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Manufacture of Cellulose Fibres from Alkaline Solutions of Hydrothermally-Treated Cellulose Pulp

Abstract

The use of hydrothermally treated cellulose pulp for the manufacture of cellulose fibres is described. Hydrothermal treatment allows for the preparation of cellulose pulp characterised by a polymerisation degree, DP, within the range of 290 - 405 and a low polydispersity Pd of 2.0 - 3.0. A method of preparing alkaline solutions with a 7.45% content of cellulose, and alkali ratio of 1.05 is described. The impact of sulfuric acid concentration, the temperature of the coagulation bath, the as-spun draw of the fibre, the total draw ratio and drying conditions upon the mechanical properties of the fibres obtained was investigated. Trials at a high laboratory scale were conducted to spin multifilament cellulose fibres with a tenacity of 20 - 22.5 cN/tex and an elongation at break of 10 - 15%.

Key words: cellulose pulp, hydrothermal treatment, alkaline cellulose solutions, cellulose fibres.

Introduction

Several procedures were elaborated and proposed herein for the manufacture of cellulose fibres employing either cellulose derivatives or specific solvents that are capable of directly dissolving cellulose pulp [1 - 5]. Few of these methods have been developed to the stage of industrial technology which could be regarded as competitive to the well-established viscose route [6 - 8]. The method presented here for the preparation of cellulose fibres based on alkaline solutions of hydrothermally treated cellulose pulp may be regarded as an alternative to the viscose process. Extensive research on the modification of cellulose pulp by means of cellulolytic enzymes and consecutive hydrothermal treatment resulted in the preparation of a cellulose pulp that directly dissolves in alkalis, giving solutions from which fibres can be spun [9 - 13]. Hydrothermal treatment was originally applied in the utilisation and depolymerisation of biomass, mainly wood scrapes, waste paper and plant residues [14]. The method was also employed in the depolymerisation of other polysaccharides like starch and guar gum. The process, conducted at a pressure of 5 to 100 MPa and temperature of 140 to 300 °C in water with a content of carbon dioxide, produces monosaccharides like glucose or galactose [15]. When applied to the activation of lignin at a temperature of 653 - 673 °C under nitrogen atmospheric pressure, the method yields such products as catechol, phenol and o-cresol [16].

Hydrothermal activation of cellulose in water or methanol at 100 - 170 °C and

a relevant pressure yields a pulp which, when used in the viscose process, allows to substantially lower the consumption of CS₂. By improving the pulp's solubility, the method may also contribute to the effectiveness of the carbamate- and NMMO processes [17 - 20].

The hydrothermal modification of cellulose pulp is an environment-friendly process; it also is a technologically simple method consisting in the treatment of pulp with water at an elevated temperature. When carried out at appropriate conditions, it enables to lower the average polymerisation degree and polydispersity and to increase the solubility of the pulp in aqueous sodium hydroxide [21 - 25]. Alkaline solutions of the pulp reveal satisfactory stability and are suitable for the forming of fibres in a coagulation bath with a content of sulfuric acid and sodium sulfate.

The aim of the study was to define the impact of coagulation (fibre forming) and fibre drawing conditions upon the properties of the fibres prepared. The influence of the polymerisation degree of the modified cellulose pulp on the properties of the spinning solution was also investigated. The spinning process of the cellulose fibres was examined, including the impact of the concentration of sulfuric acid, the temperature of the coagulation bath, the spin extension and drying conditions on the mechanical properties of the fibres obtained. In the study the fibres prepared were assumed to have a tenacity of at least 20 cN/tex and an improved water absorption.

Materials used

A commercial cellulose pulp supplied by Buckeye Co, USA was used as the main material. It was characterised by a humidity of 7.8 % and an average polymerisation degree of 553. Chemical reagents were acquired from POCh Co., Gliwice, Poland.

