Dariusz Wawro,
Włodzimierz Stęplewski

Institute of Biopolymers and Chemical Fibres,
Łódź, Poland
contact: dariusz.wawro@ibwch.lodz.pl

Producing of Continuous Cellulose Fibres Modified with Plant Proteins

Abstract
Presented is a method of producing cellulose-protein fibres from modified cellulose dissolved in aqueous sodium hydroxide, as well as from isolates of rape- and sunflower-derived proteins. Fibres were spun from alkaline cellulose-protein solutions in a coagulation bath containing sulfuric acid and sodium sulfate. Mechanical and morphological properties of the protein-modified cellulose fibres are given. The fibres revealed a high water retention value (WRV) of up to 139 %. The concentration and kind of protein are the main factors influencing the stability of the spinning process and the mechanical properties of the resulting fibres. The morphology and structure of the fibres were investigated by means of the SEM and WAXS methods. Also presented are test results of microbiological activity against the Staphylococcus aureus bacterial strain.

Key words: *modified cellulose, cellulose solutions, plant proteins isolates, cellulose-protein fibres.*

Introduction

For many years attempts have been made to modify cellulose fibres with a variety of proteins. In one of the oldest methods, casein is either added in the course of viscose preparation or the viscose is blended with an alkaline solution of casein, followed by the forming of fibres in an acidic bath [1]. The purpose of the modification was to conform cellulose fibres to protein fibres, and to reduce production costs. Animal-derived proteins were mainly used, such as casein, keratin, collagen and fibroin (from silkworm cocoons); rarely plant proteins. Cellulose-fibroin fibres are spun from a spinning solution prepared by blending a viscose containing 9% of cellulose and 5% of NaOH with 10% of an aqueous fibroin. The addition of fibroin to cellulose fibres results in a decrease in their strength and increase in their linear mass [2]. Cellulose with fibroin can be dissolved in the cuproamine complex $Cu(NH_3)_4(OH)_2$ [3, 4] and NaOH [2]. Examinations of a cellulose/fibroin film prepared from the cuproamine complex showed that bonds are formed between active groups of the singular polymer molecules in the solution [3, 4]. The cellulose/fibroin film shows a higher moisture content and amount of amorphous regions in comparison to a pure cellulose product.

Compatible solutions of cellulose and fibroin can be obtained in N-methylmorpholine oxide (NMM0) [5]. Film cast from such a solution has good mechanical properties. Cellulose and fibroin also dissolve in the ionic liquid 1-buthyl-3-methylimidazolium chloride (BMIMCl) [6]. Film cast from a solution of cellulose with 20% of fibroin is amorphous and of lower strength [6].

The authors of this paper carried out research on the use of regenerated fibroin and keratin in the forming of cellulose fibres based on alkaline solutions of modified cellulose [7, 8].

Harvesting oil plants has increased remarkably in Poland and other European countries. With the growing demand for bio-fuels, countries are leaving behind substantial amounts of proteins as by products. These can be used not only as fodder but also as a material in technical applications. Considering that the composition of aminoacides (lysine, cysteine and methionine) in the proteins of rape and soy is similar, it may appear that the proteins of rape are suited to the modification of cellulose fibres [9]. Protein isolates contain a substantial amount of macroelements like calcium, magnesium and phosphorus, as well as microelements like iron, zinc and copper [10].

Fibres spun from alkaline cellulose-protein solutions are often presented as new types of cellulose fibres since they differ from typical cellulose varieties in their physical structure and other properties. Potential uses of the fibres are in apparel, filtration cloth and bacteriostatic sanitary products.

The objective of the present work was to evidence the suitability of protein isolates derived from rape and sunflower for the modification of cellulose fibres prepared from a modified cellulose directly dissolvable in aqueous alkalis. A further goal was to examine the impact of the kind and concentration of the protein in the spinning solution upon the mechanical, morphological and structural properties of the cellulose-protein fibres, as well as to determine the antibacterial action of the fibres against the *Staphylococcus aureus* bacterial strain.

Materials

The following materials were used in the research:

- Cellulose pulp modified at IBWCh according to the procedure described in EP 1317573, with an average molecular mass of DP_w=346, dissolvable in aqueous sodium hydroxide

- Protein isolates from the seeds of rape and sunflower prepared at the Institute of Technical Biochemistry of the Faculty of Biotechnology and Food Sciences of the Technical University, Łódź. The protein solutions contained 15% of protein and 5% of NaOH.
- Reagents made by POCh. S.A., Gliwice, Poland were used in the preparation of the solutions and coagulation baths as well as in the analyses.

