

Cellulose fibers modified by Eu^{3+} -doped yttria-stabilized zirconia nanoparticles

Piotr Kulpinski · Aleksandra Erdman ·
Marek Namyslak · Janusz D. Fidelus

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Abstract This paper describes a method for manufacturing luminescent cellulose fibers. Good optical properties of cellulose fibers under UV-C illumination were achieved by incorporating ZrO_2 (0.5 mol% of Eu^{3+}) stabilized by Y_2O_3 (7 mol%) into the fiber structure's particles. Fibers were obtained from 8 wt% cellulose solution in *N*-methylmorpholine *N*-oxide (NMMO) with the addition of a luminescent modifier in the range between 0.5 and 10 wt%. The physico-chemical and mechanical parameters and the structure of these fibers were examined.

Keywords Interactive fibers · Lyocell fibers · Photoluminescent materials · Optical markers

Introduction

Modern technologies have reached almost every discipline of science. A great development in the field of man-made fibers has been observed, which allows us to

produce fibers in a manner which is not only environmentally friendly but also with greater efficiency and with a significant reduction in costs. The new technologies have also allowed us to modify standard synthetic and artificial fibers in order to obtain fibers with completely new properties. New fibers with special properties and for special applications can be used to improve human life. There is much interest in the use of biopolymers, which due to their properties are human—and environment—friendly. One of the areas of interests is cellulose, the most abundant natural polymer, and one of the oldest raw materials used in the chemical industry. Cellulose is a biodegradable, biocompatible and hydrophilic material with many promising properties, and it has been widely described in the literature (Klemm et al. 1997, 2005; Vigo 1998).

Cellulose is a biopolymer built on *D*-glucose units linked in long unbranched chains by β -1,4-glycosidic bonds. This relatively cheap natural polymer with hydrophilic properties is an important material for various applications, ranging from composite technology to medicine.

Because its chemical structures contain many intra- and intermacromolecular hydrogen bonds, cellulose is soluble in very limited numbers of solvent systems. Among them, from the point of view of application in the industry, only *N*-methylmorpholine *N*-oxide (NMMO) seems to be a promising organic solvent for cellulose. One of the advantages of the NMMO method is that NMMO is a direct solvent of cellulose, and the preparation of the spinning dope can be

P. Kulpinski (✉) · A. Erdman · M. Namyslak
Department of Man-Made Fibers, Technical University
of Lodz, ul. Zeromskiego 116, 90-924 Lodz, Poland
e-mail: Piotr.Kulpinski@p.lodz.pl

J. D. Fidelus
Institute of High Pressure Physics, Polish Academy
of Sciences, ul. Sokolowska 29/37, 01-142 Warszawa,
Poland

achieved in practically a one-step process. Intensive research over recent years has led to the development of a green and economic technology for manufacturing man-made cellulose fibers (Perepelkin 2007).

From the chemical point of view, the solubility of cellulose is possible because of NMMO's ability to replace the hydrogen bonds between polymer macromolecules with hydrogen bonds between hydroxyl groups of *D-glucopyranose* units and the highly polar $N \rightarrow O$ group in the NMMO compound. Cellulose dissolved in NMMO forms a relatively stable system which crystallizes at room temperature. The solution of cellulose in NMMO can be spun by a dry-wet method. In this process, the α -cellulose is regenerated from a concentrated, homogenous solution of polymer in the form of fibers (Fink et al. 2001; Zhao et al. 2007).

Due to the above-mentioned advantages of the NMMO method, there is a wide range of possible modifications of cellulose fibers, which offers new potential applications. Innovative and unique functional cellulose fibers, with electrical conductivity, antimicrobial activity, UV- and X-ray protection, magnetic-, photo- and thermoactivity properties, can be achieved by the addition of inorganic as well as organic modifiers to the system during the cellulose pulp dissolution process in aqueous NMMO. Adding modifiers into the polymer matrix (instead of modifying the surface of fibers during the finishing process) makes the modified fibers more wash-proof and guarantees long-lasting use.

One very interesting and promising area, from the point of view of application, is that of luminescent materials. Luminescence is very attractive phenomenon with many areas of application, and there is great interest in research into this effect (Peng et al. 2006; Shioi et al. 2008; Wang et al. 2008).

Many kinds of luminescent nanomaterials with lanthanide ions have been reported (Fidelus et al. 2009; Trexler et al. 2010 and references therein), and their structures and properties have been studied in detail. Nanocrystalline materials have found applications in various fields of engineering (Kulpinski 2007). Photoactive inorganic complexes based on trivalent rare-earth ions and metal oxides have been successfully incorporated into polymer matrices such as PUR (Ryszkowska et al. 2007; Liu et al. 2008), PMMA, PLA (Sheng et al. 2011), and PEO (Ninjbadgar et al. 2009). Also, europium ions, complexes containing

ions of this rare earth metal, and polymers doped with it, have been investigated and reported in the literature (Yakimanskii et al. 2008; Ribeiro et al. 1998; Mardaleishvili et al. 2009; Rybaltovskii et al. 2009). The zirconia, which was used in the investigation presented in this paper, is also a very interesting compound due to its characteristics, especially at nanoscale size (Gu et al. 2004).

