

Luminescent cellulose fibers activated by Eu^{3+} -doped nanoparticles

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Received: 8 September 2011 / Accepted: 20 April 2012 / Published online: 3 May 2012
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Abstract UV- active cellulose fibers were obtained by dry-wet method spinning an 8 % by weight α -cellulose solution in *N*-methylmorpholine-*N*-oxide (NMMO) modified by europium-doped gadolinium oxyfluoride $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ containing 5 mol (%) of the dopant. Photoluminescent nanoparticles were introduced in the in powder form into a polymer matrix during the process of cellulose dissolution in NMMO. The dependencies of emission intensity on excitation energy and the concentration of $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ nanoparticles in the final cellulosic products were examined by photoluminescence spectroscopy (excitation and emission). The fiber structure was studied by X-ray powder diffraction analysis. The size and dispersity of the nanoparticles in the polymer matrix were evaluated using scanning electron microscopy and X-ray microanalysis. The influence of different concentration particles (in the range from 0.5 to 5 % by weight) on the mechanical properties of the fibers, such as tenacity and elongation at break, were determined.

Keywords Interactive cellulose fibers · Nanoparticles · Photoluminescent materials

Introduction

Cellulose is an abundant natural polymer, which is of great importance in the production of various products such as textile fibers, paper etc. In the textile fiber industry, the oldest method for the manufacture of man-made cellulose fibers currently used is the viscose process (Ullmann's Fibers 2008).

Today, one of the relatively newer and most promising methods of making cellulose fibers from wood cellulose pulp is the so-called Lyocell process. This eco-friendly technology is based on the tertiary amine oxide *N*-methylmorpholine-*N*-oxide (NMMO) as the polymer direct solvent (Rosenau et al. 2001; Perepelkin 2007; Diener and Raouzeos 1999, 2001; Ik-Hyun et al. 2006). The NMMO process is very attractive and flexible because it permits the fabrication of a wide assortment of fibers, from classic fibers with microsize diameter to nanofibers formed by electrospinning (Kulpinski 2005). However, the latter is still far from being used at commercial level, but initial improvements of the method with a view towards scaling up the process have already been made. The addition of polymers, carbon black, metals and ceramics etc. to cellulose/NMMO-water mixture during the dissolving process leads to obtaining composite fibers with new functional properties

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(Laszkiewicz et al. 2005; Smiechowicz et al. 2011; Kulpinski 2007).

Recently, considerable interest in the group of luminescent nanomaterials has been focused on the oxide matrices containing optically active lanthanide ions (Dhanaraj et al. 2003; Liu et al. 2007; Wiglusz et al. 2009). Nonlinear optical materials are capable of emitting visible light of wavelengths above 400 nm under ultraviolet radiation. Also, infrared and near-infrared light-stimulated visible emissions in lanthanide-doped materials can be obtained by the up-conversion process (Liu and Chen 2007). These phenomena are related to the electron transitions inside the 4f subshell of lanthanide ions. Methods for synthesizing nanoscaled, luminescent inorganic particles, like the sol–gel process (Fu et al. 2006; Rzepka et al. 2007), the Pechini method (Ninjabdar et al. 2009), high-pressure hydrothermal synthesis (Chen et al. 2004; Fidelus et al. 2009), chemical coprecipitation (Karbowski et al. 2005) and the solvothermal method (Ninjabdar et al. 2009; Wiglusz et al. 2010) give excellent opportunities to obtain a wide range of nanoscaled powders doped with rare earth ions of various chemical structures, doping levels, and particle sizes & shapes (Karbowski et al. 2005; Wiglusz et al. 2010; Pechini 1967; Lu et al. 2010). These parameters influence the optical properties and chemical activity of such materials.

Photoactive inorganic complexes based on trivalent lanthanide ions and metal oxides can be successfully integrated with many kinds of polymer matrices, such as PUR (Ryszkowska et al. 2007), PMMA, PLA (Althues et al. 2007), PEO (Goubard et al. 2007).

