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Novel Method of Preparing Flame Retardant Cellulose-Silicate Fibres

Abstract

Presented herein are the results of research on the preparation of a novel environment-friendly method of spinning cellulose-silicate (Cel/Si) fibres obtained from enzymatically modified a pulp which could be directly dissolved in aqueous sodium hydroxide. Fibres were formed from spinning solutions in a coagulation bath containing sodium silicate and sodium sulphate. For selected spinning conditions, test results are shown for the physical-mechanical properties of the Cel/Si fibres obtained and their relative flammability represented by the limiting oxygen index (LOI). Cel/Si fibres are characterised by a favourable LOI value reaching as high as 46.5%. The impact of zinc concentration in the spinning solution is shown, which largely contributes to the stability of the spinning process as well as to the mechanical properties of the fibre and the LOI value. The surface and cross-section of the Cel/Si fibres were inspected by scanning electron microscopy (SEM), including those subjected to high temperatures and a naked flame. It was found that the fibres reveal a skin/core structure in which zinc silicates are the main constituent of the skin, while cellulose forms the core. Also presented are test results of Cel/Si fibre washing durability. Proof is also given of the excellent antibacterial properties of the fibre against the Staphylococus aureus strain.

Key words: *silicate, wet spinning, fire retardant, cellulose fibres.*

Introduction

The feature of flame retardation can be conferred upon fibres in two ways: either by impregnating products like fibres or in the course of fibre forming by the admixing of flame retardant agents into the spinning solution. From impregnation methods of cellulose materials reported that are capable of providing genuine washing resistance, barely two: Proban® [1, 2] and Pyrovatex® [3] have found wide commercial application. In Proban® technology, cellulose fibres are drenched with a preparation containing phosphonium salt $[(CH_2OH)_4P]Cl$ (THPC) and urea. A complex compound is formed in the fibre, which must be fixed by drying and processing with gaseous ammonia. The danger of substantial formaldehyde emission both in the course of drenching and during the utilisation of the products is a big disadvantage of the Pyrovatex® method [4]. Also reported is a method for the impregnation of cellulose materials with compounds that poses no risk of formaldehyde emissions, in which the impregnation mixture contains an organo-phosphorus ester with hydroxy-alkyl groups and polycarboxylic acid as a cross-linking agent [5].

Most of the flame retardant agents reported are based on organophosphates. Agents suitable for cellulose fibres can be introduced to the viscose in the form of an emulsion or solution [6, 7]. In one of the methods, aqueous dispersion of the organo-phosphorus additive Sandoflam 5060 is introduced to the viscose [8]. The organo-phosphorus compound may be introduced to the viscose along with some other additives like the bromine-containing antipyrene tetrabromobisphenol A, sodium silicate or their mixtures [9]. Viscose fibres made that way represent an oxygen index (LOI) in the 28 - 30% range, while standard viscose fibres reveal 18%.

The Finnish company Säteri have launched new technology for producing flame retardant viscose fibres called VIS-IL®. The process, based on silicon and aluminium compounds [10,11], employs a blend of viscose and sodium silicate, as well as an acidic coagulation bath which regenerates the cellulose and precipitates the contained sodium silicate in the form of polysilicic acid. The fibres obtained are additionally modified with aluminium compounds, primarily sodium aluminate, to form a cross-linked aluminium silicate structure upon the fibre surface. A complementary fixation may also be accomplished in aqueous polyaluminium chloride [12] or in a magnesium compounds-containing bath [13]. VISIL® fibres have a LOI in the range of 28- 32%, which drops only insignificantly after 20-fold washing [14]. Using the viscose method in the manufacture of cellulose fibres has been curtailed or stopped in many countries due to environmental problems. Alternative technologies have been created in which the solubility of cellulose in alkalis required is achieved by the enzymatic or hydrothermal treatment of cellulose pulp [15 - 19].

The authors herein elaborated a novel method of preparing flame retardant cellulose fibres from enzymatically-modified cellulose dissolved in aqueous sodium hydroxide containing zinc compounds. Fibres are spun from the solution by coagulation in an alkaline spinning bath containing silicon compounds [20]. Compared to known methods of preparing flame retardant fibres, the process presented herein is more advantageous due to the absence of hazardous emissions, and greatly reduced amount of salts as by-products. Besides, the process is simple, and easy to operate. The enzymatic modification of pulp and addition of zinc oxide to the aqueous sodium hydroxide provide the cellulose in alkalis with good solubility [21]. Potential uses of Cel/Si fibres are in fire-resistant upholstery for public buildings, in the furniture industry, in protective clothing, in insulation and filter materials, and as bioactive fibres in sanitary and medical devices.

Compared to known technologies for the spinning of fibres from alkaline solutions of cellulose or its derivatives, in the new process presented sulphuric acid in the coagulation bath is replaced by a distinctly alkaline solution of sodium silicate. One of the main reasons why the spinning solution streaming from the spinneret coagulates is the reaction between the sodium silicate and zincate anion contained in the spinning solution.

The reaction produces an insoluble layer of zinc silicates which settles on the fibre surface. The silicates play a double role: as the main constituent of the coagulation bath and fire–retardant agent. The method offers the preparation of fire retardant Cel/Si fibres of the skin/core type in which the skin is mainly built up of inorganic silicates, with cellulose forming the core.

