20]Sorptions were performed at 25 °C and concentrations of free MB were determined with a Shimadzu UV-2600 UV-Vis spectrophotometer (Japan).

Fibre morphology

Changes in the morphological structure of the primary cell wall of the pulps and HCS-pulps were examined with a field emission scanning electron microscope (FE-SEM) and an optical microscope. Selected native and HCS-pulps were sputter-coated with carbon with an Agar coater and studied with a JEOL JSM-6335 FE-SEM with an in-lens detector. Accelerating voltage was 5.0 kV and magnifications of 5,000 and 30,000xwere used. An optical microscope Nikon Eclipse E200 coupled to a Nikon DS-Fi2 camera was used to detect ballooning during the dissolution of the fibres. 0.2 M CED was used as a solvent.

RESULTS AND DISCUSSION

Role of the acid and ethanol moieties in HyCellSolv-treatment

Hydrolysis with hydrochloric acid in water yielded DPv 291 (Fig. 1). The degradation of cellulose remained at the same level (DPv 291-299) until ethanol concentration increased above 36%, and the slope of the linear region became negative, since the degradation of cellulose was more intensive. It is possible that ethanolysis was a competing reaction to the hydrolysis in the region where the ethanol concentration was 36-76% (Fig. 2). Also, it is noteworthy that when the ethanol concentration increased above 76%, the activity coefficient of the hydrochloric acid was more than 5 and it increased exponentially with increasing ethanol concentration.[18] This caused the slope c(EtOH)/DPvto decrease even more.

Hemicellulose composition was drastically different between the treatments with and without ethanol, even when the ethanol concentration was only 9% (Fig. 3). Water with hydrochloric acid yielded a high loss of glucose, which increased the relative xylose and mannose content of the hydrolysate. The plateau in DPv (Fig. 1) between 9-36% ethanol had slightly less glucose than the next region, 44-76%. It could be speculated that the ethanol prevents the hydrolysis of cellulose to soluble sugars even at low amounts, and enhances the degradation to smaller but still insoluble units.

Hydrolysis with 4.7 and 12.3 times higher concentrations of HCl without ethanol resulted in DPv values of 123 and 158. Values are slightly lower than what was expected from the estimated activity coefficient of hydrochloric acid in 71% and 89% ethanol environments, where the DPv values were 238 and 177, respectively. This can be explained by different swelling properties of these two solvents; water is an approximately 2-8 times better swelling agent than ethanol, depending on fibre type.[21]

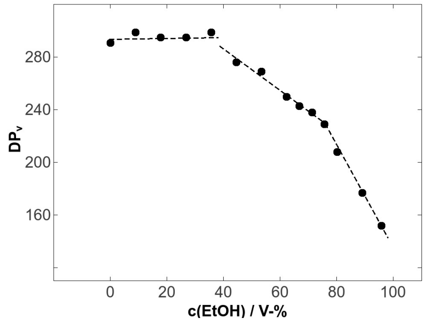

Figure 1: DPv of HCS-Domsjö pulp with various ethanol concentrations in HyCellSolv-treatment (dashed lines are given to guide the eye, indicating the three possible regions of depolymerisation kinetics)

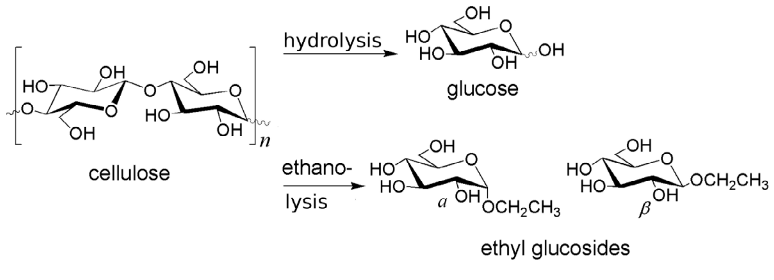

Figure 2: Products of hydrolysis and ethanolysis from cellulose (adapted from Deng*et al.*[35])

