Luminescent properties of nano-SiO$_2$:Eu^{3+}/polypropylene composite

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In this paper the luminescent properties of a composite made from isotactic polypropylene and silicate nanopowder doped with trivalent europium ion were investigated. The method for obtaining the investigated composite is presented. Thermochemical properties of the composite were determined by DSC and TG measurements, while the structure was checked by X-ray diffraction measurements. Luminescent properties for two differently crystallized nanocomposites were determined by measuring room temperature excitation and emission spectra, as well as the emission lifetime of the $^5D_0 \rightarrow {}^7F_2$ transition. It is established that the synthesized nanocomposites exhibits strong luminescent emission characteristic for a trivalent europium ion. Spectral analysis reveals that the europium ion local environment is inherent to changes of polypropylene crystallinity, suggesting that the efficient encapsulation of rare earth ions into polymers may be achieved using nano-silica. In addition, much stronger luminescence intensity was noticed for the case of polypropylene of higher crystallinity. The same was found for the $^5D_0$ emission lifetime (1.19 ms), which is a quite high value for this type of materials and may be favorable for future applications.

1. Introduction

In recent years a lot of research were focused on obtaining and investigating composites consisting of nanoparticles and polymer materials [1,2]. There are many reasons for this. Nanoparticles in such a composite retain their unique size-dependant specific properties. Favorable properties of the polymer material also remain preserved in the composite formed. In addition, novel and significantly enhanced physical, chemical, and biological properties, functions, phenomena, and processes often emerge due to synergistic effects. Like all nanostructured materials, the properties of nanostructured composites are highly structure/size dependent. To take the exceptional properties observed at the nanoscale and use these properties at the macroscale require a fundamental understanding of the properties and their interactions across various length scales. Ultimately a basic understanding of the structure-property relations will enable the nanoscale design of multi-functional materials for engineering applications ranging from structural and functional materials to biomaterials and beyond [3].

Nowadays a well established fact is that incorporation of inorganic particulate fillers into polymeric material is an effective method to improve polymers mechanical and thermal properties [4]. Nanosized fillers have capabilities to improve these properties even more on account of much larger interface area and stronger interfacial interaction with the adjacent polymer phase. This greatly reduces required filler content in the composites, making them lighter in weight and easier to be processed then the classical. The above mentioned effects are well investigated and documented for the case of nano-silica/thermoplastics composites, where several thermoplastic components were used: polypropylene, [5-8] acrylic latex, [9] polyethyleneterephthalate, [10] polyethylene, [11] polyethersulfone, [12] etc.

Polymers are increasingly recognized as important photonic media. They can be conveniently processed into various bulk forms to perform both active and passive functions [13]. A lot of research is focused on inorganic quantum dots/polymer nanocomposites for application as photovoltaic devices, [14] electroluminescent devices, [15] white light sources, [16] temperature probes, [17] optical fibers, [18] etc.

Rare-earth materials have drawn a great deal of attention due to their inherent thermal stability in optical transition. Owing to this advantage, many of them have been utilized in laser and optical fiber applications. Their unique optical properties result from the fact that the electrons of the partially filled 4f shell are shielded from the surrounding completely filled 5s and 5p shells. The energy levels of the 4f shell have equal parity, and hence electric dipole transitions are forbidden. In a solid, the small mixing with odd-parity wave functions makes the transition slightly allowed. The absorption and emission cross sections are therefore small, and the luminescence lifetimes can be quite long.

To use characteristic rare-earth optical properties several investigations have been conducted with organic rare earth complexes which can be dissolved in a polymer matrix [19-21]. Most of these complexes contain C–H bonds of which the second vibrational overtone can quench the rare earth luminescence [22]. Therefore an alternative approach to encapsulate rare-earth in a polymer is desired [23,24]. It is well known that silica is an

excellent host for rare earth ions yielding long luminescent lifetimes [25,26]. It would therefore be interesting to study if the material properties of silica (long rare-earth luminescence lifetime) could be combined with the properties of polymers (easy processing).

In this paper we analyzed luminescent properties of nano-SiO_2:Eu^{3+}/polypropylene composite prepared by dispersive mixing of hydrothermaly synthesized SiO_2:Eu^{3+} nanoparticles and polypropylene. Luminescence excitation, emission and emission lifetime are found for two composites having different polypropylene crystallinity.

