EFFECT OF ACID AND ENZYMATIC TREATMENTS OF TCF DISSOLVING PULP ON THE PROPERTIES OF WET SPUN CELLULOSIC FIBRES

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Dissolving-grade softwood pulp was treated with EG-rich enzymes and hot diluted sulphuric acid, to decrease the molecular weight of cellulose. The treated samples were dissolved in aqueous sodium zincate and spun into cellulosic fibres by a wet spinning method. The effects of cellulose concentration in the spinning solution and of cellulose molecular weight on the fibre properties were studied. The molecular weight (M_w) of the treated cellulose decreased by 38 to 63%, depending on the treatment parameters. The falling ball viscosity of the alkaline solution prepared from the differently treated pulps correlated linearly with the M_w of the treated cellulose. At constant M_w of cellulose, the tenacity of the obtained wet spun fibres correlated positively with the cellulose concentration of the spinning solution. However, a higher cellulose concentration could not compensate the lowered M_w as to the fibre properties.

Keywords: enzymatic treatment of cellulose, cellulosic fibres, wet spinning

INTRODUCTION

Native cellulose fibres have a complex physical structure, due to their different layers, composed of oriented microfibril lamellas.[1] The microfibrils are built up from aggregated elementary fibrils formed of cellulose molecules attached to each other by intermolecular hydrogen bonds. The molecules also have large intramolecular hydrogen bondings, which makes the structure rigid.[2] The cellulose fibres as such are considered to be insoluble in aqueous solutions. Consequently, derivatisation with carbon disulphide is used in the viscose process to dissolve and convert them into variously shaped articles. However, carbon disulphide is a highly toxic chemical, which requires special care in handling and recovery.[3] Therefore, an ecological method to dissolve cellulose in an aqueous environment is still being sought.

Enzymes have proved to be powerful biocatalysts that modify the cellulosic material into an alkaline soluble form.[4-6] In nature, the synergistic action of different cellulases leads to the degradation of native crystalline cellulose into glucose monomers.[7] However, when using specially tailored enzymes with a controlled ratio of different cellulases, it is possible to obtain alkali-soluble cellulose with a reasonable degree of polymerisation.[4,5]

The first alkaline solutions prepared from enzyme-treated cellulose for fibre spinning[5,8] had relatively low cellulose (3-5 wt%), and high sodium hydroxide (9 wt%) and zinc oxide (1.9 wt%) concentrations. Thereafter,

cellulose concentration increased to 6 wt%, while the sodium hydroxide and zinc oxide concentrations decreased to 7.8 wt% and 0.84 wt%, respectively.[9] The ratio between sodium hydroxide and cellulose in the spinning solution determines the amount of sulphuric acid needed for regeneration, as well as the amount of sodium salt formed as a by-product. Thus, the ratio is critical for the economy of the wet spinning process and it should desirably be below 1.

In the present investigation, the molecular weight of enzyme-treated cellulose was lowered prior to dissolution, which permitted to increase the cellulose concentration of the spinning solution. Degradation was carried out by dilute acid hydrolysis. The effects of cellulose molecular weight and cellulose concentration of the spinning solution on the properties of wet spun fibres are discussed.

MATERIALS AND METHOD

The raw material used was a commercial dissolving-grade sulphite pulp produced from a mixture of pine and spruce, by a total chlorine-free process. The pulp was delivered by Domsjoe Fabriker Ab, Sweden.

The starting pulp was first treated mechanically and with enzymes, as previously described,[9] then subjected to 0.1 M H_2SO_4 for 30 min at 80 °C or at 100 °C. Finally, the pulp was washed with demineralised water until an acid-free condition was reached. The reference samples prepared represented mechanically shredded pulp without further treatments, with enzymatic treatment only or with acid treatment (100 °C) only (Fig. 1).

