

# Green Luminescence System Containing a Tb<sup>3+</sup>- $\beta$ -Diketonate Complex Doped in the Epoxy Resin as Sensitizer

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**ABSTRACT:** Photoluminescent properties of the terbium tris(acetylacetonate)tetrahydrated [Tb(acac)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>], doped in the epoxy resin, in the solid state are reported. The polymeric Tb<sup>3+</sup> system and the precursor terbium complex were characterized by elemental analysis, thermogravimetry, differential scanning calorimetry, and infrared and electronic spectroscopy. The excitation and emission spectra of the samples containing the Tb<sup>3+</sup> complex doped diglycidyl epoxy resin were recorded at 298 and 77 K and exhibited the characteristic bands arising from the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> transitions (*J* = 6–0). The system shows an increase in the luminescence intensity with the increase in the Tb<sup>3+</sup> complex in the 1, 5,

and 10% concentrations due to the energy transfer from the polymer to the rare earth ion. On the other hand, the concentration quenching of luminescence of polymer doped with 15% of the Tb<sup>3+</sup> complex was observed. The lifetime measurements ( $\tau$  = 0.81, 0.80, 0.79, and 0.78 ms) decrease with the increase of Tb<sup>3+</sup>-complex concentration (1, 5, 10, and 15%) doped in polymer. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 865–870, 2004

**Key words:** thermogravimetric analysis; films; luminescence; stabilization

## INTRODUCTION

Luminescent compounds containing rare earth (RE) ions have various applications such as biological and analytical probes.<sup>1–4</sup> Terbium complexes can be seen as light conversion molecular devices (LCMD), assuming the term antenna effect in the sequence of absorption, energy transfer, and emission involving distinct absorbing and emitting components,<sup>1</sup> resulting in a monochromatic green color emission. The technological applications of epoxy resins in adhesives demonstrated their better wetting ability, superior mechanical properties, and good chemical and high-temperature resistance. The physical properties of epoxy films such as transparency, resistance, and good compatibility with plasticizers are important features to the application of many technological devices.<sup>5–8</sup> However, fully cured epoxies have the limitation of high brittleness and, to overcome this limitation, extensive research was carried out to modify ep-

oxies.<sup>9,10</sup> Epoxy resins are derived from the bisphenol-A/epichlorohydrin, characterized by the oxirane rings (epoxy groups). This kind of resin can be crosslinked with a variety of curing agents for obtaining high-performance and high-strength materials with very good mechanical properties, adhesive, dielectric, and chemical resistance properties in various applications such as coatings, encapsulates, and laminates, other than adhesives.<sup>6</sup> The RE systems in gas, solid, or liquid environments present narrow spectral lines characteristic of 4f<sup>N</sup>-intraconfigurational transitions retaining more or less the atomic characters that are of great help in interpreting their energy-level structure. Considering that the 4f orbitals are effectively shielded from the external influence of the ligand field by the 5s<sup>2</sup> and 5p<sup>6</sup> orbitals with a splitting of <sup>2S+1</sup>L<sub>J</sub> states around 200 cm<sup>-1</sup>,<sup>11</sup> polymers doped with RE ions present advantages, under the limitations of inorganic doped materials, of processibility and mechanical properties. The polymer acts as an immobilization matrix of the doping complex, owing to the coordination of the metallic ions with the oxirane polymer ring. The structural properties are determined by the local configuration in the vicinity of the incorporated ion.<sup>12</sup> Polymer sensitized RE presents luminescence because of the intramolecular energy transfer between the absorbing ligand and the luminescent ion that results in a strong narrow-band fluorescence with a large Stokes