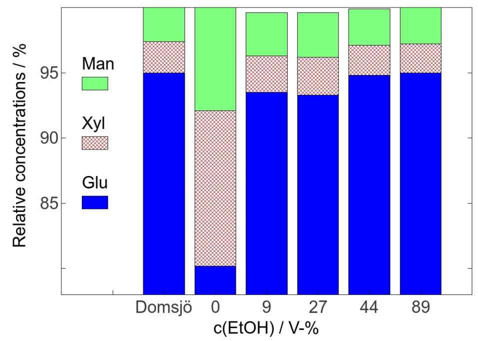

Figure 3: Relative concentrations of hydrolysates of Domsjö pulp before (Domsjö) and after (0-89%) HyCellSolv-treatment in various ethanol concentrations

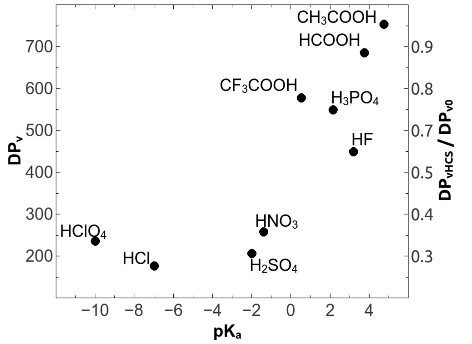

Figure 4: DPv of Domsjö-pulp after HyCellSolv-treatment with various acids (see Table 2). Right y-axis denotes the ratio between measured DPv *HCS* of HCS-Domsjö and initial DPv0 of Domsjö-pulp

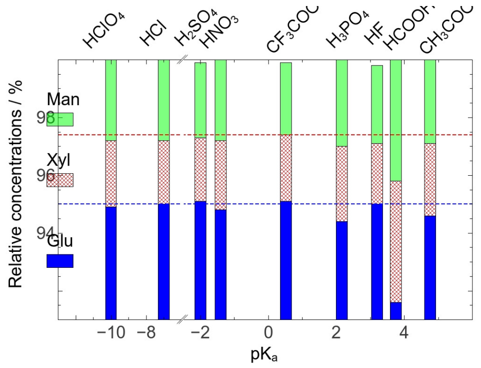

Figure 5: Relative concentrations of hydrolysates of HCS-Domsjö after the treatment with different acids. Horizontal lines indicate composition of the untreated Domsjö-pulp

Various acids (Table 2) were added in ethanol and the amount of water was kept constant by adding required amounts so that the concentration was the same as with hydrochloric acid. Even the use of pK*a* values in the ethanol environment and at high temperatures is questionable, computed DPv values were plotted against pK*a* values (Fig. 4). The acids can be divided into two groups; strong acids with pK*a* below 0 and weak acids with pK*a* above that. The former produced HCS-Domsjö with a DPv between 177-258 and the latter – with a DPvof 449-754.

It is known that the LODP is dependent on the acid and its concentration, i.e. the concentration of the hydrogen ions in the solution.[17] Since the dissociation constants of the acid increases in ethanolenvironment,[18,22] the increased concentration of hydrogen ions in reaction solution explains the decrease in DPv values. Furthermore, it seems that the local, or perhaps absolute minimum in DPv, can be reached when the pK*a* is below 0, under these experimental conditions. An increase of temperature, pressure, and ethanol concentration (and hence the activity coefficient of the acid) might result in even lower LODP.

While the viscosity averaged degree of polymerisation of cellulose decreased together with the pK*a* values of different acids, the composition of cellulose and hemicelluloses did not change (Fig. 5). Only clearly different composition was measured when the Domsjö pulp was treated with ethanol and formic acid; the amount of glucose decreased from 95.0% (untreated Domsjö) to 91.6%. This is at least 3 percentage points lower than after the treatment with any other acid. While the standard deviation of the results is ±0.5%, the glucose content in HCS-Domsjö treated with other acids was between 94.4-95.1%. It is possible that formic acid, as a small carbonyl compound that easily forms hydrogen bonds with cellulose lattice,[23] could cause swelling of the cellulose matrix and in this way enhance the degradation of cellulose into soluble glucose during the HyCellSolv-treatment.

