



COTTON MATERIALS GRAPPED WITH LUMINESCENT ORGANOSILAZANE COATINGS

Cite this: *INEOS OPEN*,
2020, 3 (6), 214–218
DOI: 10.32931/io2027a

E. N. Rodlovskaya* and V. A. Vasnev

*Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia*

Received 29 October 2020,
Accepted 15 February 2021

<http://ineosopen.org>

Abstract

The textile materials with polymeric coatings bearing rare-earth element conjugates of variable color spectrum are obtained. The polymer basis in use is a new polyorganosilazane, which, on the one hand, features high adhesion to the material fibers and, on the other hand, hampers the hydrolysis of the REE conjugates during storage of the textile materials. It is shown that the duration of luminescent glow of the coatings on the surface of the textile materials reaches 8 h at the REE conjugate content in them ranging from 6 to 26 mmol.

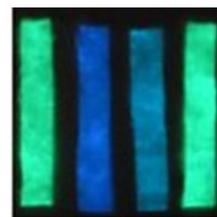
Key words: rare-earth element conjugates, oligosilazanes, filled polymeric materials, luminescence.

Introduction

In recent years, growing attention has been drawn to the conjugates of rare-earth elements (REEs) since they display appreciable mechanoluminescence [1, 2], thermoluminescence [3], and photoluminescence [4] properties along with long-lasting afterglow [5–7]. This makes them promising materials for the production of shock detectors [1, 2] and light-accumulating coatings and fabrics [8–10]. Moreover, these compounds feature low toxicity and high thermal stability and inherently refer to the crystal phosphors [11, 12]. However, an essential drawback of this class of compounds is the low moisture resistance. During storage in a humid atmosphere, they are gradually hydrolyzed to afford separate components: SrCO₃, Al₂O₃, Dy₂O₃, and H₃BO₃ [13].

Traditionally the REE conjugate powders are used in the compositions of polymeric coatings as functional fillers and additives. The typical binding agents are polydimethylsiloxane [1, 2] and poly(methyl methacrylate) [14]. The coatings based on these polymers endow the finished products with rigidity. The application of (3-aminopropyl)triethoxysilane in a combination with an epoxy resin as the binding agent [8] or the addition of the REE conjugates during the spinning of polymer fibers from a melt [10] cannot hamper leaching of the conjugates upon contact of materials with water or their hydrolysis during storage under humid conditions.

The production of textile materials with lasting prints and soft handle imposes certain requirements to polymer dispersions that are used for the processing of fabrics. The most important requirement is the formation of a strong, elastic, and transparent coating on the surface of a textile material that would possess high stability to the action of light, heat, oxidizing agents, organic solvents, and household washing. To reach the required characteristics, textile materials are treated with emulsions or



Emission of the samples in 15 min after exposure to sunlight

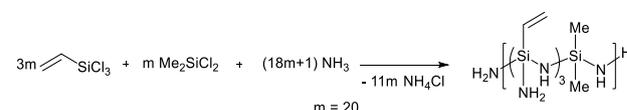
latexes based on the copolymers which macromolecular chains include monomers of different nature. The largest group of the agents used in the technologies for fabric finishing is presented by aqueous dispersions of copolymers of (meth)acrylic monomers [15–17].

Nowadays, the realization of a light-accumulating coloristic effect on textile materials is a marked trend [18–20]. The fabrics that glow in the dark are widely used in the production of clothing, in particular, for the personnel of metro systems, airports and railway, miners, rescuers, firemen, and so on [4, 5]. A search for new promising coloring and binding agents for the creation of textile materials that would be resistant to weather factors and sunlight and would exhibit a light-accumulating coloristic effect is an urgent task.

In this work, in order to create new luminescent textile materials, the REE conjugates were immobilized on the surface of cotton fabric using an organosilazane polymer coating, which, on the one hand, acts as a binding agent for the filled systems and, on the other hand, hampers the hydrolysis of the REE conjugates during storage of the final fabrics.