2. Experimental

Nanocomposites in a form of 250 μm thick films were obtained by melting a mixture of isotactic polypropylene powder and SiO_2 nanopowder doped with europium in a press at 195 °C. The nano-SiO_2:Eu^{3+} content in the composite was 1 vol%. A commercial isotactic polypropylene powder (Odžaci, Serbia) was used. SiO_2:Eu^{3+} nanopowder was obtained using the hydrothermal method. Starting silicate sol was obtained by leaching water glass, composition $Na_2O \cdot SiO_2$, SiO_2/ Na_2O ratio 3.75 and viscosity 2.2 mPa using 0.1M HCl solution. After adding entire volume of acid needed for fully leaching-neutralization of water glass, system was introduced into autoclave and under 120 °C temperature and 3 bar pressure leaching proceeded for 5 hours. Silica acid precipitate was promoted into sol in the second preparation step in autoclave under above given leaching conditions. After hydrothermal treatment pH of silica acid sol was adjusted at pH=9. The sol was then doped with 3 at% of europium. Eu_2O_3 (LABOSI, 99.99%) dissolved in nitric acid (Zorka Šabac, p.a., Serbia) was used as a europium precursor. Gelling was performed by slow dripping of 0.1M NH_4OH (Zorka Šabac, p.a., Serbia) into the silicate sol doped with europium until a monolithic gel formed. The gel obtained was then heated at 550 °C for 5 h to produce nanopowder. The mixture of these polymer and nanopowder was formed in a mill and then the mixture was melted in a press in molds. The foils obtained were cooled in two ways: fast, by soaking in an ice-water mixture and slowly, by cooling in the press. This way, thin nanocomposite foils with different polypropylene crystallinity were made.

Transmission electron microscopy of nanopowder was performed on a "JEOL JAM 2000 FX" device. Light scattering was measured in the dynamical mode on a "Light Scattering System BI-200SM, Brookhaven Instruments" device equipped with BI-200SM goniometer, BI-9000AT correlator, temperature controller and Coherent INOVA 70C argon-ion laser. Dynamic light scattering measurements were performed using 135 mW Argon laser excitation at 514.5 nm and 90° of detection angle. Particle size distributions are calculated using Brookhaven Instruments Particle sizing software. Wide-angle X-ray diffraction radiation was performed on a PHILIPS 1050 instrument using Ni filtered Cu $K_{\alpha1,2}$

radiation. Diffraction data were recorded in a 2θ range from 10° to 40°. Thermogravimetric analyses were conducted in a temperature range from 300 K to 870 K on a "Perkin-Elmer model TGS-2" instrument in air flow. DSC measurements were performed in the temperature range from 320 K to 450 K on a "Perkin-Elmer DSC-2" in nitrogen flow. The heating rate was 20 K/min.

Luminescence excitation spectrum was measured on a "Perkin-Elmer LS45 Luminescence Spectrometer" instrument. The emission spectra of europium embedded in nano-SiO_2/PP nanostructured host lattice have been performed at room temperature after excitation into the $^7F_0 \rightarrow {}^5D_2$ absorption band. The excitation source was an Optical Parametric Oscillator (O.P.O.) pumped by the third harmonic of the Nd:YAG laser. The emission has been analysed using HR250 monochromator (Jobin-Yvon) and then detected by an ICCD camera (Princeton Instrument). Lifetime measurements have been recorded under pumping by the O.P.O. in the Eu^{3+} absorption bands at room temperature.

3. Results and discussion

In order to correlate luminescent properties of nanocomposites with their structure the basic characterization has been performed. First, the size distribution of nano-silica was found. This was accomplished by measuring particle diffusion coefficients using dynamic light scattering method (quasi-elastic light scattering). Particle size distributions are calculated from the measured data using built-in instrument particle size software (Brookhaven Instruments Particle size software) and presented in the Table 1. The obtained results show very narrow size distribution of the silica sol particles: 98% of all particles have diameter of 7.7±0.5 nm, while the 2% surplus were agglomerates. Silica sol particle sizes were also checked by transmission electron microscopy and spherical particles smaller then 10 nm were found (figure not shown here).