Inorganic pigments with activators could be added to the spinning dope in the viscose, cuprum and NMMO process. Luminescent cellulose fibers can be used to verify the authenticity of textiles, as well as documents and papers of value (Gu et al. 2004). As reported elsewhere, the security fibers with various shapes of cross-section from synthetic polymers containing luminescent pigments, copolymers or dyes, has been investigated (Fu et al. 2006).

The aim of the present research was to obtain fibers from a cellulose/NMMO/water system containing particles of an inorganic lanthanide complex with luminescent properties. UV-active cellulose fibers which are able to emit visible light under UV-C radiation might have a potential application as an optical marker for protection of textiles and documents.

Experimental

Materials

Cellulose containing 98 wt% of α -cellulose with an average polymerization degree of about 1,250 (\overline{DP}) was used as a starting material for making regenerated cellulose fibers. In this research, NMMO in the form of a 50 % (v/v) aqueous solution from Huntsman Holland BV (Rotterdam, the Netherlands) was used as a direct cellulose solvent in the process of preparing the spinning dope. The propyl ester of gallic acid (Tenox PG[®]) from Aldrich (Gillingham, Dorset, UK) was used as an antioxidant agent to minimize the reduction of cellulose polymerization degree during the dissolution process.

The modifier of the cellulose fibers' properties used in this study was Ee^{3+} doped ZrO_2 nanoscale particles stabilized by 7 mol% of Y_2O_3 . The concentration of Eu^{3+} ions in this complex was 0.5 mol% per ZrO_2 . The compound was prepared according to the published procedure (Fidelus et al. 2009). The modifier's

particle were suspended in a mixture of distilled water and isopropyl alcohol. The concentration of suspension was c. 5.5 % by weight. In this work the above-mentioned compound is marked as 7YSZ-0.5Eu. The high-resolution scanning microscopy image of the 7YSZ-0.5Eu is given in Fig. 1.

As can be seen in the Fig. 1, the particles are slightly aggregated what is typical for the products of hydrothermal synthesis. The particles of the modifier have a relatively round shape, and the diameter of a single particle does not exceed 100 nm.

Instrumentation

The spinning solutions were obtained using an IKA-VISC[®] high-efficiency laboratory-scale kneader type MKD 0.6-H60, supplied by IKA-Analysentechnik (Heitersheim, Germany).

The regenerated cellulose fibers were made by the means of the dry-wet spinning method on a piston, oil-heated lab-scale spinning device with the use of an 18-hole spinneret.

The thermal gravimetric analyses (TGA) of the fibers obtained were carried out with the PerkinElmer TGA-6 Thermal Gravimetric Analyzer (US Instrument Division, Norwalk, Conn.). The measurement procedure was as follow: in the first step 40–50 mg of powdered cellulose fibers were dried in the thermo gravimetric device oven in an atmosphere of dry gas at 105 °C. The drying mode usually lasted 20 min, till no more weight loss of sample was observed. Then, the sample was again tarred and heated using a heating

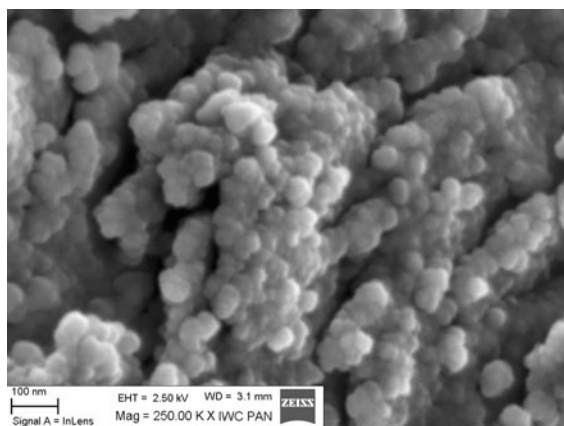


Fig. 1 High-resolution SEM photograph of 0.5 mol% of Eu^{3+} -doped ZrO_2 stabilized by 7 mol% Y_2O_3

ramp of 10 °C/min from 50 to 800 °C, under air atmosphere at a flow rate of 20 mL/min (Kulpinski 2005b).

The densities of the fibers obtained were measured at room temperature using the flotation technique in a mixture of toluene and carbon tetrachloride.

The mechanical properties of the cellulose fibers were checked on a Zwick tensile testing machine type Z2.5/TN1S from Zwick GmbH (Ulm, Germany). The data was analyzed using TestXpert software.

The crystal structures of the unmodified cellulose fibers and the fibers with an additive were analyzed by X-powder diffraction using a Siemens DV 5000 polycrystalline diffractometer (XPRT-PRO system) with $\text{Cu-K}\alpha_1$ and $\text{Cu-K}\alpha_2$ radiation. The X-ray diffraction (XRD) patterns were recorded from 5 to 90° (2θ) with a scanning step of 0.001°.