Investigating the impact of zinc concentration in the spinning solution upon mechanical and thermal barrier properties of the Cel/Si fibres obtained, as well as their fire retardancy by LOI measurement, were amongst the objectives of the research. Moreover, the influence of washing detergents and the environment's pH on the fire retardancy of the fibres was studied, and preliminary tests of the fibres' bioactivity were carried out.

■ Materials

Commercial cellulose pulp supplied by Buckeye Co, USA was used in the investigation, which was characterised by an average polymerisation degree of $\overline{DP}_w$ = 666 determined by gel chromatography (GPC). Sodium silicate (water glass) marked R140 by Rudniki Co, Częstochowa, Poland was employed in the preparation of the coagulation bath, characterised by the following: a total content of $SiO_2 + Na_2O$ = 39%, molar ratio $SiO_2 : Na_2O$ = 3.1, density at 20 °C = 1.41 g/cm^3, and a content of insoluble substance in H_2O = 0.02%. All other reagents were supplied by POCh Co, Gliwice Poland.

■ Methodology

Preparation of the enzymatically modified cellulose pulp

The cellulose pulp was first swollen in demi water at ambient temperature and defibrillated in a tearing machine. Then the wet pulp was bio-modified by means of enzyme marked Ecostone L 300 by AB Enzymes Oy, Finland in an acetate buffer at pH 4.8 and 50°C. A detailed description of the process can be found in the patent [16]. After the modification, water was removed from the pulp by filtration, the pulp was then washed with hot water to deactivate the enzyme, and finally rinsed with demi water. The pulp obtained (with $\overline{DP}_w$= 385 (GPC)) was used directly in the preparation of the alkaline spinning solution.

Preparation of the alkaline cellulose solution

The enzyme-modified cellulose pulp with a 75% water content was used in the preparation of the alkaline spinning solution. 10.2% aqueous sodium hydroxide was used as a solvent, which contained zinc oxide in an amount sufficient to provide the assumed ultimate concentration in the cellulose solution. During 60 minutes of the dissolving process, the temperature of the cellulose solution rose from 2 °C to 12 °C. The zinc content in the spinning solution, determined as ZnO, was varied in the individual trials within the range of 1.3 to 2.2%. The solution was next filtered and de-aerated while its temperature was rose to 16 °C.

Fibres spinning

From the solution prepared as above, Cel/Si fibres were formed on a wet-spinning line equipped with a spinning head holding a platinum/rhodium spinneret with 1000 openings (diameter of a single opening - 60 µm).

An aqueous solution of 17.5% sodium silicate ($SiO_2 + Na_2O$) and 7.9% sodium sulfate at 19 °C served as a coagulation bath. The solidified fibre tow was directed to a second bath with water at 85 °C, where it was drawn by 65%, and then to a third bath with water at 40 °C. Afterwards, the fibres were dried under tension in two consecutive sections, each consisting of a heated godet duo with a surface temperature of 60 °C. The fibre tow was collected in the form of continuous filaments at a final speed of 11.8 m/min. Alternatively, the fibre was collected after the washing bath and dried in loose bundles at 40 °C.

Analytical methods

The average molecular weight of the cellulose was determined by gel chromatography (GPC) [22 - 24] using Hewlett Packard HP 1050 apparatus equipped with a refractometric detector of the type RI HP 1047A and a set of columns with a hydrophilic rigid filling based on polymeric gel.

The method of determining the cellulose content in aqueous NaOH and the total alkalinity can be found elsewhere [18].

The clogging index K_w is a measure of the solution quality based on the declining filtrate output during filtration of the solution. In contrast to the K_w, the cor-

rected clogging index K_w* also takes into account the falling ball viscosity of the polymer solution and the air permeability of the filtering material. Measurements of both indices were made according to a description found elsewhere [25].

Images of the cross-section and fibre surface were made by means of a SEM/ESEM Quanta 200 (W) scanning electron microscope, Fei Co., USA.

The relative flammability of the fibre, expressed by the limiting oxygen index (LOI), was tested according to Standard PN-EN ISO 4589-2:2006.

The mechanical properties of the fibres were tested according to Standards PN-ISO-1973:1997 and PN-EN ISO 5075:1999.

To estimate the zinc content, fibre samples were mineralised with 70% HNO_3 in a microwave oven. The zinc content in the mineralised material was estimated directly by flame absorption atomic spectrometry (FAAS) at a wavelength of 213.9 nm. The sodium content in the fibres was estimated by atomic emission spectrometry (AES) at a wavelength of 589.0 nm.

Fourier-transform infrared spectra were performed with the use of a FTIR spectrometer from Unicam, controlled by Winfirst ATI Mattson software. The spectra were recorded within a wavelength number of 4000-650 cm^{-1}.

The antibacterial activity of the Cel/Si fibres against the *Staphylococcus aureus* ATTC 6538 strain was examined in a quantitative test according to Standard JIS L 1902:2002. The amount of live bacterial growth after 24 hours of incubation was estimated in the Cel/Si fibre sample and in a standard reference medium (cotton). The antifungal activity against the *Aspergillus niger* ATCC 6257 strain was estimated in a qualitative diffusion test on agar according to Standard SN 195921:1994. The samples were sterilised with overheated steam at 121 °C for 15 minutes.

For the testing of washing durability, washing was done according to Standard PN-EN ISO 6330:2002 with the use of Persil washing powder. The ratio of washing powder to water in the washing bath was 16 cm^3 per 1dm^3, and the washing temperature was 40 °C.