Table 1. Particle size distribution the nano-SiO_2 determined by dynamic light scattering measurements.

d (nm)	Participation (%)	d (nm)	Participation (%)
< 4.5	0	13.7	0
5.0	0	15.8	0
5.8	0	18.3	0
6.6	0	21.1	0
7.7	98	24.4	0
8.9	0	28.2	1
10.3	0	32.6	1
11.8	0	> 33.0	0

Structures of the composite synthesized were checked using wide-angle X-ray diffraction radiation. Diffractograms of the nanocomposite cooled in the ice-

water mixture (a) and in the press (b) are given in Fig. 2. One can note characteristic reflections typical for α-forms of isotactic polypropylene with a C2/c space group [27]. From the shape of the peaks in Fig. 2. the crystallinity of polymer foils can be estimated as higher in the case of the sample cooled in the press in relation to the sample cooled in the ice-water mixture. The reason for this is that the cooling time of the sample in the press is significantly longer so the system had more time for better ordering than the system cooled much faster in the ice-water mixture.
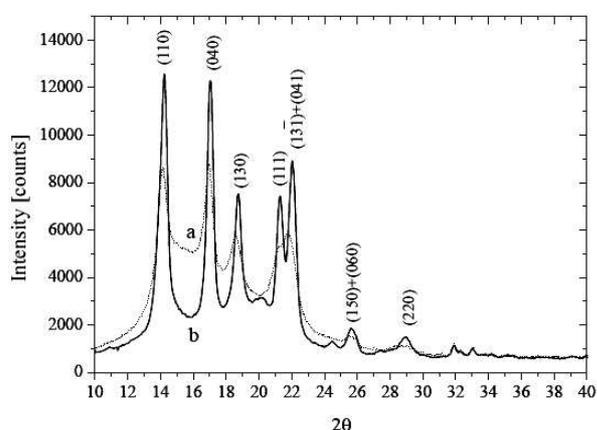
Fig. 1. XRD of the nano-SiO$_2$:Eu^{3+}/polypropylene composites obtained by: a) cooling in an ice - water mixture and b) cooling in a press.

Thermochemical properties of the composites obtained were determined by TG and DSC measurements. TG analysis showed almost identical behavior of pure polypropylene and the obtained composites (for this reason the TG plot is not presented here). Degradation starts at about 480 K and occurs in two steps until about 760 K. The only difference is in the residue on 760 K that is somewhat higher in the composite and can be attributed to the inorganic component added - SiO$_2$:Eu^{3+}.

It is a well established fact that properties of semicrystalline polymers, like polypropylene, are firmly related to their crystalline characteristics. To examine the influence of crystallinity on luminescence properties of nanocomposites we have estimated crystallinity, in addition to XRD, using DSC measurements. DSC curves of nanocomposites obtained using different cooling methods are given in Fig. 2. The presented picture indicates different crystallinity degrees in the composites. Calculation of the areas below the peaks gave the following values: 99.6 J/g for the sample cooled in the press and 74.7 J/g for the sample cooled in the ice-water mixture.
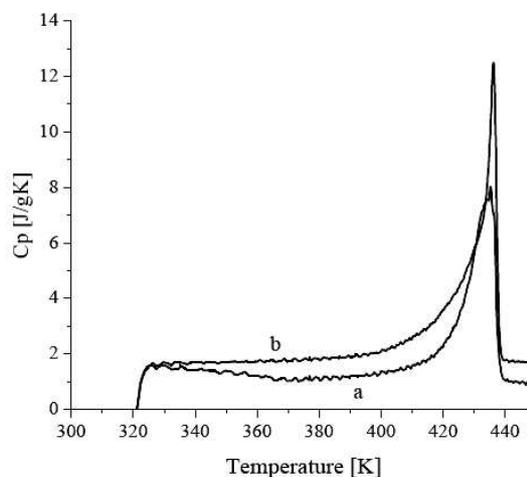
Fig. 2. DSC curves the nano-SiO$_2$:Eu^{3+}/polypropylene obtained by: a) cooling in an ice-water mixture and b) cooling in a press; the calculated crystallanities are 37.5% and 47.7%, respectively.

A comparison of these values with literature data [28] for absolutely crystalline isotactic polypropylene of 209 J/g resulted in the following crystallinity for the composites: 47.7% for the sample cooled slower in the press and 37.5% for the sample cooled faster in the ice-water mixture. These values are in accordance with the trend observed by X-ray diffraction measurements, Fig. 1. There are also several interesting issues related to the influence of nanofillers on the crystallization characteristics of polypropylene which were not subject of this research but deserve to be mentioned here in brief. Nanofillers may have some nucleation influence on the crystallinity of polypropylene. It was found[7] that the supercooling temperature of nano-SiO$_2$/polypropylene composite decreases with increasing the filler content indicating that the crystallization becomes easier in the nanocomposites due to nucleation effects of the fillers. However, the same research [7] reported unchanged crystallization enthalpy and melting point of nanocomposites compared to pure polypropylene.

