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Effects of gamma radiation on the photoluminescence properties of polycarbonate matrices doped with terbium complex

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A B S T R A C T

Luminescent films containing terbium complex $[Tb(acac)_3(H_2O)_3]$ (acac = acetylacetonate) doped into a polycarbonate (PC) matrix were prepared and irradiated at low-dose gamma radiation with ratio of 5 and 10 kGy. The PC polymer was doped with 5% (w/w) of the Tb^{3+} complex. The thermal behavior was investigated by utilization of differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA). Changes in thermal stability due to the addition of doping agent into the polycarbonate matrix. Based on the emission spectra of PC:5% $Tb(acac)_3$ film were observed the characteristic bands arising from the $^5D_4 \rightarrow {}^7F_J$ transitions of Tb^{3+} ion ($J = 0$–6), indicating the ability to obtain the luminescent films. Doped samples irradiated at low dose of gamma irradiation showed a decrease in luminescence intensity with increasing of the dose.

1. Introduction

Trivalent rare-earth (RE^{3+}) complexes have singular spectroscopic properties due to the long decay time of luminescence, very narrow band emission lines, large Stokes shift between excitation and emission of the RE^{3+} ion, (Arnaud and Georges, 2003; Bunzli and Piguet, 2002; Evans et al., 2006; Lehn, 1990; Malta et al., 1998; Uekawa et al., 1998). In addition, the high luminescence emission efficiency of the RE^{3+} complexes is attributed to the high absorption coefficient of ligands and efficient energy transfer from the triplet (T) state of the ligand to energy levels of the RE^{3+} ion (Brito et al., 1999; Teotonio et al., 2004). Acetylacetonate anion ($acac^-$) is an excellent antenna that acts as bidentate chelate protecting the terbium ion. There is a possibility to increase the luminescence efficiency of this β-diketonate by partial substitution of coordinated water molecules by other ligands that operate as co-sensitizer in the energy transfer of rare earths systems (Parra et al., 2003).

Usually, the luminescent Tb^{3+} complexes present the energy transferred ligand to metal ion from the triplet state **T** of ligand to the excited energy $^5D_4$ level of terbium ion, showing the luminescent transitions to the ground state mainfold ^7F_J ($J = 0$–6) (Teotonio et al., 2004; Bunzli and Piguet, 2002; Parra et al., 2004). In general, the most intense transition of Tb^{3+} ion is the energy level $^5D_4 \rightarrow {}^7F_5$, corresponding to a green emission band near 546 nm.

The hard acid character of rare-earth ions has a strong affinity for the compounds that contain fluoride, oxygen and nitrogen as donor atoms make possible utilize as dopant in the host polycarbonate (PC) matrices. Recent research has developed luminescent materials doped into a polymeric matrix (Parra et al., 2003, 2005, 2006; Soares-Santos et al., 2003). Polycarbonate has excellent optical properties, such as transparency and ratio of refractive indices, low water absorption and high glass transition temperature, around 145 °C. The carbonyl groups present in polycarbonate can coordinate the rare-earth complex, a property that makes polycarbonate an interesting matrix for this purpose.

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

2. Experimental

2.1. Synthesis

The polycarbonate used was obtained from Bayer Corporation, (Makrolon®), in the form of cylindrical cut granules (∅ 2–3 mm, length 2–3 mm). The $[Tb(acac)_3(H_2O)_3]$ complex was prepared by addition of terbium chloride aqueous solution to acetylacetonate

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ethanol solution of 1:3 molar ratio; followed by addition of concentrated ammonium hydroxide until around pH∼7.

The luminescent system containing the polymer doped with the terbium complex in concentration of 5% was prepared by dissolving the polymer in THF, then mixing it with the required amount of the luminescent Tb^{3+} complex dissolved in acetone. The homogeneous solutions were heated at around 60 °C 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

Thermogravimetric (TG) curves were obtained with an SDTA-822 thermobalance (Mettler Toledo), using samples of about 2 mg in saphire crucibles, under flowing nitrogen atmosphere (50 mL min^{-1}), at heating rate of 10 °C min^{-1} in inert atmosphere.