Results and discussion

A multifunctional oligomer, namely, polyvinyl dimethylsilazane was obtained by the coammonolysis of a mixture of vinyltrichlorosilane and dimethyldichlorosilane in a 3:1 molar ratio under bubbling of gaseous ammonia in toluene according to the following scheme [21–23]:



The structure of polyvinyl dimethylsilazane was confirmed by the IR and NMR spectroscopic data.

The resulting oligosilazane is a yellowish resin-like product, which is soluble in aliphatic and aromatic hydrocarbons, alcohol, diethyl ether, THF, and dioxane and is not soluble in water. It can be used as a solution in organic solvents and suspensions for the finishing of textile materials from different fibers in order to provide them luminescence properties.

To produce luminescent organosilazane coatings on the surface of textile materials, the fabric samples were impregnated with a butyl acetate suspension of the organosilazane and REE conjugate. Then, the fabric samples were dried in air and heated at 140 °C for 5 min. The short thermal impact was chosen to avoid complete hydrolysis of the resulting silazane as it was shown elsewhere [24–26]. The impregnation, drying, and thermal processing were repeated multiple times to achieve a 1, 5, 10, and 15 wt % increase in the sample masses. It should be noted that the resulting coatings did not dissolve in water and organic solvents.

The ATR-IR spectra of the modified fabrics show the absorption bands in the range of 2926–2856 cm^{-1} , which correspond to the vibrations of the CH_2 units, the overlapping absorption bands at *ca.* 1440 cm^{-1} , which can be attributed to the Si–NH–Si vibrations, and the absorption bands at 1530 and 3385 cm^{-1} , which answer to the vibrations of the amino groups. A strong absorption band in the range of 897–643 cm^{-1} refers to the boron surrounding of the corresponding REE conjugate.

Figure 1 depicts the micrographs of the fabric surface before and after modification. The processing of the cotton fabric with the organosilicon agent and REE conjugate does not lead to gluing of fabric fibers and does not damage weaving patterns. The REE conjugate particles are observed both on the thread

surface and between the fibers.

The absence of a continuous film on the surface of the modified fabric and the presence of voids between its threads and fibers suggest the retention of vapor and gas permeability of the processed material. This assumption is supported also by the previously reported data about the formation of macroporous polysilazane coatings on the surfaces of different materials [27, 28].

The duration of the luminescent glow of the modified cotton samples was determined by physical methods and visually after lighting with a 150 W electric filament lamp at a distance of 5 cm for 15 min. Table 1 presents the data on the duration of the luminescent glow of the fabric samples.

Table 1. Duration of the luminescent glow of the modified fabric samples

REE conjugate ^a	ΔM , wt % ^b	REE content, mmol	λ_{max} , nm	T, h ^c
LDP-2mA	1	1.74	525	5.0
LDP-2mA	5	8.7	525	6.5
LDP-2mA	10	17.4	520	8.0
LDP-2mA	15	26.1	490	8.0
LDP-3mA	1	0.39	520	4.5
LDP-3mA	5	1.95	490	6.0
LDP-3mA	10	3.9	490	7.5
LDP-3mA	15	5.85	475	8.0

^a LDP-2mA is the REE conjugate with the composition $\text{SeAl}_2\text{O}_4\text{:EuDyB}$ (yellow-green afterglow); LDP-3mA is the REE conjugate with the composition $\text{Se}_2\text{Al}_{14}\text{O}_{25}\text{:EuDyB}$ (blue afterglow);

^b coating content;

^c afterglow duration.