Methodology

Preparation of the modified hydrothermal cellulose pulp

Cellulose pulp was heat-treated in an aqueous medium at a pH of 4.75 in the presence of activators to obtain a modified cellulose pulp entirely soluble in aqueous sodium hydroxide, according to the European Patent [14]. First a suspension of the starting cellulose in water was prepared by means of a high-speed agitator. The suspension was then put into a pressure reactor and heated up to 173 °C, which was maintained for 30 - 70 minutes. After that time the reactor content was quenched, washed with cold water and eventually pressed out to a water content of 70 %. The cellulose pulp thus prepared was used for the preparation of an alkaline solution.

Preparation of the alkaline pulp solution

Moist hydrothermally modified pulp at 2 °C and aqueous sodium hydroxide of 10.2% concentration containing urea and zinc oxide were used for the preparation of the alkaline cellulose solution. Urea prevents the formation of secondary bonds between the hydroxyl groups of the cellulose chain. The dissolving lasted 12 minutes, during which time the temperature rose from 2 °C to 12 °C. The solution was next filtered and deaerated with the temperature rising to 16 °C.

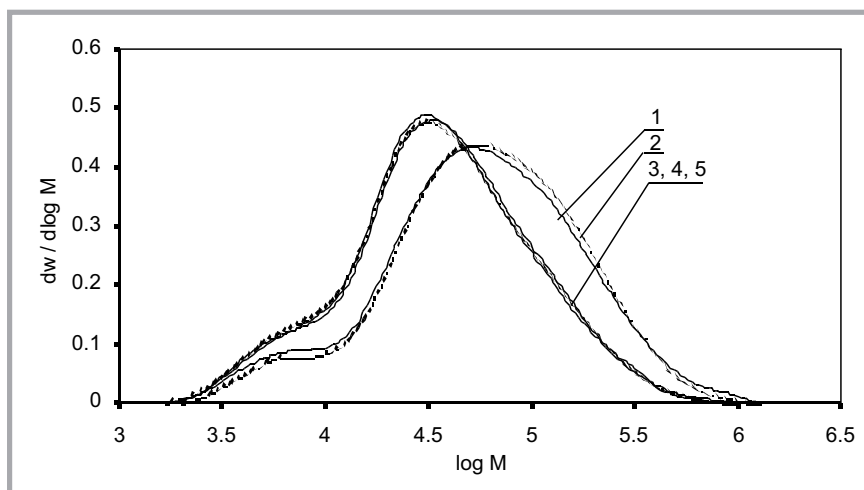


Figure 1. Function of the molecular weight distribution of cellulose pulp: unmodified (1, 2) and hydrothermally modified (3, 4, 5).

The solutions prepared were used for the forming of fibres.

Fibre spinning

Fibres were wet-spun from the prepared solution on a small pilot spinning line with the use of platinum-rhodium 1000 hole spinnerets, the diameter of the holes being 55, 60 & 80 µm. An aqueous solution of sulfuric acid with varied concentrations of 55, 65, 70, 90, 110 & 130 g/l, containing 150 g/l of sodium sulfate, was used as a coagulation bath. The impact of the coagulation bath temperature was investigated. The solidified filament cable was transported through a water bath at a temperature in the 50 to 90 °C range, in which it was 20 to 45% drawn. Next, the fibres were passed through a water washing bath at 50 °C and then through a spin finish bath. The fibre cable was dried on metal godets at 95 °C and taken up at a speed of 40 m/min. For reference purposes, the fibre was also collected directly from the washing bath as a loose bundle, which was dried at 60 °C.

Analytical methods

The average polymerisation degree of the pulp and fibres was estimated viscometrically in ethylene diamine cuprate (CED) according to ISO 5351/1:1981.

The content of cellulose in the solution was measured according to Standard ZN-70/MPCH-WS-81 using a coagulation bath with 130 g/l of sulfuric acid and 150 g/l of sodium sulfate.

A Brookfield LVT viscometer was used in measurements of the dynamic viscosity of the solutions.