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, and a heating rate of 10 °C min^{-1}. The DSC apparatus was calibrated with In metal (m.p. 156.61 °C; $\Delta H = 28.4\,J\,g^{-1}$).

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 m 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), with, operating at 5.72 kGy h^{-1}. The doses applied in the PC:5%Tb$(acac)_3$ samples were 5 and 10 kGy.

3. Results and discussion

3.1. Thermal properties

The TGA results showed a loss mass single event for all PC:5%Tb$(acac)_3$ doped systems in comparison with the undoped PC resin (Fig. 1). The TG curves obtained under inert atmosphere showed a decrease of the decomposition temperature of the doped polymeric films, indicating lower thermal stability when compared to the undoped polymeric sample, 382 and 369 °C, respectively.

The TG of PC:5%Tb$(acac)_3$ systems showed no mass loss in the range of 90–130 °C, suggesting the absence of water molecules in the system doped with the hydrated complex, [Tb$(acac)_3(H_2O)_3$]. The formation of the luminescent polymeric system could occur via interaction of oxygen atom of the polycarbonate with the Tb^{3+} ion. In addition, comparing to previous work, the thermal stability of doped system PC:5%Tb$(acac)_3$ is increased in comparison with [Tb$(acac)_3(H_2O)_3$] complex (Parra et al., 2002).

The gamma irradiation effect was observed on the thermal behavior of the PC:5%Tb$(acac)_3$ doped system at 5 and 10 kGy. It is observed that the thermal stability of the irradiated films increases when comparing with the non-irradiated PC:5%Tb$(acac)_3$ system, suggesting the occurrence of crosslink as effect of irradiation. On the other hand, there is no significant alteration between profiles of thermal decomposition curves of PC:5%Tb$(acac)_3$ system irradiated at low doses of 5 and 10 kGy.

The DSC curves presented in Fig. 2 show the glass transition event of irradiated doped polymeric systems compared with non-irradiated PC:5%Tb$(acac)_3$ film. The glass transition temperatures were 104, 94 and 93.6 °C for unirradiated, 5 and 10 kGy, respectively, while undoped PC has *Tg* temperature at 140 °C indicating the decrease in both comparison. In this aspect, the doping of Tb$(acac)_3$ complex changed physically the polycarbonate polymeric matrix.

3.2. Photoluminescent investigation

Fig. 3 shows the excitation spectra of PC:5%Tb$(acac)_3$ polymeric systems with non-irradiated and low dose of gamma irradiated (5 and 10 kGy) recorded at room temperature (298 K), under emission at $^5D_4 \rightarrow {}^7F_5$ transition (546 nm). The broaden band observed in spectral range of 250–375 nm of non-irradiated PC:5%Tb$(acac)_3$ film is assigned to the acetylacetonate ligand and PC polymer (Fig. 3a). At low dose of gamma irradiation (5 and 10 kGy) the excitation spectra for the irradiated gamma films (Fig. 3b and c) present a splitting of the absorption broadband (Fig. 3a) into two peaks. However, the narrow bands from intraconfigurational 4f transitions of the Tb^{3+} ion are absent.

