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Polymer 46 (2005) 253–259

polymer

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Effects of europium (III) acetylacetonate doping on the miscibility and photoluminescent properties of polycarbonate and poly(methyl methacrylate) blends

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Received 2 August 2004; received in revised form 7 October 2004; accepted 15 October 2004
Available online 19 November 2004

Abstract

Blends stand out as simple and cheap materials with unique properties. The miscibility of blends formed by bisphenol-A polycarbonate (PC) with poly(methyl methacrylate) (PMMA) doped with europium (III) acetylacetonate have been studied by differential scanning calorimetry (DSC), infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and photoluminescent (PL) spectroscopy. DSC studies demonstrated that undoped PC/PMMA blends obtained by precipitation method present one glass transition temperature, evidencing their apparent miscibility. FTIR spectra revealed synergic effects in the PC/PMMA system as well as the incorporation of the Eu^{3+} complex. TGA analysis suggested that the Eu^{3+} complex remains preferably in the PC micro-phase. SEM analysis showed that europium (III) acetylacetonate is homogeneously distributed within the blend and PL spectra evidenced the photoluminescence of Eu^{3+} incorporated into the blend.

Keywords: Poly(methylmethacrylate); Bisphenol-A polycarbonate; Europium

1. Introduction

The luminescent properties of rare earth complexes have been widely studied due to their exciting applications such as lasers, fluorescent sensors, electroluminescent displays, computer devices, and optical imaging [1–5]. The application of rare earth-doped metal polymers in fluorescent and laser systems has been much stimulated [6–9]. Because of the shielding effect of 5s and 5p electrons, it is accepted that 4f electrons of rare earth metal ions do not participate directly in the ligand bond, and that the 4f→4f transitions act as those of free atoms, resulting in very narrow absorption and emission bands [6]. Sm (III), Eu (III), and Tb (III) complexes with β-diketones (or other ligands that can absorb and transfer energy to the central metal) provide very strong luminescence due to increased absorbability [6,10–12]. Europium is one of the most important elements among the lanthanides, especially in its 3+ oxidation state. Due to the narrow f–f transition, a good sensitization of Eu^{3+} luminescence can be achieved through the antenna effect [10]. Europium (III) acetylacetonate complex [$Eu(acac)_3$] is used as an europium source in polymeric matrixes and presents luminescent properties due to the energy transfer between the acetylacetonate triplet state and the emitter $^5D_0$ level of Eu^{3+}. Moreover, the acetylacetonate anion acts as a chelate and can protect the rare earth ion from water molecules [13], thus increasing luminescence efficiency [14].

Doping acrylic polymeric systems with rare earth ions results in very narrow emission bands, which allows their application as luminescent probes and sensors [8,9]. Parra et al. [15] synthesized poly(acrylic acid) doped with Eu^{3+}. The authors reported that the lanthanide ion could be immobilized into the polymeric matrix through a strong chemical bond between europium and oxygen (Eu–O). This feature led to a homogeneous distribution of Eu^{3+} within

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0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.10.042

the composite, thus inhibiting the agglomeration of Eu^{3+} ions and reducing the quenching effect. Bermudez et al. [16] studied the supra-molecular interaction between poly(oxyethylene) (POE) and an europium complex. The authors showed that the molecular structure of the doped complex and the interactions between matrix and guest are factors important for miscibility and luminescent properties.

Polymeric blends are gazed at due to their simple and low cost preparation. In addition, the resulting materials may present unique characteristics as a consequence of a synergic effect. Different methods have been used to prepare blends, including casting, precipitation, and melt mixing [17].

Blends of bisphenol-A polycarbonate (PC) and poly (methyl methacrylate) (PMMA) have been reported on [18–25]. Gardlund [18] and Viville [26] showed that PC/PMMA blends are partially miscible due to the formation of an n–π complex between the PMMA ester group and the phenyl ring of PC. Agari et al. [18] reported miscible PC/PMMA blends obtained by casting. These authors demonstrated that this blend is a single-phase system under low critical solution temperature (LCST, 180–220 °C, depending on the composition). Kyu and Saldanha [22] discussed the effect of the solvent on the morphology of PC/PMMA films prepared by casting. This study suggests that the morphology is mostly controlled by the competition between a phase-separation phenomenon and solvent-induced crystallization. Many authors discuss the phase behavior of PC/PMMA blends based on the preparation method and on the nature of the solvent [21,25,27]. Two procedures can be used to prepare PC/PMMA blends using tetrahydrofuran (THF) as a solvent. In one, the solvent is removed by heating (47–60 °C) the polymer solution [20,22,28,29], and in the other, the solvent is removed by precipitation using a nonsolvent [21,29,30].