Methodology

Preparation of the cellulose alkaline solution

A modified cellulose pulp with a 75% content of water was used in the preparation of the cellulose solutions. An aqueous sodium hydroxide solution with a concentration of 10.2% served as a solvent, in which zinc oxide was dissolved in an amount sufficient to attain the assumed zinc concentration in the solution of cellulose. The dissolution proceeded at 2°C – 12°C for 60 minutes. The zinc content, calculated as ZnO, in the spinning solution was 1.3%. The solution was next filtered and deaerated at a temperature of up to 16°C. The cellulose solution thus prepared was blended with an alkaline solution of protein which contained 15% of protein and 5% of NaOH. Cellulose-protein fibres were spun from the prepared blend at 20°C.

Forming of cellulose-protein fibres

Fibres were spun on an experimental wet spinning line equipped with a spinning head holding a platinum/ rhodium spinneret with 150 holes of 80 μm diameter. An aqueous solution of 17°C containing 110 g/l of sulfuric acid and 150 g/l of sodium sulfate constituted the coagulation bath. The tow of solidified fibres was led through a second trough with water at 85°C, in which a drawing rate of R = 30% was applied. Next the tow passed a third trough holding water at 40°C. Then the fibres were tension-dried in two drying sections, each equipped with two heated godets of 40°C on the surface. The fibres were taken up at a speed of 30 m/min.

Analytical methods

The cellulose content in the aqueous NaOH solution and the total alkalinity (sodium hydroxide and carbonate) were determined according to a description given elsewhere [11].

Table 1. *Properties of the alkaline cellulose-protein solutions.*

Symbol of solution	Kind of protein	Concentration of protein, wt%	Concentration of cellulose, wt%	Total alkalinity, wt%	Dynamic viscosity at temp. 10°C, mPas	Clogging value	
						K_w	K_w*
C-1	–	–	6.35	7.84	17250	1230	105
CP-1	Sun-flower	0.47	5.82	7.74	7600	1988	178
CP-2		0.89	5.56	7.71	7625	3326	296
CP-3		1.26	5.25	7.63	5600	4192	361
CP-4	Rape	0.53	5.15	7.16	6250	–	–
CP-5		0.76	5.15	7.66	5750	–	–
CP-6		1.26	5.56	7.53	4000	–	–

The method of measuring the clogging value K_w and corrected clogging value K_w* of the alkaline cellulose solution can be found in publication [12].

Images of the fibres cross-section and surface were taken by means of a scanning electron microscope – SEM/ESEM, Quanta 200 (W), FEI Co., USA.

The mechanical properties of the cellulose fibres were tested according to Standards PN-ISO-1973:1997 and PN-EN ISO 5075:1999 in an air-conditioned room at 65±4 % relative humidity and temperature of 20±2°C.

Samples of the fibres were mineralised with 70% HNO_3 in a microwave oven to determine the content of zinc, which was measured in the mineralised residue by flame atomic absorption spectrometry (FAAS) at a wave length of 213.9 nm.

The antibacterial activity of the fibres against *Staphylococcus aureus* ATTC 6538 was tested quantitatively according to Standard JIS L 1902:2002. The number of bacteria grown after a 24 hour incubation in the fibres sample tested was estimated, as well as in cotton as reference.

Spectrophotometric spectra in the infrared range were prepared with the use of FTIR apparatus of Unicam Co equipped with the control programme Winfirst ATI Mattson. Samples were prepared in the form of pressed cubes in potassium bromide (KBr Aldrich Co).The water retention value (WRV) was determined according to Standard ISO/FDIS 23714.

The rheology properties of the cellulose-protein solutions were measured by means of a digital viscometer – Brookfield model RV DV-II +, with the Rheocalc V3.1-1 programme, at a temperature of 20°C, 25°C & 30°C.

The fibres were subjected to wide- angle x-ray diffractometry examination – WAXS – by means of a URD-6 diffractometer (Seifert Co.) in the reflection mode. The diffraction curves prepared were divided into crystalline peaks and amorphous components. The degree of crystallisation was calculated by a modified version of the Hindelecha-Johnsona method [13,14]. The average size of the crystallites was calculated according to the Scherrer equation with the use of a WAXSFIT programme [15].

The Kiejdahl method was applied to determine the nitrogen content in the fibres.

The relative flammability of the fibres, expressed by the LOI index was tested according to standard PN-EN ISO 4589 – 2:2006.