Molar mass distribution shifted towards lower molar masses along with the decreasing DPv when the acid was changed from formic to nitric, and further to hydrochloric acid (Fig. 6). The fraction of the highest molar mass cellulose was degraded and it increased the peaks at 4-7x104 Da. The increase of low molar mass polymers (M*w* < 104 Da) was observed especially when hydrochloric acid was used and the treatment time was prolonged from 0.5 to 5 h; this widened the distributions and increased the PDI rapidly (Fig. 6, inset). Since the molar masses below 104 Da consist mainly of hemicelluloses, which were not degraded during the treatment (Fig. 5), it is reasonable to presume that the relative increase in M*w* < 104 Da region is due to the increase in low M*w* and to the decrease in high M*w* celluloses.

Selectivity of HyCellSolv-treatment

Birch has the highest initial DPv0 from the pulps and the lowest glucose content in the hydrolysate (Table 3 and Fig. 7). After the HyCellSolv-treatment, the DPv was still the highest from the treated pulps, and the treatment was the most effective for Birch. Euca had a slightly lower DPv0 and a similar composition, but the HCS-treatment was the most ineffective on Euca in terms of DPv.

The anionic groups of the pulps mainly yield from uronic acids and hemicelluloses. Dissolving pulps Domsjö and Enoalfa did not change notably in their composition (Fig. 7). Xylose was slightly lower in HCS-Enoalfa, but the amounts were low compared to paper-grade hardwoods. BNP was the only pulp where the decrease in the mannose concentration was measured, but it also had initially the highest amount of mannose in the hydrolysate.

Table 3
DPv and the charge of pulps before and after HyCellSolv-treatment and the ratio of DPv values

Pulp	DPv0	DPvHCS	DPvHCS	Charge (μmol g^{-1})	
			DPv0	Initial	HCS
Domsjö	737	291*/183	0.248	39	35*/25
Enoalfa	652	159	0.244	53	42
BNP	1182	252	0.213	56	42
Euca	1238	252	0.204	75	46
Birch	1318	331	0.251	94	46

*without ethanol

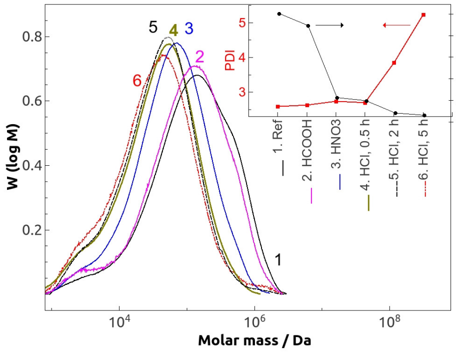

Figure 6: Molar mass distributions, polydispersity indices and DPv values of Domsjö-pulp before and after HyCellSolv-treatment with formic (2) and nitric (3) acids for 2 h, and HCl for 0.5 (4), 2 (5) and 5 h (6)