In general, the lanthanide complex should either be used as a dopant or dispersed into host matrixes for practical use and improved thermal and mechanical stabilities. Moreover, this procedure can improve processability and prevent luminescence quenching caused by aggregation of the chelating complex [6]. Due to their unique properties, polymeric materials doped with rare earth ions are materials suitable for this purpose, and can fulfill specific technological applications. Poly(methyl methacrylate) exhibits excellent transparency and good compatibility with additives and plasticizers. However, the use of PMMA presents some practical disadvantages, e.g. 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 losses in transparency. Among a number PMMA blends studied for miscibility, the mixture of PMMA and PC is one of the most investigated polymeric systems. This may be attributed to the excellent properties of PC, including outstanding ductility, low water absorption, and high glass transition temperature. This work describes the miscibility properties of blends formed by bisphenol-A polycarbonate and poly(methyl methacrylate) prepared through different methods. The blends were characterized using DSC, FTIR, TGA, PL spectroscopy, and SEM. To investigate the performance of these blends as luminescent materials, they were doped with europium (III) acetylacetonate and similarly characterized. These key studies are useful for a better comprehension of the energy transfer mechanisms, antenna and quenching effects involved in the luminescence of doped blends (PC/PMMA or others).

2. Experimental

Bisphenol-A polycarbonate (PC, 64,000 g mol^{-1}, Aldrich) and poly(methyl methacrylate) (PMMA, 120,000 g mol^{-1}, Aldrich) were used as received. Distilled tetrahydrofuran (THF, Merck), *n*-heptane (Merck), and hexane (Chemco) were previously distilled and used as solvents. Europium (III) acetylacetonate hydrate (Aldrich, hereafter called [$Eu(acac)_3$]) was used as received.

Five different procedures were used to prepare PC/PMMA blends by casting and precipitation. The melting procedure was not used due to the impossibility of mixing the europium source. The five procedures were labeled M1, M2, M3, M4, and M5. Details of each one are described below.

*M*1. The blend was prepared as films by casting. Weighed fractions of the polymers (0.25 g of each) were dissolved in THF (25 ml) at room temperature and homogenized for 24 h. The films were prepared by casting the solution (25 ml) onto Petri dishes at room temperature for 3 h. Soon afterwards, the films were detached from the dish and transferred to a vacuum oven for 40 h at 85 °C.

*M*2. Prepared similarly to M1, except that the homogenized solution was heated at 50 °C before its transfer to the Petri dishes and the detached films were dried in a vacuum chamber at room temperature for 3 h.

*M*3. Similarly to M1, and M2, except for film drying in a vacuum oven at 60 °C for 3 h.

*M*4. The blend was prepared as a powder by precipitation. Weighed fractions of the polymers (1:1 wt/wt) were dissolved into THF at room temperature and homogenized for 24 h. The blend was prepared by slowly pouring the mixture into a beaker containing *n*-heptane under vigorous stirring. The white precipitate was filtered, extensively washed using *n*-heptane, and dried in a vacuum oven at 85 °C for 40 h.

*M*5. Similarly to M4, except that the nonsolvent used was hexane instead of *n*-heptane.

An extraction procedure was employed in the SEM qualitative analysis of the blend microstructure. First, PC/PMMA 50/50 samples were fractured in liquid nitrogen. Soon afterwards, they were soxhlet extracted using formic