Results and discussion

The miscibility of the alkaline solutions of cellulose and plant protein was utilised in the preparation of protein-modified cellulose fibres. Both solutions can be blended at ambient temperature in a defined range of weight proportion. Alkaline cellulose-protein solutions are stable at ambient temperature and suitable for spinning at conditions typical for the spinning of cellulose fibres. In the process described herein, an additional chemical treatment was not employed.

Impact of the kind and concentration of the protein in the cellulose solution upon its properties.

The cellulose content in the solution was in the range of 5.15-6.35%., while the total alkalinity was kept in the 7.16-7.84%. range. The apparent dynamic viscosity was measured at 10°C of the cellulose solutions. The corrected clogging value K_w* is an essential coefficient characterising the filterability of the solution and stability of the spinning process. Alkaline

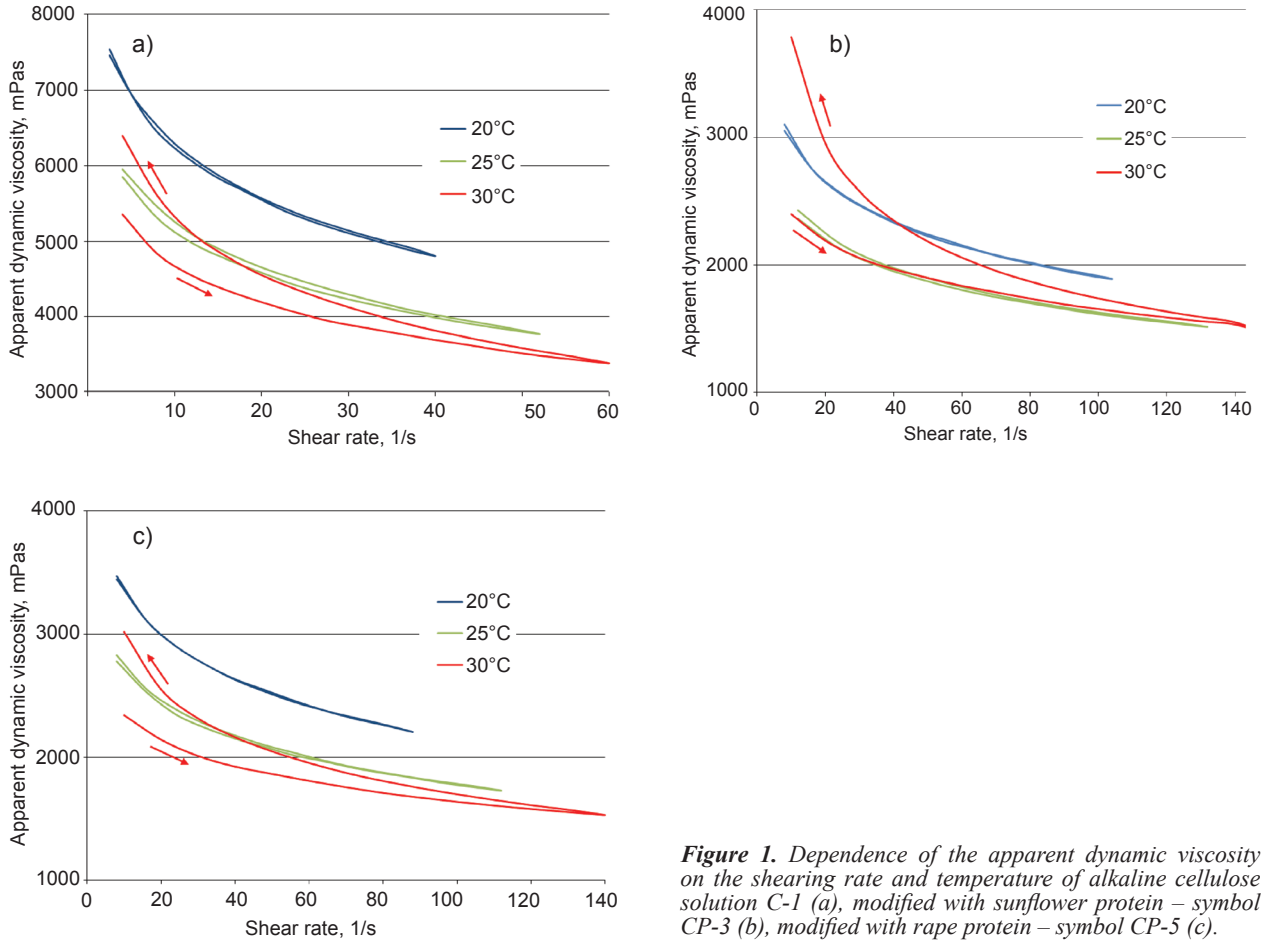

Figure 1. *Dependence of the apparent dynamic viscosity on the shearing rate and temperature of alkaline cellulose solution C-1 (a), modified with sunflower protein – symbol CP-3 (b), modified with rape protein – symbol CP-5 (c).*

solutions of cellulose show the most favourable corrected clogging value K_w*. Depending upon the amount of protein introduced, alkaline cellulose-protein solutions are characterised by a lower cellulose content, lower total alkalinity and lower apparent dynamic viscosity. Higher amounts of the protein introduced result in lower viscosity and an increased clogging value.