Table 1. *Properties of alkaline cellulose solutions.*

Symbol of solution	Cellulose content in solution, % wt.	Zinc conc. (as ZnO) in solution, % wt.	Total alkalinity, % wt.	Dynamic viscosity at 10 °C, mPas	Clogging index	
					K_w	K_w^*
C-1	6.11	1.3	7.76	15750	1147	101
C-2	6.15	1.5	7.78	15500	679	61
C-3	6.17	1.7	7.63	13500	586	53
C-4	6.12	1.9	7.78	12800	1827	157
C-5	6.15	2.2	7.83	11750	1413	122

Table 2. *Impact of zinc concentration in the spinning solution upon mechanical properties, LOI value and ash content (800 °C) of the Cel/Si fibres;* [1]- *fibres formed in an acidic bath containing 8,6% H_2SO_4, 12,9% Na_2SO_4, without fire retardants.* [2]- *fibres dried in loose condition.* [3]- *fibres formed in a bath not containing sodium sulfate: concentration of sodium silicate in the bath - 17.5%.*

Symbol of fibre	Symbol of cellulose solution	Titre, dtex	Tenacity conditioned, cN/tex	Elongation at break, %	LOI, %	Ash content, %
FC[1]	C-1	2.51	17.8	16.5	17.9	0.30
FC-1	C-1	6.57	9.1	15.2	30.1	23.8
FC-2	C-2	4.96	10.7	14.3	32.9	27.5
FC-2a[2]	C-2	5.88	10.3	42.0	34.5	31.9
FC-3	C-3	3.92	12.3	11.8	38.0	33.1
FC-3b[3]	C-3	4.93	8.9	9.5	36.2	32.9
FC-4	C-4	4.79	11.1	13.4	41.7	34.6
FC-5	C-5	5.46	10.8	16.1	43.4	35.8
FC-5a[2]	C-5	6.35	8.7	34.8	46.5	37.9

Results of the investigation and discussions

In the process according to which VIS-IL® fibres are made [10], the fibres are additionally modified in a separate operation by aluminum compounds due to the polysilicic acid showing insufficient resistance to aqueous solutions of washing detergents. In contrast, the process presented herein does not require such additional finishing.

Impact of the zinc concentration in the cellulose solution upon the mechanical and flame resistant properties of the Cel/Si fibres

Table 1 presents the main properties of the cellulose alkaline solutions from which the Cel/Si fibres were formed by coagulation in a sodium silicate-containing bath. Cellulose concentration in the solution was 6.11 to 6.17%, while the total alkalinity was kept within the 7.63 to 7.83% range. The temperature of the cellulose spinning solution was 18 °C in the course of spinning. The corrected clogging index K_w^* is an important technological factor indicating the filterability of the spinning solution and, consequently, the stability of the spinning process. The solutions marked C-2 and C-3, with a zinc concentration (as ZnO) of 1.5 and 1.7%, respectively, show the most favourable K_w^* values. An increase in zinc concentration in the solution improves, to a certain extent, the cellulose solubility, as witnessed by the dropping dynamic viscosity (from 15750 to 11750 mPa·s). Above a zinc (as ZnO) concentration of 1.7%, microscope inspection reveals in such solutions (C-4, C-5) a substantial amount of precipitated crystals of zinc compounds, causing an increase in the K_w^* index and, in consequence, disturbing coagulation in the area around the spinneret.

Amongst all the spinning solutions stored for 30 days at 20 °C, the solution marked C-3 manifested the best stability of dynamic viscosity without symptoms of undesired sedimentation.

The impact of the zinc concentration in the spinning solution on the LOI value of Cel/Si fibres, as well as their mechanical properties and ash content (after heating at 800 °C) are presented in *Table 2*. Compared with standard cellulose fibres, Cel/Si ones are characterised by higher titre values, in the range 3.92 - 6.57 dtex, and lower tenacity, falling within the 8.7 - 12.3 cN/tex range. Their elongation at break varies in the range of 9.5 to 42.0%, largely depending upon drying conditions. When dried in a loose bundle, the fibres manifest a 2 to 3-fold higher elongation than fibres which were tension-dried on heated godets. The dif-

ference in tenacity between the fibres dried differently appears surprisingly low at 0.4 - 2.1 cN/tex. Tension-drying usually induces an increase in the orientation of both the crystalline and amorphous regions, leading to a distinct increase in tenacity and drop in elongation at break. The alleged reason for the comparatively low tenacity of tension-dried Cel/Si fibres can be related to a certain unhomogeneity in the macro-structure of the cellulose core which may cause local inner stresses. This supposition has support in the image of broken fibre (*Figure 1*), which shows a coarse grain structure of the core and smooth intact skin.

The highest tenacity - 12.3 cN/tex - was found for fibres from cellulose solution with a zinc concentration of 1.7%, which correlates with the high stability of the spinning solution used and its low clogging index K_w^* (*Table 1*, C-3). Fibres spun in a silicate bath without sodium sulfate and tension-dried are characterised by the lowest elongation at break - 9.5% and tenacity - 8.9 cN/tex.

The distinct radial differentiation of Cel/Si material properties makes the fiber inclined to crimping after drawing and drying. In the course of drying they show a 2-fold higher shrinkage when compared to one-component cellulose fibres formed in an acidic bath.