In this paper, the properties of photoactive regenerated cellulose fibers prepared with the NMMO method are reported. The luminescence emission spectra of $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ nanopowder incorporated into a polymer matrix shows good photoluminescence, to be associated with the f–f transitions of the europium dope. The oxyfluoride based luminophors are excellent candidates for industrial applications due to their effective luminescence as well as high chemical and thermal stability (Grzyb and Lis 2011; Grzyb et al. 2010).

Luminescent modifications can be introduced to the various polymer materials and processed by different methods to produce films, fibers, molded pieces etc. Modified plastics can be used for ID-card and credit-card protection as well as for marking plastic products.

Among many other engineering materials, fibers appear to be one of the most interesting objects with huge potential applications.

The unique properties of luminescent cellulose fibers, together with the fact that the fibers can be very easily introduced into the paper pulp, make them a very suitable material for verifying the authenticity of documents. According to the experience of this paper's authors, adding a fraction of weight percent of luminescent fibers to the paper pulp is a good way of guaranteeing a document against falsification, because only a small quantity of the fibers is required to make sufficiently protected paper. This factor means the cost of such protection can be reduced. The use of yarn or threads containing the luminescent fibers when sewing the documents is another possible application. In this case, the addition of 10–20 % of luminescent cellulose fibers is enough to give the luminescent effect to the product obtained.

In the near future, cellulose fibers containing a precisely selected blend of luminescent modifiers could achieve the so-called fingerprint effect, with a unique photoluminescence spectrum which would be almost impossible to forge.

Luminescent yarn or threads can be also used for the protection of clothes and garments.

Experimental

Materials

Cellulose pulp containing 98 wt (%) of α -cellulose with an average polymerization degree of about 1,250 (\overline{DP}) and NMMO as 50 % aqueous solution (from Huntsman Holland BV, the Netherlands) were used for the preparation of the spinning dope. The propyl ester of gallic acid (Tenox PG[®]) from Aldrich (Gillingham, Dorset, UK) was applied as an antioxidant (stabilizers of molecular weight).

The cellulose fibers' properties were modified with Eu^{3+} doped gadolinium oxyfluoride. The $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ nanopowders with a dopant concentration of 5 mol (%) were obtained by the precipitation of fluorides by means of NH_4F in the melt stearic acid. In a typical way 1 M $\text{Eu}(\text{NO}_3)_3$ and $\text{Gd}(\text{NO}_3)_3$ solutions were prepared by dissolving oxides in nitric acid HNO_3 . Stearic acid (100 g) were put in the

round-bottomed flask and heated to 80 °C (stearic acid melts at 70 °C). Appropriate amounts (per 1 g of the product) of Ln^{3+} solutions were added to molten stearic acid and the flask was heated until water from added solutions was evaporated. In second flask, stearic acid (50 g) and ammonium fluoride (with 25 % excess to the stoichiometric amount) were mixed and the mixture was heated. To begin the reaction, solution from second flask was slowly added to first flask under vigorously stirring and the whole mixture was heated at 350 °C for 1 h. The final nanoparticles were obtained by annealing the precursor for 45 and 60 min at 700 °C.

Instrumentation

The cellulose solutions in NMMO with additive were obtained using a high-efficiency laboratory-scale IKAVISC[®] kneader type MKD 0.6-H60, supplied by IKA-Analysentechnik GmbH (Heitersheim, Germany).

The fibers were formed by the dry-wet method on a laboratory-scale piston-spinning device using a spinneret with 18 orifices of 0.4 mm diameter.

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 additive were analyzed by X-powder diffraction using a Siemens DV 5000 polycrystalline diffractometer (XPART-PRO system) with Cu-K α 1 and Cu-K α 2 radiation ($\lambda = 1.5418$ and $\lambda = 1.5444$ Å). 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 the modified fibers were recorded at room temperature on a Hitachi F-7000 spectrofluorometer.

The SEM images of the fiber surfaces and cross-sections were obtained with a JEOL 5200 LV SEM (scanning electron microscope) from JEOL Ltd. (Tokyo, Japan).

The photoluminescent particles' distribution on the fibers' surface was determined by X-ray microanalyses with the use of the SEM JSM 5400 equipped with an EDX LINK ISIS energy dispersion analyzer with specific X-ray radiation (Oxford Instruments).

