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# Formation of Fibres from Bio-modified Cellulose Pulp

## Abstract

*A process to produce fibres from bio-modified cellulose pulp has been developed. The spinning process was investigated on a large laboratory scale. Alkaline spinning solutions were first prepared from enzyme-processed cellulose, followed by wet spinning. In the course of this research, the physical-chemical properties of the bio-modified cellulose (including its solutions), were estimated. We studied the dependence of the mechanical properties of the obtained cellulosic fibres on the composition of the coagulation bath, and on process conditions such as spinning speed. Cellulosic fibres could be manufactured which were characterised by tenacity in the range of 17-19 cN/tex and an elongation of 12-13%.*

**Key words:** bio-modified cellulose, sodium hydroxide, cellulosic fibres, environment-friendly technologies.

## Introduction

For several years, investigations have been conducted in the Institute of Chemical Fibres aimed at developing new environment-friendly technologies to produce cellulosic fibres [1-5]. The processes elaborated here are based mainly on aqueous sodium hydroxide employed as a cellulose solvent. The production of cellulose fibres, which are usually manufactured by the hazardous viscose method, has been abandoned in Poland and drastically decreased in Europe as a whole, giving way to innovative ecological processes.

Amongst others, a method has been developed characterised by the use of bio-modified cellulose pulp. Such pulp is distinguished by its solubility in aqueous alkalis enabling further processing such as wet-spinning. The process was first investigated in cooperation between the Institute of Chemical Fibres and the Tampere University of Technology. It was afterwards further developed within the COST 628 project. Since March 2004 the process has been the objective of the "Biocelso!" European Project within the 5th Framework of the European Union. The process is designed to replace the viscose method, and may be implemented

in existing viscose plants without major capital investment.

The objective of the investigations made at the Institute of Chemical Fibres, presented in this paper, was to elaborate the process parameters of manufacturing cellulosic fibres from bio-modified pulp.

The research included the following aspects: estimation of the properties of the enzyme-processed cellulose pulp, preparation and quality assessment of spinning solutions prepared from the pulp, the impact of the coagulation bath's composition and spinning speed upon the mechanical properties of the fibres obtained.

## Materials and reagents

Cellulose pulp from spruce was used in the study. It is characterised by an polymerisation degree of  $\overline{DP} = 670$ .

A commercial enzymatic preparation produced by AB Enzymes Oy (Finland) under the trade name of Econase CE was used as the bio-modifying agent.

Alkaline cellulose solutions were made with the use of sodium hydroxide. Sulphuric acid was the base material for preparing the coagulation bath. Some preparations supplied by Akzo Nobel (Sweden) were also used to improve the filterability of the spinning solution, and as fibre spin-finish.

## Methodology

The dry cellulose pulp is first swollen for 2 hours in demineralised water at

ambient temperature, and disintegrated with an agitator at 1250 rpm. The surplus water is then squeezed out, and the pulp is fed to a Werner Pfleiderer tearing machine, where it is torn for 90 minutes at 35 °C. The wet pulp is then subjected to the bio-modification procedure. The mechanically pre-treated pulp is treated with Econase CE in a 0.05 M acetate buffer with a pH 4.8. The bio-modification process is described in more detail in the European Patent Application EP 122 80 98. The bio-modified cellulose pulp is separated from the enzyme liquor on a 'Nutsche' filter and washed with water.

To prepare the alkaline spinning solution, the bio-modified cellulose pulp containing 75% of water is put into a 10.2% aqueous solution of sodium hydroxide, which also contains zinc oxide, urea and surfactants. The bio-modified pulp is dissolved in a mixing tank equipped with a high-speed agitator and cooling jacket. The process is completed over 10 to 60 minutes at a temperature rising from 0 to 13 °C. The spinning solution obtained is filtered on a frame press through a standard filter cloth used in the viscose fibre industry, and then de-aerated.

The cellulose fibres are wet-spun on a large laboratory spinning line. The spinning solution is conveyed to the spinning bath by means of a 6.0 cm<sup>3</sup>/rev metering pump through a Pt-Rh spinneret with 300 holes of a single-hole diameter of 0.08 mm; or alternatively, 1000 holes of 0.06 mm in diameter.