The main properties of the solutions from which cellulose-protein fibres were spun are shown in ***Table 1***.

Distinct differences in the amount of particles can be seen between the microscopic images of cellulose-, protein-and cellulose-protein solutions. The image of the cellulose solution reveals a few small particles with a size of up to 3µm (probably mechanical impurities), and a rhomb-like crystal. More numerous and larger are the particles in the colloidal protein solution. The particles of rape proteins are larger than those of sunflower. It seems that the particle size depends upon the kind of protein. Essential differences also appear in the images of the cellulose-protein solutions. In the solutions with rape protein, large protein agglomerates emerged in the course of blending. The solutions thus prepared were not filtered, hence fragments of protein may be expected to appear in the cross-section of fibres. In the solution with sunflower protein, uniformly distributed particles are visible. It may be concluded that the type of protein used has a definite influence on the quality of the alkaline cellulose-protein solution.

Examination of the rheology of the cellulose-protein solutions

The rheology of the solutions was examined at 20, 25 and 30°C to compare the properties of the solutions and to establish a temperature suitable for fibres spinning. ***Figure 1 a-c*** present the impact of the shearing rate and temperature upon the apparent dynamic viscosity of alkaline solutions without a protein content and of those modified with sunflower or rape protein. Flow curves were drawn for an increasing and decreasing shearing rate.

A non-newtonian chara cter of the alkaline solutions of modified cellulose may be concluded from the diagrams. Two basic groups can be discerned regardless of the kind of protein added. To the first group solutions may be qualified whose viscosity at 20 and 25°C decreases with increasing shearing rate and for which the run of the flow curves at increasing and decreasing shearing rate coincidence. Such cellulose solutions reveal pseudo-plastic fluid characteristics (thinned by shearing) typical for polymer solutions [16]. Increasing the solution temperature from 20 to 25°C causes a distinct decrease in the apparent dynamic viscosity. As regards the second group of cellulose solutions, examined at 30°C, they show a hysteresis in the flow curves for both the ups and downs of the shearing rate. The arrows in the figures indicate the direction of change in the shearing rate. The solutions reveal anti-thixotropic fluid characteristics, in which the apparent viscosity increases at a constant shearing rate after a particular time. The viscosity depends on the time of shearing, hence these solutions are unstable in respect of rheology.

The anti-thixotropic character at shearing is related to the building of a mo-

lecular structure. The phenomenon observed at 30°C in the flow curves of the alkaline cellulose solutions is probably connected to the initiation of gel formation. Hysteresis is particularly pronounced in the flow curve of the cellulose solution modified with sunflower protein (***Figure 1b***). With this protein, a temperature increase of the cellulose solution from 25 to 30°C does not result in a lowering of the apparent dynamic viscosity, which is not the case for rape protein-modified cellulose solutions or solutions without protein.

The spinning of fibres from alkaline solutions of protein-modified cellulose is accomplished at about 20°C, hence the stability of the solutions at that temperature, confirmed by rheology examination, is quite important considering the long lasting process of fibres formation.

Mechanical properties of the cellulose-protein fibres

Table 2 (see page 36) illustrates the impact of the protein concentration in a solution of cellulose on the mechanical properties of fibres and their nitrogen content. Comparison of the properties of cellulose fibres with those of the protein modified ones shows a higher linear mass of the latter in the range of 3.02-3.62 dtex, as well as lower tenacity, ranging from 11.2 to 15.4 cN/tex. The elongation at break amounts to 5.1-9.4 %, largely depending upon the amount of protein added and drying conditions. The increase in linear density aroused interest, suggesting that further investigation of the drawing process should be undertaken. Research on the formation of fibres from alkaline cellulose solutions documented that the reorientation of tension-dried fibres usually increases the arrangement of both crystalline and amorphous regions, causing a distinct increase in tenacity along with a lowered elongation at break. Presumably the lower tenacity of cellulose-protein fibres can be related to the macrostructure of the fibres and the inconsistency of the fibres interior, which may cause local inner tensions. Analysis of the fibres cross-section in ***Figure 2*** supports such an explanation. The image shows fragments of protein, the structure of the core layer and the developed brim of the fibres cross-section.