From the results in *Table 2*, it ensues that, along with the increase in zinc concentration in the spinning solution, the LOI value and ash content (after heating at 800 °C) of the fibre increase. The highest LOI value - 46.5% - was found for fibres marked FC-5a, in which the high ash content of 37.9% allegedly caused a drop in tenacity to barely 8.7 cN/tex. In all the tests made, the LOI value was above
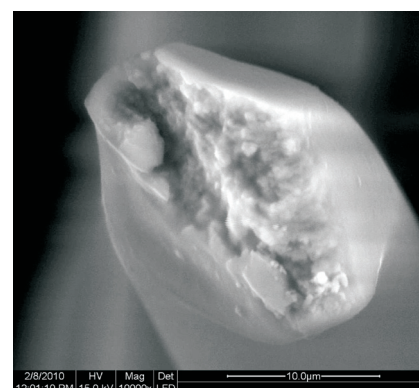

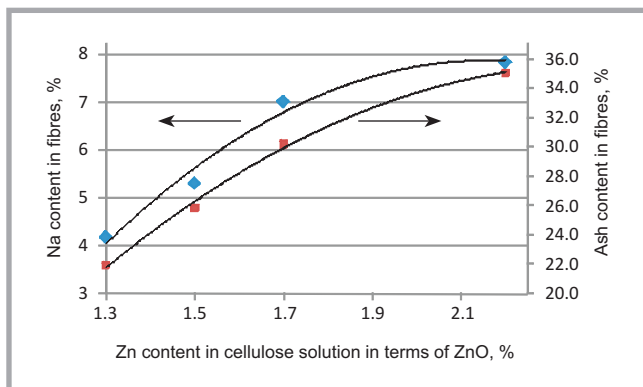**Figure 1.** *SEM image of a Cel/Si filament broken by drawing (10000×).*

Figure 2. *Impact of the zinc concentration in the cellulose solution on the amount of zinc and ash in the fibre.*
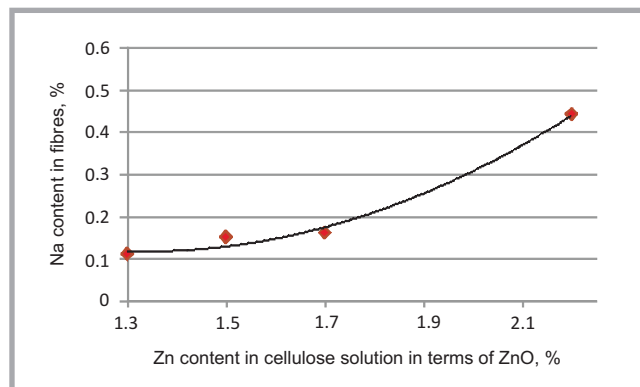

Figure 3. *Impact of the zinc concentration in the cellulose solution on the amount of sodium in the fibre.*

30%. The LOI index was slightly higher for loose-dried fibres (see **Table 2** FC-2a, FC-5a). Formed in a bath without sodium sulfate, fibres FC-3b, despite their lower tenacity, showed an LOI value and ash content similar to fibres formed in a silicate-sulfate bath.

Investigation into the chemical composition and morphology of the Cel/Si fibres

Figures 1 and *2* present the impact of the zinc concentration in the cellulose solution upon the content of zinc, ash and sodium in the Cel/Si fibres. An increase in zinc concentration (as ZnO) from 1.3 to 2.2% in the spinning solution augments its content in the fibre from 3.6 to 7.6%, and that of ash from 23.8 to 35.8%.

The content of sodium in the fibres was much lower than that of zinc and amounted to 0.11 - 0.44%. It is proof of the active role which zinc plays in the process of fibre solidification entering into bonds with silicates contained in the coagulation bath, thus influencing the shaping of the skin/core structure.

It was proven by ^{29}Si and ^{67}Zn nuclear magnetic resonance NMR tests of the interaction between silicate and zinc(II) ions in the alkaline solutions [26] that the silicate ions form complex compounds with Zn(II) appearing as zincate, $Zn(OH)_3^-$ or $Zn(OH)_4^{2-}$. The zincate enters into a reaction with the silicate monomer $[(HO)_2SiO_2]^{2-}$ at pH 14 - 15, forming $[(HO)O_2Si-O-Zn(OH)_3]^{4-}$, and with the silicate dimer, giving $[HO-SiO_2-O-SiO_2-O-Zn(OH)_3]^{6-}$ accordingly. The cyclic silicate trimer reacts slowly and incompletely with the zincate, yielding $[(HO)_3Zn(SiO_3)_3]^{7-}$. Theoretical calculations of quantum chemistry assist the identification of these zinc/silicate com-

plexes. The mechanism of the solidification of Cel/Si fibres in the aqueous sodium silicate and of the forming silicate layer upon the fibre surface is quite complex; a univocal interpretation is still needed.

It may be assumed that a difference appears between the diffusion rate of the solvent's and precipitating agent's molecules in the course of solidification of the streaming cellulose solution. The diffusion of the silicate bath to the fibre's interior is probably limited by the on-going sol-gel reaction in the inorganic portion, through which the sol undergoes transformation into a gel-like two-phase system containing both a liquid and a solid phase. In the course of the sol-gel reaction, inorganic material can be deposited on the cellulose matrix with hydrogen bonds forming between the compounds of the organic and inorganic phases [27]. From the Cel/Si fibre spinning trials, it ensues that the "never dried" inorganic layer is poorly formed and prone to me-

chanical deformation; for example, a too strong pressure applied on the wet fibre causes the out-squeezing of a part of the zinc silicate compounds along with water, which may result in a 25% decrease in the ash content of the fibre. The zinc-silicate layer is ultimately solidified only after drying, which gives the layer adequate mechanical resistance, resembling commercial preparations used as silicate-zinc protective coatings.