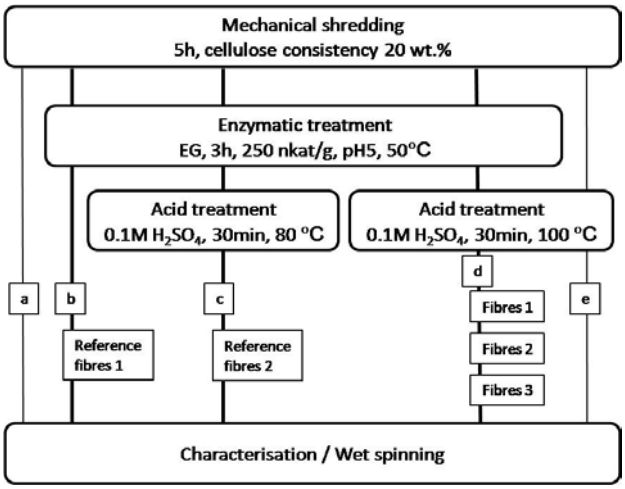

Figure 1: Schematic presentation of the treatments

The molecular weights of the differently treated samples were measured with an HPLC at Domsjoe Fabriker Ab.

The treated pulps were dissolved into aqueous sodium zincate, according to a previously described method,[10] the only exception being that no urea was used. Viscosity of the obtained alkaline cellulose solutions was measured by the modified Ball-Drop Method (ASTM D 1343-86) with stainless steel balls (1/8", 130 mg), at a measuring distance of 20 cm. Viscosity was measured immediately after dissolution and then again on the next day, in the solutions applied for fibre spinning. The cellulose content (alpha) of the alkaline solution was measured by weighing the dried films prepared by casting the solution into 10% H_2SO_4.

The cellulosic fibres were spun from the selected alkaline solutions by the wet spinning method.[9] Two types of reference fibres were prepared, one from the mechanically and enzyme-treated pulp without acid treatment, and another one with subsequent acid treatment, at 80 °C. Three fibre samples were prepared from the mechanically and enzyme-treated pulp with subsequent acid treatment, at 100 °C, to study the effect of dope cellulose concentration on the fibre properties. The coagulation bath had either a low (50 g/L) or a high (168-246 g/L) amount of sulphuric acid. The mechanical properties of the fibres were determined as described previously.[9]

RESULTS AND DISCUSSION

The acid treatment at 100 °C decreased the molecular weight of the mechanically shredded pulp by 52%, while the enzymatic treatment decreased it by 38%. The acid treatments of the enzyme-treated pulp further decreased the M_w by 39 or 21%, as

depending on the temperature the acid treatment was carried out at: 100 or 80 °C (Table 1). Each treatment decreased the polydispersity of molecular weight distribution, as compared to that of the sample treated only mechanically. The acid treatment of the mechanically shredded pulp at 100 °C produced a nearly identical shape of the molecular weight distribution curve with that obtained after the acid treatment of the mechanically and enzyme-treated pulp at 80 °C. The acid treatment of the mechanically and enzyme-treated pulp at 100 °C degraded cellulose to a higher extent, and increased clearly the share of low molecular weight cellulose – compared to the other samples (Fig. 2).

The molecular weight of the differently treated pulps correlated linearly with the falling ball viscosity of the alkaline solution, at constant cellulose concentration (Fig. 3). On the other hand, at constant M_w, falling ball viscosity increased very fast above a certain cellulose concentration, indicating a rapid gelling behaviour of the alkaline solution at a higher cellulose content (Fig. 4).

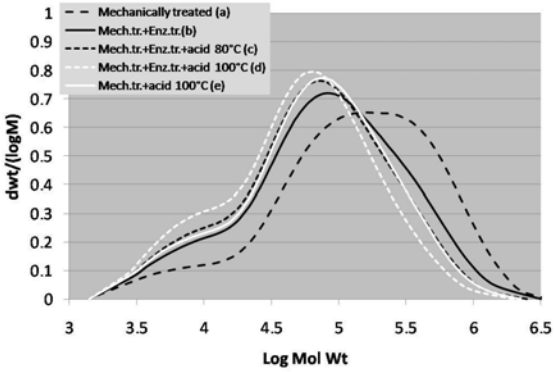

Figure 2: Average molecular weight distribution curves of differently treated pulp samples