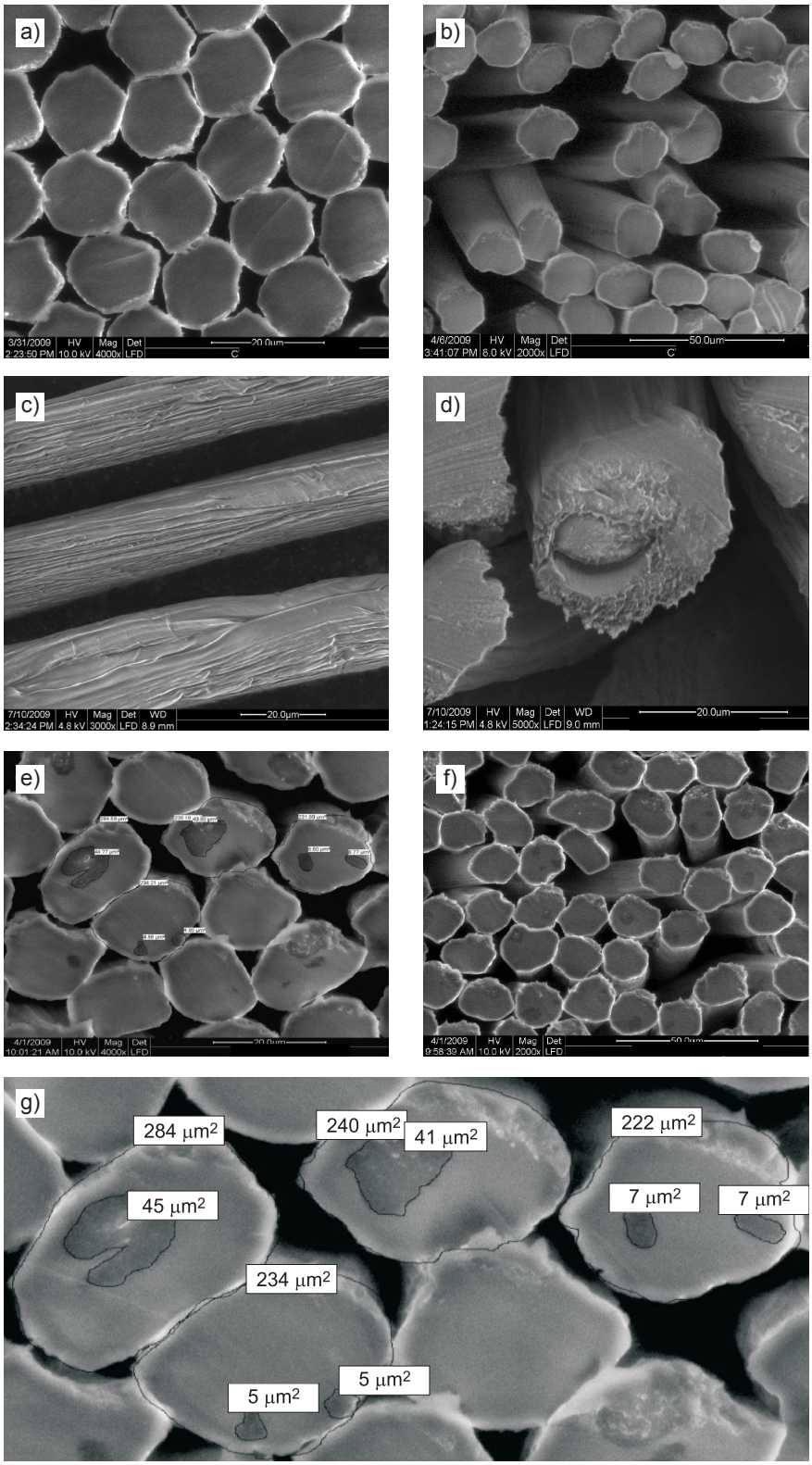

Figure 2. *SEM images of the surface and cross-section of cellulose fibres – (a, b), cellulose-protein fibres modified with rape protein – (c, d) and cellulose-protein fibres modified with sunflower protein – (e, f, g).*

Fibres prepared from cellulose solution show the highest tenacity, which corresponds well with the good stability of the solution and its low corrected clogging value K_w*. Fibres spun and dried under tension are characterised by an elongation at break of 9.2% and tenacity of 18.7 cN/tex.

