

Thermal behavior of the highly luminescent poly(3-hydroxybutyrate):Eu(tta)₃(H₂O)₂ red-emissive complex

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Abstract The aim of this study has been to gain a fundamental understanding of the mechanisms governing thermal degradation of luminescent poly(3-hydroxybutyrate) (PHB). PHB was doped with diaquabis(thenoyltrifluoroacetate) europium(III) complex, [Eu(tta)₃(H₂O)₂], and different luminescent systems were obtained. The thermal-stability of the luminescent films was discussed and the products of decomposition were analyzed. Thermal degradation of PHB:Eu(tta)₃x % systems (x = 0, 1, 5, 10, and 15 %) was elucidated by means of thermogravimetric analysis (TG), the thermal-stability decreases with the increase of europium complex concentration. The PHB polymer decomposed with evolution of carbon dioxide and 2-butenic acid molecules. The TG–FTIR results, of the gaseous degradation products of PHB in nitrogen atmosphere, indicated that the polymer is stable at temperatures up to 200 °C. Polymer matrix at concentrations above 5 % decomposed with evolution of water molecules among the other gaseous products, which implied the presence of a hydrated complex in the system. The luminescent films showed more flexibility due to a loss in crystallinity, which suggested a potential usefulness in technical applications.

Keywords Lanthanides · Poly(3-hydroxybutyrate) · Thenoyltrifluoroacetate · Thermal behavior

Introduction

The lanthanide β-diketonates are widely used in the development of luminescent materials due to monochromatic emission as one of their intrinsic properties. The narrow emission bands arising from the 4f-transitions and long lifetimes make these ions unique among the luminescent coordination compounds [1].

One of the most studied lanthanide β-diketonates is the precursor complex diaquabis(thenoyltrifluoroacetate)europium(III) [Eu(tta)₃(H₂O)₂]. For the Eu³⁺ complexes, energy is primarily transferred from the ligand triplet to the ⁵D₀ level leading to luminescent transitions to the ground state manifold ⁷F_J (J = 0–4) which are observed in the red spectral region. The most intense transition of Eu³⁺ is the ⁵D₀ → ⁷F₂, corresponding to a red emission band at 613 nm [2]. The high luminescence is due to the efficient energy transfer via the triplet state (T) from the tta ligand to the emitter ⁵D₀ level of the Eu³⁺ ion. The tta[−] anion acts as an excellent bidentate chelate which protects the lanthanide ion from binding with other water molecules by the chelate effect [3].

However, it is a difficult task to synthesize lanthanide complexes with high luminescent performance and to maintain their thermodynamic stability. An investigated and interesting way to enhance the Ln³⁺ complex thermal-stability is through the design of luminescent systems by combining lanthanide complexes with polymers. Thermodynamic analysis is useful to establish the degradation profiles of the coordination compounds which concerns to the theoretical research in lanthanide science aiming the design of new materials for relevant applications.

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Study of coordination compounds are reported based on Ln^{3+} ions in which Locatelli et al. [4] have synthesized solid-state compounds, where Ln stands for trivalent ion yttrium or lanthanide, and benzoate as ligand. Simultaneous thermogravimetry and differential thermal analysis (TG/DTA) was used to characterize the thermal behavior of these compounds. The results provided information about the compound composition, dehydration, thermal-stability, and the thermal decomposition into isolated compounds.

Studies of the europium complex in polyacrylonitrile composite fibers prepared by electrospinning showed that better thermal-stability can be achieved if rigid polyaniline (PANI) matrices provide a rigid environment for the complex, making it more stable, reinforcing the importance of using a polymer with good thermal-stability as the matrix for doping. Under these conditions, improvements in the photoluminescence properties of the referred europium complex were reported [5].

Luminescent europium complexes encapsulated in cage-like cubic ordered mesoporous silica showed an increase in the thermal decomposition temperature due to the encapsulation strategy [6]. Also, highly fluorescent Eu-containing polymers synthesized through the copolymerization of acrylic acid with Eu-complex were an example of the matrix-cage performance. In this case, decomposition between 390 and 450 °C was mostly caused by the loss of the complex structure units [7]. However, the decomposition temperature was higher than that of the europium complex itself (at around 270 °C), suggesting that the stability of the complex structure units was enhanced after the incorporation into the PMMA-co-AA chains [8].

According to the literature the Eu(III) ion can attract more than six oxygen atoms, effectively cross-linking the chains through intra and intermolecular coordination with the carbonyl oxygen of the MMA unit [9].

Thermal-stability was characterized in biodegradable polymers [10, 11] and could be extended for luminescent polymer systems. Kai et al. [12] reported TG results indicating that the Eu^{3+} precursor complex was immobilized in the polymer matrix by the interaction between the Eu^{3+} complex and the oxygen atoms of the PHB polymer when incorporated into the polymer host matrix. The thermal behavior of these luminescent systems was similar to that of the undoped polymer, however, a comprehensive study of the doping effect on the PHB crystallinity was yet to be reported.