A solution containing 60 to 120 g/dm<sup>3</sup> of sulphuric acid and 150 g/dm<sup>3</sup> of sodium sulphate serves as a coagulation bath, whose temperature is maintained

at the level of 15 °C. The spun fibres are stretched ( $R_{\max} = 30\%$ ) in water at 85 °C, rinsed with water at 40 °C, passed through a spin-finish solution containing 7 g/dm<sup>3</sup> of Berol Fintex, dried on cylinders at 85 to 90 °C, and finally tension-collected on spools as multifilament yarn. The applied spinning speed amounts to 20-50 m/min.

## Analytical methods

The enzyme preparations are analysed according to Good Laboratory Practice procedures (GLP), certificate No G-016 (SPR/BBP/8, SPR/BBP/9, SPR/BBP/10).

The content of reducing sugars is estimated by the colorimetric method SPR/BBP/15 [6, 7].

The content of  $\alpha$ -cellulose is measured according to standard [8], in which the cellulose pulp is dissolved in 17.5% sodium hydroxide.

The average polymerisation degree is estimated by the viscometric method at  $20 \pm 0.1^\circ\text{C}$  in an EWNN solution (ferro-tartaric complex). The measurements of viscosity are carried out in an Ubbelohde viscometer according to a method described elsewhere [9].

Water retention value (WRV) is estimated according to a method described in technical literature [10].

Mass loss in cellulose after the enzyme treatment is assessed by the gravimetric method.

A method described elsewhere [11] was applied to estimate the cellulose solubility in alkaline solutions.

The estimation of the viscosity of the alkaline cellulose solution measured by the falling ball viscometer consists in measuring the time in which a steel ball falls over a distance of 20 cm in a vertical glass cylinder filled with the solution at 2.2 and  $12.5 \pm 0.1^\circ\text{C}$ . The ball used has a mass of  $130 \pm 1$  mg and a diameter of 3.17 mm. The diameter of the cylinder is 30 mm.

A Brookfield type NP/3/4 viscometer was used in measuring the dynamic viscosity of the cellulose solution.

The cellulose content in the solution is found by weighing the regenerated cellulose after coagulation, washing and drying [12].

The measurement of the total alkalinity of the solution consists in neutralising it with excessive sulphuric acid, and next, by titrating the acid surplus with sodium hydroxide [13].

The clogging values  $K_w$  and  $K_w^*$  are estimated in the following manner: the cellulose solution is passed through a filter in two time sequences, the amount of the filtrate is weighed and the filter clogging constant is calculated, and then corrected on the basis of the simultaneously measured viscosity [14].

The images of the alkaline cellulose solutions were taken with the use of the Biolar optical microscope and an IMAL computer image analyser.

The amount of undissolved parts in the cellulose solution are estimated according to a method adopted in the IWCh which runs as follows: first, a solution of 50 g of cellulose in a 8% aqueous sodium hydroxide is prepared, to produce a solution with a polymer content within the range of 5.5-6.8% wt. Next, a 9% sodium hydroxide-chilled solution is added in the weight proportion of 1:1. 100 g of the diluted cellulose solution is centrifuged at 8000 rpm and 1 to 2 °C for 30 minutes, the sediment is washed four times with a 9% sodium hydroxide, and then centrifuged at 8000 rpm during 15 minutes. It is then neutralised with 10% aqueous acetic acid over 20 hours, washed with distilled water and dried at 105 °C to constant weight. The dry sediment is weighed, and the content of the insoluble parts of the cellulose is calculated from:

$$S = w \times 100 / a, [\%]$$

where:

$w$  – the mass of the dry sediment, g

**Table 1.** Some properties of the enzyme treated cellulose pulp.

Symbol of sample	Content of $\alpha$ -cellulose, %	Water retention value WRV, %	Average polymerisation degree DP <sub>v</sub>	Solubility of cellulose S <sub>a</sub> , %	Mass loss of cellulose, %
VP 27	94.5	89.0	380	99.4	4.70
VP 28	96.2	78.2	370	99.3	4.24
VP 29/1	94.1	82.1	380	99.6	5.46
VP 29/2	94.3	82.5	360	99.0	5.08

**Table 2.** Some properties of the enzyme treated cellulose pulp prepared in big lab scale.

Trial symbol	Content of $\alpha$ -cellulose, %	Water retention value WRV, %	Average polymerisation degree DP <sub>v</sub>	Solubility of cellulose S <sub>a</sub> , %	Mass loss of cellulose, %
VP 30/1	94.6	81.0	350	99.4	4.90

$a$  – the polymer content in 100 g of diluted cellulose solution before centrifugation, g

The mechanical properties of the cellulose fibres were tested in accordance with suitable standards [15, 16].