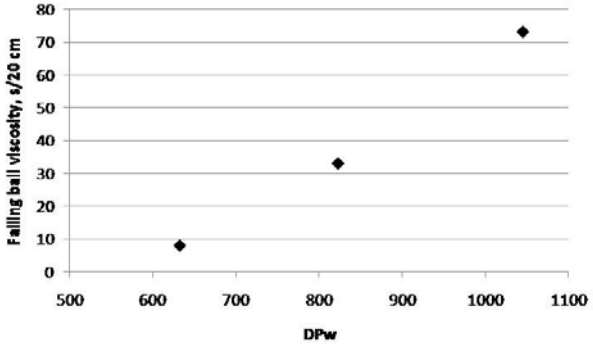

Figure 3: Falling ball viscosity of alkaline cellulose solution at constant cellulose concentration (~6 wt%)

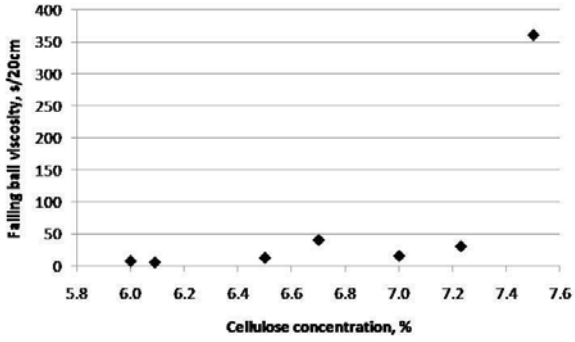

Figure 4: Falling ball viscosity of alkaline cellulose solution at constant weight average molecular weight (103153)

Table 1
Weight average (M_w) and number average (M_n) molecular weights of the samples
(Pd = polydispersity, DP_w = weight average degree of polymerisation)

Sample		Mw	Mn	Pd	DP_w
A	Mechanically treated	276160	40445	6.83	1694
B	Mechanically + enzyme-treated	170384	28843	5.91	1045
C	Mechanically + enzyme-treated + acid-treated at 80 °C	134154	25446	5.27	823
D	Mechanically + enzyme-treated + acid-treated at 100 °C	103153	21729	4.75	633
E	Mechanically treated + acid-treated at 100 °C	132810	26028	5.10	815

M_w was shown to have a positive linear correlation with the tenacity of the obtained fibres (Fig. 5). However, the slightly weaker fibres, with lower M_w, have the extensibility equal (~16%) to that of the fibres with higher M_w (Fig. 6). At the same molecular weight, the cellulose concentration of the spinning solution was nearly linearly correlated with fibre tenacity (Fig. 7), but did not present an equally clear correlation with elongation (Fig. 8). Instead, the high sulphuric acid concentration of the spin bath seemed to increase fibre elasticity (Fig. 9), while the effect on tenacity was not so obvious (Fig. 10).

At the same M_w and spin bath acid values, a higher cellulose concentration of the spinning solution produced stronger and more elastic fibres than those produced at a lower cellulose concentration (Table 2). As tenacity increased without any extensibility loss, the fine structure of the fibres was improved,[11] as due to an increased cellulose concentration. However, it was shown that the higher cellulose concentration of the spinning dope could not compensate the lowered M_w of cellulose (Fig. 7), which is most likely due to a too severe degradation of cellulose during the acid treatment.

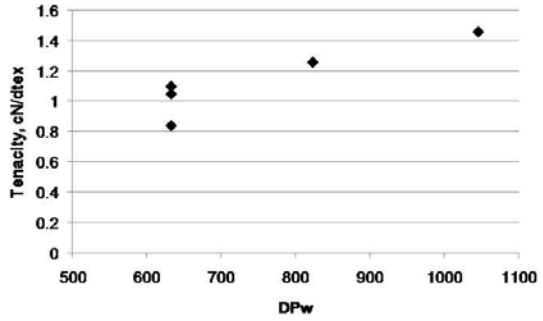

Figure 5: Tenacity of fibres as a function of the average degree of cellulose polymerisation (DP_w)