Increasing the protein content in the spinning solution results in a higher nitrogen content in the fibres. The highest nitrogen content appears in fibres marked F CP-3 and F CP-6. The high nitrogen content could have been the reason for the dis-

Table 2. Impact of the protein concentration in the solution of cellulose on the mechanical properties of fibres and their nitrogen content.

Symbol of fibre	Kind of protein	Symbol of cellulose solution	Linear density, dtex	Tenacity, conditioned, cN/tex	Elongation at break, %	Nitrogen content, %
F C-1	–	RC-1	2.57	18.7	9.2	–
F CP-1	Sunflower	CP-1	3.06	15.4	9.4	0.4
F CP-2		CP-2	3.23	12.9	7.6	0.8
F CP-3		CP-3	3.36	11.2	5.1	1.4
F CP-4	Rape	CP-4	3.02	14.6	7.8	0,5
F CP-5		CP-5	3.30	13.1	6.5	0.8
F CP-6		CP-6	3.62	12.5	9.4	1.4

Table 3. Selected properties of the cellulose-protein fibres.

Symbol of fibres	Kind of protein	Nitrogen content, %	WRV, %	LOI, %	Zinc content, mg/kg
F C-1	–	–	116	17.8	8.2
F CP-1	Sunflower	0.4	123	–	–
F CP-2		0.8	134	18.4	116.3
F CP-3		1.4	139	18.4	217.8
F CP-4	Rape	0.5	–	–	–
F CP-5		0.8	127	–	–
F CP-6		1.4	133	19.3	184.2

tinctly lowered tenacity (11-15,4 cN/tex) and elongation.

Chemical and morphological structure of the cellulose-protein fibres.

It may be assumed that when the stream of cellulose and protein undergoes solidification, a difference appears in the diffusion speed of the solvent molecules and coagulating substance. In the course of solidification, the protein may be deposited on the cellulose matrix, leading to the forming of bonds between the polymers. It appeared from the spinning trials that the fibres formed are insufficiently solidified and prone to mechanical damage; for example, an excessive squeezing of wet fibres causes the removal of a part of the proteins in the pressed out bath, which may result in a reduction in the nitrogen content in the fibres of up to 15%. It is only the drying which completes the forming of the structure, conferring adequate mechanical strength upon the fibres. ***Figure 3*** presents the FTIR spectra of cellulose and cellulose-protein fibres.

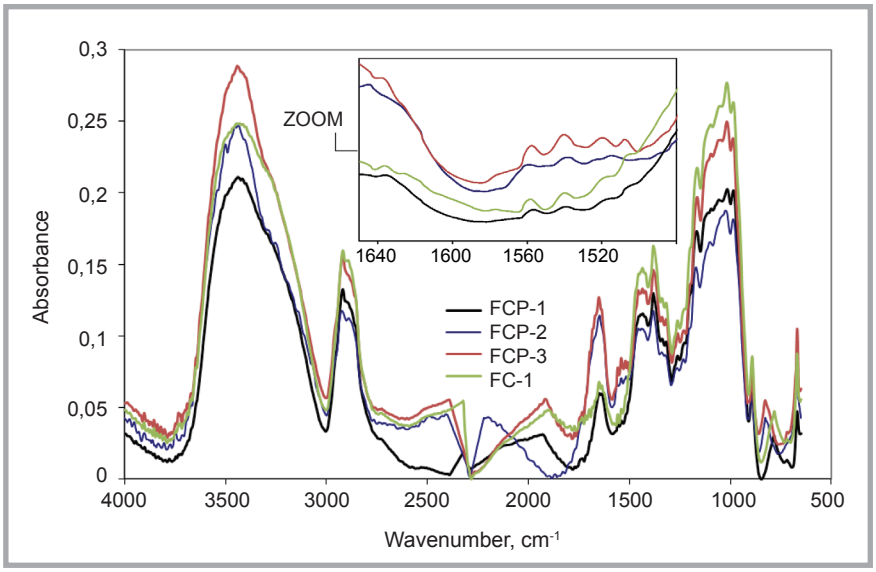

Figure 3. *FTIR spectra of cellulose and cellulose-protein fibres modified with sunflower protein, denoted as F CP-3 (N = 1,26%), F CP-2 (N = 0,89%), F CP-1 (N = 0,47%), and FC-1 (N = 0%).*

Analysis of the cellulose-protein fibres modified with sunflower protein reveals amide I bonds (oscillating extension vibrations C = O, 1600-1690 cm^{-1}) at a wave length of 1633-1644cm^{-1} that distinctly correlate with the nitrogen content in the fibres. Similarly, amide II bonds (extension vibrations CN = O and bending vibrations NH 1480-1575cm^{-1}) at a wave length of 1508-1517cm^{-1} correlate with the nitrogen content in the fibres [17].