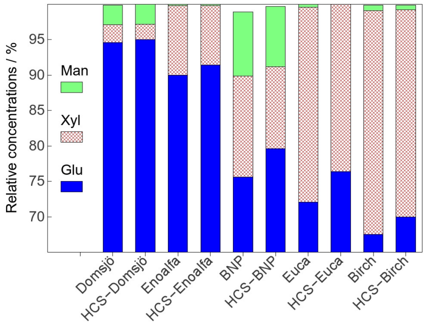

Figure 7: Relative concentrations of hydrolysates of pulps and HCS-pulps

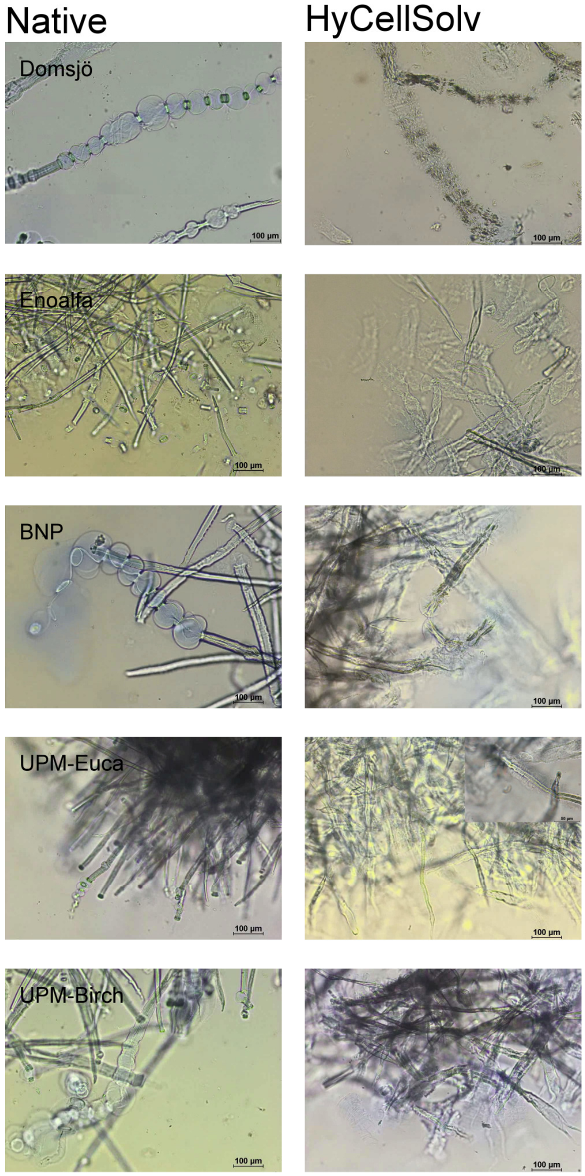

Figure 8: Native (left column) and HyCellSolv-treated (right column) pulps in 0.2 M CED solution. From top to bottom: Domsjö, Enoalfa, BNP, Euca and Birch

As the glucose content also decreased, the relative ratio of the xylose increased in the HCS-treatment In kraft pulps, the loss of a small portion of hemicelluloses resulted in a decrease in the charge (Table 3). It could be concluded that the HyCellSolv-treatment removes only a small portion of the hemicelluloses from the pulps, but mainly it decreases the degree of polymerisation of the cellulose chains. The decrease of the charge to a nearly constant level indicates that the hemicelluloses with acidic groups might be more targeted than the neutral ones.

Cell wall morphology and dissolution mechanism

Differences in the morphology of the pulp and HCS-pulp fibres were observed with FE-SEM. Clear differences could not be observed in the morphology of Domsjö and HCS-Domsjo pulps (figure not shown). HCS-Domsjö was, however, the only pulp that dissolved solely via the fragmenting mechanism in 0.2 M CED, whereas all the other HCS pulps were more resistant to the solvent and swelled uniformly before dissolving and demonstrated fragmenting only to some extent (Table 4, Fig.8). Ballooning was not observed in any HCS-pulps.

The S2-layer was clearly visible in HCS treated Enoalfa, BNP and Birch. However, the surface of Euca and HCS-Euca showed a randomly oriented network of microfibrils (Fig.9). Microfibrils are known to have a clear orientation in the S2 layer, but the orientation in S1 and in the transition lamella S12 between S1 and S2 is less consensual.[24]It is possible that this observed layer in Euca and HCS-Euca is either S1 or S12, or a mixture of the two. HCS-Euca was more resistant than other HCS-pulps against the dissolution, but it swelled uniformly without ballooning.