In the following part of the paper is presented luminescence characterization of nanocomposites. Excitation spectra of the nano-SiO$_2$:Eu^{3+}/polypropylene composites are given in Fig. 3. Emission was detected at 614 nm. The spectra are dominated by the emission from the europium ions. Excitation bands related to characteristic trivalent europium ion transitions of f-electrons: $^5L_6$, $^5D_3$, $^5D_2$, $^5D_1 \rightarrow \, ^5F_2$ are clearly observable [29]. These characteristic bands are equally situated for both composites; however the better crystallized nanocomposite exhibits noticeable stronger luminescence emission.
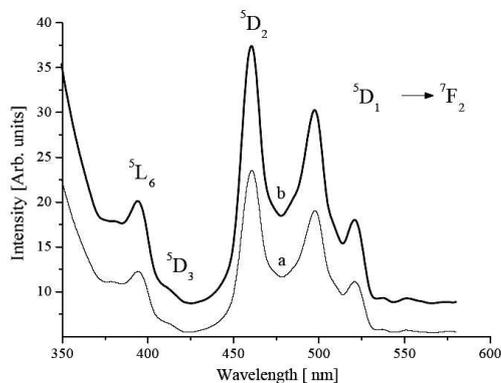
Fig. 3. Excitation spectra of the nano-SiO$_2$:Eu^{3+}/polypropylene composite: a) cooled in the ice-water mixture, b) cooled in a press; the emission is detected at 614 nm ($^7F_2$ emission).

Emission spectra of the nanocomposites excited at 460 nm are given in Fig. 4. In this picture, five emission bands centered on 578.5, 592.5, 614, 652 and 702 nm associated to $^5D_0{\rightarrow}^7F_i$ (i = 0, 1, 2, 3 and 4) spin forbidden f-f transitions, respectively, can be observed.
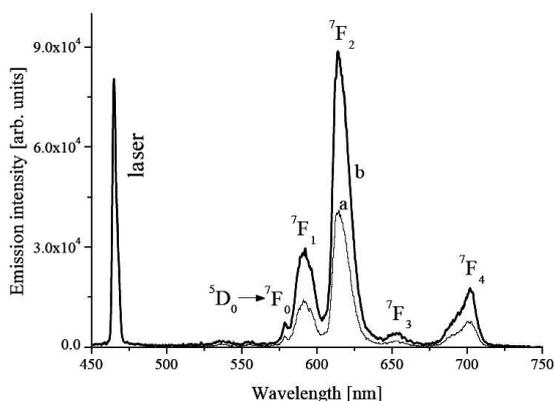
Fig. 4. Emission spectra of the nano-SiO$_2$:Eu^{3+}/polypropylene composite: a) cooled in the ice-water mixture, b) cooled in a press; the excitation is 460 nm ($^5D_2$ excitation).

There is a single line, rather weak and broad, on 578.5 nm for the $^5D_0{\rightarrow}^7F_0$ transition. Based on selection rules the band at 594 nm is attributed to the $^5D_0{\rightarrow}^7F_1$ parity-allowed magnetic dipole transition ($\Delta J = 1$) independent of the surroundings symmetry. $^5D_0{\rightarrow}^7F_{2,3,4}$ transitions are allowed electrical-dipole transitions. The most intensive line at 614 nm belongs to the $^5D_0{\rightarrow}^7F_2$ transition ($\Delta J = 2$) that is hyper-sensitive to the symmetry of the crystal field surrounding the europium ion and will be relatively strong if the surroundings symmetry is low. In this sense, it is generally admitted that the ratio of the emission intensities R = I($^5D_0{\rightarrow}^7F_2$)/ I($^5D_0{\rightarrow}^7F_1$) is an asymmetry parameter for the Eu^{3+} sites and a measure of the extent of its interaction with surrounding ligands. This

parameter, also often named chromaticity, is found to be similar in both nanocomposites (3.12 for better crystallized polypropylene and 2.87 for lower), showing that the environment of the Eu^{3+} is similar and that is predominantly defined by the nano-SiO$_2$ host. The values are quite high and very comparable to one obtained in glass and sol-gel system. Regarding the values of asymmetry parameter one may note that the found low crystal symmetry and the subsequent good chromaticity can be achieved in nanoparticles due to their high degree of disorder near the surface, as pointed out by many authors. Also, on Fig. 4 one can clearly observe well developed emission lines centered on 652 and 702 nm that originate from $^5D_0{\rightarrow}^7F_3$ and $^5D_0{\rightarrow}^7F_4$ transitions, respectively. At this point it is important to say that it was impossible on the emission features to properly correlate the size of particles to the broadness of the emission because of the insufficient resolution of the optical apparatus used. It is also important to note that better crystallized nanocomposite exhibits much stronger luminescence emission. The intensity measured at 614 nm ($^5D_0{\rightarrow}^7F_2$ transition) of the nanocomposite with 47.7% crystallinity has 2.25 times larger emission compared to compound with 37.5% crystallinity.