The presence of amide I and II bonds in cellulose-protein fibres enables the formation of hydrogen bonds with water [18]. All this is confirmed by the increase in WRV, which depends upon the content of nitrogen in the fibres, and by the change in absorbance at wave lengths corresponding to inter and intra hydrogen bonds i.e. 2900 & 3450cm^{-1}.

Figures 2a and ***2b*** show SEM images of the surface and cross-section of cellulose fibres. The surface is smooth, without distinct recesses and flaws (***Fig. 2a*** magnification-2000x). The fibres have an oval cross-section (***Fig. 2a***, 4000x).

In ***Figure 2c*** the surface of cellulose-protein fibres modified with rape protein is shown at a magnification of 3000x. The picture reveals a distinctly developed brim with deep flaws and protruding oval protein agglomerates. The outer layer on the circumference of the fibres is about 1-2 μm thick. In the cross-section of the fibres (***Fig. 2d***), an irregular core is seen that has a fine granular structure with apparent protein inclusions. For comparison, a cross-section of fibres modified with sunflower protein is also presented (***Fig. 2e***, ***f***, ***g*** 2000x and 4000x), in which some irregular dark objects can be seen. A developed brim does not appear despite a comparable nitrogen content. There are, however, fragments of the protein confined in the fibres' interior. The cross-section surface of a single fibres amounts to 220 to 280 μm^2, while that of the protein fragments is in the range of 5 to 50 μm^2, comprising a significant part.

Fibres of different nitrogen content, from about 0.4 to 1.4 %, were examined. A relation could be detected between the nitrogen content and zinc content in the fibres (***Table 3***), amounting to 217.8 mg/kg, which is evidence of zinc bonding in the course of fibres formation (zinc ap-

pears in the cellulose-protein solution), which may influence the building of the fibres structure.

Assuming that the nitrogen content in the protein is equal to 6.25%, the cellulose fibres marked F CP-3 contain 8.75% of protein. The limiting oxygen index – LOI – of the cellulose -nitrogen fibres did not increase markedly, while the WRV increased by about 20% for fibres with a higher nitrogen content. The increase in zinc content in the fibres is closely related to the nitrogen content. In conclusion, the content WRV and zinc increases with an increase in the nitrogen content.

Examination of the cellulose-protein fibres by wide angle x-ray diffractometry – WAXS

Fibres with a varying nitrogen content modified with isolates of sunflower protein (F CP-1, F CP-2, F CP-3) and with isolates of rape protein (F CP-6) were chosen for WAXS investigation. Results are presented in ***Table 4.***

It can be concluded from ***Table 4*** that the addition of sunflower protein has a distinct impact on the content of the crystalline phase of the fibres. It is, however, difficult to univocally define the relationship between the protein content and the crystallinity degree of the samples marked F CP-1, F CP-2 i F CP-3, since the lowest addition of the protein (Sample F CP-1) increased the crystallinity by about 8%, whereas the highest amount of protein (F CP-3) decreased the crystallinity by 6%, compared with unmodified fibres. Such results may suggest that a concentration of the modifying protein exists which does not cause any change in the crystalline content in the cellulose fibres matrix.

Modification of cellulose fibres with rape protein (F CP-6) distinctly reduces the crystallinity degree.

The average dimensions of crystallites perpendicular to the plane point to physical changes in the fibres structure under the influence of any of the additives. Defining the character and reason for the changes occurring is rather difficult because information concerning the protein isolates used is too scant.

Figure 4 and ***5*** present WAXS roentgenograms of the cellulose-protein fibres analysed.

Table 4. *Results of the diffraction investigation – WAXS – of the cellulose-protein fibres.*

Symbol of fibres	Kind of protein isolate	Nitrogen kontent, %	Degree of crystallinity, %	Dimensions of crystallites L_{hkl}, A		
				101	10(-1)	002
F C-1*)	–	–	39.0	36.8	40.5	38.6
F CP-1	Sunflower	0.4	46.7	25.9	43.9	44.2
F CP-2		0.8	41.3	32.4	41.9	41.3
F CP-3		1.4	37.5	36.2	44.7	43.9
F CP-6	Rape	1.4	33.2	32.5	38.7	47.4

*) – *cellulose fibres*

Table 5. *Antibacterial activity of cellulose-protein fibres against Staphylococcus aureus.*