Preparation of the fibers

The spinning dope was prepared from appropriate amounts of cellulose pulp, a 50 % aqueous solution of NMMO, and propyl ester of gallic acid. The modifier was applied in powder form, and was introduced to the system at the beginning of the dissolution process in such a quantity as to reach a suitable concentration between 0.5 and 5 % w/w of $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ nanopowder in the dry cellulose fibers. Before the modifier was introduced to the NMMO-water-cellulose system, the particles of the modifier were disintegrated in a ball mill. The starting mixture was continuously stirred and heated for about 100 min; during this time the temperature in the kneader was raised to 120 °C. The water was removed from the reaction mixture under low-pressure conditions until the water content in solution reached a level of about 14 wt (%).

The fibers were formed by the dry-wet method from an 8 wt (%) cellulose solution in NMMO-H₂O. The spinning dope was placed in the cylinder and heated to a temperature of around 115 °C. The spinning solution was forced in a melt state through the set of steel meshes (250 Mesh) and then through the spinneret holes into an airspace of 10 mm in length, and then immersed in an aqueous solidification bath at 20 °C. The spinning solution flow rate through individually capillary was about 1 m/min. The cellulose filaments were spun at a take-up speed of 70 m/min. Finally, the fibers were washed out in cold water and dried at room temperature.

Results and discussion

X-ray powder diffraction

X-powder diffraction (XRD) was used to examine both the pure cellulose fibers and those with additions of 0.5, 1 and 5 wt (%) of $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$. The XRD data are shown in Fig. 1.

It is known that the diffraction peak at about (110): 14.7°(2θ) and (002): 22.5°(2θ) are from cellulose I, and the peak at about (110): 12.3°(2θ), (1–10): 20.1°(2θ) and (020): 21.9°(2θ) are 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 about

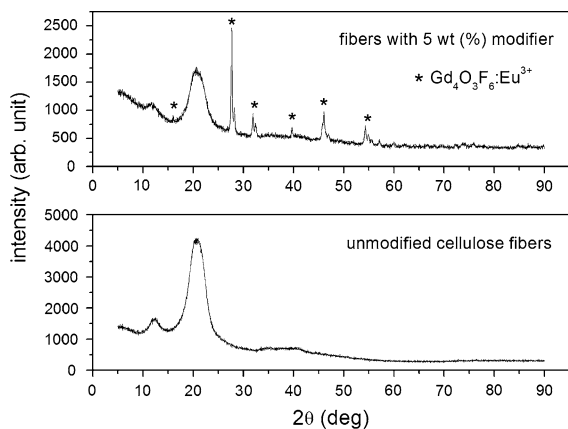


Fig. 1 X-ray diffraction patterns of regenerated cellulose and cellulose with $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$

27° , 32° , 39° , 46° , 54° , 57° (2θ) are recognized as the characteristic peaks of the modifier, and originate from tetragonal $\text{Gd}_4\text{O}_3\text{F}_6$ (JCPDS database no. 026–0658). The intensities of all these peaks are proportional to the content of modifier in the polymer matrices. The results obtained by XRD measurements suggest that the presence of additive in the cellulose fibers does not influence the structure of the cellulose matrix.

Mechanical properties

The mechanical properties of the fibers were checked on a Zwick Z2.5/TN1S tensile testing machine, according to 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 depends on the concentration of the modifier in the fibers, and fell within the range from 0.220 to 0.274 tex.

The results of the measurements of mechanical properties such as tenacity and elongation at break of

cellulose fibers with different modifier concentrations are shown in Table 1.

However, the measured mechanical properties of the fibers have a relatively high value of standard deviation, but the data suggest that the tenacity and elongation at break of the cellulose fibers obtained are dependent on the concentration of $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ particles. The unmodified fibers have the highest tenacity, equal to about 28.4 cN/tex. The presence of modifier in the final fibers reduced the products' tenacity. Increasing the concentration of inorganic particles in the cellulose fibers to values up to 5 wt (%) led to a reduced fiber tenacity at break of about 40 %.

Increasing the concentration of the modifier also affected the fibers' elongation at break. Introducing inorganic additive into the cellulose fibers decreased elongation. This phenomenon may have occurred because the rising concentration of inorganic particles reduces the elasticity of the fibers. The relatively low elongation at break could be adjusted to some extent by changing the fibers' solidification conditions during the spinning process.

