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Optical characteristics of the Eu^{3+} - β -diketonate complex doped into epoxy resin

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Abstract

Preparation of epoxy resins doped with triaquatris(acetylacetonate)europium(III) $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ at 1%, 5%, 10% and 15% and their luminescent properties in the solid state are reported. In addition, the catalytic properties of samples doped with $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ (I) and $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ (II) have been compared to that of a physical mixture of epoxy resin containing dicyandiamide (III) in the DSC curing process under heating. It was verified that the product (I) was cured under the same conditions as (III), but that product (II) was not cured. The compounds were characterized by elemental analysis, thermogravimetry (TG), differential scanning calorimetry (DSC) and infrared spectroscopy. The emission spectra of the Eu^{3+} -ACAC complex doped in the epoxy resin recorded at 298 and 77 K exhibited the characteristic bands arising from the ${}^5D_0 \rightarrow {}^7F_J$ transitions ($J = 0-4$). The experimental intensity parameter, Ω_2 , indicated that the Eu^{3+} ion in the precursor complex is in a more polarizable chemical environment than in the doped system. The emitter 5D_0 level lifetimes for doped samples (1%, 5%, 10% and 15%) show the luminescence decay curve profiles as single exponentials. The Eu-doped system containing the TTA ligand presented a higher emission quantum efficiency than that with ACAC. The emission quantum efficiencies (η) are also discussed.

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1. Introduction

The epoxy structure of the diglycidylether of bisphenol-A (DGEBA) allows the creation of epoxide networks by ring opening polymerization. A variety of cross-linking agents known as hardeners or catalysts that promote self-polymerization are reported [1]. The catalytic activity of trivalent rare-earth (RE^{3+}) triflates in the polymerization of epoxy resin of diglycidylether of bisphenol A has been discussed in Refs. [2,3]. These RE^{3+} compounds promote the ring opening of oxiranes and induce the thermal cross-linking process.

In a recent study [4] the europium β -diketonate complex $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$, was used to dope epoxy resin at proportions of 1%, 5% and 10% (where TTA = thenoyltrifluoroacetate). These systems were synthesized at around 60°C. The photoluminescence properties were described for the epoxy compounds

doped with the Eu^{3+} - β -diketonate. The TTA anion has electron-withdrawing capacity. This characteristic allows the rare-earth ions to coordinate to the epoxide oxygen weakening the C–O bond as described in the literature for the compounds of rare-earth triflates [5,6]. The $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ complex has been used as a precursor in the preparation nanophase of europium oxide polycrystalline thin films deposited on Si substrates [7]. Synthesis and luminescence properties of Eu^{3+} - β -diketonate complexes incorporated into solid matrices have been studied [8].

The luminescent properties of rare-earth complexes with various organic ligands have been reported in the literature [9–16]. In particular, the employment of rare-earth ions in display technologies plays an important role in optical electronic devices [17]. The trivalent europium ion has advantageous photoluminescent properties for the complex: narrow emission bands ($4f \leftrightarrow 4f$ transitions forbidden by the Laporte rule) leading to monochromatic red emission color; the main excited state is the emitter 5D_0 level separated around of

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12 000 cm^{-1} from the ground terms 7F_J ($J = 0$ up to 6); long lifetimes of the emitter 5D_0 level (ms); and large Stokes shift among others [18].

In the last decade, the synthesis and spectroscopic properties of rare-earth ions have been studied [19–23] including examples of ions doped into polymers as polyethylene glycol. In this system an increase in the luminescence intensity and decay time was observed when the polymer concentration increases. On the other hand, when polyacrylic acid was doped with Eu^{3+} ion, a decrease of the polymer phosphorescent intensity with increasing Eu^{3+} ion concentration was observed [20].

The $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ complex used as precursor into the polymeric matrix presents luminescence properties owing to the energy transfer efficiency via the triplet state (T) of the ACAC ligand to the emitter 5D_0 level of the trivalent europium ion. The ACAC anion acts as a chelate, which protects the rare-earth ion from additional water molecules by the chelating effect [24]. In addition, there is the possibility to increase the luminescence efficiency of this Eu^{3+} - β -diketonate complex by substitution of the coordinated water molecules by a ligand that will act in the chelate complex as a sensitizer [10].

Dyakonov et al. [25] point out important factors related to amine cured model epoxy resins using infrared spectroscopy. They reported that the ratio of epoxy: phenyl absorbance decreased from the uncured resin to the post-cured resin indicating the formation of a network through the reaction of epoxide groups with the curative. The reactivity of the amines as the explanation of the acceleration of the epoxy cure reaction was discussed.