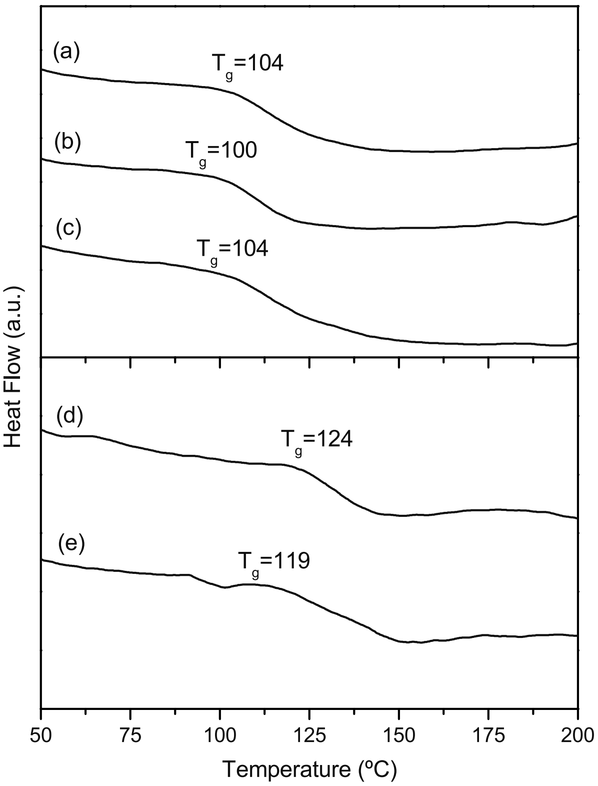

Fig. 1. DSC thermographs of blends prepared by different procedures: (a) M1, (b) M2, (c) M3, (d) M4, and (c) M5.

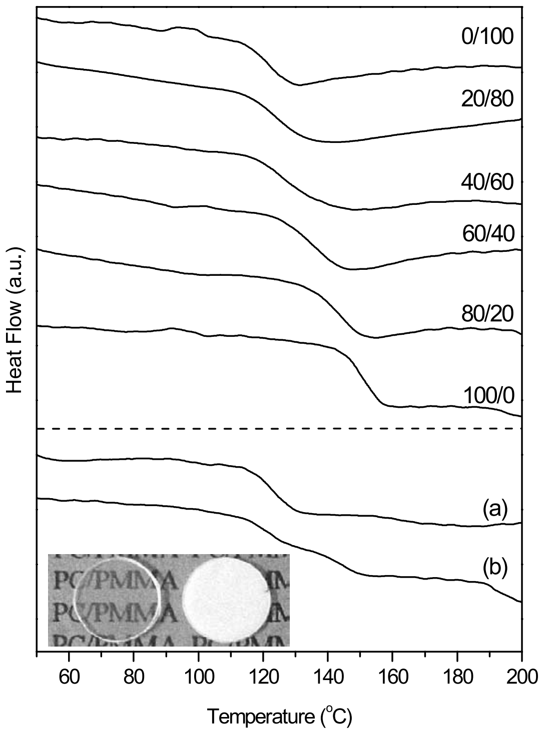

Fig. 2. DSC thermographs of blends prepared by procedure M5 with different composition ratios (top plot), and PC/PMMA (50:50) prepared by pressing piled thin sheets (bottom plot), (a) 150 °C for 30 min (transparent), and (b) 165 °C for 4 h (opaque). The photograph presents the transparent and opaque samples.

acid for 48 h. Finally, dried samples were gold coated and analyzed microscopically.

Doped PC/PMMA blends were prepared using procedure M5 by adding 0.5, 1, 2, 4, 8, 16, and 50% (wt/wt) of [Eu(acac)$_3$] to the polymeric solution (see Section 2 for M5). After pouring the solution into hexane, the yellowish precipitate formed was treated similarly.

Differential scanning calorimetry (DSC) analyses were carried out in a Shimadzu calorimeter, model 50. Thermogravimetric analyses (TGA) were carried out using a TGA Shimadzu apparatus, model 50 with N_2 flux of 20 ml min^{-1} and heating rate of 10 °C min^{-1} for both techniques. To determine glass transition temperature (T_g), samples with ca. 6 mg were closed into aluminum pans and submitted to two distinct heating processes. In the first heating, the temperature was raised from room temperature up to 180 °C to avoid thermal history. Afterwards, the sample was quickly cooled in liquid nitrogen, and then re-heated up to 200 °C. FTIR spectra were obtained in the 4000–400 cm^{-1} range using a Bomem spectrophotometer, model MB-100. Scanning electron microscopy (SEM) analyses were made in a Shimadzu microscope, model SS-550. Eu^{3+} emission spectra were obtained at room temperature with an SPEX 1704 spectrometer. The excitation source used was a 150 W Xe lamp coupled to a Kratos GM-252 monochromator.