Therefore, the aim of this study is to investigate the thermal behavior of high luminescent systems poly-(3-hydroxybutyrate): $\text{Eu}(\text{tta})_3$, using thermogravimetry analysis (TG), differential scanning calorimeter (DSC), and TG-FTIR analysis, exploring the physical-chemical properties of polymers privileged with the lanthanide β -diketonates high luminescence, as

well to understand the mechanism of the PHB degradation under oxidative and inert atmosphere. The TG-FTIR technique enables us to conduct simultaneous and continuous real time analysis and it can provide information about relevant products of thermal decomposition that could be used in potential applications.

Another purpose is to evaluate the influence of the doping complex into this highly crystalline polymer as a strategy to modify the PHB physical properties. In addition, there is the opportunity to improve the luminescence efficiency of these systems by partial substitution of coordinated water molecules shielding the Ln^{3+} ions from the deleterious effects of quenching processes [13] while other authors promote the enhancement of luminescence of Eu^{3+} by introducing Li^+ ion or after core-shell formation on Tb^{3+} doped in molybdates [14, 15].

Moreover, it has become evident that the detrimental effects of the synthetic polymer disposal to the environment due to their resistance to water, oxidation, and microorganism degradation of those products [16]. The biobased polymers are important materials to be developed using all the technologies that has been employed to improve the synthetic polymers.

Experimental

Materials

The poly(3-hydroxybutyrate) thermoplastic polymer, isotactic, orthorhombic, high crystallinity, optically active was supplied in powder form by PHB do Brasil S.A. (Serrana, SP, Brazil) with an average molecular mass (M_w) of 380,000 g mol^{-1} (polydispersion expressed as $M_w/M_n = 1.8$) and PHB accounting for 99.9 % of the dry material.

The $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex was prepared by adding europium chloride aqueous solution to thenoyltrifluoroacetate in ethanol solution at 1:3 molar ratio then mixing concentrated ammonium hydroxide of pH ~ 7 , following previous work [12].

The luminescent system containing the polymer doped with europium with doping percentages at 1, 5, 10, and 15 % (w/w) were prepared by dissolving the polymer in chloroform (30 % w/w) and mixing it with the required amount of the luminescent Eu^{3+} -complex dissolved in acetone. The homogeneous solutions were heated at 40 °C for 10 min and the films were obtained by solution casting in Petri dishes followed by solvent evaporation at room temperature of 25 °C. Following that, samples were heated to 60 °C when residual solvent evaporation occurred. The solid products, in film form with homogeneous surfaces,

were stored in vacuum desiccators over anhydrous calcium chloride at room temperature.

Methods

Thermogravimetry (TG) curves were obtained with an SDTA-822 thermobalance (Mettler Toledo), using samples of about 2 mg in sapphire crucibles, under dynamic nitrogen atmosphere (50 mL min^{-1}) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Heat flow curves were obtained using a differential scanning calorimeter (Mettler-Toledo, DSC 822e, Switzerland) under atmosphere of nitrogen (N_2), at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Two heating cycles were used for samples of 5 mg, the PHB was initially heated to $150 \text{ }^\circ\text{C}$ to eliminate the thermal history of the sample, cooled down to 0° (at $-10 \text{ }^\circ\text{C min}^{-1}$) and reheated to $200 \text{ }^\circ\text{C}$. The second scan (-50 to $200 \text{ }^\circ\text{C}$) was done at the same heating rate. All DSC experiments were performed in duplicate and the curves refer to the recorded curves. The crystallinity of the PHB in the blends was calculated according to the Eq. (1), where:

$$X_c(\%) = \frac{\Delta H_f \times 100}{\Delta H_o \times w(\text{PHB})} \quad (1)$$

ΔH_f is the sample melting enthalpy; ΔH_o is melting enthalpy of the 100 % crystalline PHB, assumed to be 146 J g^{-1} , and $w(\text{PHB})$ is the mass fraction of PHB in the sample. The DSC apparatus was calibrated with Indium (m.p. $156.61 \text{ }^\circ\text{C}$; $\Delta H = 28.54 \text{ J g}^{-1}$). Direct analysis of the surface topology was done using a Digital Instruments Nanoscope IIIa—Phase Atomic Force Microscopy (AFM), equipped with a $40 \mu\text{m} \times 40 \mu\text{m}$ scanner. Images were taken with standard silicon cantilevers operating in scanning mode. Samples for AFM analysis were crystallized in film form and analyzed by contact cantilever AFM.

TG–FTIR system consisted of a TA Instruments Q5000 thermoanalyzer and a Nexus 670 Thermo Nicolet Fourier Transform Infrared Spectrometer. The samples of 0.5 to 1.8 mg were heated in $100 \mu\text{L}$ open ceramic crucibles at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ in high purity (99.999 %) under nitrogen atmosphere (25 mL min^{-1}), from ambient temperature to $800 \text{ }^\circ\text{C}$. The transfer line and the gas cell were kept at constant temperature of 250 and $240 \text{ }^\circ\text{C}$, respectively.

Results and discussion

Thermal behavior

The curves of TG for PHB: $\text{Eu}(\text{tta})_3$ x % samples are similar, profiles of a one-step decomposition.

