

STUDY OF STABILITY IN GAMMA IRRADIATION OF LUMINESCENT FILM OF PMMA WITH EU³⁺/AG NANOPARTICLES

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ABSTRACT

Lanthanides, which are part of rare earths, have attracted attention due to their optical properties not only in research field, but also, in industrial and technological areas. Eu³⁺ ions are among the most studied of the rare earth complexes because they present higher luminescence, due to the structures of their energy levels. The combination with ligands of high molar absorptivity can promote a higher emission of the rare earth ions. The luminescent polymer system used as markers was obtained from doping with rare earth complexes, incorporating a Europium complex containing tenoyltrifluoroacetate (TTA) and triphenylphosphine oxide (TPPO) anion in the process of encapsulating silver nanoparticles in methyl polymethacrylate (PMMA). The luminescent and thermal properties of the material were analyzed in the luminescent films before and after exposure to ionizing radiation in a ⁶⁰Co source at doses of 10, 30 and 50 kGy. The TTA ligand undergoes decay of the luminescence when the precursor complex is exposed to ionizing radiation. Once doped in the PMMA polymer matrix it will be possible to protect stabilizing the luminescence of the complex. The study of the luminescence properties was performed by the spectrofluorimetry technique. The thermal properties and the decomposition profile of the material were obtained by the Thermogravimetric Analysis (TGA / DTG) in N₂ atmosphere. To investigate the enthalpic variations of the samples, the Differential Exploration Calorimetry (DSC) technique was used in N₂ atmosphere.

1. INTRODUCTION

Lanthanide ions have high quality optical properties. The discovery of the corresponding elements and their first industrial uses were closely linked to their optical properties. To date, these properties have been investigated for optical applications of lanthanides in high technology materials [1]. Rare earth compounds have been performing important functions in a number of areas of knowledge and have been applied in the following areas [2]: (a) Luminophores for illumination, (b) Electroluminescent devices with high efficiency, (c) Contrast agent for resonance (d) Luminescent probe for biomolecules, (e) Markers for proteins and amino acids, (f) Light emitting sensors in fluoroimmunoassays.

A characteristic of the RE³⁺ ions is that the electrons of the subfloor 4f are more internal than the electrons of the layers 5s and 5p, so the electrons 4f are protected due to the shielding effect exerted by the outermost electrons, so that they are not influenced by the environment around them [3]. Due to the low absorptivity of rare earth ions, its combination with high absorptivity binders can promote high emissions of these ions. In this way, the objective is that the transfer of binder energy - rare earth ion in the complex is efficient and gives rise to the emission of

light. The rare earth ion is connected to eight oxygen and / or nitrogen atoms that are derived from the ligands, forming octacoordinate complexes. The central trivalent ion is bound by a β -diketone linker, in this case tenoyltrifluoroacetate (TTA), and another organic auxiliary linker, triphenylphosphine oxide (TPPO). It should be noted that the β -diketone linker (TTA) is responsible for the absorption of the excitation energy and the transfer of this energy to the central ion. The auxiliary binder (TPPO) acts as a complement to the eight coordinates, avoiding the coordination of water molecules to the rare earth ion, contributing to energy transfer. The substitution of the solvent molecules by the TPPO ligand in the complexes increases its luminescence [4].

Rare earth complexes have been incorporated into various materials, such as polymers. Doping of rare earth complexes into polymers allows an improvement of polymer properties with flexibility, optical quality and processing conditions. The polymer acts as an immobilization matrix according to the chemical interaction but can also act as an antenna that sensitizes and intensifies the monochromatic emission of the 4f-4f transitions [5]. PMMA, a polymer used in this work, is part of the class of acrylic polymers and is a rigid and translucent thermoplastic material with excellent optical properties and resistance to ultraviolet rays, thus revealing potential use for the doping of this rare earth complex material, is derived from acrylic acid $C_3H_4O_2$ and methacrylic acid $C_4H_6O_2$. The use of new materials in the improvement of the emission of luminescence began to study the introduction of metallic nanoparticles, such as silver and gold, that can increase the emission intensity in the luminescence processes of the lanthanide compounds. by means of electron excitation modes collectively correlated in materials, as is the example of metals; raising ideas and investigations that have been of great interest for this field of action [6].

2. MATERIALS AND METHODS

2.1. Materials

Methyl polymethacrylate (PMMA) supplied by Sigma-Aldrich.