3. Results and discussion

3.1. Casting procedures (M1, M2, and M3)

All PC/PMMA blends cast from THF were transparent and had average thickness of ca. 55 μm. Similarly as reported elsewhere [21], the cloud point caused by the low critical temperature behavior of the 1:1 (wt/wt) PC/PMMA blend prepared in this work was visually measured, being ca. 200 °C. Thus, no phase separation owing to LCST behavior that might interfere with the interpretation of the second DSC scan should occur. Hence, all second DSC scans reported were performed after heating the sample to 180 °C and quenching in liquid nitrogen. Fig. 1(a)–(c) displays DSC thermograms of samples M1, M2, and M3, respectively. One glass transition is observed, suggesting an apparent miscible mixture. However, these transitions lie below PMMA T_g (106 °C), indicating a plasticization effect on PMMA. To obtain thicker samples, 10 film sheets were piled up and pressed (at 65 Pa) at 150 °C for 30 min. Unfortunately, the specimens were brittle and opaque, indicating an ineffective densification.

3.2. Precipitation procedures (M4 and M5)

N-Heptane and hexane were used as nonsolvents. The

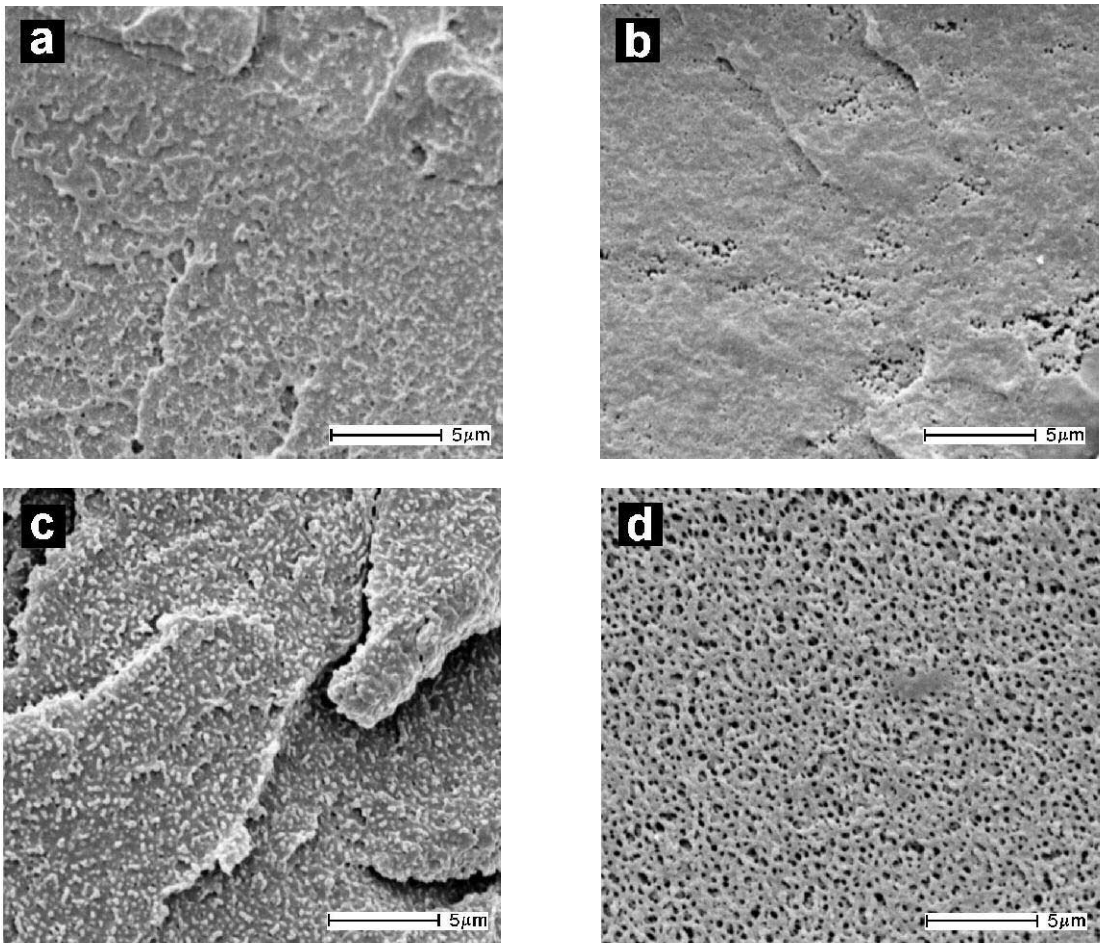

Fig. 3. Fracture surface SEM micrograph showing the microstructure of PC/PMMA 50/50 blends, (a) pressed at 150 °C for 30 min (transparent), and (b) sample pressed at 150 °C for 30 min extracted with formic acid, (c) pressed at 165 °C for 4 h (opaque), and (d) sample pressed at 165 °C for 4 h treated with formic acid.