The comparatively good tolerance to deformation e.g. during drawing (R_{max} = 85%), drying (15-16% shrinkage in loose-drying) and thermal processing (heating at 450 °C) is a characteristic feature of the surface layer of Cel/Si fibres. SEM images of the fibre surface (*Figures 3, 5, 6*) confirm that in any of such treatments, the fibre surface remains smooth without visible defects like cracks and fractures.

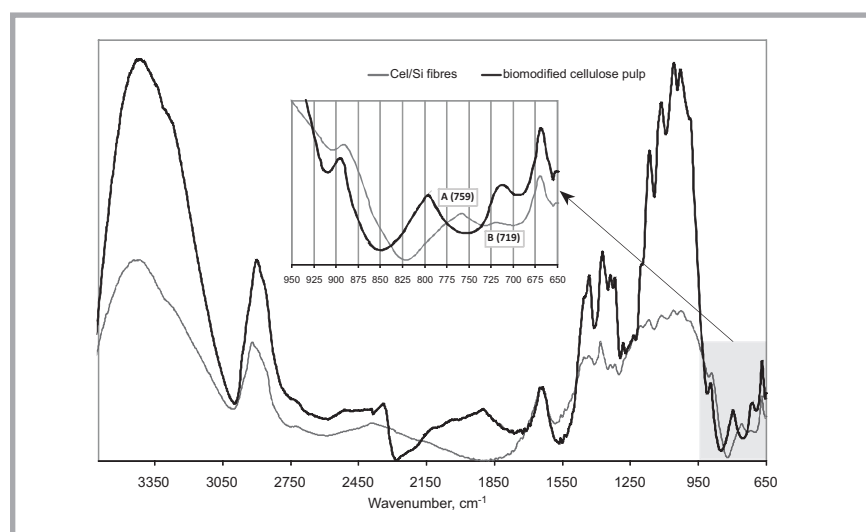*Figure 3* presents an image of a Cel/Si filament which underwent breaking elon-

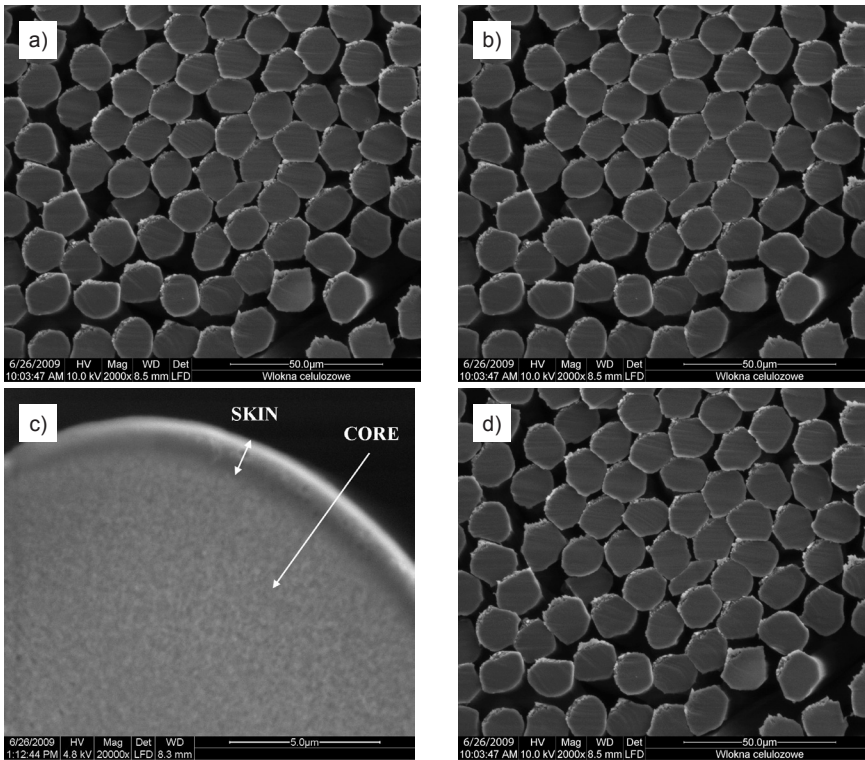**Figure 4.** *FTIR analysis of Cel/Si fibres and enzyme-modified cellulose pulp.*

Figure 5. SEM images of the surface and cross-section of the Cel/Si skin/core fibres (a, b, c),and of a cross-section of cellulose fibres spun in an acidic bath without flame retardants (d).
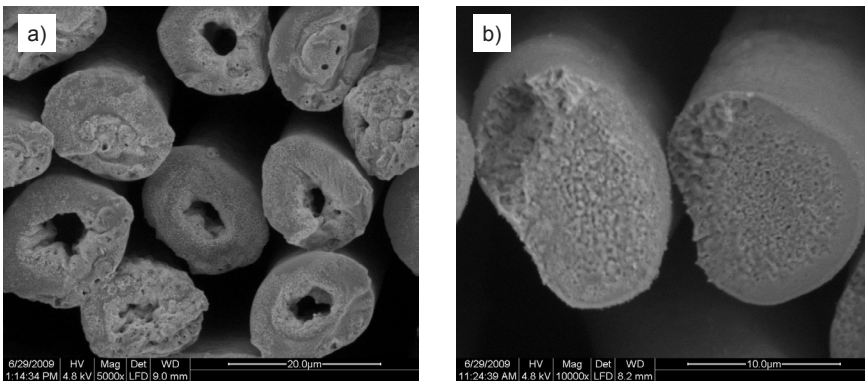