Europium oxide (99,999%) supplied by Sigma-Aldrich.

Tenoyltrifluoroacetone 99.9% supplied by Sigma-Aldrich.

Triphenylphosphinoxide 99.9% supplied by Sigma-Aldrich.

Acetone P.A. supplied by Synth.

Silver nitrate supplied by Plat-Lab.

N-N, Dimethylformamide P.A. supplied by Synth.

Polyvinylpyrrolidone K30 supplied by Synth.

2.2. Methods

The $[Eu(tta)_3(TPPO)_2]$ complex was obtained from the dissolution of a precursor complex in acetone, followed by the addition of the already dissolved TPPO linker in complex stoichiometric ratio: secondary binder 1: 2. 5.1 mg of the precursor complex dissolved in 5 mL of acetone was placed, then 10.0 mg of the secondary TPPO binder dissolved in 5 mL of acetone was prepared. The two solutions were mixed and stirred for one and a half hours under

heating for solvent evaporation. After drying the complex $[\text{Eu}(\text{tta})_3(\text{TPPO})_2]$ was stored in the vacuum desiccator.

Silver nanoparticles were synthesized from weighing and dissolving silver acetate in acetone, separately a concentration of 0.05% PVP was weighed and dissolved in acetone. The two solutions were mixed and kept under heating at about 60 °C for one hour.

The films were synthesized from the doping of the $[\text{Eu}(\text{tta})_3(\text{TPPO})_2]$ complex with the methyl polymethacrylate in solution with acetone. This material was added to the silver nanoparticle solution and allowed to stir for a period of 30 minutes until there was complete dissolution of the complex; the mixture was heated to 60 °C under stirring. The films were obtained via casting as can be observed in Fig. 1.



Figure 1: PMMA:Ag:Eu(tta)₃(TPPO)₂ film without and with the presence of UV radiation.

The thermal stability was determined by thermogravimetric analysis (TGA/DTG) in TGA-51 and TGA-50 and Shimadzu systems under the conditions: 25 °C → 600 °C, with 10 °C.min⁻¹, under Ar atmosphere. The physical properties of the new material were evaluated by differential scanning calorimetry (DSC) in the DSC-50 Shimadzu system, under the conditions: 25 °C → 150 °C, with 20 °C.min⁻¹, under Ar atmosphere. The photoluminescent properties were obtained by emission and excitation electron spectroscopy in a SPEX Fluorolog spectrofluorimeter model FL212 with double monochromators 0.22 mSPEX 1680 and 450W continuous xenon lamp.

The methyl polymethacrylate films doped with europium complex were exposed to ionizing radiation at doses ranging from 0 to 50 kGy resulting in changes in the emission spectrum bands of the luminescent films.

3. RESULTS AND DISCUSSIONS

The photoluminescent properties were investigated from the emission spectra of the Eu³⁺ complex and showed bands characteristic of the intraconfiguration transitions from Eu³⁺ ions (⁵D₀ → ⁷F_J, J = 0-6), showing red color emissions.

Emission photoluminescence data of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ doped PMMA polymer exhibited thin bands from the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ (Eu^{3+}) transitions, dominated by the hypersensitive transitions $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (~614 nm) indicating that the Eu^{3+} ion is in a non-centrosymmetric chemical environment. In Fig. 2 it is possible to observe under excitation at 350 nm the characteristic lines of the following transitions: $^5\text{D}_0 \rightarrow ^7\text{F}_0$ (579 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (592 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (612 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (656 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (699 nm). The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, referred to as hypersensitive, is the one with the highest intensity in non-centrosymmetric systems and thus responsible for the emission of red color in all compounds containing the Eu^{3+} ion emitting center.