Cross-section and surface images of the fibres were taken with the use of the Quanta 200 scanning electron microscope made by FEI Co, USA.

## Results and discussion

### Research in the preparation of spinning solutions of the enzyme treated cellulose

Several bio-modified cellulose pulps were first prepared on laboratory scale, characterised by an average polymerisation degree DP<sub>v</sub> in the range of 360 to 380, and a solubility in aqueous NaOH (S<sub>a</sub>) of above 99%. The properties of the bio-modified cellulose are presented in Table 1.

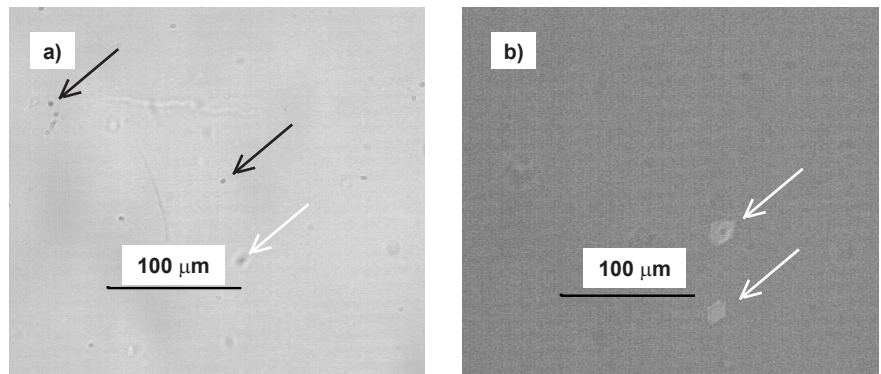
For further trials, more bio-modified cellulose was prepared in a reactor V=250 dm<sup>3</sup>. The quality of the pulp is presented in Table 2.

The properties of the bio-modified pulp, the composition of the solution (content of cellulose, NaOH, urea, zinc oxide) and the way in which the solution was prepared are factors that determine its quality.

Up-scaling to a larger laboratory scale required a change of equipment and some process parameters such as the agitator speed and the temperature of the cooling medium. After the first trials, it was found that the turbine agitator produces

too much heat, causing the solution to increase its temperature rapidly. In consequence, the dissolving time must be shortened to below 20 minutes. For the same reason, urea was added to improve the solution's stability at temperatures above zero. In consecutive trials, the temperature of the cooling medium was decreased by a few degrees, and additives were admixed to the solution (polyethylene glycol-PEG 400, Berol Visco) to improve its stability, filterability, and spinnability. The resulting spinning solutions manifested good properties; filtration, for example, proceeded smoothly at a pressure of about 0.25 MPa. Improvements in the construction of the mixing tank included a variable speed drive of the agitator, allowing precise control of the dissolving process. Such arrangements enabled the preparation of spinning solutions without the use of urea. The conditions under which the spinning solutions were prepared and their properties are compiled in Tables 3 and 4.

As can be seen in Table 4, the spinning solutions obtained are characterised by a cellulose content in the range of 5.5 - 6.0% wt, a total alkalinity of 7.64 -



**Figure 1.** Microscope images of enzyme treated cellulose in solution before filtration; a) CO – 89, b) CO –92 in polarized light (spinning solutions); In the photos, small objects of undissolved cellulose particles sized about 10 µm can be seen (white arrow), as well as tiny mechanical impurities (black arrow).

7.97% wt, low clogging values, and low content of the insoluble part. The spinning solutions presented in Table 4 were next used in spinning trials.

In Figure 1 microscope images of the alkaline cellulose solutions before filtration are presented.

#### Research in the spinning of CELSOL fibres and evaluation of their properties.

In this phase of the research, the effect of the spinning conditions, the composition

of the spinning bath, the type of spinneret used, the draw ratio and spinning speed upon the mechanical properties of the formed CELSOL fibres was investigated.