The total alkalinity of the cellulose solutions was estimated according to Standard ZN-70/MPCH-WS-81 after neutralisation of the alkalis contained in the solution using an excessive amount of sulfuric acid and by estimation of the excess acid using NaOH titration.

The clogging coefficient Kw and corrected clogging coefficient Kw* of the alkaline cellulose solutions were traced by the method outlined in [15].

Tabela 1. Parameters to prepare and properties of the alkaline cellulose solutions; ZnO concentration of 0.8% in the solution.

DPv of the hydrothermally modified cellulose pulp	Cellulose content in the solution, %	Total alkalinity, %	Alkali ratio	Urea concentration, %	Coefficient of the clogging value before filtration		Pressure increase during filtration at 16 °C, MPa	Dynamic viscosity at a temp. of, mPas / °C	Viscosity of the solution during spinning at 20 °C, mPas
					Kw	Kw*			
370	6.01	7.53	1.25	4.2	1901	145	0.05	6150 / 12	7200
325	6.31	7.92	1.26	4.2	1182	92	0.03	5350 / 14	6800
285	6.49	7.97	1.23	4.2	1087	79	0.02	7450 / 11	7850
313	6.21	7.77	1.25	4.2	1272	107	0.03	4350 / 12	4350
339	6.27	7.89	1.26	3.0	1987	151	0.03	6250 / 12	7750
368	6.16	7.94	1.29	3.7	3661	272	0.05	6800 / 12	7350
388	5.48	8.09	1.48	4.2	5652	422	0.07	6650 / 12	7500
405	5.44	7.89	1.45	4.2	-	-	0.09	6150 / 13	7250
317	7.45	7.82	1.05	3.7	1861	177	0.04	7500 / 13	7850

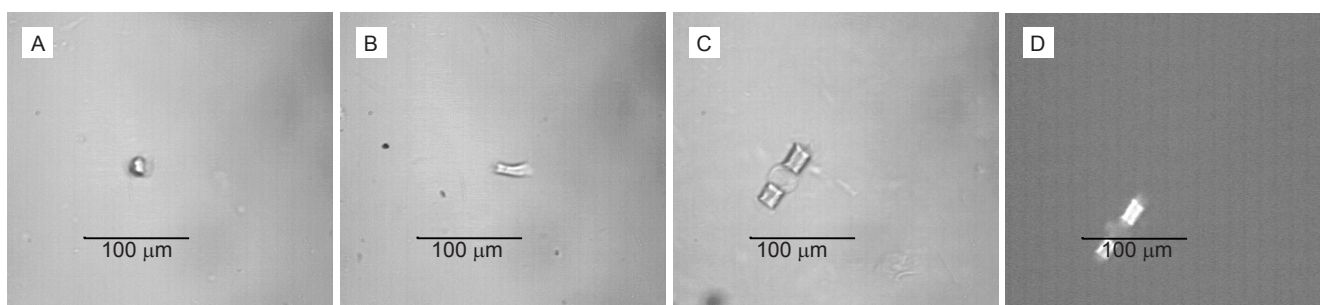


Figure 2. Microscopic images of a spinning solution (cellulose concentration - 7.45 wt%, total alkalinity - 7.82 %). A, B, C – in regular light, D – in polarized light.

The appearance of the cellulose solutions and the cross-sections of the fibres obtained were inspected under a Biolar polarizing microscope, made by ZPO Co, Warsaw, Poland, equipped with a digital analyser and image recorder. A JOEL electron scanning microscope was also used to inspect the cross-sections.

The water retention value WRV was found according to Standard ISO FDIS 23714.

The mechanical properties of the cellulose fibres were estimated according to PN-ISO-1973:1997,16 and PN-ISO-5073 :1999.

