Luminescent Cellulose Fibers Modified With Cerium Fluoride Doped With Terbium Particles

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This article describes UV-active cellulose fibers obtained by dry-wet spinning method. The fibers have been formed from an 8% by weight cellulose solution in N-methylomorpholine-N-oxide (NMMO) modified by Ce0.85Tb0.15F3 nanocrystals. The modifier was synthesized by wet chemical method, coprecipitation approach. The host was chosen as the most promising one for the green emitting Tb3+ ions. Photoluminescent nanoparticles were introduced into the polymer matrix during the process of dissolving cellulose in NMMO. The modifier occurred in the form of white paste, consisting of luminescent nanoparticles dispersed in glycerine. The dependencies between the concentration of nanocrystals, emission intensity, and excitation energy of the final cellulosic luminescent products were examined by photoluminescence spectroscopy. The size and structure of Ce0.85Tb0.15F3 nanocrystals were studied by X-ray powder diffraction analysis. The dispersion of the nanoparticles in the polymer matrix was evaluated using scanning electron microscopy and transmission electron microscopy. The real content of luminescent nanocrystals in the fibers was estimated as well. The influence of different concentrations of modifier particles (in the range from 0.5 to 5% by weight) on the mechanical properties of the fibers was determined. POLYM. COMPOS., 37:153–160, 2016. © 2014 Society of Plastics Engineers

INTRODUCTION

The world we live in undergoes a technical revolution that has affected our lives in every kind of aspects. People have access to unusual and innovative products that can be used for special applications and improve our lives. The creativity of scientists is endless and, as it is said in the introduction to Transmaterial “more new products have been developed in the last twenty years than in the prior history of materials science” [1]. This revolution also includes a transformation of the existing and well-known technologies into advanced, environmentally friendly and forward-looking industry sectors with the use of the newest, cutting-edge ideas. The changes have occurred not only in fields like electronics or medicine but also in the textile and fibers industry, and turned the traditional technologies into creative manufacturing of modified textile products. Department of Man-Made Fibers has been involved in this activity for many years. With the use of cellulose, which is one of the most widespread biopolymers possessing numerous advantages [2, 3], and the N-methylomorpholine-N-oxide (NMMO) method of forming modified regenerated cellulose fibers [4], the creation of innovative fibers with special applications has been widely developed. Importantly, there is much interest in incorporating nanomaterials as modifiers into the polymer matrix. Nanomaterials, due to their properties, provide many additional advantages [5]. Thanks to the use of a patented method [6], the following modified cellulose fibers have been obtained: fibers with silver nanoparticles [7], thermochromic fibers [8], magnetically active cellulose fibers [9], or fibers modified with silicon dioxide nanoparticles [10]. There is also much interest in luminescent modifications of regenerated cellulose fibers, and some of the investigations connected with this issue are shown below.

In this article, the results of forming luminescent cellulose fibers, with the application of nanomaterials doped with lanthanide ions (Ln3+) are presented. This kind of nanomaterials has been widely investigated in recent years due to their spectroscopic properties, as well as a wide range of potential applications. The properties of Ln3+ ions could be useful in designing new phosphors for optoelectronics; however, medicine and biology can also benefit from their properties [11, 12]. Such effects like charge transfer and energy transfer (ET), typical for Ln3+-doped materials, could effectively enhance the observed luminescence and colour of the materials [13]. Moreover, the nanocrystalline structure of Ln3+-doped compounds is advantageous and makes it possible to use
the compounds in the areas where micro-size particles materials could not be applied. Our previous studies, concerning modification of cellulose fibers by Eu$^{3+}$-doped nanomaterials have proven that the morphology and size of modifiers are important factors [14, 15]. They must be small enough to be introduced into fiber structure without negative effects on its mechanical properties. Rare earth fluorides are excellent hosts for luminescent ions like Eu$^{3+}$ and Tb$^{3+}$ [16–18]. Low phonon energy of fluorides is responsible for small quenching of luminescent dopants, and therefore bright and effective emission [19]. Fluorides could be synthesized by a relatively easy wet chemical method, like the coprecipitation approach. The presence of organic compounds or surfactants usually results in smaller nanocrystals with low aggregation factor. By selecting an appropriate composition of the fluoride host being a matrix for luminescent Tb$^{3+}$ ions, green luminescence, as well as absorption of excitation light can be strongly improved. In our previous report, we have studied various rare-earth fluorides as the matrices for Tb$^{3+}$ activators [20]. The most promising system, investigated and used as modifier for cellulose fibers, was CeF$_3$ doped with 15% of Tb$^{3+}$ ions. This material, due to the allowed f-d transition of Ce$^{3+}$ ions, could effectively absorb UV light in the range of 200–300 nm. The energy could be transferred to the Tb$^{3+}$ ions, which resulted in green emission.