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shift and long decay times. In the last decade, the  $\text{Eu}^{3+}$  ion ( $4f^6$ ) was intensively studied because of the presence of the monochromatic red emission ( $\sim 612$  nm) and the nondegenerate ( $^5\text{D}_0$ ) emitting level, which is not split in any site symmetry. Another advantage is that the intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition is used as reference and is practically insensitive to the chemical environment.<sup>13,14</sup> On the other hand, the luminescence study of the compounds containing  $\text{Tb}^{3+}$  ion ( $4f^8$  configuration) is less investigated than those with the  $\text{Eu}^{3+}$  ion, owing to the complexity of the energy-level structure with the emitting  $^5\text{D}_4$  ninefold degenerated level, which complicates the assignments of their spectral data at room (298 K) and liquid-nitrogen (77 K) temperatures.<sup>15</sup> The  $\text{Tb}^{3+}$  compounds exhibit a series of bands arising from  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  transitions (where  $j = 6-0$ ), with the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  hypersensitive transition, around 540 nm, as the dominant one.<sup>16</sup> Consequently,  $\text{Tb}^{3+}$  compounds generally exhibit green color in the presence of UV radiation. Photoluminescence properties of the europium tris(thenoyl-trifluoroacetate) dehydrated,  $[\text{Eu}(\text{TТА})_3(\text{H}_2\text{O})_2]$ , incorporated in epoxy resin, in the solid state were reported.<sup>17</sup> Because of efficient energy transfer from the polymer to the RE ion, the polymer phosphorescence intensity was observed to decrease with the increase in the  $\text{Eu}^{3+}$  ion concentration. The luminescence decay profiles of the epoxy resin doped with triaquatrakis(acetylacetonate)europium(III) at 1, 5, 10, and 15% are single exponentials as reported.<sup>18</sup>

In the present article, the properties of RE polymeric systems were studied. An organic matrix, the epoxy resin, was doped with a terbium  $\beta$ -diketonate complex in ratios of 1, 5, 10, and 15% in mass percentages. The polymeric matrices substitute the water molecules of the complex precursor (luminescent suppressor) and allow efficient energy transfer for the RE ion and consequently the increase in the luminescent intensity in these systems was verified.

## EXPERIMENTAL

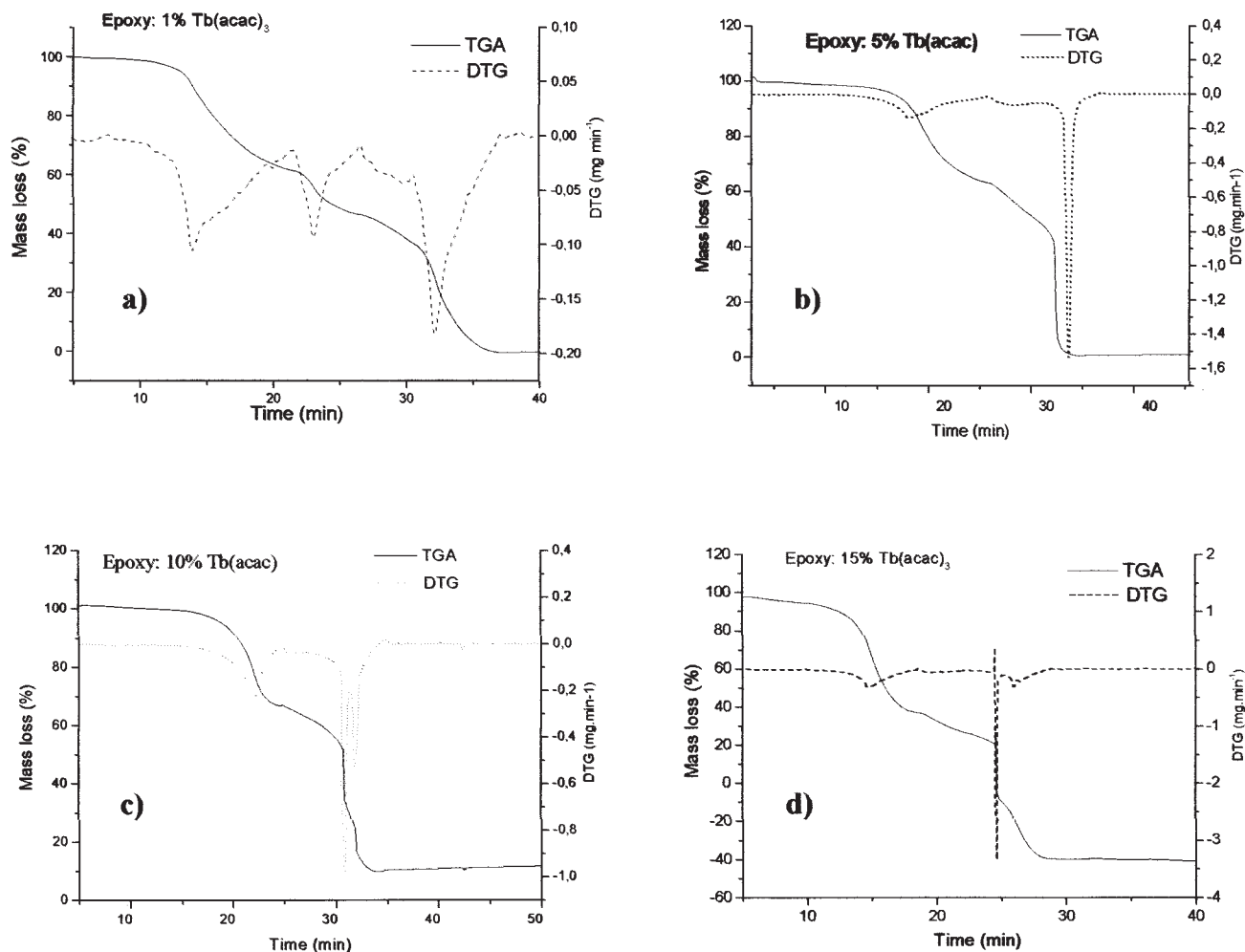
The  $[\text{Tb}(\text{acac})_3(\text{H}_2\text{O})_4]$  complex was prepared by an addition of terbium chloride (99.9% from Aldrich) aqueous solution to acetyl acetone (99.5% from Aldrich) in ethanol solution 1 : 3M ratio followed by the addition of concentrated ammonium hydroxide until  $\text{pH} \sim 7$ .<sup>18</sup> The obtained solid complex was filtrated and dried under vacuum. The epoxy resin was doped with this  $\text{Tb}^{3+}$  complex in proportions of 1, 5, 10, and 15% in mass, which were prepared by dissolving the epoxy resin (Ciba-Geigy, GT7004 with epoxy 720 g/ $\sim$ ) in acetone (Merck) and mixing it with the required amount of the  $\text{Tb}^{3+}$  complex in acetone solution. The resultant solution was stirred and heated at 60°C until complete evaporation of the solvent to obtain the solid product that was dried under vacuum for 5 h. The systems containing the  $\text{Tb}^{3+}$   $\beta$ -diketonate doped in