Results and discussion

Impact of the hydrothermally modified cellulose pulp and the composition of the solution on its properties

A modified cellulose pulp with a polymerisation degree in the 290 to 405 range

was prepared for the investigations. The function of the polymerisation degree distribution is presented in **Figure 1**. The shift of the curve towards lower molecular weights can be seen in the Figure as well as a narrowing of the curve and a higher peak, confirming the high quality of the modified cellulose pulp. Undoubtedly, the method ensures the preparation of pulps with assumed properties. As a result of earlier investigations undertaken by the authors, it is known that the modified cellulose pulp is soluble in aqueous sodium hydroxide [7, 9]. For the dissolution it is advisable to use modified cellulose pulp with a 60 to 70 % water content.

Urea and zinc oxide were added to the spinning solution to improve the dissolving process and stability of the solution obtained in the course of spinning. Solutions were prepared with a cellulose content in the range of 5.47 - 7.45 wt%. The conditions at which the solutions were prepared and the properties of the cellulose spinning solutions are shown

in **Table 1**. A reduction in the amount of admixed urea from 4.2 to 3.0% did not deteriorate the solution stability. The fact that solutions could be prepared at an alkali modulus (amount of alkalis in relation to the amount of pulp) within the range of 1.05 to 1.30 and with a viscosity at the level of 4350 to 7500 mPas is proof that the solutions are suitable for forming fibres (see **Table 1**). A distinct influence of the polymerization degree of the dissolved cellulose pulp on the filterability of the solution could be observed; the corrected clogging coefficient Kw^* in particular. The Kw^* value and the pressure during filtration go up if there is an increase in the polymerisation degree of the cellulose.

In the course of deaeration, which lasted 24 hours, the temperature rose up to 20 °C with an insignificant increase in viscosity. The increase in apparent dynamic viscosity at higher temperatures is evidence of progressive gelatinisation (ageing) caused by the formation of

Table 2. Mechanical properties of the cellulose fibres in dependence on: the concentration of sulfuric acid in the coagulation bath, temperature of coagulation bath, the as-spun draw, total drawing, the temperature of the coagulation bath, drying conditions; Na_2SO_4 – 150 g/l, speed of formation - 40 m/min, * - Distinctly deteriorated elongation conditions, maximal draw ratio 32%.

	Concentration of sulfuric acid in the coagulation bath, g/l					Temperature of coagulation bath, °C					As-spun draw ratio, %			Total drawing, %					Temperature of drawing bath, °C					Drying conditions of the fibre	
	130	110	90	70	55	18	15	14	13	12	-40,7	-20,9	11.6	45	40	35	30	20	90	75	70	60	50*	in loose bundle	under tension
Diameter of the spinneret openings, mm	1000/0.06										0.055	0.06	0.08	1000/0,06											
Concentration of sulfuric acid in the coagulation bath, g/l											H ₂ SO ₄ – 110 g/l,														
Temperature of coagulation bath, °C	15.0					15,0																			
Total drawing, %	40										40														
Temperature of drawing bath, °C	90										90											90			
Drying conditions of the fibre	under tension, at 100 °C																								
Fibre linear density, dtex	1.75	1.79	1.74	1.92	2.34	1.84	1.72	1.67	1.70	1.94	1.45	1.72	1.70	1.59	1.51	1.47	1.51	1.45	1.63	1.69	1.60	1.74	1.82	1.88	1.51
Tenacity, cN/tex	19.7	21.7	21.0	16.9	14.5	19.8	20.5	20.1	21.4	22.7	17.9	21.5	17.7	20.0	21.2	18.2	21.2	17.9	22.5	18.3	17.6	16.0	10.4	14.6	20.2
Variability coefficient of the breaking force, %	13.1	8.7	12.8	19.5	27.5	18.5	15.2	11.1	11.5	17.7	9.5	15.2	11.4	9.5	8.8	11.4	8.8	9.5	9.4	14.5	13.7	15.5	22.6	11.8	8.8
Elongation at break, %	12.9	10.2	10.2	15.3	18.8	12.3	10.4	12.8	11.1	8.2	13.8	10.4	11.3	10.5	12.0	12.5	12.0	13.8	10.5	12.2	12.6	12.9	11.8	18.4	12.0
Variability coefficient of the elongation, %	15.4	10.9	19.7	27.3	28.6	20.4	15.1	15.9	19.5	21.1	18.3	15.1	24.4	17.4	18.8	17.2	18.8	18.3	14.4	17.7	16.3	14.4	23.1	20.4	18.8

secondary bonds between the hydroxyl groups. Single fragments of swollen undissolved cellulose can also be seen in the microscopic images (*Figure 2*).