The results given above concerning the mechanical properties of the cellulose fibers may suggest that more attention should be paid optimizing the modifier synthesis process. The process should at the final step result in the water- or alcohol-stable dispersion of nanoparticles with minimum agglomerations.

The method applied at present requires annealing, which inevitably leads to the generation of agglomerates. The presence of relatively large particles and agglomerates in the polymer matrix affected the mechanical properties, which is apparent not only in significant falls of the estimated values of the modified fibers, but also in the high value of standard deviations of the results obtained.

The other possible reason for the fibers' irregularity is the small scale of the spinning device, which results

Table 1 Effect of the modifier 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	0.230	28.40	6.59	7.79	1.51
0.5	0.220	27.56	5.22	8.88	1.60
1.0	0.274	17.38	4.04	7.55	1.67
3.0	0.250	16.17	4.25	7.11	1.62
5.0	0.250	16.38	4.38	7.38	1.64

in a relatively large spread of estimated values of the filament fibers produced.

The luminescent cellulose fibers are thought to be a kind of security marker rather than a real raw material for textile production. When used as protection, those fibers could only be added in a small quantity to the supporting material such as paper, cotton or polyester yarn or polymer films. From this point of view, the fibers' excellent mechanical property is not an essential feature for many applications.

The photoluminescence (PL) properties of fibers

The luminescent properties of the modified cellulose man-made fibers were examined. As shown in Fig. 2, the excitation spectra of Eu^{3+} doped gadolinium oxyfluoride particles introduced into the celluloses were obtained by monitoring the strongest emission wavelength from the Eu^{3+} ion under a 258 nm excitation wavelength. The excitation spectra consist of a broad, large excitation band extending from 226 to 298 nm, dominated by a peak centred at 254 nm (maximum), and multiple small peaks with their center localized at longer wavelengths in powder form respectively. The broad band is characteristic of charge transfer between O^{2-} and Eu^{3+} ions (Dorenbos 2003). The narrow peaks at 274, 294, 303, 312 and 318 nm are connected with f–f transitions of the Gd^{3+} ion, and demonstrated the energy transfer from Gd^{3+} to Eu^{3+} ions (Liu et al. 2006).

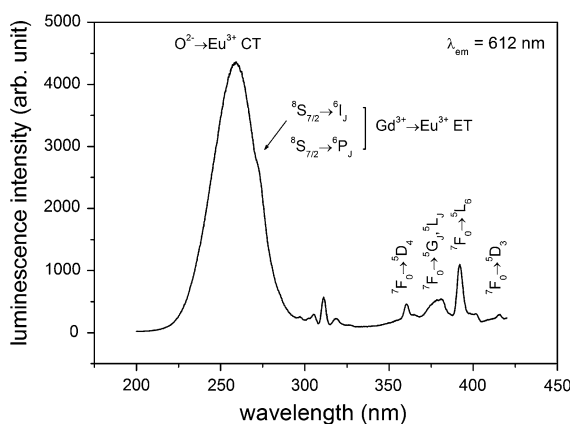


Fig. 2 Excitation spectra of cellulose fibers modified by 5 % of dopant, monitored at 612 nm

Other peaks localized above 350 nm are typical f–f transitions of the Eu^{3+} ion, with the most intense band at 392 nm.

The emission spectra of the fibers with different concentrations of lanthanide ion complexes by excitation at 258 nm are shown in Fig. 3. The emission luminescence spectra exhibits several emission peaks which are associated to the trivalent europium ion electronic transitions from excited states $^5\text{D}_1$ and $^5\text{D}_0$ to the multiplet $^7\text{F}_{0-4}$ (Lis 2002).

An analysis of the PL spectral characteristics of the modified cellulose fibers showed that the emission intensity strongly depended on the concentration of photoactive particles in the polymer matrix. Presence of the bands connected with transitions from higher $^5\text{D}_1$ level indicates small quenching of the Eu^{3+} ions by $-\text{OH}$ oscillators originating from cellulose (Klonkowski et al. 2003).