reason for not trying other nonsolvents was discussed elsewhere [21,30]. The 50% PC blend precipitated from THF by *n*-heptane and hexane exhibited a single T_g between those of PC and PMMA, Fig. 1(d) and (e). This result suggests a good degree of apparent miscibility. However, this miscibility should be judged as 'apparent' or 'constrained', since the nonsolvent effect is hypothesized (sometimes postulated [21]) to stem from the blockage of the weak interactions responsible for miscibility equilibrium.

Considering the necessity of thick and transparent samples, a subsequent study was made using procedure M5 (final product as a powder). The PC/PMMA precipitate, originally an opaque powder, was pressed at different temperatures and periods to obtain sample sheets. The pressure used was 65 Pa using a stainless steel mould (0.8 cm diameter). More detailedly, the PC/PMMA blends with different composition ratios were prepared. Fig. 2 presents DSC thermograms of these samples (top plot). Pure PMMA and PC present T_g at 106 and 145 °C, respectively, which agrees with data in literature [21]. Considering the difference of ca. 40 °C between the T_g of PC and PMMA, one can use the DSC curves to evaluate blend miscibility (or apparent miscibility in our case) [17–19,30,31]. The single T_g observed for the blends is located at temperatures intermediate to the T_g of the pure polymers, evidencing that miscibility (or a larger partial miscibility) can be reached for different percentages of the components. The specimen pressed at 150 °C for 30 min was transparent; otherwise, that pressed at 165 °C for 4 h was opaque. The bottom plot shows DSC thermograms for these samples (500 μm thick). A single transition at 119 °C was observed for the transparent sample, suggesting a larger partial miscibility between PC and PMMA. The opaque film presented two transitions, at 113 and 137 °C. Thus, the more miscible blend became less miscible after the thermal treatment (annealing-like procedure [32]). This micro-phase separation can be assigned to the heating procedure at the temperature corresponding to the two-phase region in the LCST curve of the PC/PMMA blend [21]. The PC/PMMA blends with 50 wt% PC showed a microstructurally dispersed phase/matrix morphology, as can be concluded

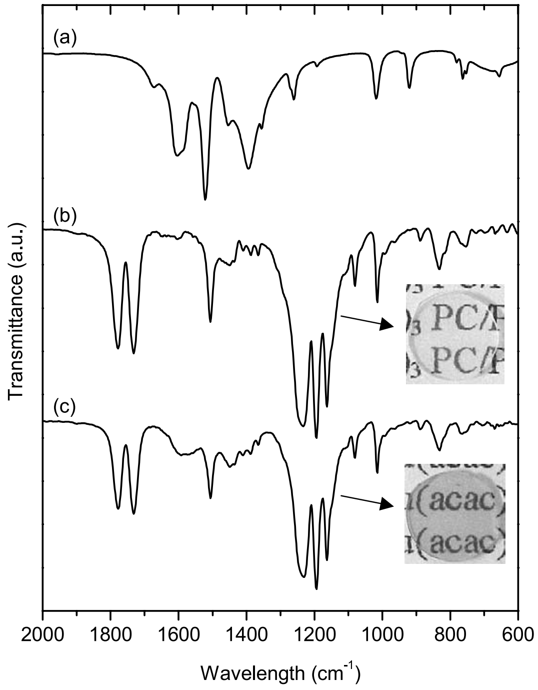

Fig. 4. FTIR spectra of (a) pure [Eu(acac)$_3$], (b) undoped PC/PMMA (60:40), and (c) doped PC/PMMA (60:40, with 50% of [Eu(acac)$_3$]). The photographs show undoped PC/PMMA (60:40), and doped PC/PMMA (60:40, with 50% Eu complex) blends.