In Fig. 1 is shown the one-step decomposition of PHB: $\text{Eu}(\text{tta})_3$ x %, in N_2 atmosphere. The samples showed thermal decomposition, under inert atmosphere indicating that the initiation of the PHB breakdown occurred in a non-oxidative process. This process was influenced by the presence of the Eu^{3+} precursor complex and as a consequence the decomposition of doped films took place at a lower temperature.

The onset temperature of the decomposition step (T_{onset}), the temperature of maximum decomposition (T_{max}), and the residue content (%) are shown in Table 1. The decomposition of undoped PHB polymer started at $272 \text{ }^\circ\text{C}$. The T_{onset} for doped PHB films were displaced to 246 , 240 , 220 , and $210 \text{ }^\circ\text{C}$, in the PHB: $\text{Eu}(\text{tta})_3$ x %; $x = 1$, 5 , 10 , and 15 %, respectively. It should be noted that the film with 15 % concentration had mass loss event of decomposition in the range 80 – $100 \text{ }^\circ\text{C}$ (Fig. 1d), suggesting the presence of precursor complex structure in the PHB: $\text{Eu}(\text{tta})_3$ system, the hydrated complex as a non-reactant excess. It was observed that the increase in the europium complex concentration also reduced the T_{max} of the doped films. The residue of thermal oxidation increased as expected, with the increasing precursor complex concentration in the luminescent films, as shown in Table 1.

Interesting information was obtained from the TG curves (Fig. 1) in the range of 50 – $200 \text{ }^\circ\text{C}$ where no mass loss event was observed for concentrations lower than 15 %, indicating that the water molecules of the hydrated complex (Fig. 1e) were absent after the doping reaction. When the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex was doped into PHB polymer, the two water molecules were replaced by interaction between the Eu^{3+} complex and polymer, yielding the form PHB: $\text{Eu}(\text{tta})_3$.

In addition, another detail to be discussed is the influence of the doping process on the crystallinity of PHB films, a highly crystallized polymer by nature. The DSC technique was applied to evaluate the temperatures of first and second melting ($T_{\text{m}1}$ and $T_{\text{m}2}$) and the crystallization temperatures during cooling ($T_{\text{c}1}$) of the melted polymer [10, 11], as shown in Fig. 2. Table 2 presents the degree of crystallinity and melting/crystallization temperature values for doped and undoped PHB polymers. A decrease in crystallinity values (%) was observed for the doped samples suggesting a hindrance of the crystallization phenomenon for the doped PHB polymers. The lowest crystallinity value (45 %) was observed in the PHB: $\text{Eu}(\text{tta})_3$ 15 % system.

The largest displacements in $T_{\text{c}1}$ values, of about $18 \text{ }^\circ\text{C}$, were observed in the 10 and 15 % PHB: $\text{Eu}(\text{tta})_3$ systems. On other hand, a slight increase of approximately $3 \text{ }^\circ\text{C}$ was observed in the PHB: $\text{Eu}(\text{tta})_3$ 5 % system. The melting temperature was not influenced as drastically as the crystallization temperature, as all systems showed a