Figure 6. SEM images of cross-sections of Cel/Si fibres heated at 450 °C for 15 (a) and 60 (b) minutes.
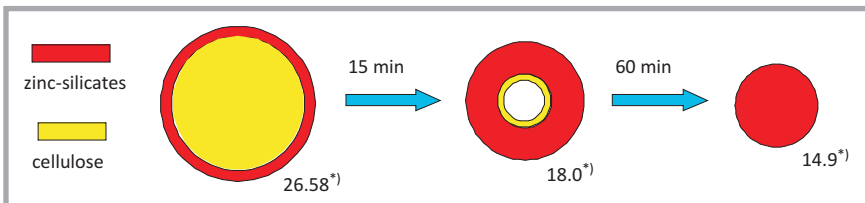

Figure 7. Scheme of the transformation of Cel/Si fibres during heating at 450 °C; *) - Average diameter, μm.

gation at ambient temperature. In the broken segment of the fibre, a coarse grain structure can be seen in the core part with distinct cavities formed at the moment of breaking. The skin portion seems to be more extended than the core: fragments of the skin obscure the core part to a major degree, and the skin remains smooth.

It may be concluded that the core, being less tolerant to deformation, burst first followed by the skin. Similar results appeared in all other SEM-inspected broken fibres.

It seems quite a simplification to regard the skin and core purely as a strict differ-

entiation between inorganic and cellulose portions. Both constituents can, to a certain degree, diffuse in each other and still maintain their general character.

Inflammability tests were made at 600 °C with cellulose fibres spun in an acidic bath without a flame retardant and with Cel/Si fibres without spin-finish. When placed in an oven, the former ignited and quickly burnt, while the latter underwent glowing, which ceased as soon as the fibres were removed from the oven. It is proof that the skin tightly isolates the cellulose interior; otherwise a flame would have appeared.

Figure 4 (see page 30) presents FTIR spectra of the Cel/Si fibres and enzyme-modified cellulose pulp. The simplest arrangement of atoms considered in the analysis of the Cel/Si fibres spectra was the tetrahedron of oxy-silicon ion SiO_4^{4-}, which constitutes the main element of the silicate's structure. The oscillating spectra of cyclosilicates are characterised by additional bands which distinguish them from mono- and disilicates (Si-O-Si in the similar region of 600-800 cm^{-1}) [28]. In the Cel/Si fibres, the symmetric stretching vibration of Si-O-Si was found, which is specific for cyclosilicates, at a wavenumber of 759 cm^{-1} and, to a lesser degree, 719 cm^{-1}. Compared to the spectrum of enzyme-modified cellulose pulp, the Cel/Si spectrum is flattened mostly in the region characterised by the presence of the strongest absorption bands of skeletal silicates including SiO_2 and its polymorphic versions. The partial overlapping in the region of absorption bands that is characteristic for both cellulose and silicates makes identification rather ambiguous; the asymmetric stretching vibration of C-O-C- (1164 cm^{-1}, cellulose) and the asymmetric stretching vibration of -Si-O-Si- (1171 cm^{-1}, silicates) being examples. The FTIR analysis of Cel/Si fibres did not reveal -Si-O-C- or Si-C bonds which would witness the existence of chemical bonds between the portion of silicates and the cellulose chains.

Figures 5.a, 5.b & ***5.c*** present SEM images of the surface and cross-section of the Cel/Si skin/core fibres. The fibre surface is rather smooth without distinct cavities and cracks (***Figure 5.a***, 10000×); the cross–section is oval (***Figure 5.b***, 2000×). The skin layer is distinctly visible at the edge of the cross-section. In the image, the layer at the edge is darker, sharply contrasting with the core. The

surface of the cross-section is smooth with scarce oval cavities a few nanometers wide.

Figure 5.c presents a fragment of a filament's cross-section at 20000 magnification. The distinct skin looks compact; its thickness on the periphery of the filament's cross-section is in the range of 1 - 2 μm. The core is regularly shaped with a fine grain structure. A cross-section of cellulose fibres spun in an acidic bath without flame retardants (*Figure 5.d*, 2000×) is shown for comparison. The diameters of the fibres presented are 26.5 μm on average and about 14.7 μm for the Cel/Si and cellulose fibres, respectively. In *Figure 6* SEM images can be seen of cross-sections of Cel/Si fibres that were heated at 450 °C for 15 and 60 minutes. The initial phase of the thermal decomposition clearly indicates the skin/core structure of the fibres (*Figure 6.a*). Cellulose constitutes the main core material which undergoes destruction, delivering gaseous products and leaving voids behind in the central segment of the cross-section.

The behaviour of the skin is in contrast with that of the core. The skin remains compact without cracks, breaks, voids, etc, which is proof of the inorganic character of the skin, which is mainly built up of zinc-silicates. Along with the thermal decomposition of the cellulose, strong diagonal shrinkage occurs, causing a distinct decrease in the fibre diameter. Silicate fibres remain after the complete decomposition of cellulose for a full cross-section (*Figure 6.b*), and a diameter barely more than half of the original. In the figure it can be seen that the smooth surface of the skin contrasts with the highly porous cross-sections.