epoxy resin were labeled as polymer 1%, polymer 5%, polymer 10%, and polymer 15%. The  $\text{Tb}^{3+}$  content was estimated by complexometric titration with EDTA, where the compound was dissolved in methanol by using xylenol orange as an indicator. The carbon and hydrogen contents were determined by usual microanalytical procedures by using elemental analyzer CHN 2400 model (Perkin-Elmer). Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained with a TG/SDTA 821 thermobalance (Mettler-Toledo), using platinum crucibles with 2 mg of the sample, under dynamic air atmosphere (50 mL  $\text{min}^{-1}$ ), at a heating rate of 10°C  $\text{min}^{-1}$ . Differential scanning calorimetry (DSC) curves were obtained with a DSC-822 cell (Mettler) by using a platinum crucible with 5 mg of the sample, in a dynamic nitrogen atmosphere (50 mL  $\text{min}^{-1}$ ) at a heating rate of 10°C  $\text{min}^{-1}$ . The DSC system was calibrated with indium [melting point (m.p.) = 156.6°C;  $\Delta H = 28.54$  J  $\text{g}^{-1}$ ]. The infrared absorption spectra of the solid samples were measured in the range of 4000–400  $\text{cm}^{-1}$  in KBr pellets by using a Bomem model MB102 FTIR spectrophotometer. The excitation and emission spectra of the powdered samples were recorded at room and liquid-nitrogen temperature in a SPEX Fluorolog-2 spectrofluorometer, model FL212 system, double grating 0.22 m SPEX 1680 monochromators, 450 W Xenon lamp as excitation source. The lifetime measurements were recorded at room temperature ( $\sim 298$  K) by using the Phosphorimeter (SPEX 1934D) accessory coupled with the spectrofluorometer.

## RESULTS AND DISCUSSION

The terbium percentage in the hydrated precursor was determined by complexometric titration with EDTA in methanol solution and the C and H contents were determined by microanalytical procedures. The percentages calculated/found are C: 34.11/33.82; H: 5.53/5.03; and  $\text{Tb}^{3+}$ : 30.09/30.45, respectively. These results are consistent with the general formula  $[\text{Tb}(\text{acac})_3(\text{H}_2\text{O})_4]$ . The TG data of the terbium complex showed one first event in the range of 90–120°C with mass loss of 4.3% corresponding to the four water molecules corroborated with the microanalytical procedures. The anhydrous compound is thermally stable until 190°C. The TG curves obtained under oxidative atmosphere of air showed a decrease of the temperature onset of oxidation to the doped polymeric system, indicating a thermal stability lower than that of undoped polymeric samples (Fig. 1).