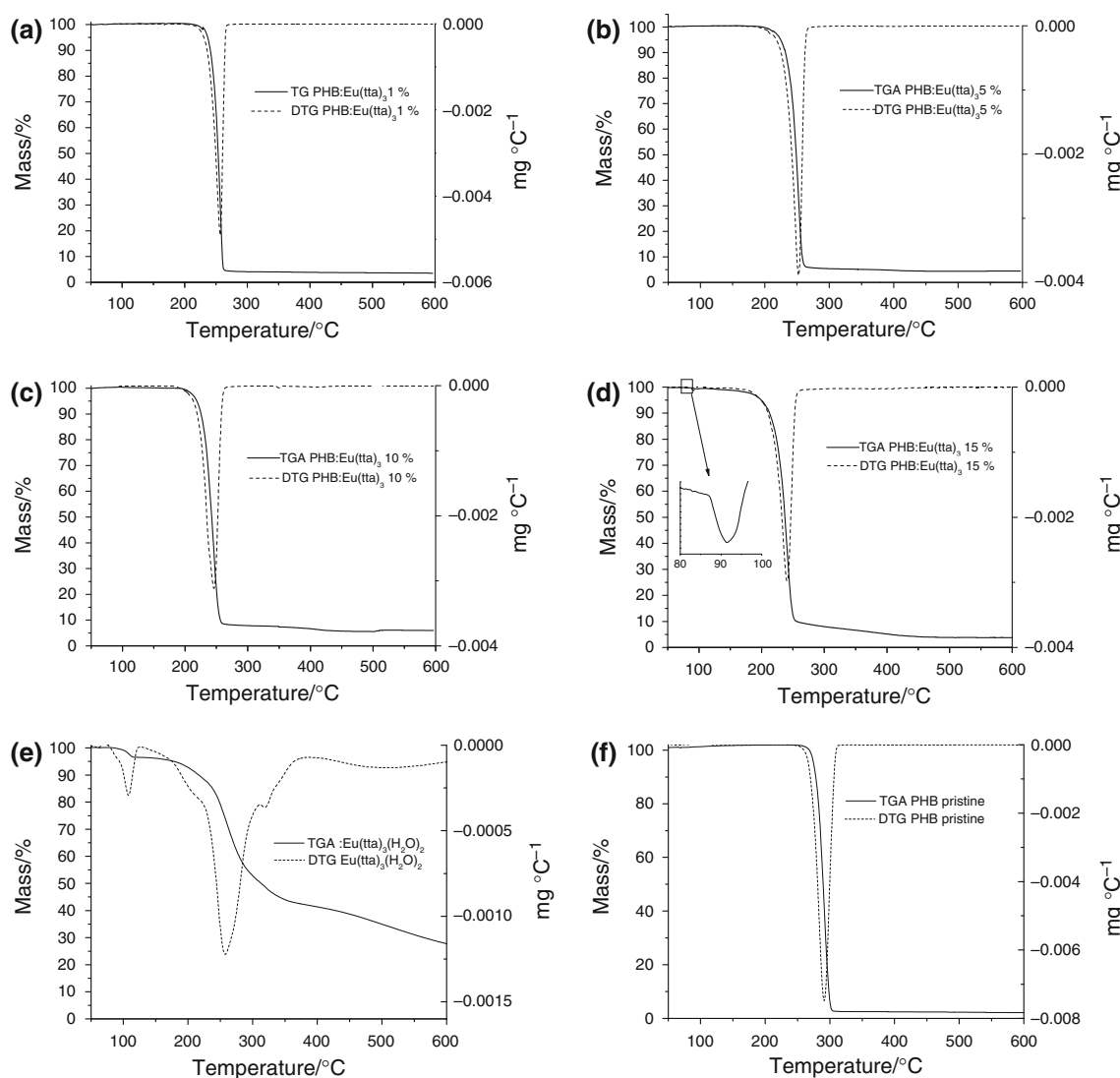


Fig. 1 Curves of TG/DTG of PHB: Eu(tta)₃ *x* % in thermal decomposition at inert atmosphere of N₂: **a** *x* = 1; **b** *x* = 5; **c** *x* = 10; **d** *x* = 15 with insert of water loss; **e** Eu(tta)₃(H₂O)₂ and **f** PHB pristine

displacement at around 5 °C for T_{m1} and T_{m2} in contrast to the undoped PHB.

Avella and Martuscelli have studied poly(3-hydroxybutyrate)/poly(ethylene oxide) blends (PHB/PEO) and reported a depression in the growth rate of PHB spherulites [17]. Crystallization temperature of the blend decreased compared to the pristine PHB, which is probably due to the lower nucleation density [10]. Similarly in regard to the PHB complex, Gunaratne and Shanks have analyzed by step-scan differential scanning calorimeter (SDSC) [18] a broad exothermic event before the melting peak in the non-reversing curve and a multiple melting reversing curve, verifying that the melting-recrystallization and remelting process is also operative [19].

The combination of PHB with europium complex, which has a low melting point, must have a plasticizer

effect and causes the decrease of the PHB melting point which was clearly observed in the first heating run. In the second heating run, where the PHB micro crystals are ordered in chain regions, the decrease of the PHB melting point was clearly observed. During the cooling at a low rate more ordered crystals were formed. The second melting peak is a double peak and its lower intensity is attributed to the imperfect crystals formed during the sample cooling.

The decrease of crystallinity observed in the doped materials, of about 12–15 % for the higher doping concentrations, is relevant regarding physical properties and processability. This level of crystallinity allows the luminescent material processability, as the flexibility is now higher, in contrast of brittleness of the PHB films and suggests potential technical applications.

Table 1 Values of thermal degradation temperatures and residue content of pure PHB and doped polymer

Sample	T_{onset} (N ₂)/K (±1 K)	T_{max} (N ₂)/K (±1 K)	Residue (N ₂) (±0.01 %)	Residue (O ₂) (±0.01 %)
PHB	545	552	0.85	0.24
[Eu(tta) ₃ (H ₂ O) ₂]	365	525	48	45
PHB:Eu(tta) ₃ 1 %	519	525	0.47	0.45
PHB:Eu(tta) ₃ 5 %	513	522	5.30	1.34
PHB:Eu(tta) ₃ 10 %	509	525	3.76	2.45
PHB:Eu(tta) ₃ 15 %	483/365	498	4.00	3.33

T_{onset} : initial degradation temperature (N₂ atmosphere); T_{max} : temperature of maximum decomposition rate obtained in derivative TG curve (N₂ atmosphere)

Atomic force microscopy (AFM)