The excitation and emission spectra of cellulose fibers and the modifier were recorded at room temperature (RT) on a CM 2203 Spectrofluorometer. The excitation spectra, monitored at 607 nm, were recorded for a spectral range extending from 220 to 600 nm. The emission characteristics, covering the red and near infra-red part of the spectrum, were obtained under excitation at 240 and 260 nm. The excitation and emission slits were 10 and 5 nm respectively.

SEM images of fiber surface and cross-sections were obtained with a JEOL 5200 LV SEM scanning electron microscope from JEOL Ltd. (Tokyo, Japan). The morphology determination of the modifier and the fibers' surface were taken on a LEO 1530 field-emission scanning microscope. The specific surface area analysis was determined by the multipoint B.E.T. method (Gemini 2360, Micromeritics Instruments).

Preparation of the regenerated cellulose fibers

Appropriate amounts of cellulose, 50 % (v/v) aqueous solution NMMO and propyl ester of gallic acid were loaded into the kneader. The modifier was applied as a water dispersion containing 5.5 wt% of 7YSZ-0.5Eu powder. It was introduced into the system at the beginning of the dissolution process within the range of 0.5–10 % by weight of 7YSZ-0.5Eu nanopowder in relation to α -cellulose. The starting mixture was continuously stirred and heated for about 100 min; in this time the temperature in the kneader was raised from 45 to 115 °C. The water was removed from the

reaction mixture under low-pressure conditions until the water content in solution achieved the level of about 14 wt%.

The fibers were spun from an 8 wt% cellulose solution of NMMO at a temperature of 115 °C, with the take-up speed of 70 m/min. The cellulose filaments were passed through an aqueous spinning bath (20 °C). The spinning dope flow rate through an individual capillary was about 1 m/min. Finally, the fibers were washed out in cool water and dried at room temperature. A simplified diagram of the manufacturing process of modified cellulose fibers is shown in Fig. 2. A similar procedure has been described elsewhere (Kulpinski 2005a, b).

Results and discussion

Determining the modifier content

The real concentration of the inorganic modifier in the cellulose fibers obtained was determined on the basis of the density measurement method and thermogravimetric analyses.

In the case of the first method, the real density of the fibers placed in a column filled with a mixture of toluene and CCl₄ was evaluated. To calculate the mass concentration of the photoluminescence modifier in the final cellulose products, the density of pure

modifier was 5.73 g/cm³, according to the specific surface area analysis. Unfortunately, in this method the upper range of measured samples is limited to the gravity of tetrachloromethane, so the results are also limited to the cellulose fibers containing up to 3 wt% of the modifier. The results shown in Table 1 demonstrate the progressive rise in the fibers' density along with the rise in the 7YSZ-0.5Eu concentration.

According to the formula:

$$\frac{m_c}{m_m} = \frac{\rho_c \times \rho_m - \rho_w \times \rho_c}{\rho_w \times \rho_m - \rho_c \times \rho_w}$$

where m_c —mass of the cellulose, g; m_m —mass of the modifier, g; ρ_c —density of the cellulose, g/cm³; ρ_m —density of the modifier, g/cm³; ρ_w —the real density value of the cellulose fibers, g/cm³; the percentage mass content of the modifier in the fibers C_m wt% was calculated from the following equation (the results are shown in Table 1):

$$C_m = \frac{1}{\frac{m_c}{m_m} + 1} \times 100$$

To prove the results acquired from the density measurement method, the thermal gravimetric analysis (TGA) was used to estimate the amount of the inorganic additive remaining in the obtained cellulose fibers. The analyses were done with a PerkinElmer TGA-6 Thermal Analyzer in a temperature range between 50 and 800 °C, at 10 °C/min heating rate