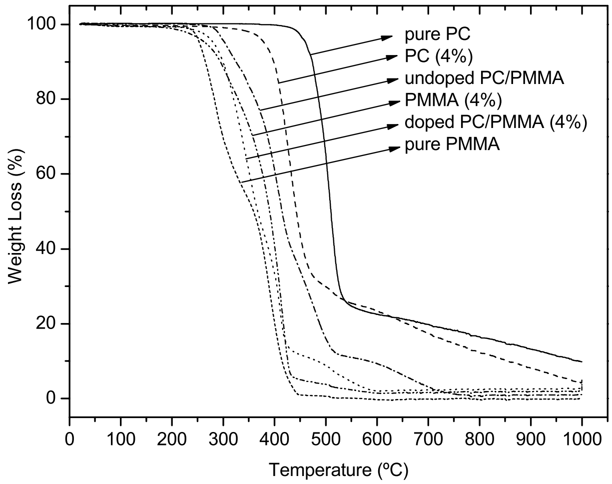

Fig. 5. TG curves of pure PC, pure PMMA, doped PC (4% [Eu(acac)$_3$]), doped PMMA (4% [Eu(acac)$_3$]), undoped PC/PMMA (50:50), doped PC/PMMA (50:50, 4% [Eu(acac)$_3$]).

from the extraction experiments, Fig. 3. The larger partial miscibility of the transparent sample, supported by Fig. 3(d), agrees with DSC measurements.

The FTIR spectra of pure PMMA, and of the 40:60 and 60:40 PC/PMMA blends (no shown) suggest that the PC/PMMA blend is a chemically interacting mixture [33, 34]. FTIR spectra of [Eu(acac)$_3$], undoped blend (60:40), and that doped with 50% (wt/wt) [Eu(acac)$_3$] are shown in Fig. 4. The blend 60:40 (%, fraction weight) was chosen based on its very high transparency when compared to other samples. Comparing to curve (b), the broader band at ca. 1600 cm^{-1} of the doped blend is probably due to the signal at 1596 cm^{-1} assigned to the C=O deformation of the acetylacetonate group. This fact suggests that europium (III) acetylacetonate was incorporated into the polymeric blend. The broadening of the signals at 756, 1227, 1362–1430, and 1505 cm^{-1} was also assigned to the europium compound.

Aiming to investigate blend thermal stability and mainly the effect of Eu complex doping, thermal analyses of the pure components, the pure blend (50:50), and doped samples were performed, Fig. 5. Analyzing the weight loss ranging between 99 and 15%, one can suggest the preferable localization of the Eu complex within the blend as follows. After considering the stabilities of PC and PMMA (pure samples) and the relative influence of [Eu(acac)$_3$] on blend thermal behavior, more specifically on decomposition temperature, the lower stability of the 50:50 doped PC/PMMA blend suggests that the Eu complex preferably remains in the PC rather than the PMMA phase. To support this statement, it is necessary to invoke the pioneering work of Rincón and McNeill [34] on the thermal behavior of PC/PMMA blends. These authors postulated that the PMMA macroradicals (created during thermal pyrolysis) abstract hydrogen atoms from isopropyl groups of PC molecules, followed by chain scission of the resulting PC radicals, leading to the destabilization of PC in 50:50 PC/PMMA blends. This mechanism is consistent with the thermal behavior presented by our blends, i.e., the higher the PMMA content (60, 70, 80, and 90%), the lower the thermal stability of the blend (thermograms not shown). Now, let us consider the effect of adding the Eu complex. Fig. 5 shows, in general, that the addition of the Eu complex increases the thermal stability of PMMA and decrease the thermal stability of PC. An important feature arises from this observation, i.e. if [Eu(acac)$_3$] were homogeneously distributed between PC and PMMA phases, the thermal stability of the doped PC/PMMA blend should be at best slightly lower than that of the undoped blend. However, the thermal stability of the doped blend is quite lower than that of the undoped one. Therefore, the only support for this occurrence is a higher [Eu(acac)$_3$] content in the PC phase; otherwise, the thermal stability of the doped blend should be closer to that of the undoped one (since [Eu(acac)$_3$] stabilizes PMMA and avoids the formation of macroradicals, which consequently, would thermally destabilize the blend). Photoacoustic spectroscopy measurements also evidenced the preferable localization of [Eu(acac)$_3$] in the PC phase [35].