SEM and SEM + EDS observation

To estimate the size and distributions of the particles on the fibers, scanning electron microscopy (SEM) and the SEM + EDS method were applied. The low vacuum technique was applied in the SEM method. This technique allows us to observe not only objects which are just on the surface of the sample, but also to perceive some particles lying just below the sample surface. Because the nature and structure of cellulose and inorganic particles ($\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$) are totally

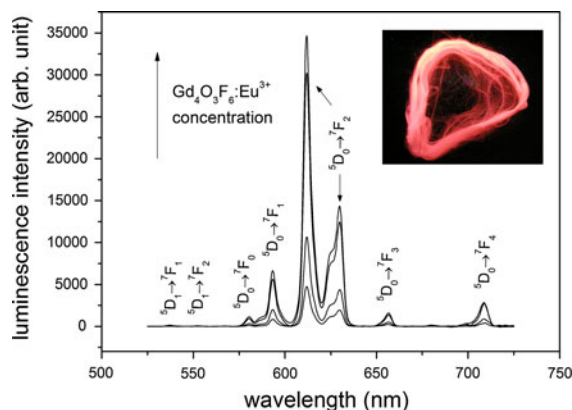


Fig. 3 Photoluminescence spectra of cellulose fibers with increasing concentration of $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ (0, 5; 1; 3 and 5 %) using excitation at 258 nm. The inset shows the emission of cellulose fibers with 3 % of $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ excited by UV lamp, 254 nm

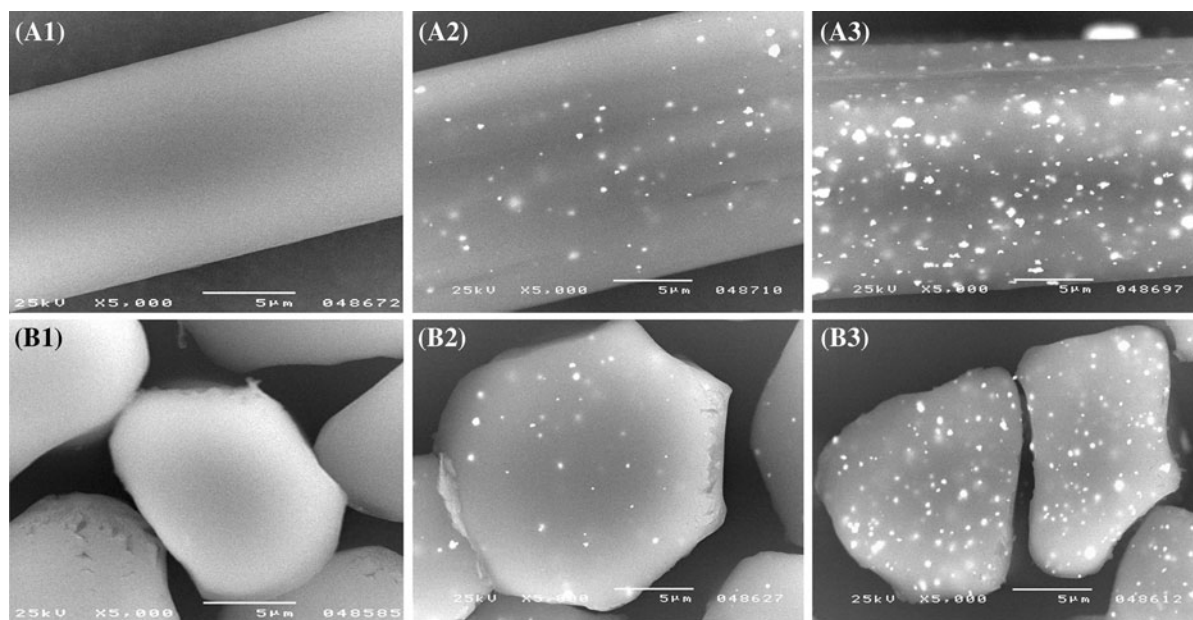


Fig. 4 SEM images of surface cellulose fibers (A1—unmodified fibers, fibers with $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$: A2—1 %, A3—5 %) and cross-section (B1—unmodified fibers, fibers with modifier: B2—1 %, B3—5 %)

different, those two phases reflect and diffuse the electron beam in different ways, so the contrast of two materials is rather high, and the modifier particles are very clearly visible in the SEM images. In Fig. 4 (A2, A3, B2 and B3) there are several intensive white spots, which are the grains of the photoactive modifier located just on a layer very close to the fibers' surface. The less intensive and dimmer white dots are the grains of modifier disposed within the depth of the cellulose matrix.