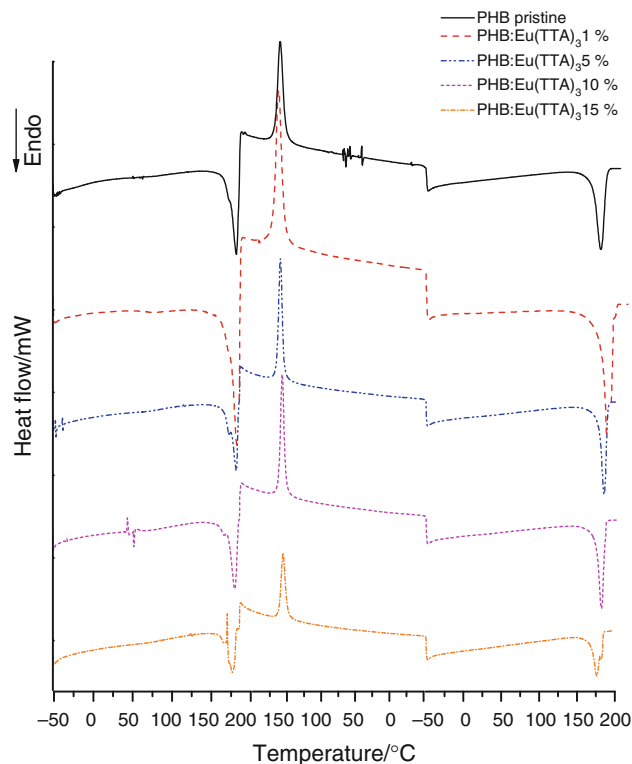
In the last years, atomic force microscopy (AFM) has become one of the most frequently used tools to understand polymer crystallization. In general, the thermal-stability of polymer crystals can be attributed to lamellar thickness and/or crystal perfection. The combination of high resolution, ease in the sample preparation and the non-destructive nature of the experiments allowed the visualization of the crystallization arrangements at the lamellar and sub-lamellar levels [19].

Hobbs et al. have studied polymer crystallization using AFM, particularly questions related to growth in polymers in situations of controlled lamellar orientation [20–22].

The initial nucleation step is crucial in the crystallization process and in the formation of a stable nucleus in the polymers. The final properties of a product can be controlled by impurity additions as nucleating agents, showing the possibility to crystallize as multiple polymorphs at the atomic level.

Madbouly et al. reported the effect of poly(vinyl alcohol) (PVA) on the crystallization behavior and morphology of PHB. The spherulitic radial growth rates were reduced by the addition of PVAc [23] and the same was observed in the blends with poly(D,L-lactic acid). The decrease in crystallinity was due to the significant melt-recrystallization observed, showing that the crystallization rates and sizes of spherulites were significantly reduced as the RPLA content increased [24].

Lima and Felisberti studied the morphology of PHB/epichlorohydrin blends and attributed the differences in the morphology of the crystalline phase to the presence of elastomeric phase in the intra-spherulitic zone and in

**Fig. 2** DSC results of PHB pristine and doped PHB:Eu(tta)₃x % (x = 1, 5, 10, and 15 %) systems**Table 2** DSC values of melting temperatures and crystallinity of undoped and doped PHB

Sample	T_{m1} /K (±1 K)	T_{m2} /K (±1 K)	T_{m2} /K second peak	T_{c1} /K (±1 K)	Crystallinity/ %
PHB	453.8	443.6	430	352.1	59.0
PHB:Eu(tta) ₃ 5 %	454.3	442.8	428	354.5	53.0
PHB:Eu(tta) ₃ 10 %	448.6	434.7	410	333.7	47.8
PHB:Eu(tta) ₃ 15 %	448.8	441.6	422	333.0	45.3

T_{m1} : melting temperature of first heating; T_{m2} : melting temperature of second heating; T_{m2} (second peak): second peak temperature of melting in the second heating; T_{c1} : crystallization temperature in cooling

consequence the texture of the PHB spherulites was strongly influenced by the elastomeric nature [25].

Figures 3, 4, and 5 allows the comparison between the superstructures of the PHB pristine film and the 5 and 10 % PHB:Eu(tta)₃ systems (after completed crystallization in closed chamber at 22 °C, at 15 × 15 μm scan size) and contour lines were drawn on the topography images to show the possible differences.

In the luminescent PHB:Eu(tta)₃ systems the occurrence of coordination may explain differences in crystallinity,

i.e., the presence of carbonyl groups (C=O) in the PHB which promotes a strong interaction with the europium complex. This kind of interaction between PHB and europium complex may constrain the nucleation rate, restricting growth of lamellae. In addition, where the molecular structure is not sufficiently regular, the crystallinity may be reduced. Molecules of regular shape may crystallize to form three-dimensionally ordered structures at sufficiently low temperatures. If disorder is added, for example, due to less regular molecular structures, the crystallization may be inhibited although the material could still undergo spontaneous aggregation, in this case to less ordered nanoscale domains [26].