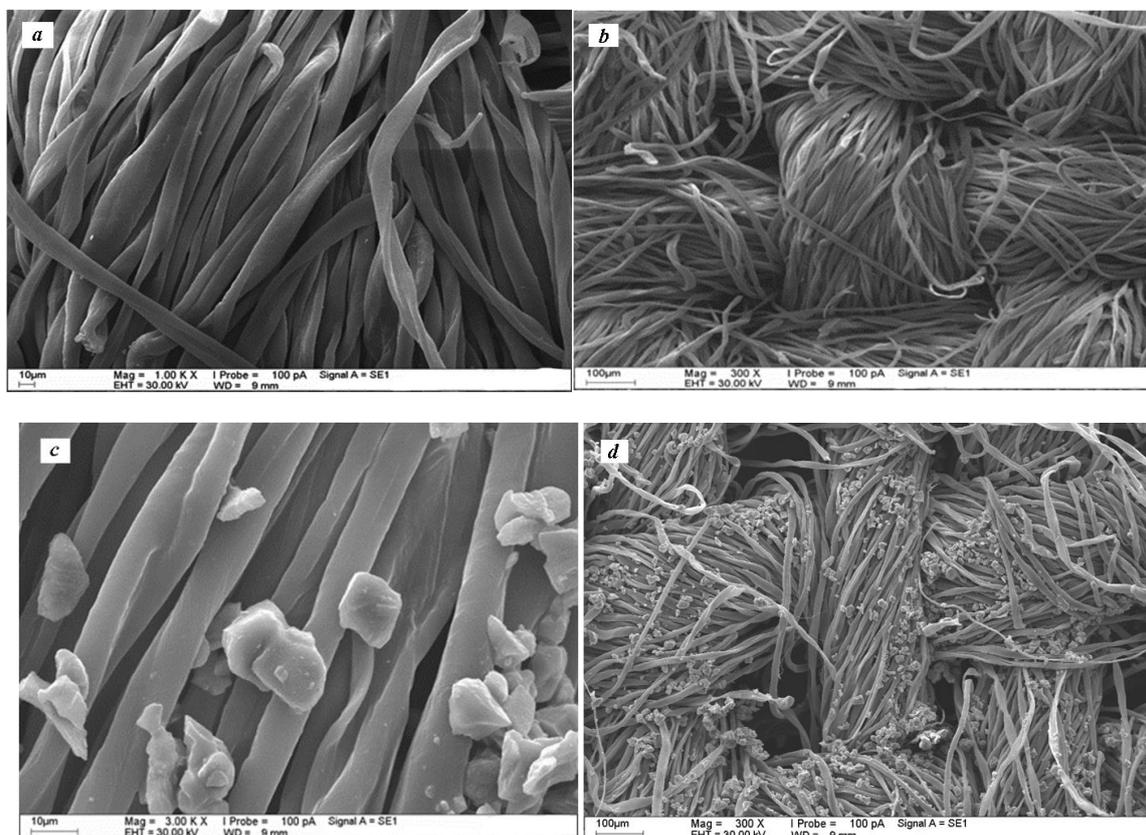


Figure 1. Micrographs of the surfaces of the initial (*a*, *b*) and modified (*c*, *d*) cotton fabrics. The modification was performed with oligodivinyldimethylsilazane bearing 15 wt % of LDP-3mA conjugate.

As can be seen from Table 1, the color (λ_{\max}) and duration of luminescent afterglow strongly depend on the conjugate composition and its content on the fabric surface. Thus, at the REE content in the coating of 0.39–1.74 mmol, the duration of luminescent glow composes 4.5–5 h. As the REE content in the coating grows 15 times, the glow duration increases by 3 h. This peculiarity is associated with a photoluminescence effect of the REE conjugates [4].

The luminescence spectra of the samples bearing LDP-2mA conjugate show green and blue-green emission bands, which correspond to the maximum glow intensity at 525, 520, and 490 nm, depending on the mass fraction of the conjugate applied to the fabric. The fluorescence spectra of the samples containing LDP-3mA conjugate demonstrate the emission bands in blue (475 nm) and green (520 nm) emission regions. There is also a dependence of the emission intensity on the conjugate content. This dependence can be explained by the fact that the luminescence yield at low contents of an emitting component is proportional to its content; however, an increase in the concentration of the luminescent component leads to a reduction in the luminosity rather than its increase. This effect is usually connected with the presence of admixtures in a solution that absorb the incident radiant or emitted energy, leading to a reduction in the luminescence yield [29].

Figure 2 depicts the micrographs of the modified fabric after 5 washing cycles. The pigment is partially leached from the fabric surface but still remains between its fibers. At the same time, there is no photoluminescence decay. Figure 3 shows the emission spectra of the samples of the modified fabric before and after 5 washing cycles. As can be seen, the spectra coincide.