In HCS-BNP, some ballooning was initiated in 0.2 M CED, but the cell walls could not hold the osmotic pressure and they broke down at the early stage of the initiated ballooning. Also, some fragmenting was observed during the dissolution. It seems that the visible changes in morphology alone cannot explain the absence of the ballooning phenomenon during the dissolution. For example, no exposed S2 layer was observed in the micrographs of HCS-Domsjö. Since the hemicellulose composition does not change drastically during the HyCellSolv-treatment, only the decrease in DPv correlates to some extent with the dissolution mechanism (Table 3). However, for example HCS-Enoalfa has a similar DPv to that of HCS-Domsjö and it still does not demonstrate pure fragmenting. One explanation could be the differences in wood species, combined with the DPv and hemicellulose (mainly xylan) composition; softwood HCS-Domsjö and HCS-BNP were the only ones where some fragmenting was observed, although some ballooning was initiated in HCS-BNP. HCS-BNP has, however, a much higher concentration of hemicelluloses and DPv, which may have caused the partial ballooning. Hardwood fibres are notably shorter and more evolved than softwood fibres,[25] leading to better solvent penetration in hardwoods and lower osmotic pressure. DPv decreased more when the pKa of the acid was lower (Fig. 4). A similar trend was observed in the dissolution mechanism: the fibres of the HCS-Domsjö pulp dissolved via fragmentation after the treatment with strong mineral acids, whereas with phosphoric acid (pK*a* 2.16), the fibres swelled uniformly and showed only some fragmentation. Fibres swelled uniformly before dissolution when hydrofluoric acid was used (pK*a* 3.2), and only balloons were observed with formic acid (pK*a* 3.75) HCS-treatment (Table 4).

Table 4
Morphological features of FE-SEM micrographs and observations of dissolution mechanism in 0.2 M CED of pulps and HCS-pulps treated with various acids and ethanol concentrations

HCS-Pulp	Morphology	Dissolution mechanism
Domsjö	R	F
Enoalfa	S2	U
BNP	S2	U
Euca	I	U
Birch	S2	U
Acid (pKa)		
Hydrochloric (-7)	R	F
Sulphuric (-2)	S2	F
Trifluoroacetic (0.52)	R	B
Phosphoric (2.16)	-	U/F
Hydrofluoric (3.2)	R	U
Formic (3.75)	I	B
c(EtOH)/%		
28-96	-	F
19	-	U/F
0-9	-	U

Abbreviations: Morphology: S2 – S2 layer exposed, R – remnants of P/S1/S12 layers present, I – intact P/S1/S12 layers; Dissolution mechanism: B – dissolution *via* ballooning, U – uniform swelling, F – fragmenting

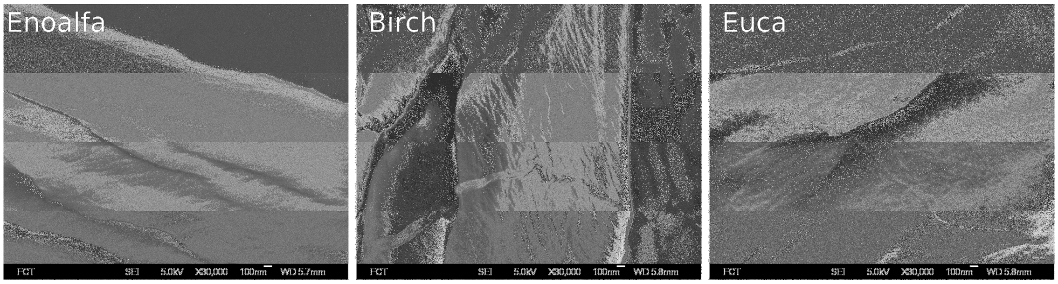

Figure 9: SEM images of HCS-Enoalfa (left), -Birch (middle) and -Euca (right), (magnification30,000x)

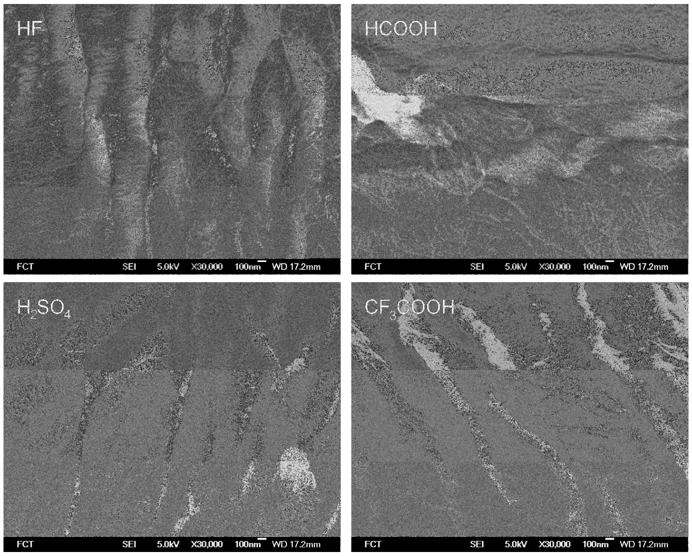

Figure 10: SEM images of HCS-Domsjö pulp treated with hydrofluoric, formic, sulphuric and trifluoroacetic acids in ethanol environment (magnification 30,000x)