The scheme of the transformation of Cel/Si fibres during heating at 450 °C is shown in *Figure 7*.

Cel/Si fibres made according to description [20], when heated at 800 °C, become partially sintered and, upon cooling down, form a homogeneous mass. The surface of the Cel/Si fibres, additionally subjected to the action of an acid, adopts the form of polysilicic acid. *Figure 8* presents images of Cel/Si fibres processed with aqueous 0.05% HCl at 20 °C for 1 hour and then heated at 800 °C. Snow-white silicate fibres were possible to obtain, but unfortunately they were weak and brittle (*Figure 8.a*). The SEM

image (*Figure 8.b*) shows a smooth surface of the skin and a highly porous surface of the cross-section.

Figure 9 shows an SEM image of a Cel/Si filament exposed to a flame for half a minute. The acceleration of cellulose pyrolysis by the direct action of the flame increases the amount of volatile products and may yield a silicate structure in the form of highly porous tubes. A overly violent process, however, causes many cracks in the skin and cross-section due to the pressure of the quickly evolving gases. The resulting product is too brittle to preserve the original fibre form with a void inside. More detailed investigations are intended on the behaviour of products made from Cel/Si fibres when subjected to a flame.

Impact of washing detergents and the pH of the environment upon the leachability of fire retardants from Cel/Si fibres

Figure 10 (see page 32) illustrates the influence of the multiple washing of Cel/Si fibres in a water solution of commercial Persil washing powder at 40°C upon the LOI value. Fibres formed from cellulose solutions with a zinc content (as ZnO) of 1.3% (symbol of fibre FC-1a, LOI = 31.5) and 1.7% (symbol of fibre FC-3a, LOI = 40.4) were selected for testing. The fibres were dried in loose bundles. Fibres spun at a higher zinc content in the cellulose solution manifested a lower decrease in LOI, particularly in the first seven washing cycles. After 15 washing cycles, the LOI value was 25.6% and 36.9% for the FC-1a and FC-3a fibres, respectively. It ensues from the testing results that a higher content of zinc in the cellulose solution produces a better resistance of Cel/Si fibres to multiple washing

Table 3 presents the influence of the processing of Cel/Si fibres (symbol FC-2a) with aqueous solutions of HCl at a concentration of 0.002 - 0.1% and NaOH at a concentration of 0.1 - 5% on the ash content. The ash content was estimated after processing, washing with water and drying.

Based on the results presented in *Table 3*, it may be concluded that the fire retardant in Cel/Si fibres reveals a much better fastness in an alkaline medium. Fibres processed with aqueous HCl at a concentration of up to 0.01% (pH 2.6) and NaOH at a concentration of up to 0.5%
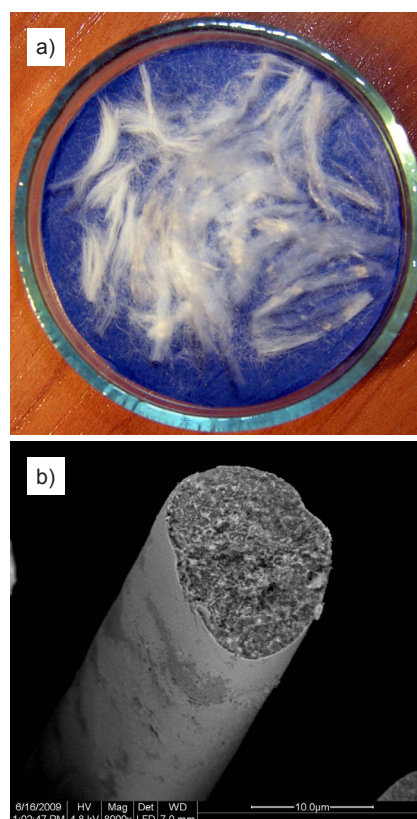

Figure 8. *Cel/Si staple fibres subjected to acidic processing after heating at 800 °C; a) Image of silicate fibres, b) SEM image of a silicate filament.*
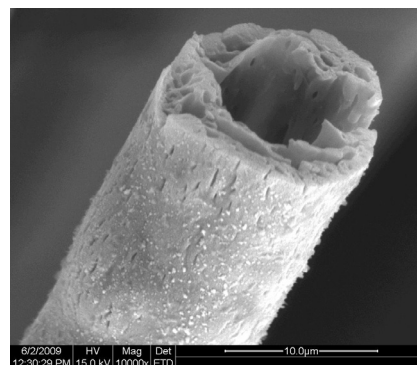

Figure 9. *SEM image of a Cel/Si filament after the action of naked flame during half a minute.*

Table 3. *Influence of the processing of Cel/Si fibres (symbol FC-2a) with aqueous HCl and NaOH on fire retardancy fastness (measured as the ash content in fibres heated at 800°C); [1] - fibres without processing.*

