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INVESTIGATIONS OF GAMMA IRRADIATION ON THE PROPERTIES OF LUMINESCENT FILMS OF POLYCARBONATE (PC) MATRIX DOPED WITH EUROPIUM COMPLEX [$Eu(tta)_3(H_2O)_2$]

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ABSTRACT

Luminescent lanthanide complexes have attracted much recent interest for their application as luminescent materials. The combination of unique spectroscopic properties from rare earth complexes associated to physical and chemical intrinsic properties of polymers became more attractive in the last years. A number of advantages of these substances have been reported or realized over the much studied conjugated polymers and non-lanthanide. Luminescent films composed by diaquatris(thenoyltrifluoroacetonate)europium(III) complex [$Eu(tta)_3(H_2O)_2$] doped into a polycarbonate (PC) matrix were prepared and irradiated at gamma radiation with 5, 10, and 20 kGy. The PC polymer was doped with 1% (w/w) of the Eu^{3+} complex. The thermal properties was investigated by utilization of differential scanning calorimeter (DSC) changes in thermal stability was observed due to the addition of doping agent into the polycarbonate matrix. Changes in photophysical properties due of gamma radiation was observed by emission, excitation spectra and fourier transformed infrared spectra (FTIR). Based on the emission spectra of PC:1% $Eu(tta)_3$ film were observed the characteristic bands arising from the $^5D_0 \rightarrow {}^7F_J$ transitions of Eu^{3+} ion (J=0-4), indicating the ability to obtain the luminescence films.

1. INTRODUCTION

The luminescent advantages of trivalent lanthanide ions is due to 4f electrons that are well shielded from the environment by the outer core 5s and 5p electrons and are thus minimally involved in bonding. Because of this shielding, the atomic properties of these ions are typically retained after complexation. The total ligand-field (LF) splitting of an f-electron term is rarely more than a few hundred cm^{-1}, where the $4f^n$ ground state configuration is crucial for many luminescence properties of phosphors. Therefore, the absorption and emission spectra of Ln(III) ions consist of sharp, narrow bands corresponding to the 4f transitions of the metal ion [1].

But lack of thermal and optical stability prevents rare earth complexes from having more applications. Also, the efficiency of lanthanide emission is rather sensitive to the vibration of neighbouring X-H bonds. Thus, emission from Ln(III) ions can often be quenched by high frequency vibrations of solvents or ligands such as those of OH, CH, or NH bonds. The

vibronic coupling between the emissive levels of the metal and the O-H bonds of coordinated water molecules is especially deleterious.[1,2]

In order to solve these problems, rare earth complexes have been incorporated into several matrices [3-8]. Built materials that combine simple methods of synthesis and high luminescent properties became more attractive in the last years. Nowadays, there is currently interest in potential applications of rare earth complexes to obtain high luminescent materials for fluorescent labels, organic light-emitting diodes (OLEDs), biological imaging, and sensory devices.[8-10]

Luminescent systems based on rare earths doped into polymeric matrices have been interesting due to the combination of unique spectroscopic properties from rare earth complexes associated to physical and chemical intrinsic properties of polymers.

Polycarbonate (PC) has excellent properties for example optical properties as high clarity, transparency and ratio of refractive indices, low water absorption, exceptional impact resistance, toughness and high glass transition temperature (T_g).

The radiation technology is preferred over the other processes due to many advantages when compared with other conventional methods. For initiation processes, radiation differs from chemical initiation. In radiation processing, no catalyst or additives are required to initiate the reaction. [2]

The molecular changes induced by γ-radiation in a polymer may be classified as main chain bond scission, resulting in a decrease in molecular weight and, thus, adversely affecting its mechanical properties; and chain crosslinking, resulting in an increase in molecular weight and formation of network structure. Both chain scission and crosslinking occur primarily in the amorphous region, while some may take place in the boundary between the crystalline and amorphous regions. Chain scission, in general, occurs to polymeric chains at a low radiation dose. At high doses, free radicals could be generated on polymeric chains, which may cause crosslinking by forming covalent bonds between polymer chains. Radiation modification is the phenomena by which the properties of the polymers can be improved. [2,5]

In this present work, we report the preparation and characterization of terbium complex doped in polycarbonate matrix. The films were irradiated with gamma radiation doses of 5, 10, and 20 kGy. The doping Effect of the $[Eu(tta)_3(H_2O)_2]$ complex into the PC film was also investigated. Photoluminescence behavior of the doped system indicates the interaction of the Eu^{3+} ions with the polymeric system.