An analysis of the modified cellulose fibers' SEM images showed that the $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ particles were distributed randomly on the surface as well as inside the fibers (cross-section images), but some of these particles had become aggregated. The tendency of the modifier to form the agglomerates into cellulose matrices increased with the increase of modifier concentration into fiber-forming polymer.

According to the image analysis based on the SEM images of the modified fibers, about 80 % of the total amount of particles were found in the diameter below 300 nm for fibers containing between 0.5 and 1 % of the modifier.

ESD linear analysis (Fig. 5) proved the presence of chemically unchanged modifier particles. The analysis showed that some places on the fibers' surfaces contain elevated concentrations of the elements such

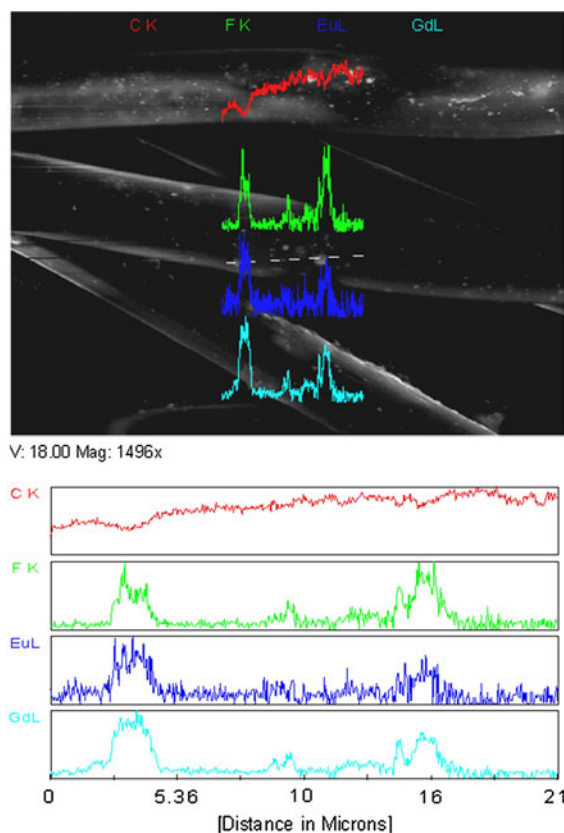


Fig. 5 Linear EDS analysis of the surface of cellulose fibers with a 5 wt (%) $\text{Gd}_4\text{O}_3\text{F}_6:\text{Eu}^{3+}$ addition

as F, Eu and Gd, which correspond to the chemical composition of the modifier.

Unfortunately the SEM + EDS linear analysis (Fig. 5) of surface fibers also confirmed the presence of large clusters of $\text{Gd}_4\text{O}_3\text{F}_6\text{:Eu}^{3+}$ particles in the fibers.

The SEM and EDS analyses showed that future research should also focus on achieving the better dispersion of the modifier throughout the cellulose matrix.

Conclusions

Cellulose fibers with luminescent properties were prepared by the NMMO method. The modifier was introduced to the spinning dope during the cellulose dissolution process, and the fibers were spun by means of the dry-wet method. The fibers obtained contained from 0.5 to 5 % w/w of modifier emitting red light upon stimulation with UV-C radiation. The intensity of optical signals was strictly dependent on the amount of additive in the polymer matrix.

The results obtained by XRD measurements suggest that the presence of additive in the cellulose fibers does not influence the structure of the cellulose matrix.

The presence of the modifier particles in the cellulose matrix causes a decrease in the fibers' tenacity. Fibers containing 5 % of the luminescent modifier have about 40 % lower tenacity than cellulose fibers without the modifier. The decrease in the fibers' tenacity is mainly caused by the presence of a non-fiber forming phase ($\text{Gd}_4\text{O}_3\text{F}_6\text{:Eu}^{3+}$), and to some extent by the fact that the particles of the modifier tend to agglomerate. Another important reason for the drop in the fibers' tenacity could be the method of preparing the modifier, which in the final step requires annealing. This causes the particles to stick together and form agglomerates, which are very difficult to disperse in the spinning dope.