A hydrothermally modified cellulose pulp with DP = 317 was prepared for spinning fibres. Solutions of the pulp were prepared, characterised by the following: content of cellulose - 7.45%, urea - 3.7%, ZnO - 0.8%, total alkalinity - 7.82%, and dynamic viscosity during spinning – 7850 mPas.

Impact of spinning conditions upon the mechanical properties of the cellulose fibres

It could be observed that the sulfuric acid concentration in the spinning bath had a distinct influence on the fibre-forming process and mechanical properties of the fibres obtained (*Table 2*). A concentration of sulfuric acid below 70 g/l badly disturbed the spinning process, yielding fibres with inferior mechanical properties. The solidification of fibres is the result of a chemical reaction, which is governed by the concentration of hydrogen ions; an insufficient concentration results in incomplete coagulation and solidification. These processes are accompanied by the gelatinisation and desolvation of the gels formed, which is caused by the presence of sodium sulfate. The highest fibre tenacity values were attained with an acid concentration in the spinning bath within the range of 90 - 130 g/l. At subsequent stages of the research, a sulfuric acid concentration of 110 g/l was adopted.

The temperature range of 13.0 - 15.0 °C appeared advantageous for the coagulation bath. From the results presented in *Table 2*, it can be assumed that fibres formed in a coagulation bath at 15 °C have a tenacity of 20.5 cN/tex. Lowering the temperature to 12 °C resulted in the instability of the fibre forming process, mainly in the spinneret area with, however, a modest increase in fibre tenacity. On the other hand, fibres formed at 18 °C revealed a lower tenacity. Based on such results, a temperature of 15 °C was selected as the optimum at which the spinning process can be smoothly conducted, the fibres being acceptable in respect of mechanical properties.

The lower tenacity attained at a higher temperature e.g. 18 °C can be explained by the temperature dependent increase in the chemical reaction rate and the result-

Table 3. Average polymerisation degree and WRV of the cellulose fibres.

Average polymerisation degree		WRV, %	Moisture imbibition, %
Hydrothermally modified pulp	Cellulose fibres		
368	326	105	11.4

ing acceleration of fibre solidification (increased mobility of the molecules). Such conditions restrain the orientation of the macromolecules of the cellulose that proceed along the velocity gradient.

In the pursuit of a lower linear fibre mass, the diameter of the spinneret openings was varied in the range of 0.055 to 0.080 mm. Since the take-up speed was kept constant at 40 m/min, the changing linear mass resulted in a varied as-spun draw. The relation between fibre tenacity and the extension at the spinneret is shown in *Table 2*.

The highest tenacity was attained with a negative extension at the spinneret, equal to - 20.9%. Any increase in the spinneret extension resulted in an inferior fibre tenacity.

Influence of the total draw ratio and bath temperature on the mechanical properties of the fibre

The drawing process of the fibres was examined in a water bath at 90 °C. The maximum draw ratio that could be applied was 45% above that value the fibre bundle was prone to rupture. The fibre strength at a 45% draw ratio was slightly worse than that at 40% (see *Table 2*). There was no distinct difference in the mechanical properties of fibres drawn at ratios of 35% and 40%, which is why a draw ratio of 40% was adopted as the optimum in most of the trials.