2. MATERIALS AND METHODS

2.1 Synthesis

The polycarbonate (PC) used was obtained from Bayer Corporation, (Makrolon®), in the form of cylindrical cut granules (Ø 2 to 3 mm, length 2 to 3 mm). The $[Eu(tta)_3(H_2O)_2]$ complex was prepared by addition of europium chloride aqueous solution to β-diketone ethanol solution of 1:3 molar ratio; followed by addition of concentrated ammonium hydroxide until pH ~7.

The luminescent system containing the polymer doped with the terbium complex in concentration 1% was prepared by dissolving the polymer in tetrahydrofuran, THF, then mixing it with the required amount of the luminescent Eu^{3+} complex dissolved in acetone. The homogeneous solutions were heated at around 60ºC until total evaporation of solvents. The mixture was cast into a pyrex® recipient and left to dry in air. The doped films were then cut in slices that were irradiated and analysed.

2.2 Measurements

The infrared absorption spectra of the solid samples were measured in the range 4000–400 cm^{-1} in film form by using a Thermo Nicolet model 6700 FTIR spectrophotometer.

Heat flow curves were obtained using a differential scanning calorimeter model DSC822e (Mettler Toledo) in an aluminum crucible with 2 mg of the sample, in a flowing nitrogen atmosphere (50 $mL \cdot min^{-1}$), and a heating rate of 10 $ºC \cdot min^{-1}$, from -20 to 220°C. The DSC apparatus was calibrated with In metal (m.p. 156.61 ºC; $\Delta H = 28.4\ J \cdot g^{-1}$).

The excitation and emission spectra of luminescent films were recorded at room temperatures in a SPEX Fluorolog-2 spectrofluorimeter, model FL212, double grating 0.22 meter SPEX monochromators, and a 450 W Xenon lamp as the excitation source.

Irradiation took place in a 6917.4 CI ^{60}Co Gamma Cell 220 from Atomic Energy of Canada Ltda (AECL), dose rate of 5.72 $kGy \cdot h^{-1}$. The radiation doses applied in the PC:1%$Eu(tta)_3$ samples were 5,10, and 20 kGy.

3. RESULTS AND DISCUSSION

3.1 Fourier transformed infrared spectroscopy

The IR spectra of the polymer Eu^{3+} complex presented a large complexity of peaks. The peaks related to the H_2O vibrational modes in the $[Eu(tta)_3(H_2O)_2]$ complex were attributed at 3500–3200 cm^{-1} (υ_s and υ_{as} OH) and at 1630–1600 cm^{-1} (HOH bending).[3]

In the case of the polymer complex system, the absence of these bands cannot be confirmed because of strong absorptions of the resin part in those regions. In the examination of the IR spectral data of the polymer doped with Eu^{3+} β-diketonate complex, the characteristics peaks at 1138 cm^{-1} attributed to $\upsilon_{as}(CF_3)$ and 933 cm^{-1} of $\upsilon(C=C + C=O)$ were verified, indicating the presence of tta in the polymer complex.

3.2 Glass transition changes

The DSC curves in Fig. 1 show the displacement in glass transition of non irradiated PC:Eu(tta)$_3$ 1% (a) from 119 to 109, 134, and 120 for irradiated doped systems at (b) 5,(c) 10, and (d) 20 kGy, respectively. These results show decrease in the glass transition on the system irradiated at 5 kGy and, that can suggest a chain scission in polymer chains, in other hand, at dose of 10 kGy in the doped systems showed an increase of glass transition temperature that can be attributed a crosslinking effect in the polycarbonate matrix[5].