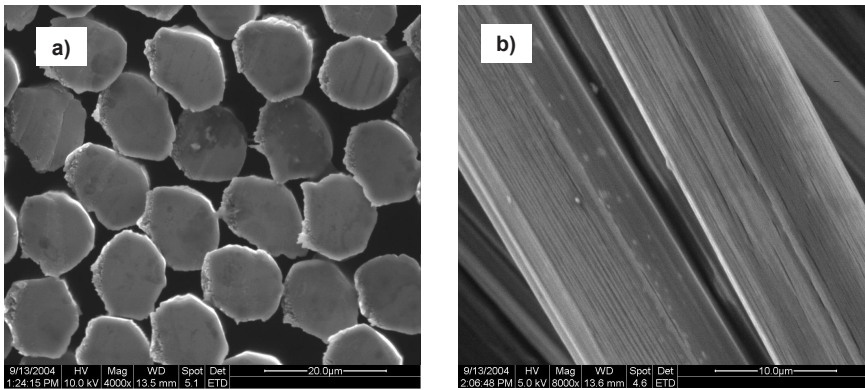
Attempts were first made to assess the usefulness of the solutions marked CO-56 through CO-66 (Table 4) for the spinning process, and to define the process parameters like godet's speed, the circulation of the spinning bath, the amount of additives applied and the temperature of drying cylinders.

**Table 3.** CELSOL spinning solutions – conditions of their preparation and properties .

Solution symbol	Cellulose symbol	Moisture of cellulose, %	Urea concentration in the solution, % wt	Type of additive	Concentr. of additive calculated on cellulose, %	Dissolving time, min	Final dissolving temperature, °C
CO - 56	VP 27	68.5	4.2	PEG 400	2.5	12	11
CO - 58			4.2	PEG 400	3.0	10	10
CO - 61	VP 28	66.6	4.2	PEG 400	3.0	11	8
CO - 66	VP 29/1	68.3	3.7	PEG 400	3.0	13	7
CO - 70	VP 29/2	66.2	4.2	PEG 400	3.0	14	8
CO - 72			0	PEG 400	3.0	18	4
CO - 75			0	PEG 400	3.0	19	4
CO - 84	VP 30/1	70.4	0	PEG 400	3.0	13	3
CO - 89			0	Berol Visco BV 31	3.0	60	1
CO - 92			0	Berol Visco BV 388	3.0	60	2

**Table 4.** Properties of CELSOL spinning solutions; • the insoluble part was estimated in the solution after filtration.

Solution symbol	Cellulose symbol	Cellulose content in solution, % wt	Total alkalinity, % wt	Alkali ratio	Viscosity measured by falling ball, s	Temp. of falling sphere viscosity measurement, °C	Dynamic viscosity after 24 h/temp, cP/ at °C	Kw	Kw*	Content of insoluble part in solution*, %
CO -56	VP 27	6.05	7.81	1.29	136.0	12.5	-	1487	86	-
CO - 58		5.79	7.64	1.32	73.2	11.4	7 550/18.0	3888	311	0.21
CO - 61	VP 28	5.68	7.97	1.40	120.6	10.0	10 250/15.5	5175	459	0.34 (0.24 <sup>a</sup> )
CO -66	VP 29/1	5.64	7.98	1.41	95.0	8.0	-	1752	157	0.21
CO - 70	VP 29/2	5.69	7.86	1.38	84.5	8.0	-	689	51	0.12
CO - 72		5.73	7.74	1.35	141.0	5.2	8 750/17.0	2386	175	1.09
CO - 75		5.68	7.79	1.37	88.5	6.0	-	1056	77	1.27
CO - 84	VP 30/1	5.79	7.72	1.33	69.5	5.0	8 400/10.0	858	80	0.44
CO - 89		6.07	7.84	1.29	110.0	2.2	13 750/10.0	-	-	-
CO - 92		5.87	7.92	1.35	71.0	4.0	8 000/9.5	-	-	• 0.41



**Figure 2.** SEM photos of cellulosic fibres – CO-89/1; a) cross-section, b) outer surface.

The fibres were spun from the solution marked CO-70 at a speed of 30m/min; the fibres were collected on spools. The mechanical properties of the fibres obtained are presented in Table 5.

Various spinning trials were made employing solutions with and without urea content. It appeared that the presence of the substance does not influence either the fibre-forming process or the mechanical properties of the fibres manufactured. Hence, urea was abandoned in all subsequent spinning trials.

The following investigations were made in relation to fibre forming :

- impact of the sulphuric acid concentration in the spinning bath on the properties of the fibres obtained. We investigated the concentration range of 60 to 120 g/dm<sup>3</sup> using the following solutions: CO-84/1 (60 g/dm<sup>3</sup>), CO-84/2 (80 g/dm<sup>3</sup>), CO-84/3 (100 g/dm<sup>3</sup>), CO-84/4 (120 g/dm<sup>3</sup>). The spinning speed was 30 m/min. In the trial with CO-84/3, the spinning had a smooth, uninterrupted run for 30 minutes, and the fibres obtained, spun

as nominal 2 dtex, revealed adequate mechanical properties.