The results obtained allow for concluding that the protective film based on oligovinylidimethylsilazane is formed not only on the fiber surface but also on the surface of the conjugate particles. In the latter case, the film around the particle surface preserves the REE conjugate from the negative impact of water (during washing), preventing its hydrolysis. The high adhesion to the fiber surface is caused by the chemical interaction of the oligomer aminosilanol groups with the hydroxy groups of the fiber polymer, which results in the release of ammonia [26].

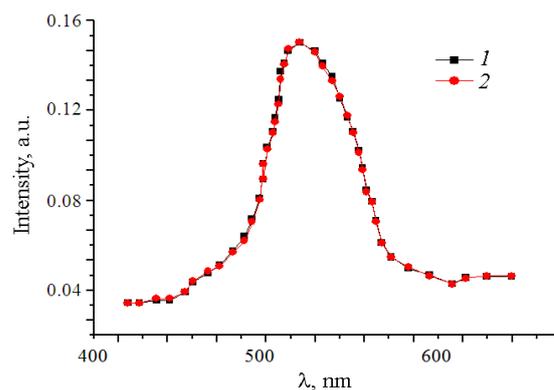


Figure 3. Luminescence spectra of the cotton fiber modified with the oligosilazane and LDP-2mA conjugate (5 wt %): before washing (1), after 5 washing cycles according to GOST (State Standard) 29298-2005 (2).

Experimental

The investigations were performed with the cotton fabric (EMPA, Switzerland) featuring the density of 100 g/m², the linear density of fibers of 0.33 tex, and the specific surface area of 4.5 m²/g, containing 20% of cellulose acetate and 80% of ethyl cellulose and the REE conjugates of long-lasting afterglow of different color spectra: LDP-2mA (SeAl₂O₄:EuDyB) with green and LDP-3mA (Se₂Al₁₄O₂₅:EuDyB) with blue emission (NPO Platan, Russia).

The luminescence spectra of the organosilazane coatings with the REE conjugates were measured on a Lumeks Fluorat-02-Panorama fluorometer (Russia). The experiments were carried out outside a cell holder using an add-on unit connected with an analyzer by a fiber-optic link. The exciting radiation source was an electric filament lamp with a wattage of 150 W. The distance between the exciting radiation source and the sample under investigation was 5 cm.

The IR spectrum of the resulting oligosilazane was recorded on a Carl Zeiss Specord M82 spectrophotometer in the range of 4000–400 cm⁻¹ on KBr, NaCl, and LiF plates.

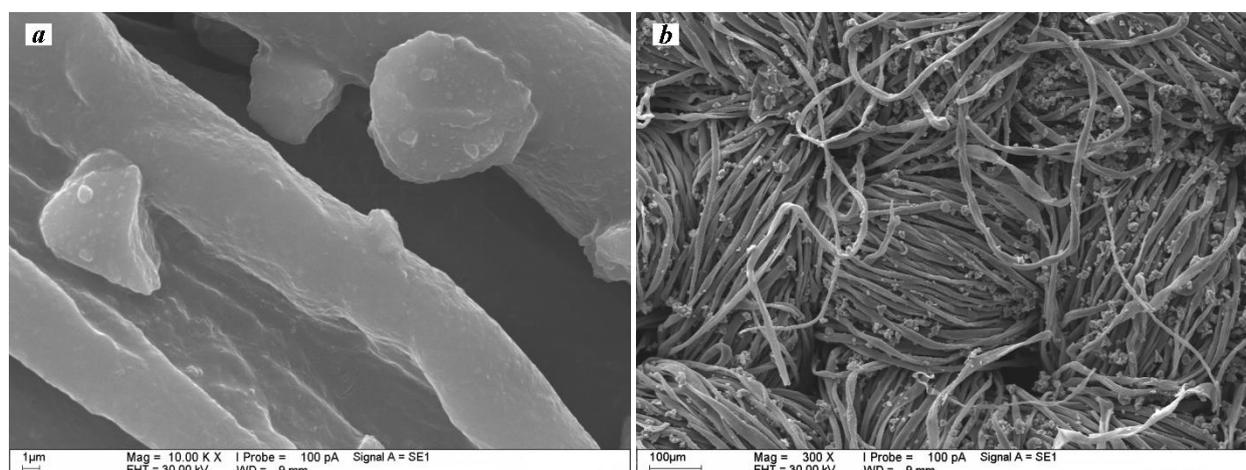


Figure 2. Micrographs of the cotton fabric samples modified with the oligosilazane and LDP-3mA conjugate after five washing cycles at $\times 10000$ (a) and $\times 300$ (b) magnification. The conjugate content in the coating is 15 wt %.