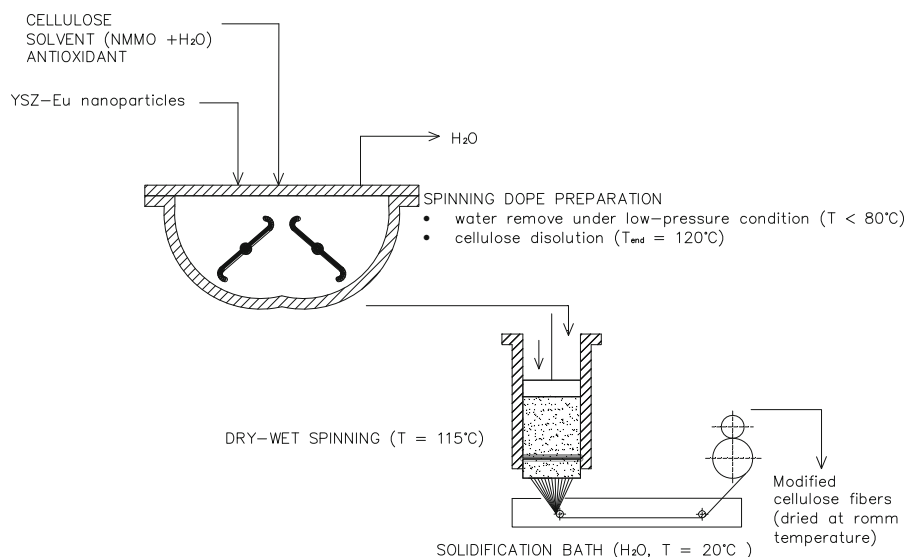
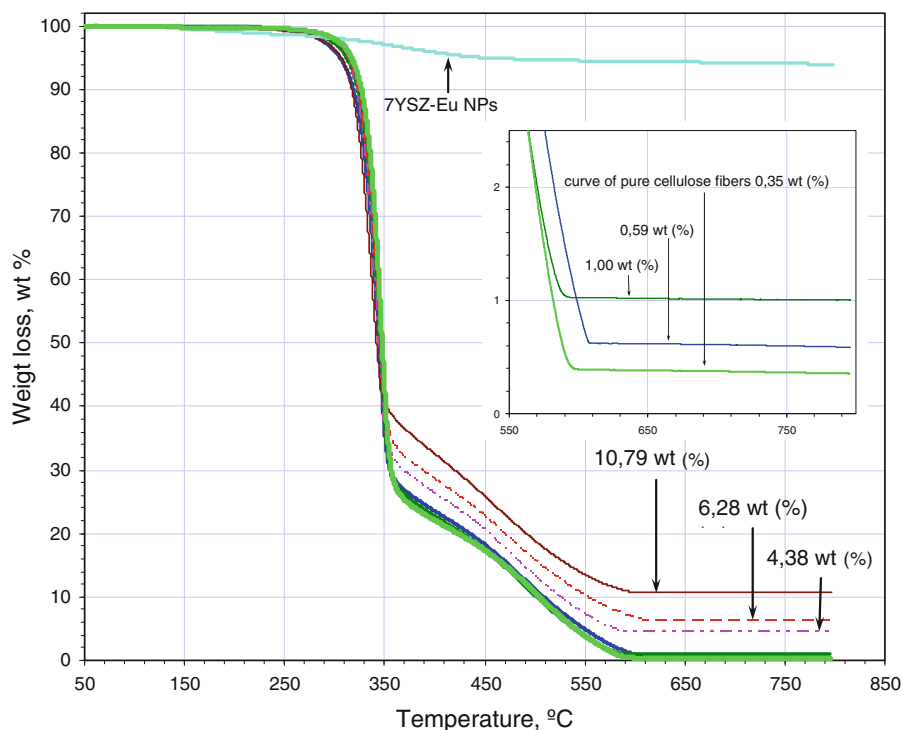


Fig. 2 Scheme and conditions for preparing modified man-made cellulose fibers in a laboratory-scale apparatus

Table 1 Investigation of concentration of 7YSZ-0.5Eu modifier in man-made cellulose fibers

Sample (theoretical concentration of the modifier, percentage by weight)	Concentration of the modifier calculated on the basis of density investigation (wt%)	Concentration of the modifier evaluated on the basis of thermal analysis (wt%)
Cellulose without modifier	0.00	0.35
Cellulose fibers with 0.5 % of modifier	0.48	0.59
Cellulose fibers with 1 % of modifier	1.09	1.00
Cellulose fibers with 3 % of modifier	3.05	4.38
Cellulose fibers with 5 % of modifier	–	6.28
Cellulose fibers with 10 % of modifier	–	10.79

Fig. 3 TGA curves of pure cellulose fibers, modifier and cellulose/7YSZ-0.5Eu composite

under an air atmosphere. Prior to the measurement, approximately 35 mg samples of the powered fibers were dried at temperatures of 105 °C for 20 min in the TGA apparatus to eliminate residual water from the hydrophilic materials until no further changes in values of weight loss were observed.

In the case of the thermal analysis of the plane modifier, weight loss associated probably with the process of dehydration was observed at temperatures between 350 and 450 °C.

The typical TGA curves for cellulose and cellulose composite (Fig. 3) show a double weight loss step. The investigation materials are thermally stable up to

250 °C, which is the starting point of the cellulose materials' thermal degradation. The main mass loss is observed within a range of temperatures between 250 and 350 °C. The second decomposition stage occurred within the temperature range of 350–610 °C. The cellulose parts of the products were completely decomposed around 570–610 °C. The results presented in the thermal gravimetric plot demonstrate that the higher concentration of luminescent complex in fibers leads to a slowdown in the rate of cellulose degradation in the second stage of this oxidation process. When the cellulose degrades completely, the remaining mass of each sample can be recognized as the mass of the

inorganic compound 7YSZ-0.5Eu; these particles are thermally stable at temperatures over 650 °C.