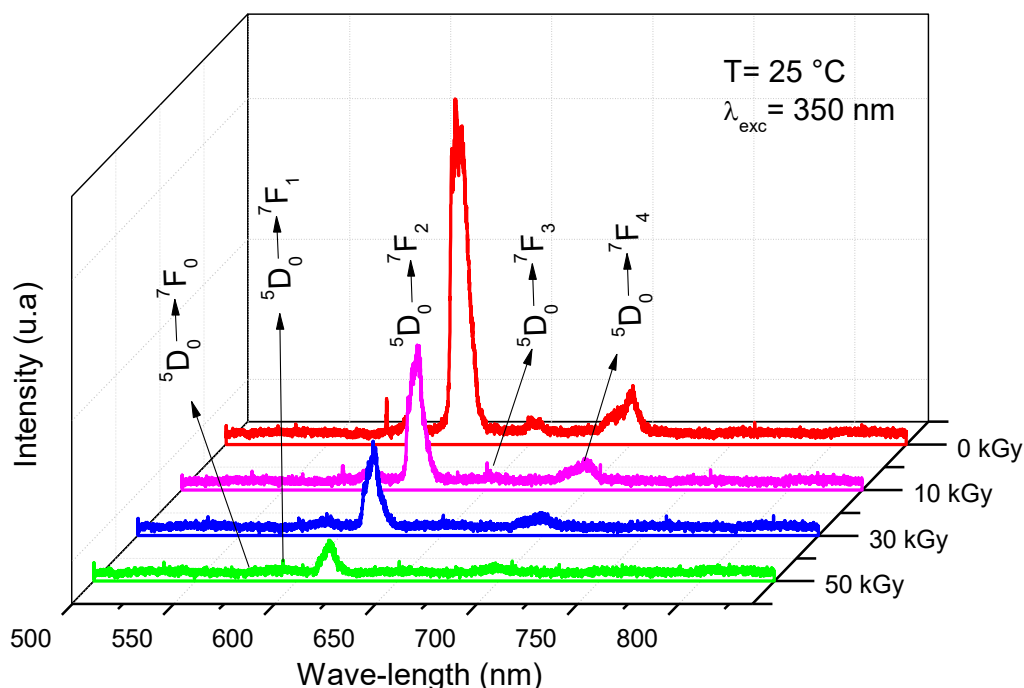


Figure 2: Emission Spectrum of the PMMA:Ag:Eu(tta)₃(TPPO)₂ polymer system at the different radiation doses.

It can be observed that in the films where the radiation exposure occurred, there was a decrease in the intensity of the emission of the luminescence, as shown in Fig. 3, through the decay as a function of the irradiation dose, attributing this effect to the absorption of luminescent energy by virtue of degradation of the polymer matrix.

It can be observed that this type of situation corroborates previous studies on rare earth complex doped polymeric materials [7,8] where it is observed that the effect of matrix degradation through exposure to ionizing radiation impairs the phosphorescence of the material, also evidencing its degree of degradation.

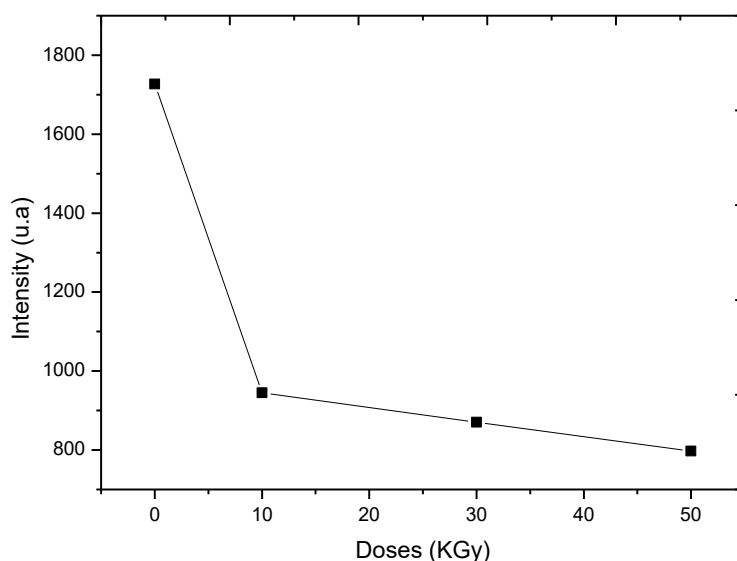


Figure 3: Luminescence decay graph of the polymer system PMMA:Ag:Eu(tta)₃(TPPO)₂ as a function of the dose of ionizing radiation.

The excitation spectrum, Fig. 4, was performed at room temperature (25 °C) and recorded in the range 250 to 550 nm, with emission monitored in the hypersensitive transition $^5D_0 \rightarrow ^7F_2$ (~ 614 nm). The spectrum shows broad bands in the range of 250 to 400 nm attributed to TTA linker absorption. In the presence of gamma irradiation doses, the excitation spectra for the irradiated films show a decrease in the absorption group of the ligand group corroborating previous results in the literature [8] where it is confirmed that the degradation of the material directly influences the phosphorescence of the irradiated films doped movies.