The ^1H NMR spectrum was registered on a Bruker AMX-400 spectrometer with the working frequency of 400.13 MHz in CDCl_3 using Me_4Si as an internal standard.

The IR spectra of the coatings were obtained with a Bruker VERTEX 70v FTIR-spectrometer in the ATR mode with the resolution of 4 cm^{-1} using a Pike GladyATR add-on unit with the diamond working element. The ATR-IR spectra were corrected using the unit software to take into account the dependence of the radiation penetration depth into a sample on its length.

The afterglow duration of the samples was determined according to *GOST* (State Standard) *R 12.2.143-2002* [30].

The afterglow duration was also evaluated visually compared to the afterglow durations of the reference samples in 15 min after turning off the light source. The references were the REE powders from this work.

The micrographs of the samples of the initial and processed fabric were obtained on a Cam-scan-S2 scanning electron microscope according to the standard procedure in the SET mode, using the accelerating voltage of 20 kV. The conducting coating was a gold-palladium melt. The application was performed in an argon atmosphere in an Eiko Ion coater IB-3 apparatus (Japan) [31, 32].

The hydrolytic resistance of the coatings on fabrics was defined by washing according to *GOST* (State Standard) *29298-2005* over 5 washing cycles [33].

Oligovinyl dimethylsilazane was synthesized according to the following procedure. A flask equipped with a stirrer, backflow condenser with a calcium chloride tube, and a bubbling system for NH_3 supply was charged with a 10–12% toluene solution of a mixture of organochlorosilanes consisting of vinyltrichlorosilane $\text{CH}_2=\text{CHSiCl}_3$ (3 mol) and dimethyldichlorosilane Me_2SiCl_2 (1 mol). The reaction mixture was cooled to $+10\text{ }^\circ\text{C}$; then, ammonia was bubbled under vigorous stirring, keeping the temperature no higher than $+10\text{ }^\circ\text{C}$. During NH_3 bubbling, the reaction mixture was intensively heated and the bulk curdy precipitate of NH_4Cl was formed. In 10–20 h, the ammonia supply was ceased to take an aliquot from the reaction mixture. The reaction was considered to be complete if the bubbling of ammonia through this sample did not afford a precipitate of ammonium chloride. In the case of precipitation, the ammonolysis was continued for further 1–2 h and again a sample was taken to control the reaction.

After completion of the coammonolysis, the resulting mixture was cooled to room temperature, filtered through a Nutsche filter with a filtration paper to separate the precipitate of NH_4Cl and afford a toluene solution of target oligovinyl dimethylsilazane.

The reaction of 4.85 g of vinyltrichlorosilane and 1,3-dimethyldichlorosilane afforded 2.6 g of polyvinyl dimethylsilazane. Yield: 90%. The silazane concentration in a toluene solution was defined by the dry residue [24, 25]. $M = 5000$ (cryoscopy in benzene). IR ν/cm^{-1} : 915, 960–980 (Si–N–Si), 1150, 1210, 1648–1638 (Si–CH=CH₂), 3320, 3385 (NH₂). ^1H NMR: δ 3.38 (m, NCH₃), 5.68 (m, SiCH=), 5.82 (m, =CH₂), 6.05 (m, =CH₂), 6.41 (br m, NH₂) ppm.

To produce the luminescent coatings on the surface of the textile materials, the fabric samples were impregnated with a suspension of the film-forming oligosilazane (2 mL) and REE

conjugate (0.8 g) in butyl acetate (10 mL). The resulting sample was dried in air and heated at $140\text{ }^\circ\text{C}$ for 5 min. The impregnation, drying, and thermal processing were repeated multiple times to achieve a 1, 5, 10, and 15 wt % increase in the sample masses. ATR-IR, ν/cm^{-1} : 897–643 (B), 1440 (Si–N–Si), 1530 (NH₂), 1648–1638 (Si–CH=CH₂), 2926–2856 (CH₂), 3385 (NH₂) (the spectra of eight samples did not exhibit significant differences).