Two independent methods for measuring the real amount of the modifier in the fibers have shown that the calculated value of the modifier is very close to the amount remaining in the cellulose fibers. It seems that the NMMO method is suitable for introducing this kind of inorganic modifier, and allows the production of fibers with the desired concentration of the modifier with acceptable accuracy.

X-ray powder diffraction

The X-powder diffraction (XRD) was used to examine pure cellulose fibers, as well as cellulose fibers with the addition of 5 and 10 wt% of 7YSZ-0.5Eu. The XRD data is shown in Fig. 4.

It is known that the diffraction peak at about 12° (2θ) is from cellulose I and the peak at ca. 22° (2θ) is from cellulose II. These results correspond to the (110) and (020) plane of the crystallites in cellulose I and II respectively. The four peaks in X-diffraction pattern centered at c. 30, 35, 50, 60, 74, 82° (2θ) are recognized as the characteristic peaks of tetragonal structure ZrO_2 crystals associated with (101)_t plane (Chen et al. 2004; Brasse et al. 2009). The intensity of all of these peaks is proportional to the content of the modifier in polymer matrices. The results obtained from XRD measurements suggest that the presence of the additive in the cellulose fibers does not influence the structure of the cellulose matrix.

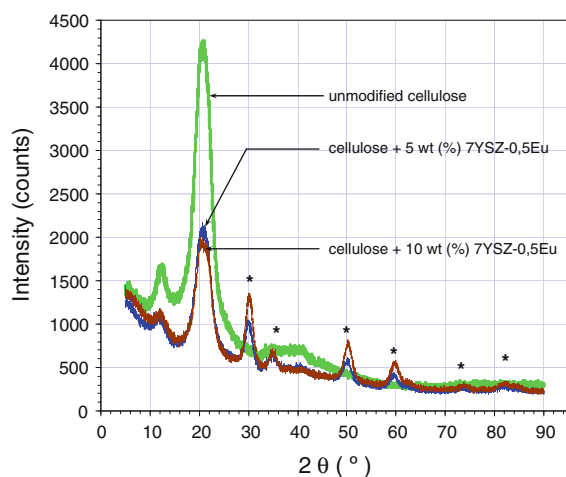


Fig. 4 X-ray diffraction patterns of regenerated cellulose and cellulose with 7YSZ-0.5Eu

Mechanical properties

The influence of the different content of $ZrO_2:Eu^{3+}$ stabilized by yttrium oxide particles on the mechanical properties of the fibers was checked on a Zwick Z2.5/TN1S tensile testing machine, in accordance with Polish standard PN-85/P-04761/04. The linear density of the fibers was measured according to Polish standard PN-72/P-04800. The linear density of obtained cellulose fibers ranges from 0.230 to 0.255 tex.

The results of the measurements of mechanical properties such as tenacity and elongation at break of cellulose fibers containing different concentrations of the modifier are shown in Table 2.

The data suggests a strong dependency of the tenacity and elongation at break of the obtained cellulose fibers on the concentration of 7YSZ-0.5 %Eu particles. Unmodified fibers have the highest tenacity, equal to ca. 28.4cN/tex. The presence of the modifier in fibers in content up to 0.5 % by weight only slightly reduced the products' tenacity. The increase in the concentration of inorganic particles in cellulose fibers to values within a range of 1–5 and 10 wt% leads to a decreased fiber tenacity at break of about 15 and 30 % respectively.

The modifier also influences the fibers' elongation at break. Introducing 0.5 wt% of the additive into cellulose fibers induced a rise of values of elongation at break, but further raising the concentration of the modifier in the fibers' material decreased elongation to a constant level of about 8.6 %, within a range of concentration 1–10 wt%. This phenomenon was also observed with a similar inorganic modifier with the nanosize particle (unpublished results). The effect is probably caused by the round shape of the added modifier, which results in a kind of plasticization effect during the spinning process. It is also very likely that the nanosize of the modifier particles caused the optimum effect, which is expressed around 0.5 % w/w. This may depend on many factors, such as the concentration of defects, the degree of crystallinity, and the nature, amount, and distribution of dopants (Armelaio et al. 2008). The real reason for this phenomenon is under investigation.

The results shown in Table 2 have a relatively high value of standard deviations for the elongation at break, which can be explained by two overlapping factors. First, the cellulose fibers presented in this

Table 2 Effect of the modifier's concentration on the linear density and mechanical properties of cellulose fibers

Concentration of the modifier (wt%)	Linear density (tex)	Tenacity (cN/tex)	Standard deviation for tenacity values	Elongation at break (%)	Standard deviation for elongation at break values
0.0	0.23	28.4	6.59	7.79	1.51
0.5	0.237	27.82	7.96	9.68	1.65
1.0	0.249	24.69	7.56	8.65	1.78
3.0	0.255	23.34	9.16	8.77	1.66
5.0	0.255	24.31	7.11	8.63	1.39
10.0	0.245	20.84	5.14	8.55	1.50

work were modified with inorganic particles, which to some extent worsen the spinning process and cause a larger scatter of results.