Chemical reactions that take place during cure determine the resin morphology and consequently will determine the polymerization mechanism of the reaction of DGEBA with boron trifluoride–ethylenediamine (BF_3 –EN) complex suggests that the complex breaks down rapidly into active species. These species react with epoxy groups producing an activated oligomer that polymerizes in sequence. Ghaemy et al. [26] using isothermal DSC and FTIR techniques suggested that cure occurs by formation of a stable HBF_4 –epoxy complex after which the polymerization can occur. The reactive catalytic species, HBF_4 , reacts quickly with the epoxy group and the polymerization occurs via carbocation. Hwang et al. [27] compare four-synthesized diamines in the cure of epoxy resin. The results suggested that electron withdrawing groups present between two nitrogen atoms in the diamine structure results in decreasing reactivity. This kind of resin is largely used in areas such as coatings, laminates and diverse other materials for technical applications [27–29]. Chemical reactions that take place during cure determine the resin morphology and the properties of the cured thermoset.

Our current study is concerned with the synthesis of DGEBA organic compounds doped with the europium acetylacetonate complex. The investigations were made in order to observe the thermal behavior in the range 120–250°C, the usual cure interval of the epoxy resins. The behavior of two Eu – β -diketonates doped into epoxy resin in reference to a mix of dicyandiamine and the resin was also compared. The aim of this work also was to report on luminescent properties of the europium acetylacetonate complex doped into the DGEBA polymer at mass percentage ratios of 1, 5, 10 and 15.

2. Experimental

2.1. Preparation of the $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ complex doped into diglycidylether of Bisphenol-A resin (DGEBA)

The epoxy resin used is a diglycidyl ether of bisphenol A (Araldite GT 7004 with epoxy 720 g/equivalent) originated Ciba-Geigy. The preparation of the luminescent polymeric materials was processed using the epoxy resin and $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ complex precursor.

The triaquatris(acetylacetonate)europium(III) complex was synthesized by the dissolution of europium chloride, $\text{EuCl}_3 \cdot 6(\text{H}_2\text{O})$, in water, addition of acetylacetonate in ethanol in a 1:3 M ratio ($\text{Eu}:\text{ACAC}$) followed by the addition of concentrated ammonium hydroxide until the pH is approximately 7 at which the Eu – β -diketonate complex precipitates [30]. The solid compound was filtered, washed with water and dried in a vacuum desiccator over anhydrous calcium chloride at room temperature.

The Eu^{3+} ion content was estimated by complexometric titration with EDTA [31], where the individual compound was dissolved in methanol using xylenol orange as an indicator. The carbon and hydrogen contents were determined by the usual microanalytical procedures using a Perkin Elmer Model CHN 2400.

The luminescent polymer samples of 1, 5, 10, and 15 mass percent were prepared by dissolving DGEBA in acetone, mixing it with the required amount of the Eu – ACAC complex dissolved in acetone, and heating at approximately 60°C until the solvent was evaporated.

The infrared spectra of the solid samples were recorded in the range 4000–400 cm^{-1} in KBr pellets at room temperature using a Bomem model MB102 FTIR spectrophotometer.

The excitation and emission spectra of the powdered samples were measured with a SPEX Fluorolog-2 spectrofluorometer (model FL212) using the front face mode. This apparatus was fully controlled by a DM3000F spectroscopic computer. The quantum efficiency values were determined with parameters appropriate to this apparatus. The luminescence decay curves