The impact of the temperature of the drawing bath on the fibre's mechanical properties was investigated within the range of 50 - 90 °C (see *Table 2*). A draw ratio of 40 % was achieved within a temperature range of 70 to 90 °C of the spinning bath. Fibres with the highest tenacity, equal to 22.5 cN/tex and 10.5% of the elongation at break, were prepared when the drawing bath was at 90 °C. Below 60 °C the fibre tenacity was distinctly lower. For a drawing bath temperature of 50%, the draw ratio had to be lowered to 32% to prevent fibre rupture. A higher drawing bath temperature allows to apply a higher draw ratio- a factor that positive influences the mechanical properties of cellulose fibres. It was interesting to learn

that a higher temperature of the drawing bath contributes to increased fibre strength. This phenomenon calls for investigations into the crystalline structure, which is probably related to the change in crystallisation degree.

Impact of drying conditions upon the mechanical properties of the fibres

The mechanical properties of fibres dried in a loose bundle and under a strain were compared. Tension drying was carried out on godets heated up to 100 °C, while the loose bundle was dried at 60 °C. The tenacity of tension-dried fibres is 38% higher than that of loose bundle dried ones, but at a distinctly lower elongation at break, amounting to 12% (*Table 2*). The results distinguish tension drying as a favourable procedure, producing better mechanical properties. Tension drying contributes to preserving macromolecule orientation during the process.

Morphological and molecular investigations of the cellulose fibres

The cellulose fibres revealed an almost round cross-section without a distinctly developed brim. The 1.5 - 1.7 dtex fibres were 11 - 12 µm in diameter. The most regular shape of the cross-section was found in fibres which were formed in a coagulation bath with 110 g/l of sulfuric acid and 150 g/l of sodium sulfate at 90 °C. In other cases the cross-section was oval-shaped without a developed brim. A regular, round shape of the fibre cross-section is an asset when a fibre high strength is sought. It must be highlighted that the hydrothermally modified cellulose pulps used for the preparation of spinning solutions were characterised by a high polymerization degree and a high concentration of 7.45% in the solution, factors which largely contribute to the regular shape of the cross-section (*Figure 3*, see page 22).

In this study the change in polymerisation degree which occurs during dissolving and spinning was also investigated. Analysis results of the average polymerisation degree of cellulose in the pulp and fibres as well as the WRV values are presented in *Table 3*. It was found that the polymerisation degree dropped by 10%

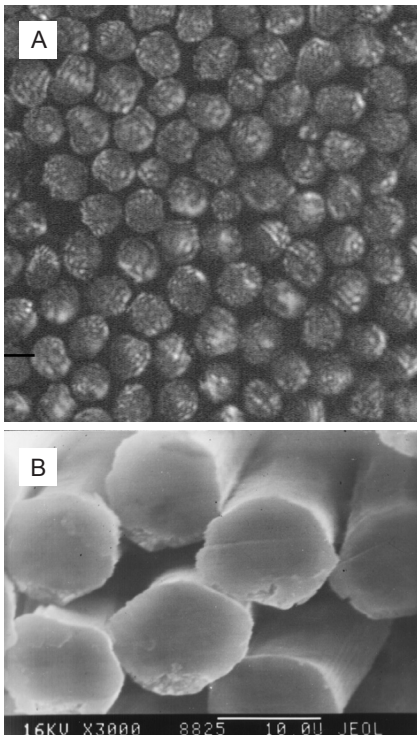


Figure 3. Cross-sections of fibres prepared from a hydrothermally modified pulp; A - optical microscopic images. B - SEM images.

during dissolving and spinning, providing evidence of the progressive degradation of cellulose. The cellulose fibres show a high WRV value, which opens the possibility of use in hygiene materials.

Summary

Hydrothermally modified cellulose pulp is a suitable starting material for the preparation of spinning solutions with a 7.45% cellulose content and an alkali ratio of 1.05. Cellulose fibres can be spun from such solutions at the follow-

ing recommended conditions: 110 g/l of sulfuric acid and 150 g/l of sodium sulfate in the coagulation bath at 15 °C; a negative as-spun draw of - 20.9%, a total draw ratio of 40% in the bath at 90 °C. The fibres obtained have a round cross-section without a developed brim and are characterised by a tenacity of 22.5 cN/tex and an elongation at break of 15%.

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