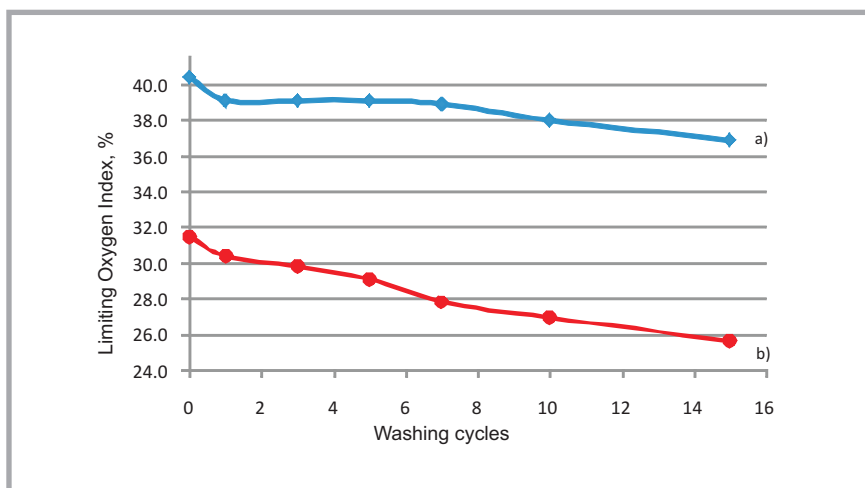| Test solution		Ash content (800°C), %
Reagent	Concentration, %	
-	-	31.9[1]
HCl	0.002	30.5
	0.01	29.9
	0.1	23.5
NaOH	0.1	31.6
	0.5	28.6
	5	12.9

Figure 10. *Impact of the number of washing cycles of Cel/Si fibres in an aqueous solution of Persil detergent at 40 °C upon the LOI value. Fibres spun with a zinc (as ZnO) content in the cellulose solution of 1.7% (a) and 1.3% (b).*

Table 4. *Antibacterial activity test of Cel/Si fibres (S. aureus); [1] – standard cellulose fibres spun into an acidic coagulation bath.*

Sample marking	Zinc content	Time, h	Number of bacteria, CFU/sample	Activity	
				Bacteriostatic	Bactericidal
Cotton	0	0	2.41×10^4	-	-
	0	24	1.02×10^7	-	-
FC [1]	< 50 ppm	24	1.15×10^7	- 0.1	- 2.6
FC-2	4.79%		2.88×10^2	4.4	1.9
FC-5	7.60%		< 20	5.7	3.2

(pH 13.1) were characterised by only a slight decrease in ash content. Thus, it may be concluded that the fire retardancy of the Cel/Si fibres showed good fastness in aqueous solutions with a pH varying in the wide range of 2.6 - 13.1.

Estimation of the bioactivity of the Cel/Si fibres

Considering the high content of zinc in the fibres, it appeared to be interesting whether the Cel/Si fibres could be suitable for other uses than in fire-resistant materials. This is the reason why preliminary testing of the bioactivity was carried out. It seems that potential uses emerge

Figure 11. *Testing of the antifungal activity of the Cel/Si fibres against A. niger (diffusion test).*

in filtration materials as well as in sanitary and medical devices where the feature of bioactivity is highly valued. Such conceptual uses call for further investigations on the specific modification of fibre properties e.g. their chemical structure.

Table 4 presents the testing results of Cel/Si fibre bioactivity against *Staphylococcus aureus*. The results show that Cel/Si fibres show bacteriostatic and bactericidal activity against the *S. aureus* strain. The activity increases with an increase in the zinc content of the fibre. The Cel/Si fibres with the highest zinc content of 7.6% showed bactericidal activity after 24 hours of incubation. Standard cellulose fibres spun in an acidic bath with a zinc content below 50 ppm are neither bacteriostatic nor bactericidal against *S. aureus*.

Figure 11 presents test results of the antifungal activity (qualitative test) of the Cel/Si fibres (symbol FC-5) against the *Aspergillus niger* strain. The Cel/Sil fibres show only limited activity against the strain. The growth on the sample was confined to below 50% of the sample tested, which may be regarded as insufficient antifungal activity.
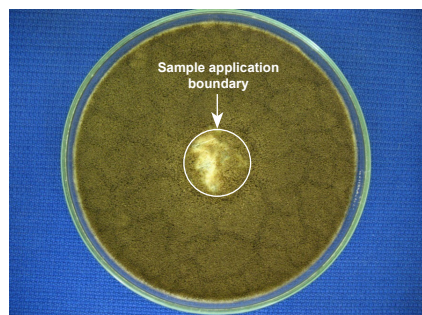
■ Summary

From enzyme–modified cellulose, stabile alkaline solutions were prepared containing zinc (as ZnO) at a concentration of 1.5- 1.7%. From such solutions flame redardant cellulose-silicate fibres were spun with a tenacity of up to 12.3 cN/tex and elongation at break of up to 42% (air conditioned). The fibres prepared attained a high LOI value of 30.1–46.5%. It was found that the zinc content in Cel/Si fibres exceeds many times that of sodium and increases up to a maximum of 7.6% with an increase in zinc concentration in the cellulose spinning solution. It was documented that fibres spun from the alkaline solutions of cellulose in a coagulation bath containing aqueous sodium silicate adopt a skin/core configuration. The skin is built up of inorganic material, while cellulose forms the core. Heated at 450-800°C, the fibres retain their fibrous form after complete decomposition of the cellulose component accompanied by a nearly two-fold reduction in the fibre diameter. Cel/Si fibres are resistant to multiple washing in water with commercial detergents. Fibres formed from cellulose solutions with a zinc concentration (as ZnO) of 1.7% revealed a comparatively low decrease in LOI, from 40.4% to 36.9% after 15 washing cycles. The fire retardancy of the Cel/Si fibres showed good fastness under the action of aqueous HCl and NaOH in a pH range of 2.6–13.1. The fibres show bactericidal activity against the *S. aureus* strain.

□

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