The emission spectra of PC:5%Tb$(acac)_3$ systems were recorded in the 450–700 nm range under excitation at around 323 nm are

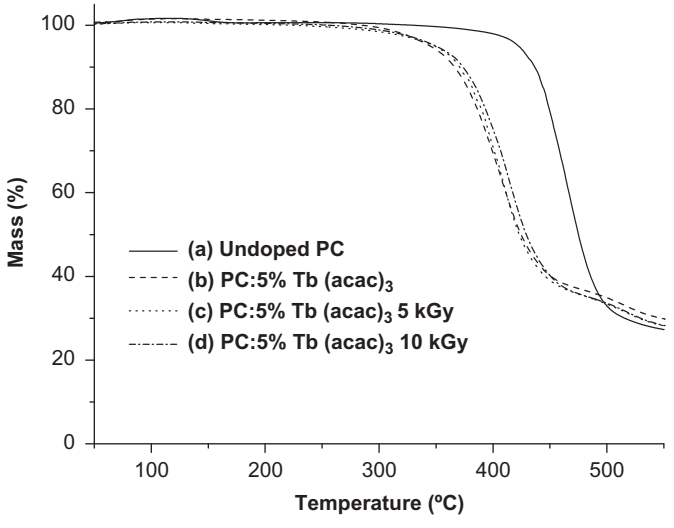

Fig. 1. Thermal decomposition curves (TGA) of films, under N_2 atmosphere: (a) undoped PC, (b) non-irradiated PC:5%Tb$(acac)_3$, (c) PC:5%Tb$(acac)_3$ irradiated at 5 kGy dose and (d) PC:5%Tb$(acac)_3$ irradiated at 10 kGy dose.

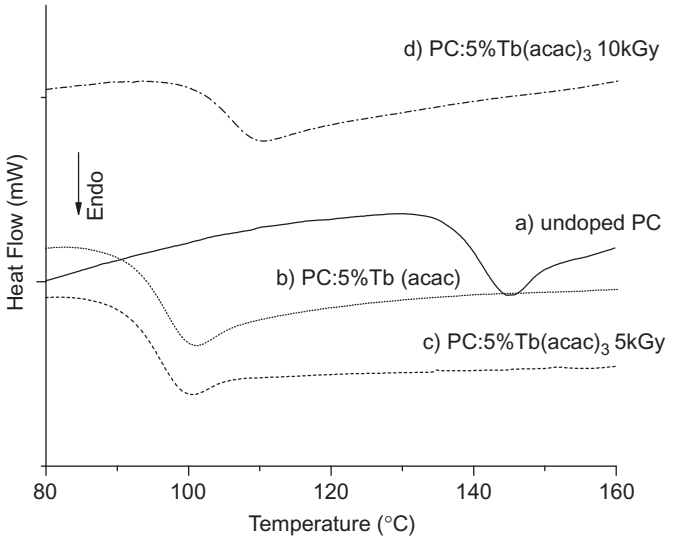

Fig. 2. Differential scanning calorimetry curves (DSC) of films, under N_2 atmosphere: (a) undoped PC, (b) non-irradiated PC:5%Tb$(acac)_3$, (c) PC:5%Tb$(acac)_3$ irradiated at 5 kGy dose and (d) PC:5%Tb$(acac)_3$ irradiated at 10 kGy dose.

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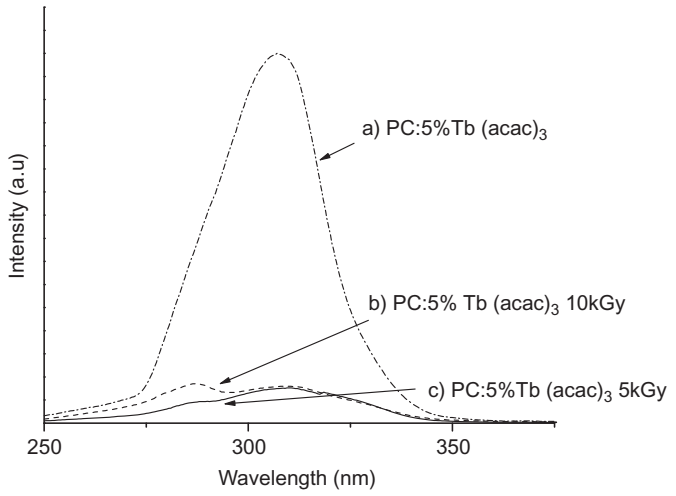

Fig. 3. Excitation spectra of PC:5%Tb(acac)$_3$ films recorded at room temperature, under emission monitored at 546 nm, with following doses of gamma irradiation: (a) sample non-irradiated (b) sample irradiated at 5 kGy and (c) sample irradiated at 10 kGy.

