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Spectroscopic properties of polycarbonate and poly(methyl methacrylate) blends doped with europium (III) acetylacetonate

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Abstract

Spectroscopic properties of blends formed by bisphenol-A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) doped with Europium (III) acetylacetonate [$Eu(acac)_3$], have been studied by photoacoustic spectroscopy (PAS) and photoluminescent (PL) spectroscopy. Emission and excitation spectra, excited state decay times, and quantum efficiency have been evaluated as well. PAS studies evidenced chemical interactions between the Europium complex and the PC/PMMA blend, which presented typical percolation threshold behavior regarding the Eu^{3+} content. PL spectra evidenced the photoluminescence of the Eu^{3+} incorporated into the blend. Photoluminescence property enhancement was observed for the composite in comparison with the precursor compound. Optimized emission quantum efficiency was observed for the 60/40 blend doped with 2% and 4% Europium (III) acetylacetonate.

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1. Introduction

The luminescence of rare earth complexes has been intensively studied mainly due to their possible applications as light conversion molecular devices (LCMD). These complexes constitute a

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class of new materials with potential applications in a wide range of processes and new technologies, such as luminescent materials [1], bioinorganic sensors, bioaffinity assay luminescent labels [2], europium zeolite supported complexes [3], and high technology optics and optoelectronic applications [4–11]. The application of rare earth-doped polymers to fluorescent and laser systems has large commercial, biomedical, and industrial interest [12–15].

The photoluminescence study of Eu^{3+} complexes with β-diketonate anions (e.g. acetylacetonate, acac, or tris(thenoyltrifluoroacetonate), TTA) increased in the last decade due to their high luminescence [16,17]. Their narrow emission bands (4f $\leftrightarrow$ 4f transitions forbidden by Laporte rule) lead to the emission of monochromatic red light. As the emitter $^5D_0$ level usually displays rather long decay times (ms) and is well separated (around 12 000 cm^{-1}) from the ground terms ^7F_J ($J = 0$ up to 6), it presents low non-radiative decay by high-energy vibrational modes. The low intensity $^5D_0 \rightarrow {}^7F_0$ transition observed in either excitation or emission spectra is non-degenerated, which facilitates the interpretation of optical data and provides information on the eventual existence of more than one symmetry site occupied by the Eu^{3+} ion. The $^5D_0 \rightarrow {}^7F_1$ transition is usually taken as a reference transition because it is allowed by magnetic dipole, and consequently the intensity of this transition is not considerably altered by the perturbing ligand field [18].

Europium (III) acetylacetonate complex is used as a doping europium source of polymeric matrixes and presents favorable luminescent properties due to the energy transfer between the acetylacetonate triplet state and the emitter $^5D_0$ level of Eu^{3+}. In their study of epoxy resins doped with $[Eu(acac)_3(H_2O)_3]$, Parra et al. [19] reported high luminescent properties (lifetime and emission quantum efficiency) due to the antenna effect of the absorbing energy that is then efficiently transferred to europium. Moreover, both acac or TTA anions act as chelates and protect the rare earth ion from water molecules [18], thus increasing luminescence efficiency [20,21]. Concerning the preparation of rare earth-doped materials, the use of the hybrid concept to tailor some spectroscopic characteristics by bringing together some interesting individual characteristics on the composite material (synergism) has greatly stimulated the study of new Eu^{3+}-doped materials. Enhanced visible emission under UV excitation may be obtained with a high UV absorption cross-section, an efficient intra-molecular energy transfer; and a high emitting level quantum efficiency [22,23].

Because of the optic applications of doped polymers, it is of great interest to study their luminescent properties [13]. In contrast to inorganic crystals, when polymeric materials are doped with rare earths, they do not present limitations in terms of mechanical properties, processability, and physico-chemical stability. Several studies have evaluated the influence of rare earth doping on polymers, mainly with europium (Eu) and terbium (Tb) complexes [2,13,14]. Europium composites are also used in alloys and in light projection systems. Its oxidized form is applied as a laser active medium and typically its red emission is used in TV sets.

Doping acrylic polymeric systems with rare earth ions results in very narrow emission bands, a requirement for their application as luminescent probes and sensors [14,15]. In general, acrylic materials, particularly, poly(methyl methacrylate), have a high resistance to UV radiation, are hardly hydrolyzed, exhibit excellent transparency, and good compatibility with additives and plasticizers. However, the use of pure PMMA presents some practical disadvantages, e.g. its brittleness and high water absorption. To circumvent these drawbacks, many efforts have been made through copolymerization and polymer blending. A homogeneous polymer mixture contributes to the performance of PMMA without loss in transparency. Among a number PMMA blends studied for miscibility [24–30], PMMA and PC is one of the most deeply investigated blends due to the excellent properties of PC, including outstanding ductility, low water absorption, and high glass transition temperature.

This work describes the investigation of the spectroscopic and luminescent properties of blends formed by bisphenol-A polycarbonate (PC) and poly (methyl methacrylate) (PMMA) doped with Eu^{3+}-β-diketonate, $[Eu(acac)_3]$ complex and the