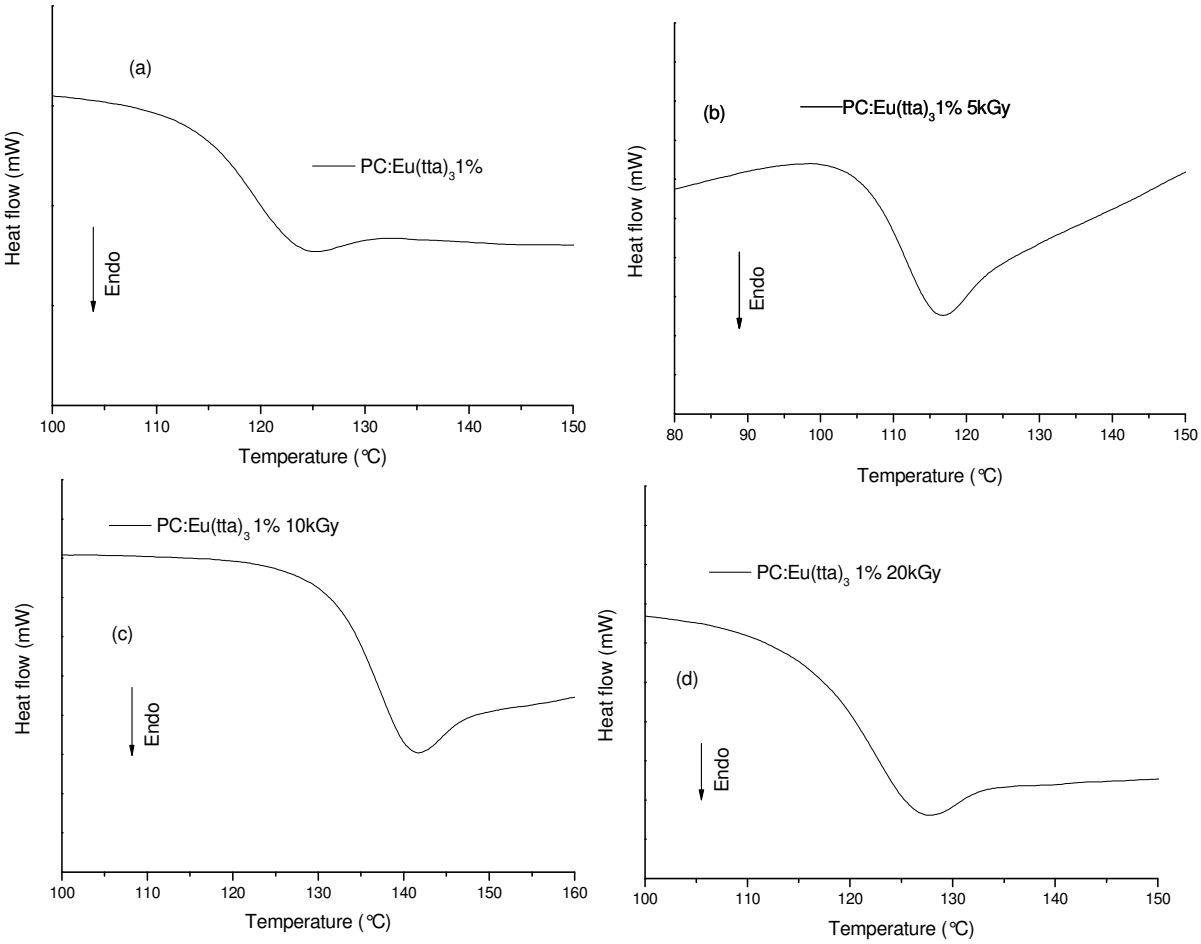

Figure 1. DSC curves of PC:Eu(TTA)$_3$ 1% systems obtained at a heating rate of 10 °C min^{-1}: at doses 0 (a) , 5 (b), 10 (c), and 20 kGy (d).

In general, the organic ligands of the europium complexes absorb light and transfer the energy to the europium ion, Eu^{3+}, through the triplet state of the ligand. The process of energy transfer from the triplet manifold of the complex to the rare earth ion, emission then occurs from the metal ion as an f – f transition. Essentially all emission originates from the

$^5D_0$ energy level of Eu^{3+} ion with the strongest emission $^5D_0 \rightarrow {}^7F_2$ transition at approximately 614 nm;