TG–FTIR analysis

The TG–FTIR analysis, as a perfect tool for identification of volatile products of thermal decomposition, was performed for the pristine poly- β -hydroxybutyrate and films doped with $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ complex at different concentrations, 1, 5, and 7 %. The stack plot of gaseous products of degradation of PHB in nitrogen showed that the polymer was stable at temperatures up to about 200 °C as can be seen from Fig. 6. The further heating resulted in the evolution of carbon dioxide as gaseous products of the PHB decomposition. Carbon dioxide refers to double-band at 2,362 and 2,338 cm^{-1} derived from stretching vibrations of ($\nu\text{C-O}$) bonds of CO_2 . In addition, a band at 657 cm^{-1} was observed due to deformation vibrations of carbon dioxide molecules. The FTIR spectrum recorded at 215 °C indicated diagnostic vibrations bands of 2-butenic acid (crotonic acid) as a product of the disintegration of poly- β -hydroxybutyrate. The bands in the range 2,980–2,840 cm^{-1} originated from stretching asymmetric and symmetric vibrations of the (CH_3) group from crotonic acid. The bending asymmetric and symmetric vibrations of the methyl group $\delta(\text{CH}_3)$ were assigned to the bands at 1,443 and 1,352 cm^{-1} ,

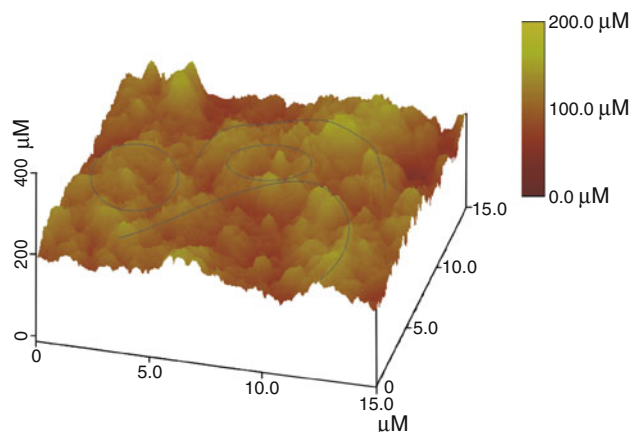


Fig. 3 AFM from PHB pristine film

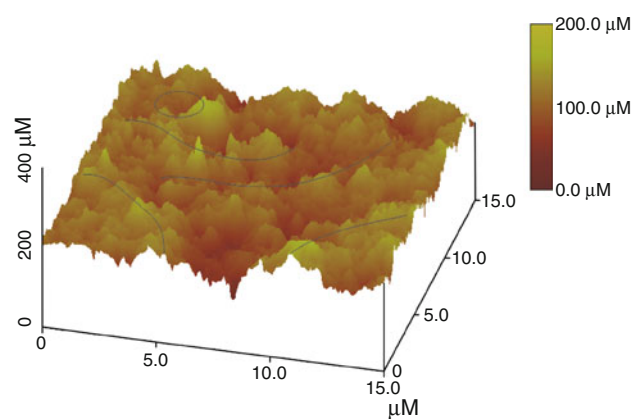


Fig. 4 AFM from PHB:Eu(tta)₃ 5 % system

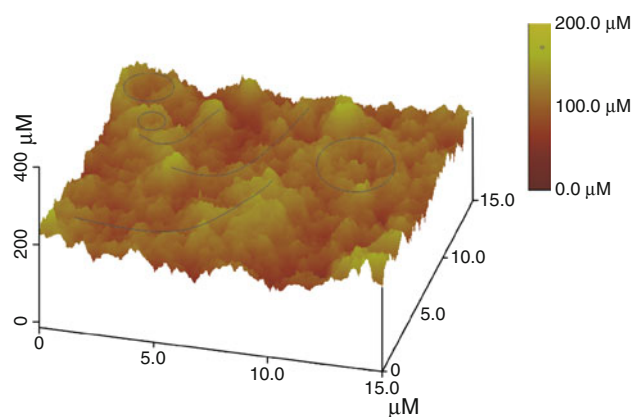


Fig. 5 AFM from PHB:Eu(tta)₃ 10 % system

respectively. At 1,768 and 1,755 cm^{-1} there were observed bands from stretching vibrations of $\nu(\text{C=O})$ group from COOH . Bonds of $-\text{CH}$ in aliphatic chains gave rise to bands in the range 3,100–3,000 cm^{-1} , 1,658, 1,144, 1,093, and 968 cm^{-1} , due to skeleton stretching vibration $\nu(=\text{CH})$, $\nu(\text{C}-\text{C})$ and out-of-plane deformation vibrations $\delta(=\text{CH})$. The most intense vibrations from crotonic acid were recorded at 280 °C (Fig. 7). At higher temperatures, only bands derived from carbon dioxide were observed [27].