The TG data show that the epoxy resin is more stable to thermal oxidation than those polymeric samples doped with  $\text{Tb}^{3+}$  complex (Table I). The incorporation of RE complex into the epoxy resin decreases the onset temperature of thermal decomposition; on



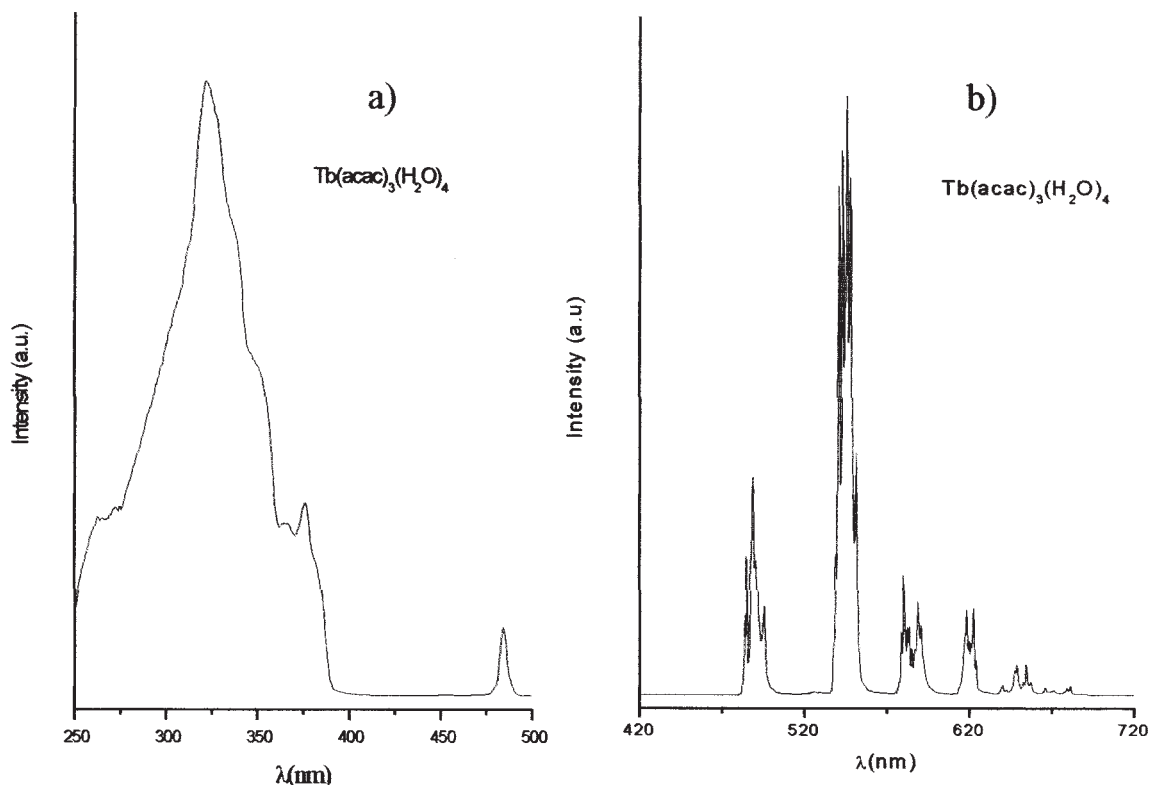
**Figure 1** Thermal analysis curves of the epoxy resin doped with 1, 5, 10, and 15% of [Tb(acac)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>], at a heating rate of 10°C/min. TG data recorded in air dynamic atmosphere of (a) Epoxy: 1% Tb(acac)<sub>3</sub>; (b) Epoxy: 5% Tb(acac)<sub>3</sub>; (c) Epoxy: 10% Tb(acac)<sub>3</sub>; and (d) Epoxy: 15% Tb(acac)<sub>3</sub>.

the other hand, the decomposition process indicates less stability of the doped system. The TG/DTG data of the Tb<sup>3+</sup> polymer system show absence of the loss mass event in the range of 90–130°C, suggesting that the interaction between the Tb<sup>3+</sup> complex and polymer occurs via replacement of the water molecules in the coordination compound. The DSC results (figure

**TABLE I**  
Temperature of Onset of Mass Loss ( $T_{\text{onset}}$ ) and Glass Transition ( $T_g$ ) of the Tb<sup>3+</sup> Complex Doped into the Epoxy Resin Compared to and the Original Polymer, at a Heating Rate of 10°C/min