The emission lifetimes of the $^5D_0{\rightarrow}^7F_2$ transition of the europium ion was determined in nanocomposite samples. Figs. 5 and 6 show the results of measurements of the emission lifetime in samples cooled in the ice-water mixture and in the sample cooled in the press, respectively. Pictures show the logarithm of emission intensity measured at 614 nm as a function of the time. For these samples the luminescence decay profiles could be adjusted by a single-exponential function in the longer times, while a non exponential part is observed for the short time. The estimated lifetimes were 0.56 ms for the nanocomposite with lower crystallinity and 1.19 ms for the better crystallized polymer. The lifetime of 1.19 ms is a quite high value, characteristic of europium species with low non-radiative energy transfer probability. This can be indeed favorable to further applications.
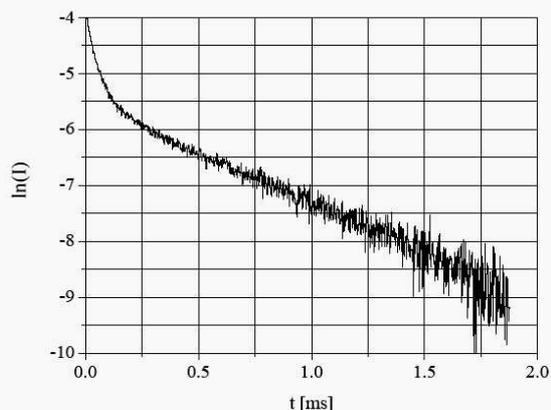
Fig. 5. $^5D_0{\rightarrow}^7F_2$ transition decay profile at room temperature of the nano-SiO$_2$:Eu^{3+}/polypropylene composite obtained by cooling in an ice-water mixture. Lifetime is estimated to be 0.56 ms.
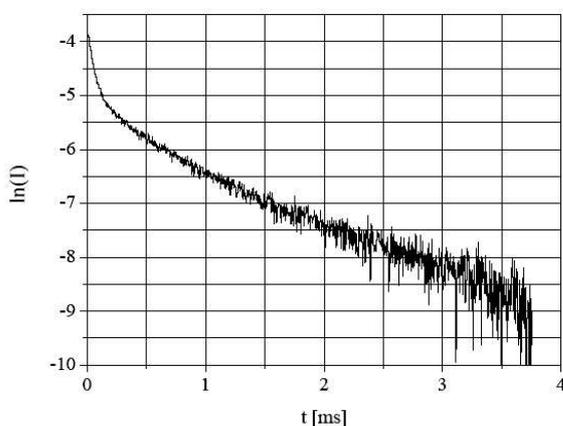
Fig. 6. $^5D_0 \rightarrow ^7F_2$ transition decay profile at room temperature of the nano-SiO$_2$:Eu^{3+}/polypropylene composite obtained by cooling in a press. Lifetime is estimated to be 1.19 ms.

4. Conclusion

In this paper luminescence properties of composites consisting of isotactic polypropylene and nano-SiO$_2$ doped with trivalent europium ion were investigated. Nanocomposites were prepared to have two different polymer crystallinities, as confirmed by XRD and DSC measurements, in order to check structural influence of polymeric component on optical properties. It was established that characteristic emission of the trivalent europium ion was present in both composite samples, though it was more intensive in the sample with the higher crystallinity. The identical positions and shapes of the emission bands and similar chromaticity factors of composites reveal very similar local environment for the europium ions. This suggests successful encapsulation of rare earth ions in polymer through nano-silica host. However, luminescence $^5D_0$ lifetime measurements showed difference between nanocomposites. Composite with the higher crystallinity has 1.19 ms lifetime, quite high value characteristic of europium species with low non-radiative energy transfer probability. With nano-silica average size less then 10 nm a number of Eu^{3+} species lying close to the nano-silica/polymer interface became significant, and therefore influence of polymer component on emission from europium may be more influential. Observed differences in $^5D_0$ lifetimes are indicative of lower luminescence quenching in polypropylene hosts with higher crystallinity.

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