The TG–FTIR spectra of the poly- β -hydroxybutyrate films doped with $\text{Eu}(\text{tta})_3$ complex at concentrations 1 and 5 % was similar to that of the PHB. Among their volatile products of decomposition, only carbon dioxide and crotonic acid were recognized. On the other hand, the polymer doped with the 7 % complex decomposed with evolution of water molecules (Fig. 7). Using simple TG analysis the hydrated complex was reached only by the system with 15 % of europium. The characteristic bands of stretching (4,000–3,500 cm^{-1}) and deformation vibrations (1,800–1,300 cm^{-1}) of OH groups from water molecules evolved across the whole temperature range (50–400 °C) [28]. The remaining products of thermal decomposition

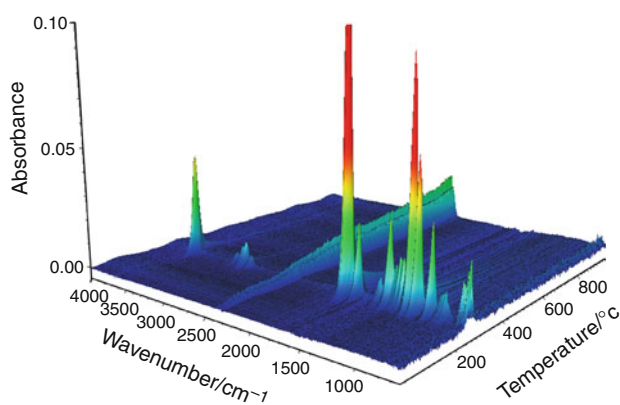


Fig. 6 FTIR spectra of the gas-phase products of undoped PHB

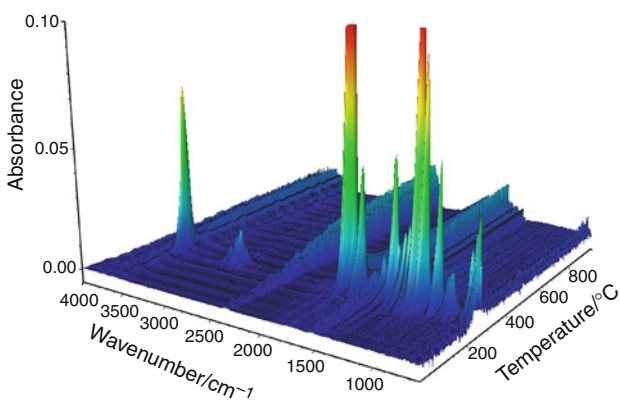


Fig. 7 FTIR spectra of the gas-phase products of PHB 7 % $\text{Eu}(\text{tta})_3$ -doped films recorded under an inert atmosphere of N_2

i.e., carbon dioxide and crotonic acid evolved at temperatures similar to that found for PHB [29].

Conclusions

The thermal-stability of the luminescent systems, under non-oxidative process of decomposition, decreased when the polymer PHB was doped with Eu^{3+} -complex. The changes in the crystallization temperatures were due to the presence of Eu^{3+} complex which hinders the growth of crystalline domains. As a consequence of the doping process, it was also observed a decrease of PHB crystallization degree as the doping with lanthanide complex increased.

The reactions between polymer and europium precursor complex occur via the replacement of the water molecules of the coordination compound, forming a new system of interaction between the Eu^{3+} -complex and the polymer. The TG–FTIR results of degradation of PHB in nitrogen (N_2) indicated that the polymer is stable up to 200 °C. The evolution of water molecules among gaseous products in the films doped with concentrations $\geq 7\%$ assigned the

presence of $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$ hydrated complex in the system other than the doped polymer material. This proved that exist one concentration, between 5 and 7 %, of saturation of the polymer for Eu^{3+} -complex doping. The doping of the polymer with europium complex affected the crystallinity of the processed films resulting in greater flexibility, usefulness for technical applications.

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References

1. Brito HF, Malta OL, Felinto MCFC, Teotonio EES. Luminescence phenomena involving metal enolates. In: Zabicky J, editor. The chemistry of metal enolates. Chichester: Wiley; 2009. p. 131–84.
2. Binnemans K. Lanthanide-based luminescent hybrid materials. *Chem Rev.* 2009;109:4283–374.
3. Parra DF, Brito HF, Matos JR, Dias LC. Enhancement of the luminescent intensity of the novel system containing Eu^{3+} - β -diketonate complex doped in the epoxy resin. *J Appl Polym Sci.* 2002;83:2716–26.
4. Locatelli JR, Rodrigues EC, Siqueira AB, Ionashiro EY, Bannach G, Ionashiro M. Synthesis, characterization and thermal behaviour of solid-state compounds of yttrium and lanthanide benzoates. *J Therm Anal Calorim.* 2007;90:737–46.
5. Wang H, Yang Q, Sun L, Zang C, Li Y, Wang S, et al. Improved photoluminescence properties of europium complex/polyacrylonitrile composite fibers prepared by electrospinning. *J Alloys Compd.* 2009;488:414–9.
6. Da Silva LCC, Martins TS, Santos Filho M, Teotônio EES, Isolani PC, Brito HF, et al. Luminescent europium complexes encapsulated in cage-like cubic ordered mesoporous silica. *Microporous Mesoporous Mater.* 2006;92:94–100.
7. Spacu P, Brezeanu M, Patron L, Contescu D, Crisan D, Segal E. Coordination compounds as raw materials for mixed oxides: part IX. Thermal decomposition of some copper-lanthanide mandelate complexes. *Thermochim Acta.* 1991;178:231–9.
8. Wang LH, Wang W, Zhang WG, Kang ET, Huang W. Synthesis and luminescence properties of novel Eu-containing copolymers consisting of Eu(III)-acrylate- β -diketonate complex monomers and methyl methacrylate. *Chem Mater.* 2000;12:2212–8.
9. Pan Y, Zheng A, Hu F, Xiao H. In the synthesis of Eu-containing copolymers consisting of Eu(III)-acrylate- β -diketonate complex monomers and methyl methacrylate. *J Appl Polym Sci.* 2006;100:1506–10.
10. Rodrigues JAFR, Parra DF, Lugão AB. Crystallization on films of PHB/PEG blends. *J Therm Anal Calorim.* 2005;79:379–81.
11. Shanks RA, Gunaratne LMWK. Comparison of reversible melting behaviour of poly(3-hydroxybutyrate) using quasi-isothermal and other modulated temperature differential scanning calorimetry techniques. *J Therm Anal Calorim.* 2011;104:1117–24.
12. Kai J, Parra DF, Brito HF. Polymer matrix sensitizing effect on photoluminescence properties of Eu^{3+} - β -diketonate complex doped into poly-beta-hydroxybutyrate (PHB) in film form. *J Mater Chem.* 2008;18:4549–54.
13. Bunzli JCG, Piguet C. Lanthanide-containing molecular and supramolecular polymeric functional assemblies. *Chem Rev.* 2002;102:1897–928.