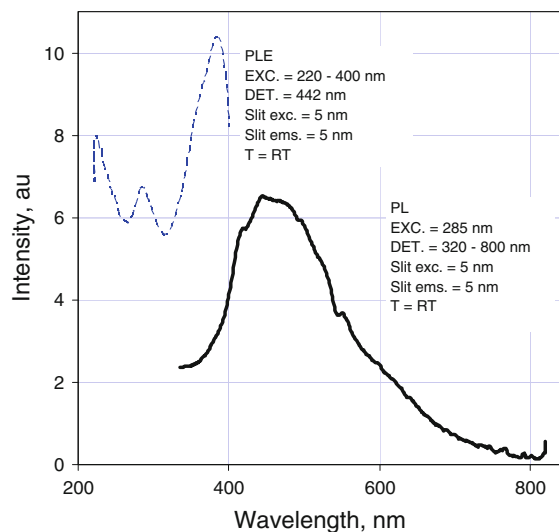
Another factor is that the uniform properties of the fibers strongly depend on the spinning conditions, as well as on the scale of the spinning device. In the presented paper, fibers were obtained as continuous fibers using a small laboratory-scale device, which results in a relatively large spread of estimated values.

The fibers' photoluminescent (PL) properties

The luminescent properties of the modified man-made cellulose fibers were examined and compared with the properties of pure cellulose fibers, as well as with the pure modifier.

The spectral characteristics of unmodified cellulose fibers, shown in Fig. 5, indicate the presence of organic compounds in the man-made fibers' chromophore, with maximal absorbance at 285 and 395 nm. The emission spectrum of the compounds obtained under excitation at the wavelength of 285 nm is in the form of a broad band extending from UV to red spectral range with a maximum at c. 440 nm. As was shown elsewhere (Rosenau et al. 2002), chromophores can be generated during the cellulose dissolution process in NMMO. However, they are extracted from the spinning jets during coagulation process in the spinning bath, but some small amount could remain in the obtained fibers. The results are consistent with the literature data, which confirms the possibility of isolating chromophoric compounds from cellulose materials, including Lyocell-type cellulose fibers (Goubard et al. 2007).

The excitation spectra of pure Eu(III) ion—doped YSZ particles and those introductions into celluloses were obtained by monitoring the strongest emission

**Fig. 5** Excitation and emission spectra of pure regenerated cellulose fibers

wavelength of the europium (III) ion at 607 nm (as shown in Fig. 6). In the case of the 7YSZ-0.5Eu additive, the excitation spectrum consists of three bands: one broad, large band of excitation extending from 255 to 320 nm, with a maximum located at 276 nm, and two less intense bands with centers localized at c. 420 and 490 nm respectively. The excitation spectra of the fibers doped with photoactive nanoparticles, monitored at the same wavelength, are completely different in character. The lines are much broader, with an indistinct local maximum observed at around 240 nm. The spectral position of this maximum, which is different from the maximum observed in the case of the pure additive, may suggest the presence of energy transfer processes between the cellulose fiber and the fillers introduced. However,

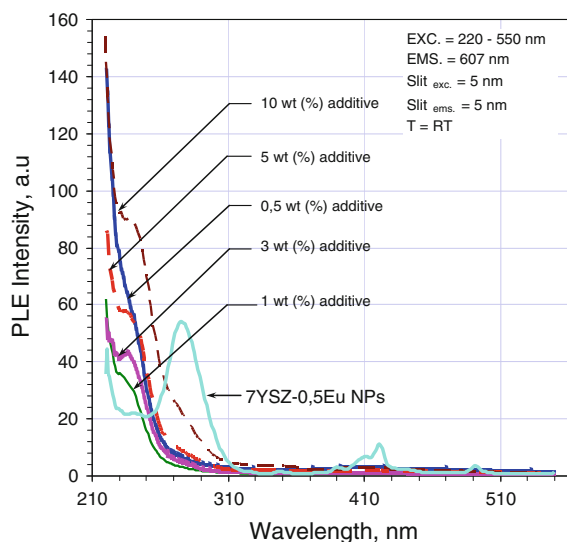
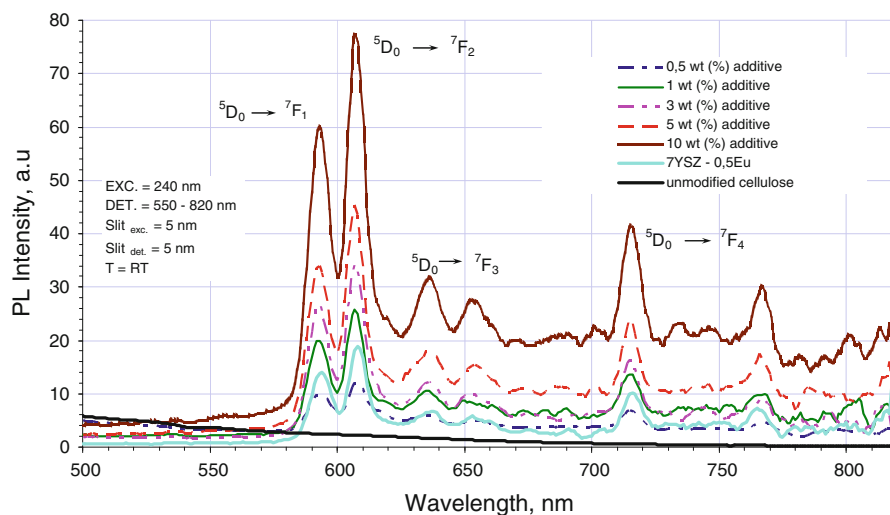