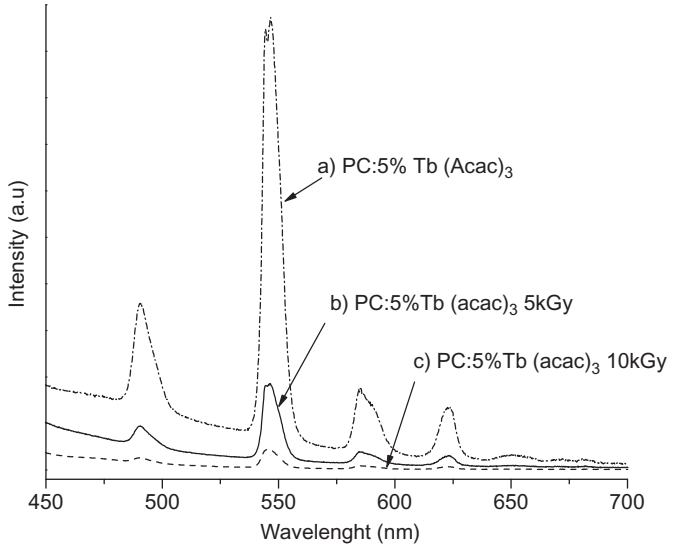

Fig. 4. Emission spectra of PC:5%Tb(acac)$_3$ films recorded at room temperature, under excitation at 323 nm,with following doses of gamma irradiation: (a) sample non-irradiated (b) sample irradiated at 5 kGy and (c) sample irradiated at 10 kGy.

shown in Fig. 4. These spectra show the emission bands corresponding to the electronic transitions $^5D_4 \rightarrow {}^7F_J$ ($J = 0$–6) of the Tb^{3+} ion, where the most intense transition are assigned to the $^5D_4 \rightarrow {}^7F_5$ transition around 546 nm. All the broaden emission bands arising from the intraconfigurational 4f of Tb^{3+} ion indicate the interaction between the Tb^{3+}-complex and PC polymer. Besides, the emission spectra of the PC:5%Tb(acac)$_3$ films (Fig. 4b and c) under low dose of gamma irradiation of 5 and 10 kGy (w/w) present a decreasing in the luminescence intensity of terbium ion with increasing of gamma irradiation. On the other hand, the PC:5%Tb(acac)$_3$ systems without gamma irradiation exhibits the highest (Fig. 4a).

4. Conclusion

The doped PC:5%Tb(acac)$_3$ system showed lower thermal stability compared to the polycarbonate resin matrix. Based on the profiles of thermal decomposition curves of PC:5%Tb(acac)$_3$ system irradiated at low doses of 5 and 10 kGy present similar thermal behavior.

The emission spectral profiles of the PC:5%Tb(acac)$_3$ system show broaden band assigned to the $^5D_4 \rightarrow {}^7F_J$ transitions of Tb^{3+} ion ($J = 0$, 1, 2, 3, 4, 5 and 6), indicating the interaction between the Tb^{3+}-complex and PC polymeric matrix. Moreover, when the PC:5%Tb (acac)$_3$ systems undergo gamma irradiation of 5 and 10 kGy (w/w) is observed a decreasing for the luminescence intensities of the Tb^{3+} ion. On the other hand, The PC:5%Tb(acac)$_3$ shows a high intensity green emission, suggesting that this polymeric system can acts as efficient light conversion molecular devices (LCMDs).