In this article, the properties of photoactive luminescent cellulose fibers obtained by dry-wet spinning method with the use of NMMO as a direct solvent of cellulose are presented. The fibers were modified with Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanocrystals doped with 15 mol% of Tb$^{3+}$ ions. This kind of an innovative material seems to be one of the most interesting, and due to its unique properties has many potential applications, for example paper and clothing protection (the so called fingerprint effect).

**EXPERIMENTAL**

**Materials**

To prepare the spinning dope cellulose pulp containing 98% wt of α-cellulose and 50% aqueous solution of NMMO (from Huntsman Holland BV, the Netherlands) were used. For the stabilization of the molecular weight (as an antioxidant), propyl ester of gallic acid (Tenox) from Aldrich (Gillingham, Dorset, UK) was used. The modifier of the cellulose luminescent fibers was cerium fluoride doped with 15% mol of terbium ions. The modifier was prepared at the Department of Rare Earths, Faculty of Chemistry at Adam Mickiewicz University, by the method described further in the text.

**Instrumentation**

To obtain cellulose solutions from which the fibers were formed, high efficiency laboratory-scale IKAVISC kneader type MKD 0.6-H60 was used. The fibers were formed with the use of dry-wet spinning method on a laboratory-scale piston-spinning device with a spinneret equipped with 18 orifices of 0.4 mm diameter.

The X-ray diffraction patterns (XRD) were measured with a Bruker AXS D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.541874$ Å) in the 2θ ranges from 20° to 60°. Scanning electron microscopy images (SEM) were measured on CAIS EVO 40 (accelerating voltage of 19–20 kV).

The excitation and emission spectra, as well as luminescence lifetime measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer at room temperature, with the use of powder samples. Excitation and emission spectra were corrected for the instrumental response. The measured luminescence decays showed nonexponential character. Lifetime decrease may be approximated by an exponential function, therefore to calculate lifetime values, the obtained decays were matched with the applied exponential function: $I = I_0 + A \exp \left(-t/\tau\right)$ Luminescence lifetimes were calculated with the help of OriginLab 8.5 software. The goodness of fit time traces was not lower than $R^2 = 0.998$ and errors not higher than $\tau_{err} < 0.01$ ms.

To determine the amounts of nanocrystals in the fibers, 0.25 g of modified fibers were annealed at 1000°C for 3 h. The calculations of dopant amounts were done on the basis of the obtained mixture of CeO$_2$ + Tb$_2$O$_3$. To estimate the real content of the modifier in the fiber material, thermogravimetric analysis (TGA) was performed, using a Perkin–Elmer TGA-6 device. Measurements were carried out in the temperature range from 100 to 800°C in the airflow.

To evaluate the distribution of modifier nanoparticles in the fiber matrix, SEM observations were performed. The SEM images of the fiber surface and cross-sections were obtained with a JEOL 5200 LV SEM (scanning electron microscope) from JEOL (Tokyo, Japan). Transmission electron microscope (TEM) technique was used to precisely evaluate the size and distribution of modifier nanoparticles in the polymer matrix. TEM images were measured by JEM 1200 EXII, JOEL transmission electron microscope, using an accelerating voltage of 80 kV. The influence of the different content of Ce$_{0.85}$Tb$_{0.15}$F$_3$ particles on the mechanical properties of the fibers was measured on a Zwick Z2.5/TN1S tensile testing machine, in accordance with Polish standard PN-85/P-04761/04. Linear density of the fibers was measured according to Polish standard PN-72/P-04800.