Species	$T_{\text{onset}}$ (°C), in air	$T_g$ (°C)
Epoxy resin	373	43.0
Epoxy 1% Tb(acac) <sub>3</sub>	325	48.0
Epoxy 5% Tb(acac) <sub>3</sub>	316	54.0
Epoxy 10% Tb(acac) <sub>3</sub>	282	58.0
Epoxy 15% Tb(acac) <sub>3</sub>	270	58.0

not shown) indicated an exothermic peak, in the interval of 210–260°C, attributed to the polymerization of the epoxy resin. The DSC curve recorded for the undoped resin does not present events in the interval of 70–300°C when submitted at the same analytical conditions. This result suggests that the Tb<sup>3+</sup> complex doped into the resin acts as a catalyzer of the polymerization process. In addition, it was noted that at >260°C the doped system presents decomposition, in agreement with the TGA data. The IR spectra of samples of the polymer Tb<sup>3+</sup> complex presented a large complexity of peaks. The bands related to the H<sub>2</sub>O vibrational modes in the [Tb(acac)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>] complex were assigned to those observed at 3500–3200 cm<sup>-1</sup> ( $\nu_s$  and  $\nu_{\text{as}}$  OH) and at 1630–1600 cm<sup>-1</sup> (HOH bending).<sup>19</sup> 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. The  $\nu(\text{C}=\text{O})$  peak at 950 cm<sup>-1</sup> of the epoxy resin presented a shift at 930 cm<sup>-1</sup> in the polymeric doped

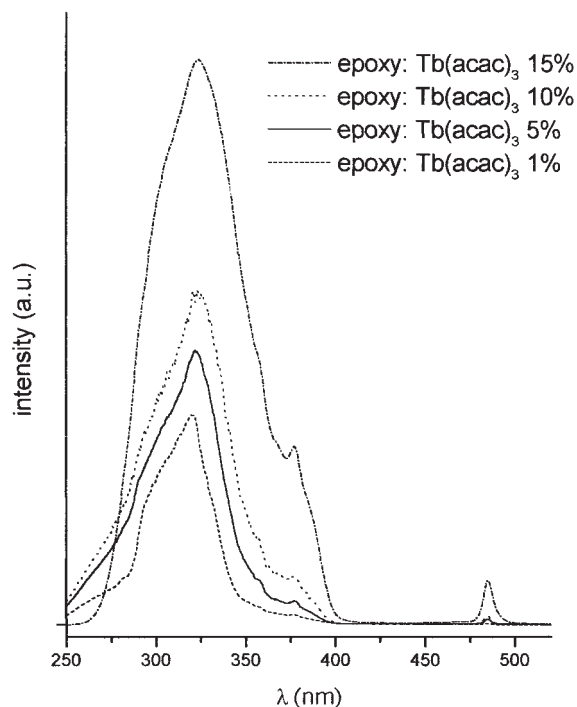


**Figure 2** Luminescence spectra of the solid-state  $[\text{Tb}(\text{acac})_3(\text{H}_2\text{O})_4]$  complex, at 77 K. (a) Excitation spectrum monitored at 543 nm and (b) emission spectrum under excitation at 323 nm.