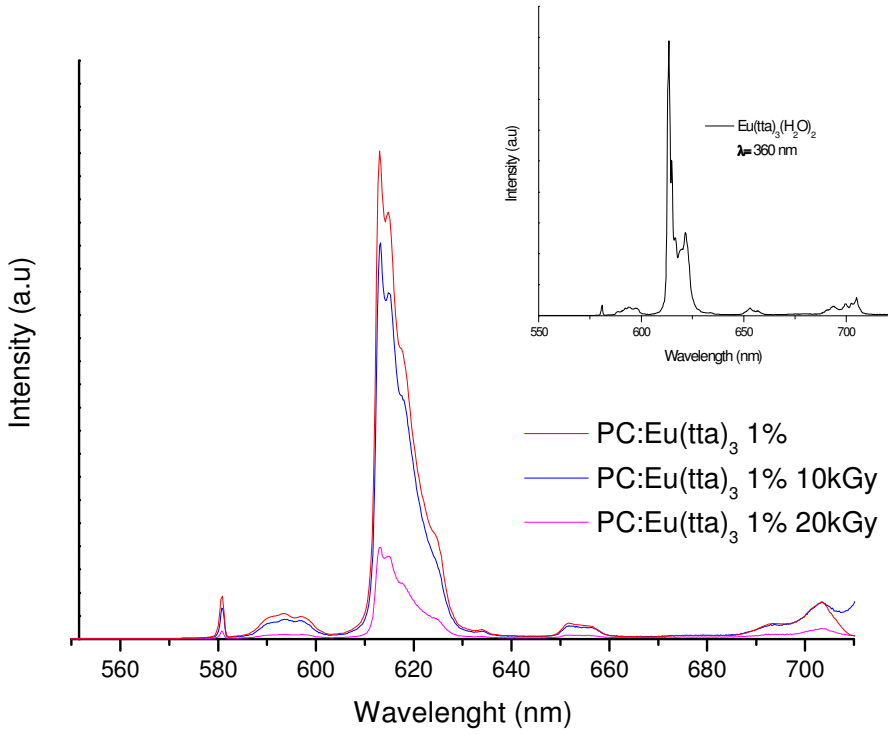

Figure 2. Emission spectra of PC:Eu(tta)$_3$ 1% irradiated and non-irradiated.

The emission spectrum of the not-irradiated PC:Eu(tta)$_3$ 1% and PC:Eu(tta)$_3$ 1% irradiated at 5, 10, and 20 kGy system exhibit broadened bands arising from excited $^5D_0$ state to ground ^5F_J states (J=0-4) of Eu^{3+} ion while the narrow bands are typical of the precursor complex in the emission spectrum (Fig. 2). This difference between complex precursor and the complex doped into the polymer is due to inhomogeneous line broadening of the intraconfigurational 4f-transitions, effect of the interaction between polymer and europium ion.

Doped samples irradiated at low dose of gamma irradiation showed a decrease in luminescence intensity with increasing of the dose.

In emission, the state most likely to emit is the $^5D_0$, thus the $^5D_0 \rightarrow {}^7F_2$ transition becomes allowed by the electric dipole effects due to the surrounding ligand fields.

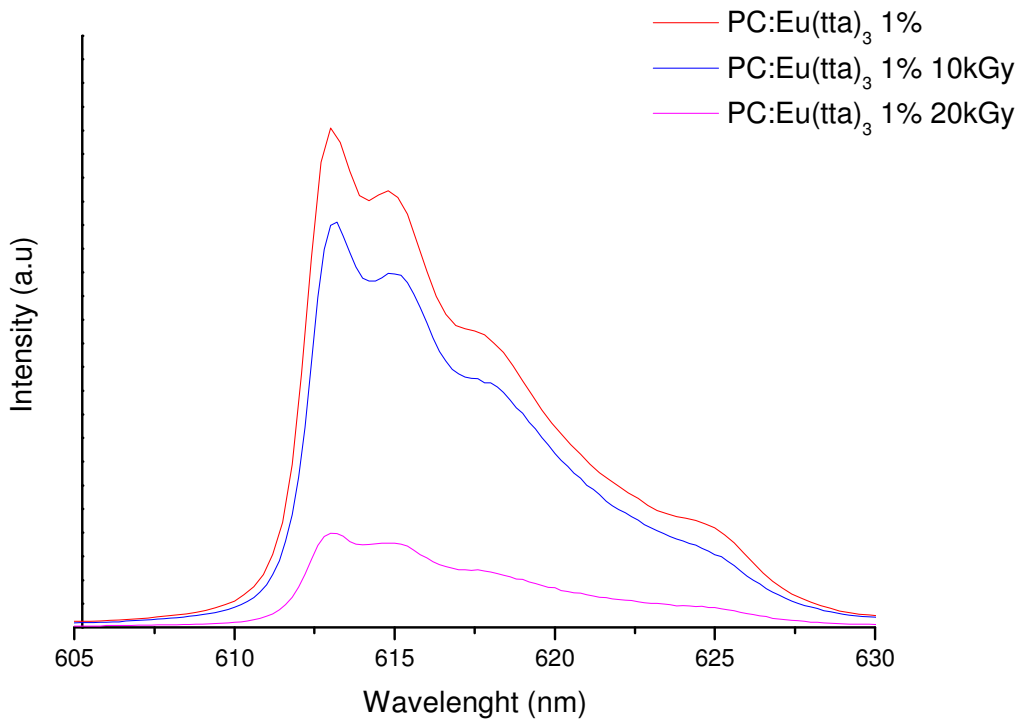

Figure 3. Emission of $^5D_0 \rightarrow {}^7F_2$ transition of PC:Eu(tta)$_3$ 1% irradiated and non-irradiated.