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References

Arnaud, N., Georges, J., 2003. Comprehensive study of the luminescent properties and lifetimes of Eu^{3+} and Tb^{3+} chelated with various ligands in aqueous solutions: influence of the synergic agent, the surfactant and the energy level of the ligand triplet. Spectrochim. Acta A 59, 1829–1840.

Brito, H.F., Carvalho, C.A.A., Malta, O.L., Passos, J.J., Menezes, J.F.S., Sinisterra, R.D., 1999. Spectroscopic study of the inclusion compound of β-cyclodextrin and tris(dibenzoylmethane)europium(III) dehydrate. Spectrochim. Acta Part A 55, 2403–2410.

Bunzli, J.C.G., Piguet, C., 2002. Lanthanide-containing molecular and supramolecular polymetallic functional assemblies. Chem. Rev. 102, 1897–1928.

Evans, R.C., Douglas, P., Winscom, C.J., 2006. Coordination complexes exhibiting room-temperature phosphorescence: evaluation of their suitability as triplet emitters in organic light emitting diodes. Coord. Chem. Rev. 250, 2093–2126.

Lehn, J.M., 1990. Perspectives in supramolecular chemistry—from molecular recognition towards molecular information-processing and self-organization. Angew. Chem. Int. Engl. 29, 1304–1319.

Malta, O.L., Brito, H.F., Menezes, J.F.S., Gonçalves e Silva, F.R., Donegá, M.C., Alves, C.M.S., 1998. Experimental and emission quantum yield in the compound Eu (thenoyltrifluoroacetonate)$_3$. 2(dibenzyl sulfoxide). Chem. Phys. Lett. 282, 233–238.

Parra, D.F., Mucciolo, A., Duarte, D.G., Brito, H.F., Lugao, A.B., 2006. Characterization and photoluminescence properties of diglycidyl methacrylic resin doped with the Eu^{3+} beta-diketonate complex. Appl. Polym. Sci. 100, 406–412.

Parra, D.F., Brito, H.F., Matos, J.D., Dias, L.C., 2002. Enhancement of the luminescent intensity of the novel system containing Eu^{3+}-beta-diketonate complex doped in the epoxy resin. Appl. Polym. Sci. 83, 2716–2726.

Parra, D.F., Brito, H.F., Lugao, A.B., 2005. Influence of the gamma irradiation on photoluminescence properties of DGMA doped with Eu^{3+}–β-diketonate complex. Nucl. Instrum. Methods Phys. Res. Sect. B. 236, 235–240.

Parra, D.F., Mucciolo, A., Brito, H.F., 2004. Green luminescence system containing a Tb^{3+}–β-diketonate complex doped into epoxy resin as sensitizer. Appl. Polym. Sci. 94, 865–870.

Parra, D.F., Mucciolo, A., Brito, H.F., Thompson, L.C., 2003. Optical characteristics of the Eu^{3+}-β-diketonate complex doped into epoxy resin. J. Solid State Chem. 171, 412–419.

Soares-Santos, P.C.R., Nogueira, H.I.S., Felix, V., Drew, M.G.B., Ferreira, R.A.S., Carlos, L.D., Trindade, T., 2003. Novel lanthanide luminescent materials based on complexes of 3-hydroxypicolinic acid and silica nanoparticles. Chem. Mater. 15, 100–108.

Teotonio, E.E.S., Felinto, M.C.F.C., Brito, H.F., Malta, O.L., Trindade, A.C., Najjar, R., Strek, W., 2004. Synthesis, crystalline structure and photoluminescence investigations of the new trivalent rare earth complexes (Sm^{3+}, Eu^{3+} and Tb^{3+}) containing 2-thiophenecarboxylate as sensitizer. Inorg. Chim. Acta 357, 451–460.

Uekawa, M., Miyamoto, Y., Ikeda, H., Kaifu, K., Nakaya, T., 1998. Synthesis and properties of europium complexes with β-diketone ligands for organic electroluminescent devices. Bull. Chem. Soc. Jpn. 71, 2253–2258.

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