**Synthesis of Ce$_{0.85}$Tb$_{0.15}$F$_3$ Nanocrystals**

Luminescent nanocrystals were synthesized by a simple, coprecipitation method in the presence of glycerine. This organic compound acted as a surface modifier, preventing uncontrolled growth of particles, and as the factor increasing solubility of nanocrystals in water. In this
method the starting materials were: glycerine $\mathrm{CH_2(OH)-CH(OH)CH_2(OH)}$ (POCh S.A., pure, 99.5%), ammonium fluoride $\mathrm{NH_4F}$ (POCh S.A., ACS grade, 98+%), $\mathrm{CeCl_3/6H_2O}$ (Carl Roth, 99.9%), and $\mathrm{Tb_4O_7}$ (Stanford Materials, 99.99%). Terbium oxide was dissolved in $\mathrm{HNO_3}$ (POCh S.A., ultra-pure) and evaporated to dryness several times to remove the excess of $\mathrm{HNO_3}$. From cerium chloride and terbium nitrate, 1 M solutions were prepared.

According to our previous report, we have chosen $\mathrm{CeF_3}$ as the most promising host for the green emitting $\mathrm{Tb^{3+}}$ ions [10]. The concentration of dopant ions has been set at 15% showing the most intensive luminescence and quantum yield. To synthesize 1 g of $\mathrm{Ce_{0.85}Tb_{0.15}F_3}$ nanocrystals, 25 mL glycerine, 4.25 mL $\mathrm{CeCl_3}$ and 0.75 mL of $\mathrm{Tb(NO_3)_3}$ solutions were mixed and diluted to 100 mL by distilled water. The second solution containing $\mathrm{NH_4F}$ was prepared in a similar way: 25 mL of glycerine, 0.56 g of $\mathrm{NH_4F}$ (with 25% excess) were mixed and diluted to 100 mL by distilled water. Next, to the intensely stirred and heated to 50$^\circ$C solution of $\mathrm{Ce^{3+}}$ and $\mathrm{Tb^{3+}}$ ions, the second mixture was slowly added over 30 min, while maintaining the temperature at 50$^\circ$C and stirring for additional 30 mins. The obtained white precipitate was collected by centrifugation and washed with water several times. The resulting white paste was used in the synthesis of fibers as luminescent modifier.

**Preparation of Luminescent Cellulose Fibers**

Regenerated cellulose fibers with luminescent properties were obtained by a well-known method described in previous reports [4]. A difference was observed in the characteristics of the modifier which was dispersed in glycerine. Appropriate amounts of cellulose pulp, 50% NMMO aqueous solution, antioxidant, and the white paste of luminescent modifier were introduced to the IKAVISC kneader. The process of dissolving cellulose was carried out under reduced pressure and with temperature rising up to around 115$^\circ$C. Water was being removed during this process until its concentration in the cellulose solution reached about 14% wt. The content of luminescent nanocrystals served as a basis for calculating the amount of modifier, which was estimated by means of thermogravimetric analysis at the level of about 40%. Based on this value, the next step was to calculate an appropriate amount of modifier, which should be incorporated into the spinning dope so as to reach the assumed content of it in the fibers (0.5, 1, 3, and 5%wt). The whole process of
preparing cellulose pulp lasted about 1.5 h. Afterwards, the fibers were formed by dry-wet spinning method. The spinning dope was introduced into a cylinder and heated to 115°C. Then, it was forced through a set of steel meshes and spinneret holes into an air gap and immersed into an aqueous solidification bath, the temperature of which was 20°C. The fiber filaments were take-up with the speed of 55 m/min. The final product was washed in distilled water and dried in room temperature.