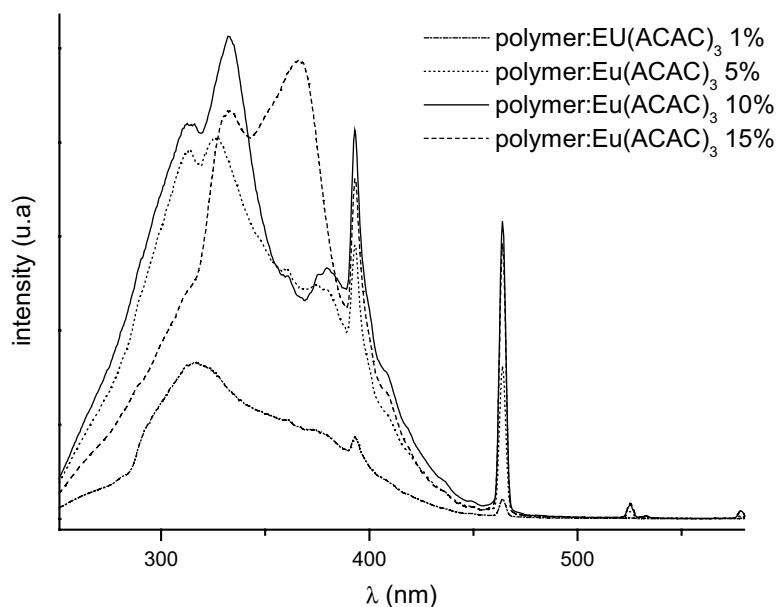


Fig. 2. Excitation spectra of the epoxy resin doped with $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ complex, at liquid nitrogen temperature monitored with emission in the hypersensitive transition around 614 nm with the following concentrations : (a) polymer 1%, (b) polymer 5% and (c) polymer 10%.

Fig. 3 shows one peak around 579 nm attributed to the ${}^5D_0 \rightarrow {}^7F_0$ transition suggesting the existence of only one site symmetry when the Eu^{3+} ion is perturbed by the ligand field from the polymer and this is confirmed by maximum number of the $(2J + 1)$ -components from the 7F_1 and 7F_2 transitions.

The inset of Fig. 3 shows the broad emission band around 450 nm arising from the organic part (ACAC-polymer) of the system. In the ACAC-polymer the ${}^5D_1 \rightarrow {}^7F_J$ transitions ($J = 0, 1$ and 2) are not observed. On the other hand, they are observed between 520 and 560 nm for the polymer doped with the $\text{Eu}(\text{TTA})_3$ complex [4] indicating higher luminescence for the TTA than the ACAC system. As expected, there is an increase in the emission intensities of the broad bands with increasing $\text{Eu}(\text{ACAC})_3$ complex concentration in the polymer. The deflection around 460 nm for all samples is due to the self-absorption of the ${}^7F_0 \rightarrow {}^5D_2$ transition.

Fig. 4 shows the emission spectra of $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ in the range 420–720 nm with excitation around 394 nm at 77 K. The profiles of the ${}^5D_0 \rightarrow {}^7F_J$ transitions are different from those observed for the emission spectra of the $\text{Eu}(\text{ACAC})_3$ complex doped into the polymer (Fig. 3) indicating that the Eu^{3+} ions are found in distinct chemical environment in the four species. When we compare the profiles for the ${}^5D_0 \rightarrow {}^7F_J$ transitions it is noted that the bands in the doped polymer systems are broader than in the precursor complex due to the inhomogeneous media of the polymeric material.

The inset of Fig. 4 presents the broaden band of low intensity in the range of 420–520 nm related to the triplet

state (T) from the ACAC ligand and narrow bands arising from the ${}^5D_1 \rightarrow {}^7F_J$ transitions ($J = 0, 1$ and 2) of Eu^{3+} ion in the range of 520–575 nm. These data suggest that the energy transfer from triplet state to europium ion is less efficient than in the $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ complex. In the inset of Fig. 3 we see that the ${}^5D_1 \rightarrow {}^7F_J$ transitions are not observed whereas they are present in the hydrated complex (inset of Fig. 4) giving evidence for the interaction between the Eu^{3+} ion and the epoxy polymer.

The radiative contribution for the depopulation of the emitter 5D_0 level was determined in order to verify the photophysical properties of the $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ complex doped into DGEBA resin on the europium luminescence characteristics, and consequently its emission quantum efficiency (η). The emission data for the ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions of the Eu^{3+} ion were used to determine the experimental intensity parameters (Ω_λ , $\lambda = 2$ and 4). As the ${}^5D_0 \rightarrow {}^7F_1$ transition is magnetic dipole allowed and its intensity is generally considered unperturbed by the ligand field, it was taken as the reference. The Ω_6 intensity parameter was not included in this study since the ${}^5D_0 \rightarrow {}^7F_6$ transition could not be observed. The emission intensity, $I = \hbar\omega AN$, is expressed in terms of the surface under the emission curve, where $\hbar\omega$ is the transition energy, and N is the population of the emitting level (5D_0). The coefficient of spontaneous emission (A) in this case may be given by

$$A_{0J} = \frac{4e^2\omega^3}{3\hbar c^3} \lambda \sum_{\lambda} \Omega_{\lambda} \langle {}^7F_J | U^{(\lambda)} | {}^5D_0 \rangle^2, \quad (1)$$