For fibers containing up to 1 % of the modifier, about 80 % of the total amount of particles have a diameter below 300 nm. The higher the concentration of the modifier, the more agglomerated the particles become. Further investigation should focus on developing more efficient methods to reduce the size of the modifier particles, as well as on methods for reducing the tendency to agglomeration.

Another open question is the stability of the composite fibers and the problem connected with leaching the modifier. However, the particles of the modifier are closed in the polymer matrix, and they seem to be firmly trapped in the polymer, but of course it is possible that some particles could have been removed from the fibers. This may take place during the mechanical wearing process, and also when the fibers are repeatedly subjected to washes or soaked with water. The aging tests carried out on cellulose-type fibers containing a modifier with thermochromic properties showed that the stability of the fibers can be extended to over 10 years. Additional research connected to the estimation of leaching, particularly for luminescent fibers, should be carried out in the near future.

Fibers with these properties can be used for the security marking of documents, papers and textile products.

Acknowledgments T. G. gratefully acknowledges the financial support in the form of the VENTURES project operated by the Foundation for Polish Science and financed by the EU European Regional Development Fund, Ventures/2009-4/2. This work was also partly supported by grant no. NN 508 623 240 of Ministry of Science and Higher Education (Poland).

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References

- Althues H, Simon P, Kaskel S (2007) Transparent and luminescent $\text{YVO}_4\text{:Eu}$ /polymer nanocomposites prepared by in situ polymerization. *J Mater Chem* 17:758–765
- Chen L, Liu Y, Li Y (2004) Preparation and characterization of $\text{ZrO}_2\text{:Eu}^{3+}$ phosphors. *J Alloy Compd* 381:266–271
- Dhanaraj J, Jagannathan R, Trivedi DC (2003) $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ nanocrystals—synthesis and luminescent properties. *J Mater Chem* 13:1778–1782
- Diener A, Raouzeos G (1999) Continuous dissolution process in direct cellulose in NMMO. *Chem Fibers Int* 49:40–42
- Diener A, Raouzeos G (2001) Optimization of cellulose dissolution stage in Lyocell process as origin for different applications. *Chem Fibers Int* 51:260–261
- Dorenbos P (2003) Systematic behaviour in trivalent lanthanide charge transfer energies. *J Phys-Condens Mat* 15:8417. doi:10.1088/0953-8984/15/49/018
- Fidelus JD, Yatsunenko S, Godlewski M, Paszkowicz W, Werner-Malento E, Lojkowski W (2009) Relation between structural properties of Pr^{3+} -doped yttria-stabilized zirconia nanopowders and their luminescence efficiency. *Scripta Mater* 61:415–418