- influence of the spinning speed in the range of 20 to 50 m/min on the fibres' properties. In these trials, the following solutions were used: CO-92/1 (20 m/min), CO-92/2 (30 m/min), CO-92/3 (40 m/min), CO-92/4 (50 m/min); the concentration of sulphuric acid in the spinning bath was set at 100 g/dm<sup>3</sup>. It could be concluded that in the range of the spinning speed amounting to 20-50 m/min, the fibres obtained were featured by similar properties: tenacity (conditioned) of 17.3 to 18.4 cN/tex and elongation at break of 10 to 14%, (see Table 5). However, it was observed that at the spinning speed of 50 m/min, the number of single filament breaks was noticeably higher than in case of the lower speeds.
- spinning of a yarn consisting of 300 single filaments at a speed of 30 m/min, and draw ratio of 1.30 (CO-89/1) and 1.35 (CO-89/2). The yarn obtained was characterised by a conditioned tenacity of 16.4 and 17.4 cN/tex, and an elongation at break of 12 and 11%, for the draw ratios of 1.30 and 1.35 respectively.

**Table 5.** Mechanical properties of cellulose fibres cellulosic.

Fibre symbol	Solution symbol	Linear density, dtex	Variation coefficient of linear density, %	Tenacity conditioned, cN/tex	Elongation at break conditioned, %
CO - 56A/1	CO - 56	3.17	1.72	15.1	22.3
CO - 56A/2		2.79	1.23	17.0	11.0
CO - 56/1		5.86	12.6	15.3	14.0
CO - 56/2		4.11	1.70	18.8	11.0
CO - 58	CO - 58	1.88	1.12	18.5	15.0
CO - 61	CO - 61	2.30	3.30	18.3	13.0
CO - 66	CO - 66	1.87	0.48	18.2	13.0
CO - 70/1	CO - 70	2.01	0.55	15.8	12.2
CO - 70/2		2.59	2.24	19.7	8.00
CO - 72/1	CO - 72	2.09	1.96	14.4	18.0
CO - 72/2		2.69	4.54	16.8	13.0
CO - 72/3		4.05	5.68	17.2	15.0
CO - 75/1	CO - 75	2.10	1.38	16.3	13.0
CO - 75/2		2.37	1.98	17.0	13.0
CO - 84/1	CO - 84	2.00	1.55	14.8	19.0
CO - 84/2		2.06	1.55	15.5	17.0
CO - 84/3		2.16	1.85	18.3	15.0
CO - 84/4		2.18	1.09	15.1	14.0
CO - 89/1	CO - 89	2.53	3.20	16.4	12.0
CO - 89/2		2.40	1.42	17.4	11.0
CO - 92/1	CO - 92	2.57	1.05	17.3	14.0
CO - 92/2		2.65	1.05	18.4	12.1
CO - 92/3		2.94	1.22	18.1	13.0
CO - 92/4		3.45	2.87	18.0	13.5

The results of the investigations are presented in Table 5.

The selected fibre samples were analysed by means of scanning electron microscopy. In Figure 2, images of the cross-section and outer surface of the cellulosic fibres are presented.

The cellulose fibres images presented in Figure 2 display an oval shape of the cross-section, while shallow wrinkles, differentiated in dimensions, can be seen on the outer fibre surface.

From the results presented in Table 5, it may be concluded that the concentration of sulphuric acid in the coagulation bath does not radically influence the fibres' conditioned tenacity. The highest value of the parameter appeared in fibres that were spun to a coagulation bath containing 100 g/dm<sup>3</sup> (fibre symbol CO 84/3). Within the range of 30-50 m/min, the spinning speed actually has no influence on the mechanical properties of the fibres obtained.

## Summary

The bio-modified cellulose prepared on a large laboratory scale is characterised by an average polymerisation degree of 350, and dissolves readily in aqueous sodium hydroxide with the dissolution degree  $S_a$  amounting to 99%. The material is suitable for the preparation of alkaline solutions containing up to 6.0% wt of cellulose at a total alkalinity of 7.9% wt. Such solutions are featured by a corrected clogging value ( $K_w^*$ ) below 200, and as low as 0.5% content of insoluble particles, which is a precondition for the forming of cellulose fibres. Spinning trials with the alkaline solutions of the bio-modified cellulose confirmed the possibility of preparing fibres with a tenacity in the range of 17 to 19 cN/tex, and an elongation in the range of 12 to 15%.



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