Fig. 6 presents SEM micrographs of fractured undoped PC/PMMA (60:40, Fig. 6(a)), and doped (60:40, Fig. 6(b) and (c)) samples. No significant phase difference was microscopically observed in these samples at this magnification level; however, the phase domains might be too small

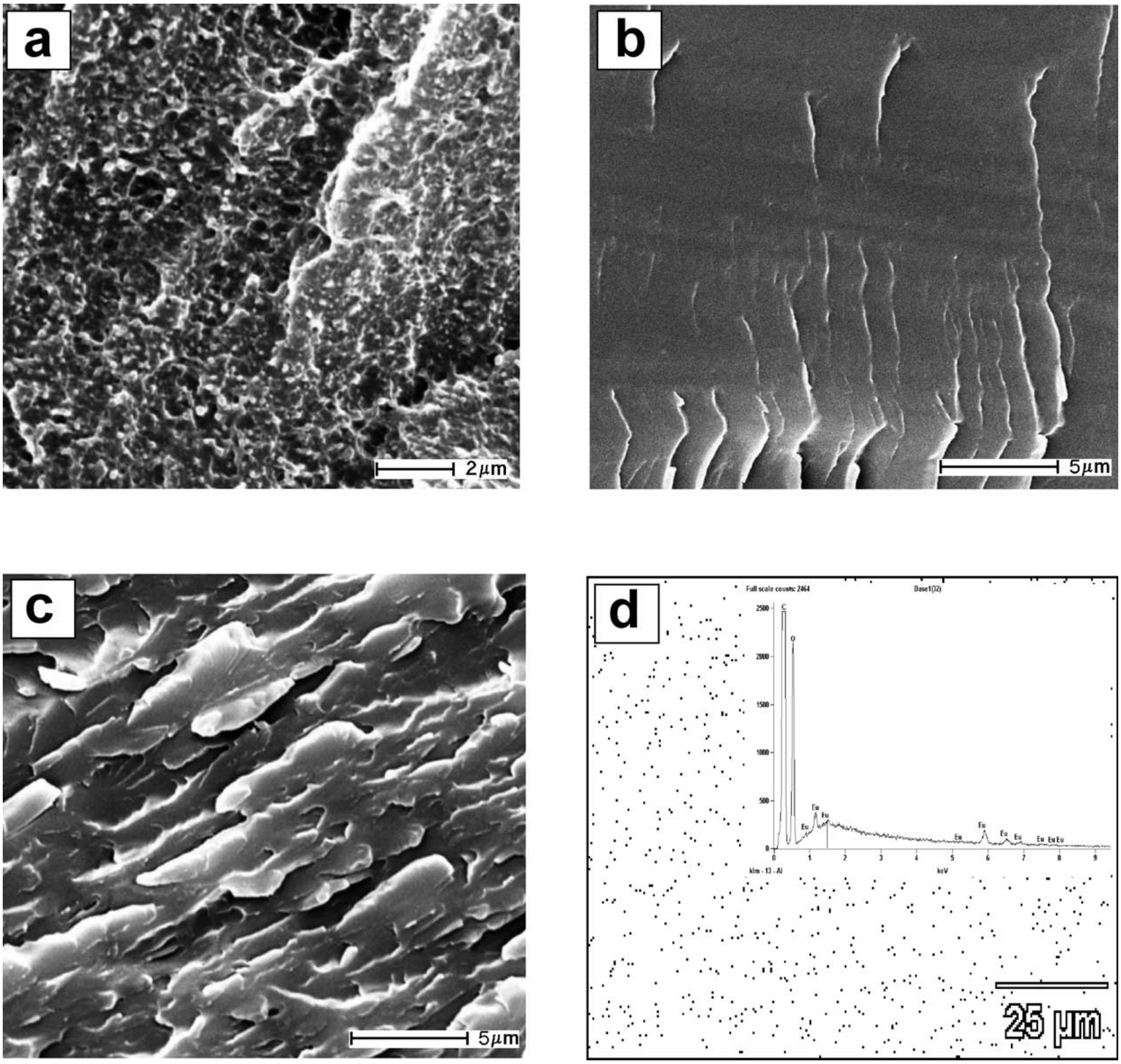

Fig. 6. Fracture surface SEM micrographs of (a) undoped PC/PMMA (60:40), (b) doped with 4% [Eu(acac)$_3$], (c) doped with 16% [Eu(acac)$_3$], (d) Eu Lα1 EDS micrograph of sample 60:40 doped with 16% [Eu(acac)$_3$] (EDS spectrum inset).

and beyond the detection sensitivity. The morphology of the 60% PC blend (Fig. 6(a)) resembles that of pure PC [36]. The addition of the Eu complex leads to a noticeable morphological alteration, Fig. 6(b) and (c). Microscopic analysis using EDS technique (energy dispersive spectroscopy) was used to check Eu dispersion within the blend, Fig. 6(d). It was possible to verify that europium (III) acetylacetonate is well distributed in the polymeric matrix.