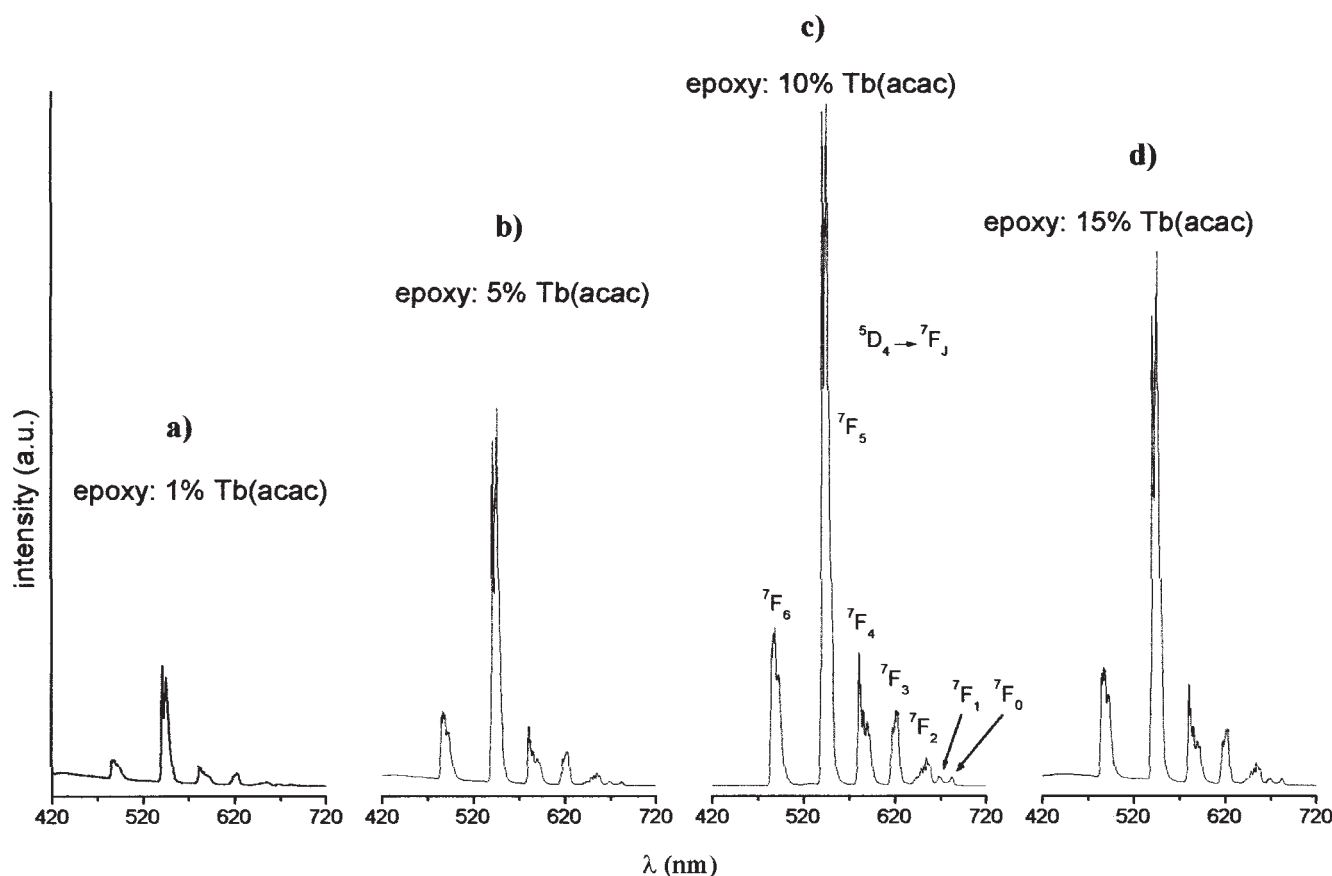
systems, indicating that the  $\text{Tb}^{3+}$  ions coordinate with the oxygen atoms of the resin.

Excitation and emission spectra (Fig. 2) were obtained from the  $[\text{Tb}(\text{acac})_3(\text{H}_2\text{O})_4]$  complex at 77 K. The excitation spectrum [Fig. 2(a)] recorded under emission at 543 nm presents intense broad bands in the range of 250–350 nm, attributed to the absorption of the acetylacetonate ligand. The shoulders arising from the 4f–4f transitions of the  $\text{Tb}^{3+}$  ion are attributed to  ${}^7\text{F}_6 \rightarrow {}^5\text{D}_1$  (323 nm),  ${}^7\text{F}_6 \rightarrow {}^5\text{L}_6$  (337 nm),  ${}^7\text{F}_6 \rightarrow {}^5\text{L}_9$  (349 nm),  ${}^7\text{F}_6 \rightarrow {}^5\text{L}_{10}$  (366 nm),  ${}^7\text{F}_6 \rightarrow {}^5\text{D}_3$  (382 nm), and also the narrow bands  ${}^7\text{F}_6 \rightarrow {}^5\text{G}_6$  (376 nm) and  ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$  (484 nm) are observed. In the case of the  $\text{Tb}^{3+}$ -complex emission spectrum [Fig. 2(b)], under excitation at 323 nm, exhibits the characteristic lines of the  $\text{Tb}^{3+}$  ion arising from the following transitions:  ${}^5\text{D}_4 \rightarrow \text{F}_6$  (490 nm),  ${}^5\text{D}_4 \rightarrow \text{F}_5$  (545 nm),  ${}^5\text{D}_4 \rightarrow \text{F}_4$  (587 nm),  ${}^5\text{D}_4 \rightarrow \text{F}_3$  (621 nm),  ${}^5\text{D}_4 \rightarrow \text{F}_2$  (653 nm),  ${}^5\text{D}_4 \rightarrow \text{F}_1$  (669 nm), and  ${}^5\text{D}_4 \rightarrow \text{F}_0$  (682 nm).