It is possible to observe that the excitation spectrum presents bands of higher intensity in the ligand absorption region (diketonate), evidencing the potential of the TTA ligand to act as "antenna" in the Eu^{3+} ligand energy transfer process.

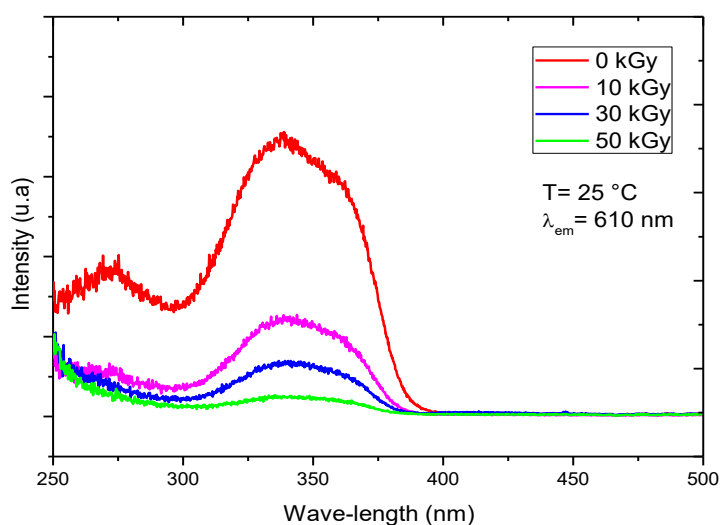


Figure 4: Excitation Spectrum of the PMMA:Ag:Eu(tta)₃(TPPO)₂ polymer system at the different radiation doses.

It was demonstrated from the TGA curves, as observed in Fig. 5, that the PMMA:Ag:Eu(tta)₃(TPPO)₂ luminescence system showed no mass loss between 80 and 120 °C thus indicating that the films doped with the complex are anhydrous. Also, comparing it with previous works [7,8], verify that the curves of the irradiated films present significant mass loss, the smallest thermal thermal variation in relation to non-irradiated films.

It is also possible to observe that the glass transition does not decrease in the luminescent systems exposed in UV chamber. This is an indication that under UV exposure the luminescent material does not alter its impact resistance property, which is a property dependent on the glass transition of the material.

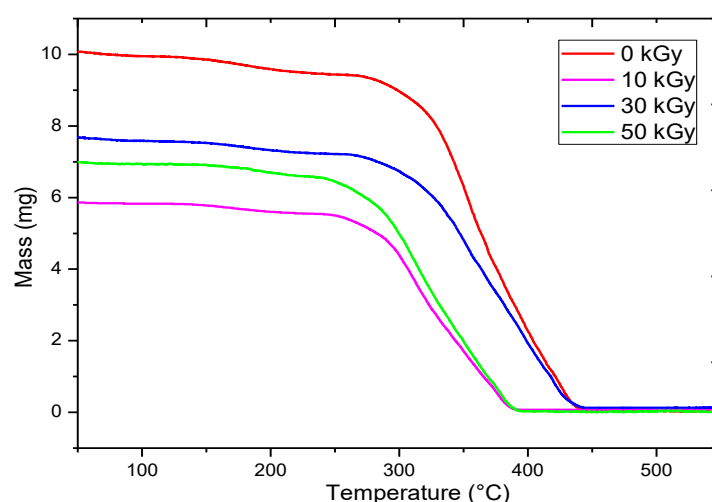


Figure 5: Thermogram of the PMMA:Ag:Eu(tta)₃(TPPO)₂ polymer system at the different radiation doses.

4. CONCLUSIONS

The PMMA:Ag:Eu(tta)₃(TPPO)₂ showed a change in its luminescence properties after exposure of the material to the ⁶⁰Co source ionizing radiation at the doses of 10, 30 and 50 kGy, and can be compared with studied films. In previous works [7,8], where it can be observed that through a degradation effect of the polymeric matrix there is a direct interaction with the luminescence of the material. This is stated based on the peak profiles presented in the emission and excitation spectrum bands where it is possible to show that the luminescence decay of the films occurs after their exposure. These results can be confirmed by the profile of the thermal decomposition curves, the irradiated material presented lower stability compared to the matrix. Based on this, through the degradation effect of PMMA it is possible to observe that its phosphorescence decays thus providing evidence of the degree of degradation of the matrix. Due to changes in material properties it will be possible to use it as an optical marker with greater efficiency under low irradiation dose conditions.

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