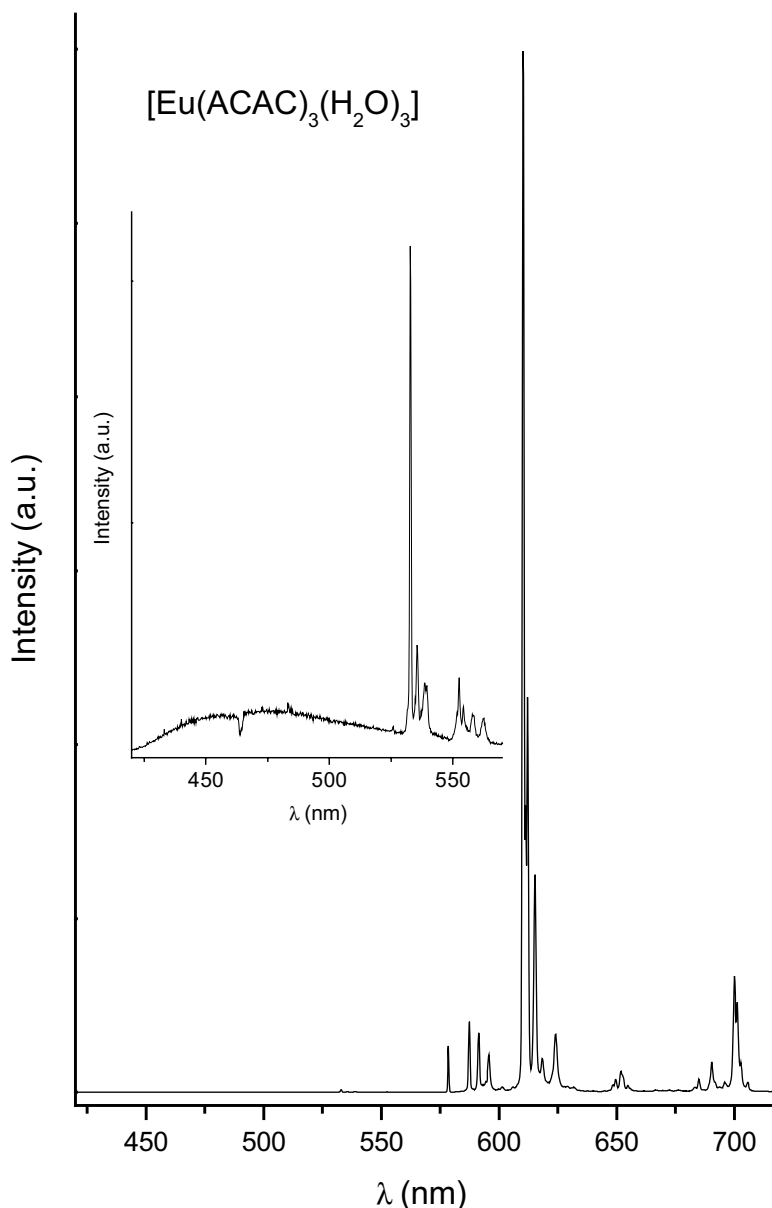


Fig. 4. Emission spectra of the [Eu(ACAC)₃(H₂O)₃] complex recorded in the range 560–720 nm under excitation at 394 nm, at 77 K. The inset shows a zoom of the ⁵D₁ → ⁷F_J levels (J = 0, 1 and 2) in the range 420–570 nm.

chemical environment than [Eu(ACAC)₃(H₂O)₃] complex.

Table 1 shows the higher values of Ω₄ parameters for the hydrated complex than for the doped polymer suggesting the sensitive character of the ⁵D₀ → ⁷F₄ transition due to the perturbation of the chelate effect of the ACAC anion and polymer on the Eu³⁺ ion.

When the DGEBA resin is doped with 1% or 10% of Eu(ACAC)₃ present values of the emission quantum efficiency lower than the hydrated complex suggesting that the non-radiative contribution is operative. However the 5% doped polymer has a value of η about twice as large as the other polymeric matrices suggesting that the polymer acts as a sensitizer reinforcing the energy

transfer from the ACAC anion to the Eu³⁺ ion considering that the band around 394 nm related to the ⁷F₀ → ⁵L₆ transition from Eu³⁺ ion is overlapped with the band from organic part.