14. Parchur AK, Prasad AI, Ansari AA, Rai SB, Ningthoujam RS. Luminescence properties of Tb³⁺-doped CaMoO₄ nanoparticles: annealing effect, polar medium dispersible, polymer film and core-shell formation. *Dalton Trans.* 2012;41:11032–45.
15. Parchur AK, Prasad AI, Rai SB, Tewari R, Sahu RK, Okram GS, Singh RA, Ningthoujam RS. Observation of intermediate bands in Eu³⁺ doped YPO₄ host: Li⁺ ion effect and blue to pink light emitter. *AIP Adv.* 2012. doi:10.1063/1.4739504.
16. Parra DF, Fusaro J, Gaboardi F, Rosa DS. Influence of poly(ethylene glycol) on the thermal, mechanical, morphological, physical-chemical and biodegradation properties of poly(3-hydroxybutyrate). *Polym Degrad Stab.* 2006;91:1954–9.
17. Avella M, Martuscelli E. Poly-D(-)(3-hydroxybutyrate)/poly(ethylene oxide) blends phase diagram, thermal and crystallization behaviour. *Polymer.* 1988;29:1731–7.
18. Gunaratne LMWK, Shanks R. Isothermal crystallisation kinetics of poly(3-hydroxybutyrate) using step-scan DSC. *J Therm Anal Calorim.* 2006;83:313–9.
19. Gunaratne LMWK, Shanks RA, Amarasinghe G. Thermal history effects on crystallisation and melting of poly(3-hydroxybutyrate). *Thermochim Acta.* 2004;423:127–35.
20. Hobbs JK, Farrance OE, Kailas L. How atomic force microscopy has contributed to our understanding of polymer crystallization. *Polymer.* 2009;50:4281–92.
21. Hobbs JK, McMaster TJ, Miles MJ, Barham PJ. Direct observations of the growth of spherulites of poly(hydroxybutyrate-co-valerate) using atomic force microscopy. *Polymer.* 1998;39:2437–46.
22. Hobbs JK, McMaster TJ, Miles MJ, Barham PJ. Cracking in spherulites of poly(hydroxybutyrate). *Polymer.* 1996;37:3241–6.
23. Madbouly SA, Mansour AA, Abdou NY. Crystallization kinetics of PHB/PVAc blends using time resolved dielectric spectroscopy. *Eur Polym J.* 2007;43:3933–42.
24. Gunaratne LMWK, Shanks RA. Miscibility, melting, and crystallization behavior of poly(hydroxybutyrate) and poly(D,L-lactic acid) blends. *Polym Eng Sci.* 2008;48:1683–92.
25. Lima JA, Felisberti MI. Poly(hydroxybutyrate) and epichlorohydrin elastomers blends: phase behavior and morphology. *Eur Polym J.* 2006;42:602–14.
26. Ikkala O, Brinke GT. Self-organized supramolecular polymer structures to control electrical conductivity. In: Nalwa HS, editor. *Handbook of advanced electronic and photonic materials and devices.* San Diego: Academic Press; 2001.
27. Silverstein RM, Webster FX. *Spectrometric identification of organic compounds.* 6th ed. New York: Wiley; 1996.
28. Teixeira KC, Moreira GF, Welber G, Quirino WQ, Legnani C, Silva RA, Cremona M, Brito HF, Achete CA. Rare-earth based OLEDs TG-FTIR thermal stability investigation of tetrakis betadiketonates complexes. *J Therm Anal Calorim.* 2011;106:587–93.
29. Gwo Hong SG, Gau TK, Huang SC. Enhancement of the crystallization and thermal stability of polyhydroxybutyrate by polymeric additives. *J Therm Anal Calorim.* 2011;103:967–75.