Conclusions

The new cotton fabrics were synthesized that are grafted with the organosilazane coatings filled with the REE conjugates. On the one hand, the polysilazane serves as a binding agent for the disperse filler, on the other hand, it hampers the hydrolysis of the REE conjugates during storage. The resulting coatings are stable not only to water but also to organic solvents, which can be used for the creation of the work clothing elements. The photoluminescence in the range of 475–525 nm with the maxima in green (520, 525 nm), blue-green (490 nm), and blue (475 nm) regions was observed. It was established that the duration of the luminescent glow of the organosilazane coatings on the surface of polymeric materials reaches 8 h at the REE conjugate contents in the coatings ranging from 6 to 26 mmol.

Acknowledgements

The IR spectroscopic studies were performed with the financial support from the Ministry of Science and Higher Education of the Russian Federation using the equipment of the Center for Molecular Composition Studies of INEOS RAS.

Corresponding author

* E-mail: rodlovskaya@mail.ru. Tel: +7(499)135-6075 (E. N. Rodlovskaya)

References

- Z. Tang, F. Zhang, Z. Zhang, C. Huang, Y. Lin, *J. Eur. Ceram. Soc.*, **2000**, *20*, 2129–2132. DOI: 10.1016/S0955-2219(00)00092-3
- P. Jha, A. Khare, *J. Alloys Compd.*, **2020**, *847*, 156428. DOI: 10.1016/j.jallcom.2020.156428
- R. E. Rojas-Hernandez, F. Rubio-Marcos, M. Á. Rodríguez, J. F. Fernández, *Renewable Sustainable Energy Rev.*, **2018**, *81*, 2759–2770. DOI: 10.1016/j.rser.2017.06.081
- T. Peng, H. Yang, X. Pu, B. Hu, Z. Jiang, C. Yan, *Mater. Lett.*, **2004**, *58*, 352–356. DOI: 10.1016/S0167-577X(03)00499-3
- V. Vitola, V. Lahti, I. Bite, A. Spustaka, D. Millers, M. Lastusaari, L. Petit, K. Smits, *Scr. Mater.*, **2021**, *190*, 86–90. DOI: 10.1016/j.scriptamat.2020.08.023
- V. Liepina, D. Millers, K. Smits, *J. Lumin.*, **2017**, *185*, 151–154. DOI: 10.1016/j.jlumin.2017.01.011
- R. E. Rojas-Hernandez, F. Rubio-Marcos, M. V. Dos Santos Rezende, M. Á. Rodríguez, A. Serrano, Á. Muñoz-Naval, J. F. Fernández, *Mater. Des.*, **2016**, *108*, 354–363. DOI: 10.1016/j.matdes.2016.06.112
- J. Li, Y. Zhao, M. Ge, S. Fu, T. Lin, *J. Rare Earths*, **2016**, *34*, 653–660. DOI: 10.1016/S1002-0721(16)60075-3
- M. Skwarczyńska, M. Runowski, P. Kulpiński, S. Lis, *Carbohydr. Polym.*, **2019**, *206*, 742–748. DOI:

- 10.1016/j.carbpol.2018.11.058
10. H. F. Brito, J. Hölsä, T. Laamanen, M. Lastusaari, M. Malkamäki, L. C. V. Rodrigues, *Opt. Mater. Express*, **2012**, *2*, 371–381. DOI: 10.1364/OME.2.000371
 11. Q. Li, B. Yan, *J. Rare Earths*, **2019**, *37*, 113–123. DOI: 10.1016/j.jre.2018.10.001
 12. S. Han, Y. Wang, W. Zeng, W. Chen, *J. Rare Earths*, **2016**, *34*, 245–250. DOI: 10.1016/S1002-0721(16)60021-2
 13. J. Nance, T. D. Sparks, *Prog. Org. Coat.*, **2020**, *144*, 105637. DOI: 10.1016/j.porgcoat.2020.105637
 14. S. Khursheed, G. A. Sheergojri, J. Sharma, *Mater. Today: Proc.*, **2020**, *21*, 2096–2104. DOI: 10.1016/j.matpr.2020.01.329
 15. O. A. Hakeim, F. Abdelghaffar, A. A. Haroun, *Dyes Pigm.*, **2020**, *177*, 108307. DOI: 10.1016/j.dyepig.2020.108307
 16. A. A. Haroun, H. A. Diab, O. A. Hakeim, *Carbohydr. Polym.*, **2016**, *146*, 102–108. DOI: 10.1016/j.carbpol.2016.03.039
 17. M. Elgammal, R. Schneider, M. Gradzielski, *Dyes Pigm.*, **2016**, *133*, 467–478. DOI: 10.1016/j.dyepig.2016.06.033
 18. A. Erdman, P. Kulpinski, T. Grzyb, S. Lis, *J. Lumin.*, **2015**, *169*, Part B, 520–527. DOI: 10.1016/j.jlumin.2015.02.049
 19. L. Bossin, I. Bailiff, I. Terry, *Radiat. Meas.*, **2020**, *134*, 106318. DOI: 10.1016/j.radmeas.2020.106318
 20. P. Zhang, J. Lan, Y. Wang, Z. H. Xiong, C. Z. Huang, *Biomaterials*, **2015**, *36*, 26–32. DOI: 10.1016/j.biomaterials.2014.08.026
 21. CN Patent 111732602, **2020**.
 22. M. Yan, Y. Tan, Z. Zhang, J. Hu, Z. Xie, *Eur. Polym. J.*, **2006**, *42*, 3068–3077. DOI: 10.1016/j.eurpolymj.2006.07.009
 23. C. Salameh, S. Bernard, C. Gervais, F. Babonneau, A. Bruma, S. Malo, P. Miele, *J. Eur. Ceram. Soc.*, **2019**, *39*, 183–194. DOI: 10.1016/j.jeurceramsoc.2018.09.027
 24. R. Chavez, E. Ionescu, C. Balan, C. Fasel, R. Riedel, *J. Appl. Polym. Sci.*, **2011**, *119*, 794–802. DOI: 10.1002/app.32777
 25. E. N. Rodlovskaya, B. A. Izmailov, V. A. Vasnev, L. I. Komarova, S. I. Luik Saar, M. M. Krayushkin, V. A. Barachevskii, O. I. Kobeleva, T. M. Valova, *Polym. Sci., Ser. B*, **2011**, *53*, 352–357. DOI: 10.1134/S156009041105006X
 26. E. N. Rodlovskaya, B. A. Izmailov, V. A. Vasnev, A. A. Amelichev, A. V. Naumkin, S. V. Dvoryak, A. S. Ivanov, *Polym. Sci., Ser. B*, **2016**, *58*, 347–350. DOI: 10.1134/S1560090416030131
 27. J. Olejarka, A. Łącz, Z. Olejniczak, M. Hasik, *Eur. Polym. J.*, **2018**, *99*, 150–164. DOI: 10.1016/j.eurpolymj.2017.12.018
 28. E. Kroke, Y.-L. Li, C. Konetschny, E. Lecomte, C. Fasel, R. Riedel, *Mater. Sci. Eng., R*, **2000**, *26*, 97–199. DOI: 10.1016/S0927-796X(00)00008-5
 29. A. Ya. Zheltov, V. P. Perevalov, *Chemistry and Technology of Organic Dyes. Colors of Compounds*, Yurait, Moscow, **2019** [in Russian].
 30. GOST (State Standard) R 12.2.143-2002, **2002**. <http://docs.cntd.ru/document/1200030896>
 31. M. A. Ali, R. Umer, K. A. Khan, W. J. Cantwell, *Composites, Part B*, **2019**, *176*, 107320. DOI: 10.1016/j.compositesb.2019.107320
 32. D. Shindo, T. Oikawa, *Analytical Electron Microscopy for Materials Science*, Springer, Luxembourg, **2002**. DOI: 10.1007/978-4-431-66988-3
 33. GOST (State Standard) 29298-2005, **2005**. <http://docs.cntd.ru/document/1200044808>