Symbol of sample	Zinc content, mg/kg	Time, h	Amount of bacteria, U/sample	Activity	
				bacteriostatic	bakterycidal
F C-1	8.19	0	6.1×10^4	–	–
		24	1.6×10^7	–	–
F CP-2	116.3	24	1.15×10^7	-0.2	-2.6
F CP-3	217.8		2.88×10^2	1.4	-1.0

Bioactivity of the cellulose-protein fibres

The cellulose-protein fibres were tested in respect of antibacterial activity against the *Staphylococcus aureus* bacterial strain, the results of which are given in ***Table 5***. Fibres with the highest protein content appear to be bacteriostatic against the aforementioned strain. The effect augments with an increasing content of zinc in the fibres (F CP-3). Fibres spun by coagulating in an acidic bath with a low content of zinc (8,19 mg/kg) are neither bactericidal nor bacteriostatic.

The preliminary testing of their bioactivity suggest that the cellulose-protein fibres may be applied due to their content of zinc, for the manufacture of bioactive sanitary and medical materials.

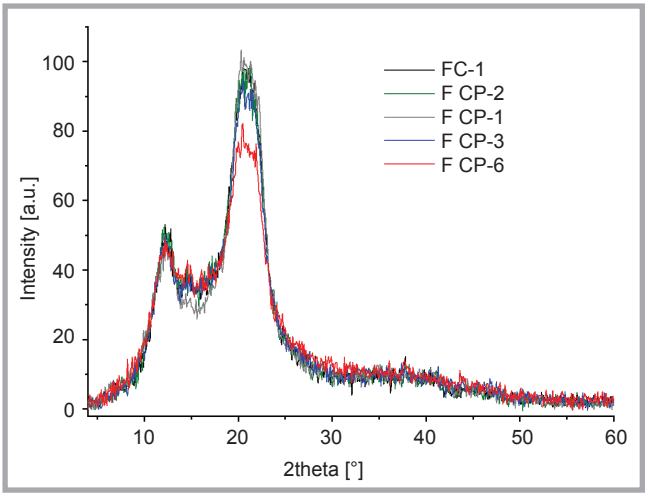

Figure 4. *Comparison of WAXS curves of the cellulose-protein fibres.*

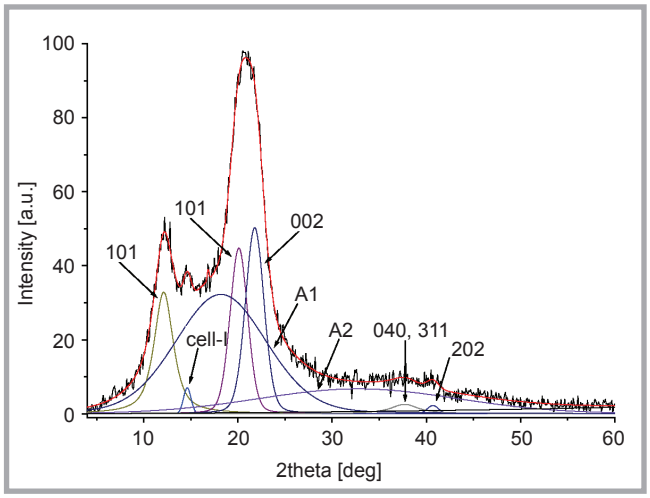

Figure 5. *WAXS curves registered for cellulose fibres F C-1 with development to crystalline peaks (Miller coefficients are marked) and amorphous components (A1 and A2).*

Conclusions

1. The method of wet-forming cellulose-protein fibres from an alkaline cellulose solution modified with isolates of plant proteins developed herein enabled the preparation of a new type of cellulose fibres characterised by a specific physical and chemical structure.

2. The essential impact of the presence of protein in the spinning solution on the sorption properties of the fibres obtained was documented**.**

3. Stable alkaline cellulose solutions with a protein content in the range of 0,47-1,26% pave the way for the preparation of cellulose-protein fibres with an improved WRV of up to 139 %, a tenacity of up to 15.4 cN/tex and an elongation at break in the range of 5.1-9.4%. The fibres have a rather low limiting oxygen index – LOI – in the range of 18.4-19.3%.

4. Cellulose-protein fibres modified with rape protein of 1.4 % nitrogen content are characterised by a fibre cross- section with a developed brim and high content of large agglomerates of the protein.

5. Cellulose-protein fibres modified with sunflower protein of 1.4 % nitrogen content and 217.8 mg/kg zinc content reveal bacteriostatic activity against *Staphylococcus aureus* bacteria.

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