Figure 3 shows the excitation spectra of the epoxy resin doped with  $\text{Tb}^{3+}$  complex in the ratio of 1, 5, 10, and 15%, which were recorded in the range of 250–550 nm at liquid nitrogen temperature, under emission monitored at 546 nm. This figure shows an intense band, in the range of 250–400 nm, broader than the relative bands observed in Figure 2(a), indicating the interaction of the  $\text{Tb}^{3+}$  complex with the polymer. This broaden band overlaps the narrow bands arising from the 4f–4f



**Figure 3** Excitation spectra of the epoxy resin doped with  $[\text{Tb}(\text{acac})_3(\text{H}_2\text{O})_4]$  complex, at 77 K, emission at hypersensitive transition around 548 nm at the following concentrations: (a) Epoxy: 1%  $\text{Tb}(\text{acac})_3$ , (b) Epoxy: 5%  $\text{Tb}(\text{acac})_3$ , (c) Epoxy: 10%  $\text{Tb}(\text{acac})_3$ ; and (d) Epoxy: 15%  $\text{Tb}(\text{acac})_3$ .



**Figure 4** Emission spectra of the epoxy resin doped with  $Tb^{3+}$  complex, at 77 K, with excitation around 358 nm. In the sequence it is shown: epoxy: 1% $Tb(acac)_3$ ; epoxy: 5% $Tb(acac)_3$ ; epoxy: 10% $Tb(acac)_3$ ; and epoxy: 15% $Tb(acac)_3$ .

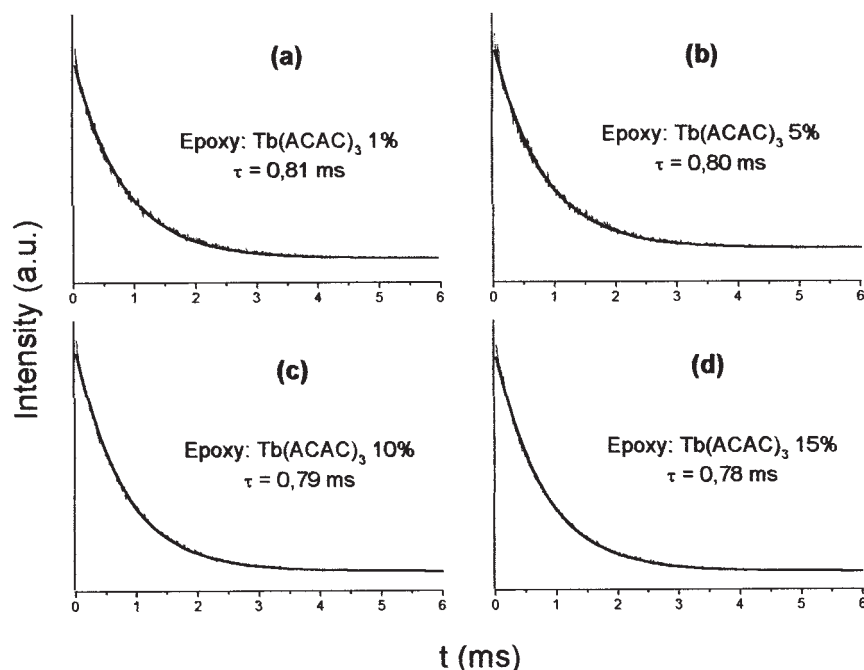
transitions of the  $Tb^{3+}$  ion for the systems doped with 1, 5, and 10%, in the range of 250–370 nm. On the other hand, the  ${}^7F_6 \rightarrow {}^5G_6$  (377 nm) and  ${}^7F_6 \rightarrow {}^5D_4$  (485 nm) transitions are noted for all doped systems. As can be seen in Figure 3, the band intensity of  $Tb^{3+}$  ion increases with the terbium complex concentration in the epoxy resin in ratios of 1, 5, 10, and 15%.