The emission spectra of the Eu-polymer systems excited at 394 nm are shown in Fig. 7. The five emission bands in each spectrum correspond to the characteristic transitions of Eu^{3+}. The inhomogeneous broadening of the $^5D_0 \rightarrow {}^7F_0$ band indicates the existence of different surrounding environments around Eu^{3+} ions [1,4,6,7,13,15]. Fig. 7(a) shows typical emission concentration quenching for more concentrated materials, which agrees with the literature [1,3,7,9,15]. The photoluminescent spectra in Fig. 7(b) allow assessing the effect of the PC fraction on the signal output. Supported by data in literature based on the interactions between the PMMA ester group and the PC phenyl ring [18,19,26], the main result of Fig. 7(b), i.e. the higher photoluminescence output for a lower PC concentration, suggests the existence of a PC killer-like effect (probably the phenyl group) on the organic antenna (specifically the ester group). Under this condition, only a weak emission of Eu^{3+} complex is observed, since the ester group of the organic antenna in the Eu complex can interact with the PC phenyl ring. The data reported on Fig. 7 constitute the preliminary results of an ongoing study to

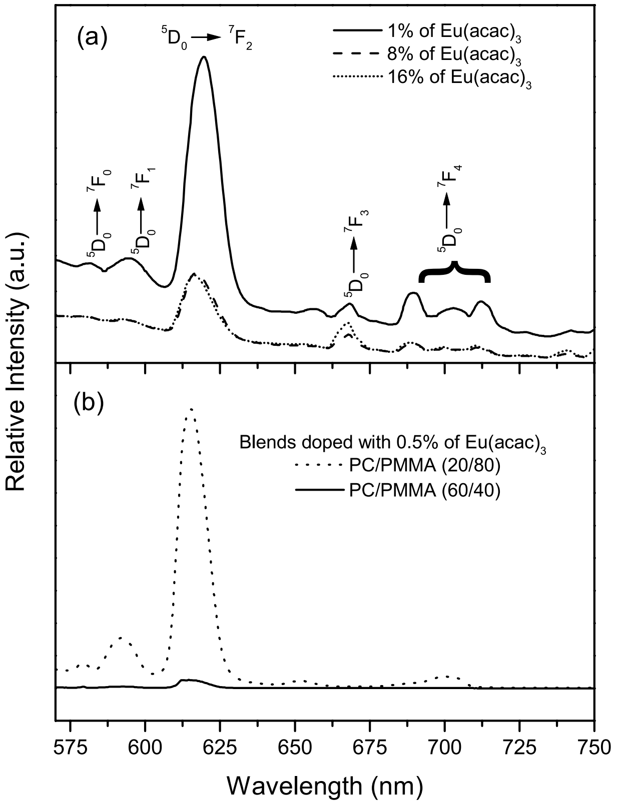

Fig. 7. Emission spectra of doped systems (films ca. 500 μm) measured at room temperature ($\lambda_{ex} = 394$ nm).

better understand the PC, PMMA, and [Eu(acac)$_3$] interactions. These study results will be published in the short future.

4. Conclusions

Eu-polymer complexes containing acetylacetonate as a ligand and prepared by precipitation method turned out to be apparently miscible and good luminescent materials. From FTIR results, it can be concluded that the doping ions could be immobilized in the polymer matrix by chemical bonds. TGA and PL properties suggested the preferable localization of the Eu complex in the PC phase (or micro-phase). SEM analysis allowed assessing the distribution of Eu^{3+} ions within the blend. However, one should keep in mind that detailed studies are necessary to elucidate the hypothesis of preferable localization of the Eu complex within the blend. In addition, it is necessary a meticulous study of the structure and properties of these systems, the host/guest interaction, and of the influence of the host and guest molecular structure on PL properties for the development of practical applications.

Acknowledgements

R.B. thanks CAPES for fellowship. CNPq and Fundação Araucária are acknowledged for the financial support. L.A.O. Nunes (IF-USP-São Carlos), S.J.L. Ribeiro and J.M.A. Caiut (Unesp-Araraquara) are gratefully acknowledged for photoluminescence measurements.

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