RESULTS AND DISCUSSION

Characteristics of the Obtained Luminescent Nanocrystals

Cerium fluoride crystallized as hexagonal nanocrystals with space group $P3_1c1$. Figure 1 shows XRD patterns of the obtained $\text{Ce}_{0.85}\text{Tb}_{0.15}\text{F}_3$ nanocrystals compared with reference from the ICSD database (Inorganic Crystal Structure Database). All peaks can be well indexed with hexagonal $\text{CeF}_3$. The slight shift of peaks maxima is connected with the substitution of $\text{Ce}^{3+}$ ions in the crystal lattice by $\text{Tb}^{3+}$ dopants. Relatively wide peaks are characteristic for nanosized crystals, and the main reasons for this observation are the decreased crystallinity and the presence of defects, comparing with ideal hexagonal structure of $\text{CeF}_3$.

Morphology of the synthesized nanomaterials was examined by TEM. Figure 2 shows TEM images of as-prepared nanocrystals. They crystallized as small nan plates with quite good dispersion of their sizes. The sizes of most of the crystals were in the range of 5–25 nm, and the average size was 13 nm. The presented images also show a small agglomeration of crystals, which is a direct result of glycerin presence on their surface [10]. An appropriate morphology of this material is an important factor for further modifications of cellulose fibers, the thickness of which does not exceed several micrometers (see Fig. 3). Small sizes of nanocrystals as well as their decreased agglomeration facilitate the introduction of particles inside the fibers during their synthesis. Furthermore, mechanical properties of such fibers are similar to those not modified.
Estimation of the Real Content of a Modifier in the Fibers

To estimate the real content of the luminescent modifier introduced into the fiber structure the fibers were examined by means of TGA method. The measurement was done according to the method described elsewhere [10]. The results obtained by thermogravimetric method are shown in Table 1.

Results showed in Table 1 refer to the measurements of the real concentration of Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanocrystals in the obtained fibers. According to the measurements, the real concentration of the modifier differs very slightly from the calculated values. It can be concluded that the annealing method used to estimate the content of luminescent nanocrystals in the white modifier paste is very precise and useful as the obtained values differ only by about 3% from the calculated ones. The method allowed to calculate an appropriate amount of the modifier which was introduced to the cellulose solution so as to reach its calculated theoretical content in final luminescent fibers.

<table>
<thead>
<tr>
<th>Calculated/theoretical concentration of modifier into fibers (wt%)</th>
<th>The real measured concentration of modifier into fibers (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>0.48</td>
</tr>
<tr>
<td>1.0</td>
<td>0.97</td>
</tr>
<tr>
<td>3.0</td>
<td>2.91</td>
</tr>
<tr>
<td>5.0</td>
<td>4.85</td>
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</table>

SEM Observation and Fibers Examination by TEM Method

SEM images presented in Fig. 3 show fibers modified with 5% of Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanocrystals compared to fibers without any modifier. Their thickness is in the range of 10–20 μm. The structure and surface of the modified fibers are similar to those of the fibers obtained by the same dry-wet spinning method but without modifier [21].

To examine precisely the size and distribution of modifier nanocrystals in fibers, as well as the size of agglomerates, TEM method and NIS-Elements software were used. The images shown in Fig. 4 confirm good distribution of the modifier in the polymer matrix. TEM images also show some characteristics of agglomerates, which consist of single, separate crystals of the modifier.