Due of the very sensitivity to the first coordination sphere around the Eu^{3+} ions the $^5D_0 \rightarrow {}^7F_2$ transition can be very useful to study the environment around. It should be noted that the similar behavior of $^5D_0 \rightarrow {}^7F_2$ transition, (Fig. 3) suggesting that Eu^{3+} ions occupy similar microenvironment them in PC:Eu(tta)$_3$ 1% luminescent systems.

The $^5D_0 \rightarrow {}^7F_0$ transition can give valuable information of the microenvironment around the Eu^{3+} ions, where the symmetry and the width of the band indicate the surrounding environment of the ions.

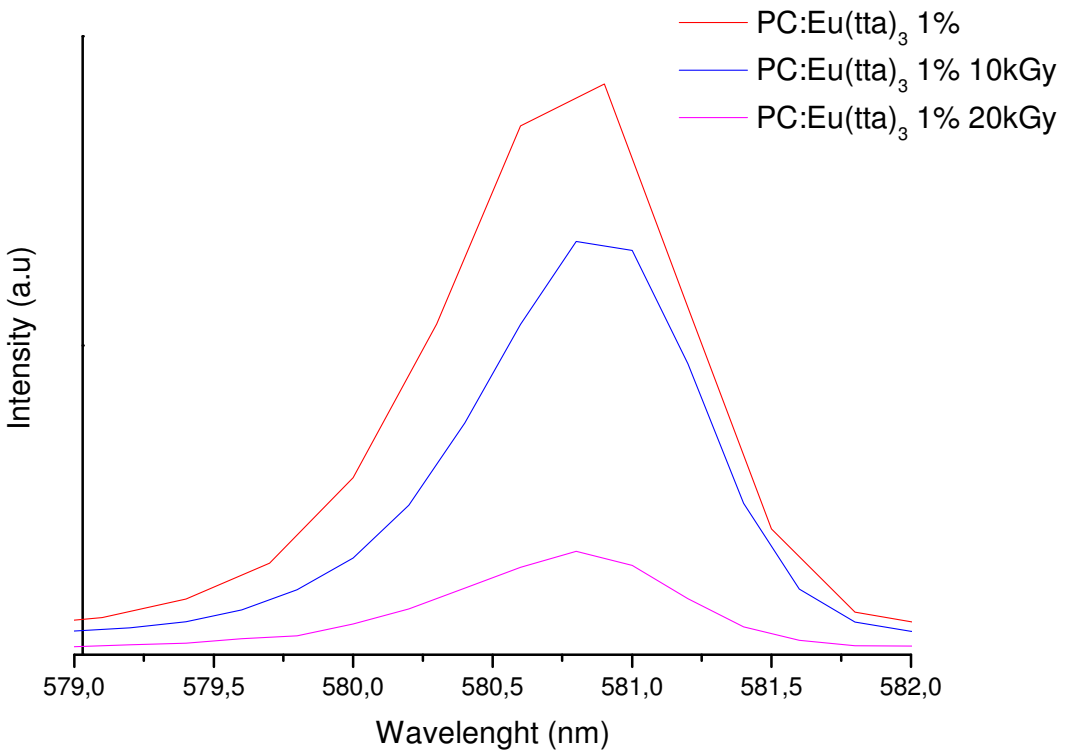

Figure 4. Emission of $^5D_0 \rightarrow {}^7F_2$ transition of PC:Eu(tta)$_3$ 1% irradiated and non-irradiated.

Due of non-degenerative in both states, one single emission transition can be seen in principle The $^5D_0 \rightarrow {}^7F_0$ transition bands of PC:Eu(tta)$_3$ (Fig. 4) shows symmetric shape and a homogenous.

4. CONCLUSION

Essentially all emission originates from the $^5D_0$ energy level of Eu^{3+} ion with the strongest emission $^5D_0 \rightarrow {}^7F_2$ transition at approximately 614 nm. The irradiated PC:Eu(tta)$_3$ doped systems show similar thermal behavior in comparison to the luminescent system PC:Eu(tta)$_3$. Doped samples irradiated at low dose of gamma irradiation showed a decrease in luminescence intensity with increasing of the dose. In conclusion, the irradiated luminescent systems are desirable for gamma radiation sensors.

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