The Figure 4 presents the emission spectra of the polymer doped with  $Tb^{3+}$  complex in the ratio 1, 5, 10, and 15%, recorded at 77 K (excitation at 324 nm). The emission spectra exhibit the characteristic lines of the  $Tb^{3+}$  ion as in Figure 2(b) but the splitting of the  ${}^5D_4 \rightarrow F_J$  transitions ( $J = 6-0$ ) are different and the attribution was done following:  ${}^5D_4 \rightarrow F_0$  (682 nm),  ${}^5D_4 \rightarrow F_1$  (669 nm),  ${}^5D_4 \rightarrow F_2$  (653 nm),  ${}^5D_4 \rightarrow F_3$  (621 nm),  ${}^5D_4 \rightarrow F_4$  (587 nm),  ${}^5D_4 \rightarrow F_5$  (545 nm), and  ${}^5D_4 \rightarrow F_6$  (490 nm). The hypersensitive  ${}^5D_4 \rightarrow F_5$  transition is the best luminescence probe for the terbium ion and when we compare the emission spectra of  $Tb^{3+}$  systems under excitation at 323 nm (Fig. 4) and 358 nm (figure not shown), similar profiles are observed. The spectra at 323 nm show highest luminescence intensities due to the absorption from the ligand, and those at 358 nm are arising from the  $Tb^{3+}$  ion. These spectral data (Fig. 4) do not exhibit the broad band from the ligand in the

range of 370–550 nm, related to triplet state,<sup>18</sup> showing an efficient energy transfer from the ligand states to the emitting  ${}^5D_4$  level of the terbium ion. The emission arising from the emitting  ${}^5D_3$  level was not recorded, indicating that a rapid  ${}^5D_3 \rightarrow {}^7F_4$  radiationless transition is induced by the high vibrational frequencies of the organic ligand.<sup>20</sup> Comparing the profiles of emission spectra in the range of 420 up to 720 nm, the increase of the luminescent intensity with the increase of the  $Tb^{3+}$  concentration is observed (1, 5, and 10%). Concentration quenching of luminescence in the system doped with 15%  $Tb(acac)_3$  with a decrease in luminescent intensity is observed. Similar to  $Eu^{3+}$  ion,<sup>17,18</sup> the terbium complexes present the phenomenon of increased luminescence efficiency with the acetylacetonate chelate, by partial substitution of water molecules once coordinated on epoxy resin. In this case, the polymer acts as a sensitizer in the chelated  $Tb^{3+}$  complex.

The luminescence decay curves (Fig. 5) of the emitting  ${}^5D_4$  level for the doped systems (1, 5, 10, and 15%) were obtained by excitation on the  ${}^7F_6 \rightarrow {}^5L_9$  transition (323 nm) and emission was monitored at the  ${}^5D_4 \rightarrow {}^7F_5$  transition (543 nm). These curves have single-exponential behavior, indicating the presence of one site of





**Figure 5** Luminescence decay curves of polymer doped with  $\text{Tb}^{3+}$  complex recorded at  $\sim 298$  K in the following concentrations: (a) Epoxy: 1%  $\text{Tb}(\text{acac})_3$ , (b) Epoxy: 5%  $\text{Tb}(\text{acac})_3$ ; (c) Epoxy: 10%  $\text{Tb}(\text{acac})_3$ ; and (d) Epoxy: 15%  $\text{Tb}(\text{acac})_3$ .

symmetry for the  $\text{Tb}^{3+}$  ion. The lifetimes ( $\tau = 0.81$ , 0.80, 0.79, and 0.78 ms) decrease with the increase in  $\text{Tb}^{3+}$ -complex concentration (1, 5, 10, and 15%) doped in polymer.

### CONCLUSION

The DSC result suggests that the  $\text{Tb}^{3+}$  complex, doped into the epoxy resin, acts as a catalyzer of the polymerization process. In addition, it was noted that above  $260^\circ\text{C}$  the doped system presents decomposition in agreement with the TGA data. The excitation spectra show narrow bands arising from the  $4f-4f$  transitions of the  $\text{Tb}^{3+}$  ion and the band intensities increase with the increase in the  $\text{Tb}^{3+}$ -complex concentration in the epoxy resin in a ratio of 1, 5, 10, and 15%. The emission intensity increases with the increase of the  $\text{Tb}^{3+}$  concentration (1, 5, and 10%) except for the system doped with 15%  $\text{Tb}(\text{acac})_3$ , suggesting the occurrence of concentration quenching of luminescence. This system presents the phenomenon of increasing the luminescence efficiency of the  $[\text{Tb}(\text{acac})_3(\text{H}_2\text{O})_4]$  complex by substitution of water molecules by the polymer. In this case, the epoxy resin may act as a sensitizer for the chelate  $\text{Tb}^{3+}$  complex.

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