Mechanical Properties of Luminescent Cellulose Fibers

Measurement results of linear density and mechanical properties, such as tenacity and elongation at break, of cellulose fibers containing different concentrations of the modifier are shown in Table 2. The measurements prove, that there is a dependency between the concentration of nanocrystals in fibers and the linear density. Linear density has greater values for fibers with a larger concentration of the modifier, especially fibers with 5% wt of nanocrystals have high linear density. It is certain that this dependency is caused by modifier particles which are introduced into the fibers. The higher the content of nanocrystals in the polymer matrix, the higher the linear density. The tenacity of the obtained fibers decreases due to the increase of the concentration of Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanocrystals, with the exception of 0.5% wt
concentration, where it is higher. It seems that this concentration of nanoparticles in the polymer matrix is the optimum one that may cause an increase in the mechanical characteristic of cellulose fibers. This phenomenon was also observed in other modified fibers and may depend on many factors, which is still under investigation. The obtained tenacity values also differ from the mechanical properties that could be observed during our previous research. What is very important and worth emphasizing, the decrease of tenacity is very small as it diminishes by only about 6%. This kind of phenomenon has not been observed before and in other publication it equalled about 15–30% [4] and 40% [5]. The great results of tenacity measurements can be explained by the character of the modifier, which was in this case dispersed in glycerine and introduced into the fibers in the form of paste. This ensures good dispersion in the polymer matrix (see SEM and TEM images) and small size of the introduced nanocrystals. Due to these features the modifier has no influence on decreasing the mechanical properties, as it could be observed when the modifier particles were in the form of a powder (inorganic particles can be dispersed unevenly in fibers and create agglomerates, which strongly decreases mechanical properties of the fibers). The values of elongation at break also differ from the ones observed in the previous research, and they slightly rise to 3% with the increase of modifier concentration in the fibers. These results can be as well ascribed to the great dispersion of the modifier in the fibers. The results presented in Table 2 show high values of standard deviations for tenacity and elongation at break. These factors can be related to irregular properties of the obtained cellulose fibers. It must be emphasized that the fibers were formed on laboratory-scale and uniform properties of cellulose fibers, obtained by dry-wet spinning method, strongly depend on the spinning conditions. As a result, the estimated values can differ significantly.

**TABLE 2. Effect of the modifier’s concentration on the linear density and mechanical properties of cellulose fibers.**

<table>
<thead>
<tr>
<th>Concentration of the modifier (wt%)</th>
<th>Linear density (tex)</th>
<th>Tenacity (cN/tex)</th>
<th>Standard deviation for tenacity values</th>
<th>Elongation at break (%)</th>
<th>Standard deviation for elongation at break values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.284</td>
<td>30.65</td>
<td>9.27</td>
<td>10.48</td>
<td>1.62</td>
</tr>
<tr>
<td>0.5</td>
<td>0.214</td>
<td>35.72</td>
<td>8.23</td>
<td>10.53</td>
<td>1.54</td>
</tr>
<tr>
<td>1.0</td>
<td>0.223</td>
<td>33.90</td>
<td>8.77</td>
<td>10.97</td>
<td>1.64</td>
</tr>
<tr>
<td>3.0</td>
<td>0.259</td>
<td>33.04</td>
<td>8.45</td>
<td>11.74</td>
<td>1.89</td>
</tr>
<tr>
<td>5.0</td>
<td>0.324</td>
<td>28.69</td>
<td>7.92</td>
<td>10.59</td>
<td>1.78</td>
</tr>
</tbody>
</table>