Clear differences could not be observed in the morphologies of sulphuric and hydrofluoric acid HCS-treated pulps (Fig. 10). Some oriented S2 layers were seen, as well as remnants of S1 and perhaps S12 lamella. The microfibrils in formic acid treated HCS-Domsjö fibres were completely randomly oriented. The decrease of glucose in the hemicellulose composition obviously did not have an effect on the morphology, which supports the fact that outer layers of the cell wall are mainly constituted of hemicelluloses.[26]

Decreasing the ethanol concentration in the HyCellSolv-treatment increased the DPv of HCS-Domsjö pulp (Fig. 1), but it did not change the dissolution mechanism until the ethanol concentration was 19% or below. At low ethanol concentrations, fibres were swelled uniformly before dissolution, but balloons were not observed even when ethanol was not used at all. In this case, the hemicellulose composition was drastically changed (Fig. 3) and DPv was still above, for example, HCS-BNP and HCS-Euca (Table 3). This indicates that the ethanol itself is not the parameter causing the dissolution mechanism to change from ballooning to fragmenting. The main factors causing the change in the dissolution mechanism seem to be the acid and its pK*a*, as well as the pulp type.

CONCLUSION

The HyCellSolv-treatment was studied by varying the ethanol concentration and acid moiety. Dissolving and kraft pulps were affected by the treatment in a similar manner: the DPv decreased to 20-25% from the initial DPv0. The hemicellulose content changed only slightly in all the pulps, except when the formic acid was used, the glucose content of the HCS-Domsjö degreased notably, increasing the relative portions of the xylose and mannose. Formic acid, as a small carbonyl compound, could swell the cellulose matrix, form hydrogen bonds and hydrolyse the cellulose chains from the end of the chain, cleaving the cellulose into soluble glucose molecules. All other acids participated only at the degradation of the DPv of cellulose in good correlation with their pK*a* values. Previously, Cuissinat[27] named five modes of dissolution for cotton and wood fibres. Here, we have shown how wood fibres change their dissolution mechanism from ballooning (mode 3) to fragmenting (mode 1) or uniform swelling (previously unnamed mode). The interior part of the fibre, mainly the thick S2, dissolves and creates an osmotic pressure inside the P layer, which forms collars around the swelling secondary cell wall layers and creates balloons.[25,6] In the HyCellSolv-treatment, the P layer is ruptured and balloons cannot form anymore, and as a result, in the case of hardwood pulps, fibres swelled uniformly. Possibly, the S1 and the intermediate lamella S12 were slowing down the dissolution, maintaining the fibre shape. Fragmenting, on the other hand, occurs when all the outer layers, that is P, S1 and S12, of the fibre are ruptured and the S2 layer dissolves rapidly due to fast solvent in flow, under the free flow of solvent and solutes. The HyCellSolv-treatment is an efficient and energy-saving method to reduce the DPv of the pulp. DPv can be targeted by choosing the suitable acid, ethanol concentration or adjusting the temperature and time.[5]Unlike most of the acid hydrolysis methods, it is quite specific to cellulose and hydrolysis/ethanolysis does not proceed to the point where the components would become soluble in water. Furthermore, the HyCellSolv-pretreatment ruptures the outermost layers of the fibres and so enhances the dissolution of all tested pulp types due to better solvent penetration.

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REFERENCES

[1] J. Quesada, M. Rubio and D. Gomez, *J. Wood Chem. Technol.*, **19**, 115 (1999).

[2] P. Kumar, D. M. Barrett, M. J. Delwiche and P. Stroeve, *Ind. Eng. Chem. Res.*, **48**, 3713 (2009).

[3] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Lee *et al.*, *Bioresour. Technol.*, **96**, 673 (2005).