Table 1 presents the lifetimes (τ) of the ⁵D₀ emitter state of the precursor compound and Eu³⁺ diketonates doped in the epoxy resin measured at room temperature. The decay curves show only a single exponential, suggesting that there is only one site of symmetry for the europium ion. Comparing the lifetimes between the hydrated precursor with those of the doped polymer an increase in the lifetimes of these systems is observed, as expected, from the non-radiative decay channel owing to vibronic coupling of the water molecules in the

Table 1

Photoluminescent data for the polymers doped with the $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_2]$ complexes in the ratios of 1%, 5%, 10% and 15%, in the solid state

Compounds	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	R_{02}	τ (ms)	η (%)
$[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]^a$	33.0	4.6	0.013	0.26	29.0
$[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$	29.6	12.1	0.016	0.288	32.6
Polymer:Eu(ACAC) ₃ 1%	18.0	9.7	0.012	0.32	23.6
Polymer:Eu(ACAC) ₃ 5%	22.9	11.1	0.095	0.47	42.4
Polymer:Eu(ACAC) ₃ 10%	20.4	10.1	0.014	0.32	26.1
Polymer:Eu(ACAC) ₃ 15%	20.0	9.8	0.014	0.33	26.4

The experimental intensity parameters (Ω_2 , Ω_4 , R_{02}), lifetimes (τ), emission coefficient and quantum efficiency (η) were obtained at room temperature.^a Ref. [4].

$[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ complex, similar to the compounds doped with the $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ complex.

It is important to note that the values of the emission quantum efficiencies determined for the epoxy resin doped with $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ are higher than for the hydrated precursor suggesting that the polymeric matrices act also as a sensitizer to improve the energy transfer from the TTA ligand to the Eu^{3+} ion in that system [4]. This fact indicates that the energy transfer from the ACAC ligand to Eu^{3+} ion into the epoxy polymeric matrix is lower than from the TTA ligand (Table 1).

The intensity parameter (R_{02}) is simply the ratio between the intensities of the ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions. The intensity of the ${}^5D_0 \rightarrow {}^7F_0$ transition has been attributed to the J -mixing effect, that is the mixing between states with different J quantum numbers via the even terms of the crystal potential. The R_{02} parameter may give information on the J -mixing effect associated with the ${}^5D_0 \rightarrow {}^7F_0$ transition. This effect is mainly due to the mixing between the 7F_2 manifold and the 7F_0 level through the rank two components of the crystal field, which is caused by the chemical environment around the rare-earth ion. Table 1 shows the R_{02} values for the $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ complex and polymer:Eu(ACAC)₃ $x\%$ ($x = 1, 5, 10$ and 15) where the highest R_{02} value was obtained for the doped polymer with 5%.

4. Conclusions

The polymer doped with $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ suffers degradation at the same cure condition applied to the mixture of the resin with dicyandiamine that normally cures in this situation. On the other hand the resin doped with the $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$ complex has shown a self-polymerization under these conditions. This suggests that the polymer doped with TTA is more stable than that doped with the ACAC anion, consequently the polymerization takes place with TTA.

The highest value of Ω_2 is observed in the system with 5% concentration reflecting the higher hypersensitive behavior of the ${}^5D_0 \rightarrow {}^7F_2$ transition. The highest lifetime

of the emitter 5D_0 level in the polymer:Eu(ACAC)₃ $x\%$ ($x = 1, 5, 10$ and 15) is associated with the absence of water molecules that would quench the luminescence in these systems. The polymer doped with 5% presents higher emission quantum efficiency value evidencing that the epoxy resin acts as a sensitizer increasing the energy transfer to the rare-earth ion. The highest R_{02} value was obtained for the polymer:Eu(ACAC)₃ 5% system indicating the higher mixing between the 7F_2 manifold and the 7F_0 level through the rank two components of the chemical environment around of Eu^{3+} ion.

The DGBA resin doped with the $[\text{Eu}(\text{ACAC})_3(\text{H}_2\text{O})_3]$ shows high luminescence due to the antenna effect of absorbing energy that is then efficiently transferred to the europium.

The emission quantum efficiencies obtained for the polymer:Eu(TTA)₃ 1% ($\eta = 45.7\%$), in comparison with that doped with Eu(ACAC)₃ 5% ($\eta = 42.5\%$) suggest that the energy transfer from the ACAC ligand to Eu^{3+} ion into the epoxy polymeric matrix is less efficient than the TTA ligand.

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