- Fu X, Niu S, Zhang H, Xin Q (2006) Photoluminescence of Dy^{3+} ions in yttrium-stabilized zirconium oxide with different phases. *Mater Sci Eng B-Adv* 129:14–17
- Goubard F, Vidal F, Bazzi R, Tillement O, Chevrot C, Teyssie D (2007) Synthesis and luminescent properties of PEO/lanthanide oxide nanoparticle hybrid films. *J Lumin* 126: 289–296
- Grzyb T, Lis S (2011) Structural and spectroscopic properties of $\text{LaOF}:\text{Eu}^{3+}$ nanocrystals prepared by the sol–gel Pechini method. *Inorg Chem* 50:8112–8120
- Grzyb T, Weclawiak M, Lis S (2010) Synthesis and photophysical properties of $\text{LaOF}:\text{Eu}^{3+}$ nanocrystals. *Terrae Rarae* 19:1–5
- Ik-Hyun K, Soo-Myung Ch, Tae-Jung L (2006) Industrial cellulose fiber and process for its production. EP 1 657 327 B1
- Karbowiak M, Mech A, Kempinski L, Mielcarek W, Hubert S (2005) Effect of crystallite size on structural and luminescent properties of nanostructured $\text{Eu}^{3+}:\text{KGdF}_4$ synthesised by co-precipitation method. *J Alloy Compd* 400:67–75
- Klonkowski AM, Lis S, Pietraszkiewicz M, Hnatejko Z, Czarnobaj K, Elbanowski M (2003) Luminescence properties of materials with $\text{Eu}(\text{III})$ complexes: role of ligand, coligand, anion, and matrix. *Chem Mater* 15:656–663
- Kulpinski P (2005) Cellulose nanofibers prepared by the N-methylmorpholine-N-oxide method. *J Appl Polym Sci* 98:1855–1859
- Kulpinski P (2007) Cellulose fibers modified by hydrophobic-type polymer. *J Appl Polym Sci* 104:398–409
- Laszkiewicz B, Kulpinski P, Niekraszewicz B, Czarnecki P, Rubacha M et al (2005) The method of making modified cellulose fibers. EP 1 601 824 B1
- Lis S (2002) Luminescence spectroscopy of lanthanide(III) ions in solution. *J Alloy Compd* 341:45–50
- Liu CH, Chen DP (2007) Controlled synthesis of hexagon shaped lanthanide-doped LaF_3 nanoplates with multicolor upconversion fluorescence. *J Mater Chem* 17:3875–3880
- Liu C, Liu J, Dou K (2006) Judd–Ofelt intensity parameters and spectral properties of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystals. *J Phys Chem B* 110:20277–20281
- Liu L, Ma E, Li R, Liu G, Chen X (2007) Effects of phonon confinement on the luminescence dynamics of Eu^{3+} in Gd_2O_3 nanotubes. *Nanotechnology* 18:015403. doi:10.1088/0957-4484/18/1/015403
- Lu C-H, Wu T-Y, Hsu C-H (2010) Synthesis and photoluminescent characteristics of Sr_2CeO_4 phosphors prepared via a microwave-assisted solvothermal process. *J Lumin* 130: 737–742
- Ninjbardgar T, Garnweitner G, Börger A, Goldenberg ML, Sakhno VO, Stumpe J (2009) Synthesis of luminescent $\text{ZrO}_2:\text{Eu}^{3+}$ nanoparticles and their holographic sub-micrometer patterning in polymer composites. *Adv Funct Mater* 19:1819–1825
- Pechini M (1967) Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor. US patent 3(330):697
- Perepelkin KE (2007) Physicochemical principles of spinning of natural fibroin fibres and ways of using them in chemical fibre technology. Part 2. Structure and properties of natural fibroin fibres. Use of principles of biomimetics in developing chemical fibre technologies. *Fibre Chem* 39: 363–371
- Rosenau T, Potthast A, Sixta H, Kosma P (2001) The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process). *Prog Polym Sci* 26: 1763–1837
- Ryszkowska J, Zawadzka EA, Hreniak D, Lojkowski W, Opalinska A, Kurzydowski KJ (2007) Structure and properties of polyurethane nanocomposites with zirconium oxide including Eu . *J Mater Sci Eng C* 27:994–997
- Rzepka A, Ryba-Rymanowski W, Diduszko R, Lipinska L, Zajaczkowska A (2007) Growth and characterization of Nd, Yb—yttrium oxide nanopowders obtained by sol-gel method. *Cryst Res Technol* 42:1314–1319
- Smiechowicz E, Kulpinski P, Niekraszewicz B, Bacciarelli A (2011) Cellulose fibers modified with silver nanoparticles. *Cellulose* 18:975–985
- Ullmann's Fibers (2008) Fiber classes, production and characterization. In: Krässig H, Schurz J, Stedman RG et al (eds) *Cellulose*. Wiley, Weinheim, pp 335–389
- Wiglusz R, Grzyb T, Lis S, Strek W (2009) Preparation and spectroscopy characterization of $\text{Eu}:\text{MgAl}_2\text{O}_4$ nanopowder prepared by modified Pechini method. *J Nanosci Nanotechnol* 9:5803–5810
- Wiglusz RJ, Grzyb T, Lis S, Strek W (2010) Hydrothermal preparation and photoluminescent properties of $\text{MgAl}_2\text{O}_4:\text{Eu}^{3+}$ spinel nanocrystals. *J Lumin* 130:434–441