[4] J.-H. Lin, Y.-H. Chang and Y.-H. Hsu, *Food Hydrocoll.*, **23**, 1548 (2009).

[5] J. Trygg and P. Fardim, *Cellulose*, **18**, 987 (2011).

[6] N. L. Moigne, M. Spinu, T. Heinze and P. Navard, *Polymer*, **51**, 447 (2010).

[7] H. Krässig and W. Kitchen, *J. Polym. Sci.*, **51**, 123 (1961).

[8] C. Woodings (Ed.), "Regenerated Cellulose Fibres", Woodhead Publishing Ltd, CRC Press, US, 2001.

[9] R. Sescousse and T. Budtova, *Cellulose*, **16**, 417 (2009).

[10] J. Trygg, P. Fardim, M. Gericke, E. Mäkilä and J. Salonen, *Carbohyd. Polym.*, **93**, 291 (2013).

[11] B. C. Saha, L. B. Iten, M. A. Cotta and Y. V. Wu, *Process Biochem.*, **40**, 3693 (2005).

[12] S.-Y. Yoon, S.-H. Han and S.-J. Shin, *Energy*, **77**, 19 (2014).

[13] E. Sjöström, "Wood Chemistry: Fundamentals and Applications", Academic Press, US, 1993.

[14] R. F. Nickerson and J. A. Habrle, *Ind. Eng. Chem.*, **39**, 1507 (1947).

[15] A. Isogai and R. H. Atalla, *Cellulose*, **5**, 309 (1998).

[16] H. Qi, C. Chang and L. Zhang, *Cellulose*, **15**, 779 (2008).

[17] H. Håkansson and P. Ahlgren, *Cellulose*, **12**, 177 (2005).

[18] H. S. Harned and M. H. Fleysher, *J. Am. Chem. Soc.*, **47**, 82 (1925).

[19] E. Immergut, J. Schurz and H. Mark, *Monatsh. Chem.*, **84**, 219 (1953).

[20] P. Fardim and B. Holmbom, *Tappi J.*, **2**, 28 (2003).

[21] O. El Seoud, L. Fidale, N. Ruiz, M. D'Almeida and E. Frollini, *Cellulose*, **15**, 371 (2008).

[22] E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951).

[23] Y. Sun, L. Lin, C. Pang, H. Deng, H. Peng *et al.*, *Energ. Fuels*, **21**, 2386 (2007).

[24] J. Brändström, S. L. Bardage, G. Daniel and T. Nilsson, *IAWA J.*, **24**, 27 (2003).

[25] W. Jensen (Ed.), "Puukemia"(Wood Chemistry), SuomenPaperi-insinöörrienYhdistyksenoppi-jakäsikirja I, Teknillisten Tieteiden Akatemia, Finland, 1977.

[26] A. J. Panshin and C. De Zeeuw, "Textbook of Wood Technology", New York, US, McGraw-Hill, 1970.

[27] C. Cuissinat and P. Navard, *Macromol. Symp.*, **244**, 19 (2006).

[28] Domsjö Specification Sheet of Domsjö Cellulose, <http://www.domsjoe.com>, accessed on 10 November 2010.

[29] StoraEnso, Specification Sheet of Enoalfa, <http://biomaterials.storaenso.com>, printed on 10 June 2014.

[30] Metsä FibreOy, Specification Sheet of Botnia Nordic Pine+, <http://www.metsafibre.com>, accessed on 11 December 2014.

[31] UPM-Kymmene Corporation, Specification Sheets of UPM Euca and UPM Betula TCF, <http://www.upmpulp.com>, accessed on 11 December 2014.

[32] D. R. Lide (Ed.), “CRC Handbook of Chemistry and Physics”, vol. 84, CRC Press, USA, 2003.

[33] R. P. Bell, “Proton in Chemistry”, Springer, US, 1973.

[34] P. Atkins and D. Shriver, “Shriver and Atkins' Inorganic Chemistry”, Oxford University Press, UK, 2010.

[35] W. Deng, M. Liu, Q. Zhang and Y. Wang, *Catal. Today*, **164**, 461 (2011).