**Luminescent Properties of Regenerated Cellulose Fibers**

Luminescent properties of cellulose fibers modified by nanophosphor are presented in Fig. 6. The modified material was examined by measuring luminescence excitation spectra (Fig. 6a), emission spectra (Fig. 6b) and luminescence decays (Fig. 6c). Figure 6d shows intensive, green luminescence of the fibers under UV lamp ($\lambda_{\text{exc}} = 254$ nm). Excitation spectrum shows a wide band with the maximum of around 246 nm. This band is connected with excitation of Ce$^{3+}$ ions and promotion of an electron into a higher excited level of 5d shell and then, ET to Tb$^{3+}$ ions. This transition is enabled by spin selection rules, which is responsible for high intensity of the connected band [22]. Absorption of UV light by cellulose fibers is responsible for the uneven structure of the band in the range of 200–250 nm. The direct excitation of Tb$^{3+}$ ions through the forbidden f-f electron transitions is relatively small and ineffective. Hence, the connected excitation bands are invisible in the registered spectra. Figure 6b presents emission spectra of the modified fibers. They are composed of f-f emission bands characteristic for Tb$^{3+}$ ions. The emission bands are evidence of radiative relaxation of Tb$^{3+}$ ions from the excited $^5D_4$ level. From the emission as well as excitation spectra it is clearly seen that fibers modified with 3 and 5% of Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanocrystals show similar intensity of emission. Therefore introducing larger amounts of the modifier nanocrystals is unnecessary and may reduce the tenacity of the fibers. Luminescence decays are typical for Tb$^{3+}$ ions and equal about 2–3 ms [23]. They have shown a nonexponential character of the registered curves. This is the result of cross relaxation process between Tb$^{3+}$ ions in nanocrystals. The kinetics of cross relaxation is complex and a model explaining this process...
has been reported [24]. The decay profiles can be matched with exponential function as the first approximation of the reported kinetics model. Emission of the obtained cellulose fibers is very intensive, which is an important factor for further applications. What is more, the use of inorganic compounds, like rare earth fluorides guarantees chemical and photophysical stability of their structure and luminescence.

CONCLUSIONS

Cellulose fibers modified with UV–active cerium fluoride doped with terbium ions nanoparticles were obtained. The modifier was dispersed in glycerin and added to the spinning dope during cellulose dissolution process, in the form of white paste. CeF$_3$Tb nanocrystals were prepared by a co-precipitation method and contained 15% mol of Tb$^{3+}$ ions, which ensured the most intensive luminescence and quantum yield. The presence of glycerine prevents uncontrolled growth of modifier particles and, as it seems from the research presented in this work, thanks to the small aggregation of crystals provides good dispersion of dopant in polymer matrix. The morphology of synthesized modifier particles examined by TEM showed small nanoplates and good dispersion of their sizes (5–25 nm, with the average size of 13 nm). The obtained interactive fibers contained from 0.5 to 5% wt of modifier, which ensures great photoluminescent effect and effective emission of green light under UV radiation of the maximum value at 543 nm. The estimated real concentration of the modifier in the fibers differs only slight from the calculated one. Based on the SEM images of the obtained cellulose fibers it can be seen that structure and surface of the obtained luminescent fibers are similar to those of fibers without the modifier. Furthermore, luminescent nanocrystals are characterized by good dispersion in the polymer matrix and small aggregation. The observations made by SEM method were confirmed by more precise TEM techniques. The analysis of fibers images obtained by TEM showed that the size of most modifier particles is smaller than 100 nm and the particles are evenly distributed in the polymer matrix. The analysis made by means of TEM techniques also proved that the method of introducing the modifier, which was suspended in glycerine, is an excellent one and helps to protect the particles from agglomeration process. The measurement results of

![Image](https://example.com/image.png)

FIG. 6. Luminescent properties of cellulose fibers doped with Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanocrystals: (a) excitation spectra, (b) emission spectra, (c) luminescence decays, and (d) luminescence of fibers under UV irradiation ($\lambda = 254$ nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
mechanical properties of the obtained fibers differ from the ones obtained before. In most cases the presence of dopant particles in the polymer matrix significantly decreases tenacity of the modified fibers (by about 15–40% with 0.5–5% concentration of the dopant in fibers). However, in this case the decrease of tenacity is very small as it decreases by only about 6%. The form of the modifier and its dispersion in glycerine resulting in the small size of the particles, small agglomerates, and great dispersion of nanocrystals in the polymer matrix may also be responsible for this phenomenon. These factors also influence the elongation at break, which slightly rises with the higher concentration of modifier nanocrystals in fibers. It seems that the presence of this inorganic modifier not only does not decrease the elasticity of the fibers, but even slightly increases it (except from the 5% wt dopant concentration, for which it slightly decreases). These cases, because of their specificity will be further investigated. The characteristic of the obtained fibers is very promising and makes it possible to find quite unique applications for this kind of luminescent material, especially for documents or textile protection.

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