Fig. 6 Excitation spectra of regenerated cellulose fibers, fibers containing 7YSZ-0.5Eu nanoparticles (NPs) and 7YSZ-0.5Eu powder

this should be confirmed by further measurements (e.g. fluorescence dynamic profiles).

The emission spectra of the fibers with different concentration of lanthanide ion complexes and pure 7YSZ-0.5Eu obtained under excitation at 240 and 260 nm are shown in Figs. 7 and 8 respectively. All the luminescence spectra exhibit several emission peaks associated with the electronic transitions within the trivalent europium ion and originating from excited 5D_0 state to the 7F_j manifolds. On the basis

Fig. 7 Photoluminescence spectra of pure cellulose fibers, cellulose fibers with 7YSZ-0.5Eu and reference powder, the samples were excited by 240 nm wavelength



of the aggregate emission spectra shown in Figs. 7 and 8, it can be concluded that the number of chromophoric groups present in the fibers' material is small, and affects the emission characteristics of luminescent cellulose fibers only minimally.

The analysis of the spectral PL characteristics of the modified cellulose fibers showed that the emission intensity depends on the photoactive particle concentration in the polymer matrix, as well as on the excitation energy. Luminescence emission intensity expressed in arbitrary units is almost 2–3 times higher in each case for the fiber excited by electromagnetic radiation of a wavelength of 240 nm than in the case of the excitation wavelength of 260 nm.

A suitable amount of the modifier with luminescent properties ensures the utility of this type of product for application as an optical marker, for the protection of textiles, documents and various products. The product's authenticity can be checked with equipment generally available on the market for document security testers. In the case of textiles, one of the most important advantages is that the modifier closed in the cellulose matrix is stable, and cannot be easily removed from the fibers when they are in use or during washing.

Scanning electron microscope (SEM) observation

The distributions of particles on the fibers were determined by scanning electron microscopy (SEM). The intense white spots visible in the SEM-photos

Fig. 8 Photoluminescence spectra of pure cellulose fibers, cellulose fibers with 7YSZ-0.5Eu and reference powder by excitation at 260 nm

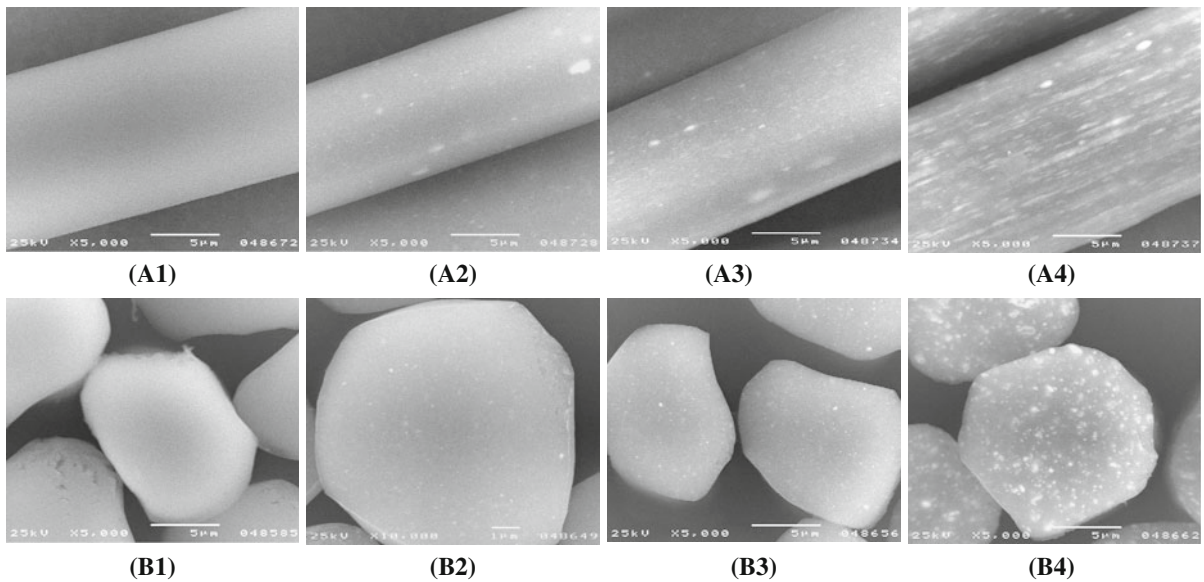
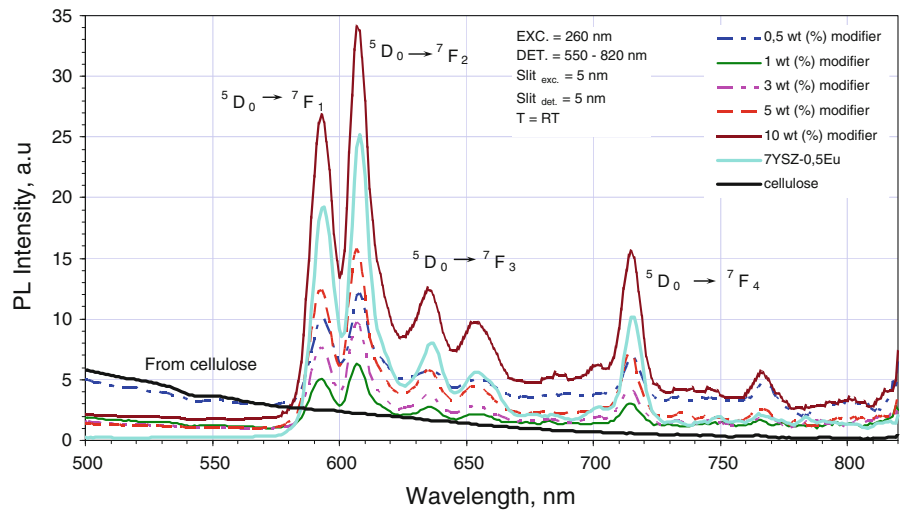