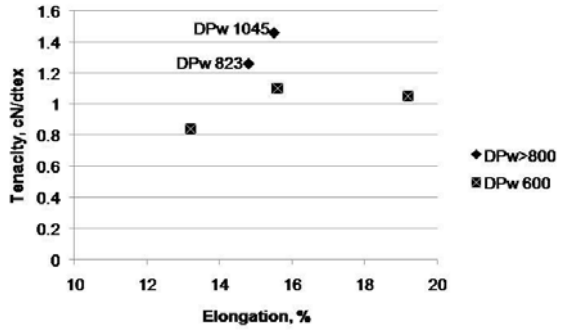

Figure 6: Mechanical properties of wet spun cellulosic fibres

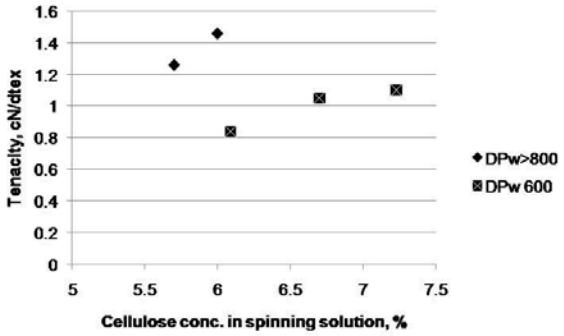

Figure 7: Tenacity of fibres as a function of cellulose concentration in the spinning solution

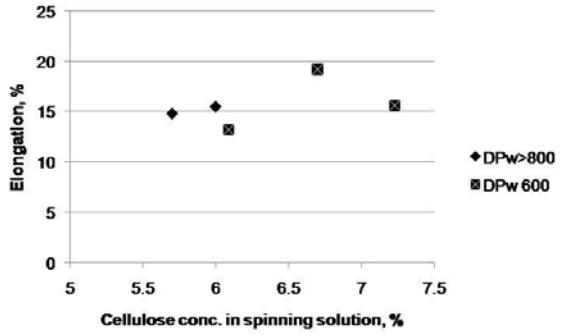

Figure 8: Elongation of fibres as a function of cellulose concentration in the spinning solution

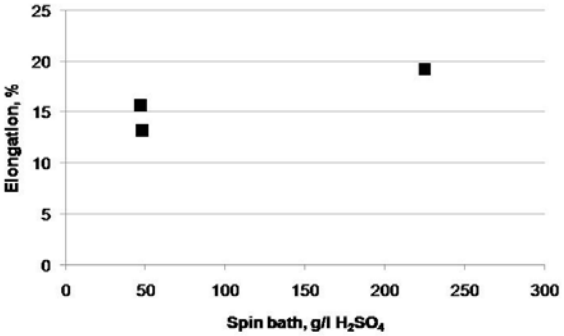

Figure 9: Elongation of fibres as a function of spin bath sulphuric acid concentration (DP_w 600)

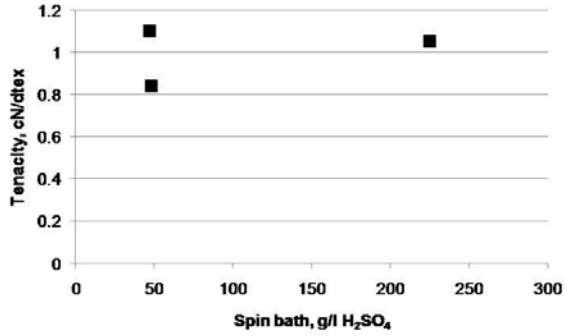

Figure 10: Tenacity of fibres as a function of spin bath sulphuric acid concentration (DP_w 600)

Table 2
Wet spinning parameters

Fibre sample	Acid treatment		Alkaline solution		Spinning	Mechanical properties of fibres	
	Temperature, °C/time, min	M_w	Cellulose concentration, wt%	Falling ball viscosity*, s/20 cm	H_2SO_4, g/L	Tenacity, cN/dtex	Elongation, %
Reference 1	0/0	170384	6.0	83	168	1.46	15.5
Reference 2	80/30	134154	5.7	27	246	1.26	14.8
Fibre 1	100/30	103153	6.1	6	48	0.84	13.2
Fibre 2	100/30	103153	6.7	33	225	1.05	19.2
Fibre 3	100/30	103153	7.2	50	47	1.10	15.6

*the next day, prior to spinning

CONCLUSIONS

The cellulose concentration of the spinning solution can be raised from 6 wt% up to 7.2 wt% by decreasing the molecular weight of cellulose. Even in such a case, the fibre properties were better at a higher cellulose concentration while, at the same M_w, a higher concentration could not compensate for the reduced M_w, because molecular weight had degraded too much. However, fibre properties might be improved by optimising the values within the limits applied in the present work.

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The text reflects only the authors' views and the Community is not liable to any use of the information provided therein.

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