Fig. 9 SEM images of surface cellulose fibers (A1—unmodified fibers, fibers with 7YSZ-0.5Eu: A2—0.5 %, A3—5 %, A4—10 %) and cross-section (B1—unmodified fibers, fibers with 7YSZ-0.5Eu: B2—0.5 %, B3—5 %, B4—10 %)

(Fig. 9) are the grains of a photoactive modifier located very close to the surface of the photographed area of fibers. The less intense white dots are the grains of a modifier disposed in the depth of the cellulose matrix.

The analysis of the SEM images from the modified cellulose fibers proved that the 7YSZ-0.5Eu particles were randomly distributed both on the surface and inside the fibers (cross-section images), but the quality

of SEM images do not allowed, without any doubts to estimate the tendency to agglomeration. The SEM studies suggest that the agglomeration effect depends on the content of the modifier in the cellulose matrix but further investigation to fully explain this phenomenon are necessary. In the next step of research the Transmission Electron Microscopy (TEM) or Dynamic Light Scattering technique (DLS) would be applied. To avoid the tendency to agglomeration the

functionalization and particles surface modification methods should be applied in further experiments.

Conclusion

Cellulose fibers modified with photoluminescent nanoparticles (0.5 mol% of Eu^{3+} -doped ZrO_2 stabilized by 7 mol% Y_2O_3) were prepared. The fibers obtained contained from 0.5 to 10 % w/w of the modifier in the cellulose matrix. The combination of modern technology for manufacturing man-made cellulose fibers and manufacturing technologies of nanostructured materials allowed us to obtain interactive fibers with photoluminescent properties. Optical investigation of the modified cellulose fibers confirmed that the material developed has a high intensity of luminescence emission when exposed to the UV-C radiation of wavelengths ranging from 240 to 260 nm.

Two independent methods for measuring the modifier's contents show that the whole amount of the additive introduced during the cellulose dissolution process remains in the cellulose fibers. The presence of the photoluminescent modifier in the cellulose fibers' material decreases the tenacity and elongation of the final product. Fibers containing 10 % of the modifier have a tenacity only about 25 % lower than cellulose fibers without the modifier. Estimated mechanical properties of the cellulose fibers have high value of standard deviations, which is caused by the presence of inorganic particles, as well as a small scale of the spinning device. To achieve more uniform properties of the fibers, more affords should be done on the quality of the modifier. Further study should be focused on the synthesis of the modifier with possibly small size of particles with low tendency to agglomeration and very good luminescent properties. Above mentioned factors should allow to lower the modifier concentration in the cellulose fibers, which certainly improve the mechanical properties of the fibers.

The data obtained from the cross-section images of the modified cellulose fibers proves that the particles of the modifier are statistically distributed within the cellulose matrix. Together with the increasing concentration of the modifier, this increases the amount of relatively big size particles, which suggests the tendency of the modifier to agglomeration. For better effects of particle dispersion, more effective disintegration techniques should be applied.

A relatively good luminescence effect combined with the exceptional properties of the natural cellulose fibers leads us to expect these fibers to be an excellent material for various applications in the textile industry, as well as for the protection of documents, in the near future.

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