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STABILIZATION OF MODIFIED POLYAMIDE MATRIX

Leonardo G. Marchini, Duclerc F. Parra, Ademar B. Lugão

Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
dfparra@ipen.br

ABSTRACT

Films of PA 6 (polyamide) doped with Europium luminescent complexes have been develop and studied for applications in advanced technologies. Development of optical marker for process monitoring is the focus of the present study. Based in doped luminescent polyamide samples were prepared for polymer processing use. Films were prepared by dissolution of PA 6 in acid moiety with addition of europium complex. Stability evaluation was done in samples submitted to irradiation with 10 and 100 kGy of ionizing source. The luminescent polymer matrices were characterized using the techniques of infrared (FTIR), thermogravimetry (TGA/DTG), differential scanning calorimetry (DSC) and photoluminescent properties by electron emission spectroscopy.

1. INTRODUCTION

The design of highly luminescence trivalent rare earth (RE^{3+}) complexes containing enolates as ligands, in particular, β-diketonates, has been intensively investigated among the RE^{3+} coordination compounds[1]. The great interest in research on the luminescence properties of rare-earth 1,3-diketonate complexes is mainly due to their potential applications such as medical diagnosis [2-4], electroluminescence [5-6], triboluminescence [7-8] optical markers and even laser materials [9-10].

The importance of optical spectroscopy of RE^{3+} ions is associated mainly with their narrow emission bands arising from the intraconfigurational 4f–4f transitions and long lifetimes, which make these ions unique among the luminescent coordination compounds [11]. Polymer doped with rare-earth ions presents singular properties which stability is under investigation due to the great importance.

The radiation technology is used some times for polymer modification. In radiation processing, no catalyst or additives are required to initiate the reaction [13]. The molecular changes induced by γ-radiation in a polymer may be classified as main chain bond scission, resulting in a decrease in molecular weight and, thus, adversely affecting its mechanical properties; and chain crosslinking, resulting in an increase in molecular weight and formation of network structure. Both chain scission and crosslinking occur primarily in the amorphous region, while some may take place in the boundary between the crystalline and amorphous regions. Chain scission, in general, occurs to polymeric chains at a low radiation dose. At high doses, free radicals could be generated on polymeric chains, which may cause crosslinking by forming covalent bonds between polymer chains. Radiation modification is the phenomena by which the properties of the polymers can be improved [13-14]. The effect of radiation in doped polymers can be concerned with the thermal and oxidative stability then these aspects are purpose of investigation.

The polyamide doped with europium complex has never been investigated before or used as optical marker in polyolefin processes. In this work, we report the preparation and characterization of Europium complex doped in polyamide 6 (PA6) matrix. The films with 5% of Europium complex were irradiated with gamma radiation doses of 10 kGy and 100 kGy. Thermal and oxidative stability were investigated for future application of this new material.

2. MATERIALS AND METHODS

2.1 Synthesis

The polyamide 6 (PA 6) used was obtained from Du Pont ™ , (Zytel® 7301 NC010), in the form of cylindrical cut granules (Ø 2 to 3 mm, length 2 to 3 mm). The $[Eu(tta)_3(H_2O)_2]$ complex was prepared by addition of europium chloride aqueous solution to β-diketone ethanol solution of 1:3 molar ratio; followed by addition of concentrated ammonium hydroxide until pH ~7 [12] .

The luminescent system containing the polymer doped with the Europium complex in concentration 5% was prepared by dissolving the polymer in acetone and then mixed it with required amount of polyamide 6 dissolved in acid moiety.

The mixture of Europium complex with polyamide 6 were cast into a pyrex® recipient and o dried in stove at 110°C. The doped films were then cut in slices that were irradiated and analyzed.

2.2 Measurements

The infrared absorption spectra of the solid samples were measured in the range 4000–400 cm^{-1} in film form by using a Thermo Nicolet model 6700 FTIR spectrophotometer.

Thermogravimetric Analysis (TGA) was recorded with a Mettler-Toledo TGA / SDTA 851 thermo balance in nitrogen or oxygen atmospheres of 50 mL min^{-1}, in the temperature program from 25 °C up to 750 °C at a heating rate of 10 °C min^{-1}. Samples about 2 - 5 mg were placed at alumina crucible. This technique is used to obtain the initial decomposition temperature (T_{onset}).

Differential Scanning Calorimetry (DSC) was carried out in a 822 Mettler-Toledo under nitrogen atmosphere of 50 mL min^{-1} at a heating rate of 10 °C min^{-1}, in the temperature program of 25 to 250 °C, keeping in 250 °C for 5 minutes and cooling from 250 to -50 °C at a rate of 50 °C min^{-1} and reheating from -50 up to 250 °C at heating rate of 10 °C min^{-1}. The polymer samples of 10 - 15 mg were placed in closed aluminum pans.

Irradiation took place in a 6917.4 CI ^{60}Co Gamma Cell 220 from Atomic Energy of Canada Ltda (AECL), dose rate of 5.72 $kGy.h^{-1}$. The radiation doses applied in the PA6:5%$Eu(tta)_3$ samples were of 10 and 100 kGy.

3. RESULTS AND DISCUSSION

3.1 Fourier transformed infrared spectroscopy

The peaks related to the H_2O vibrational modes in the $[Eu(tta)_3(H_2O)_2]$ complex were attributed at 3500–3200 cm^{-1} (υ_s and υ_{as} OH) and at 1630–1600 cm^{-1} (HOH bending) [15] are absent in the doped polyamide, fig.1.

The peaks that characterize polyamide are peptide bond 3300 cm^{-1} (υ group of NH), 1650 cm^{-1} (υ group of CO – amide I),1550 cm^{-1}(δ group of NH + υ of CN – amide II)[16]. In the irradiated samples are observed the broadening band at 3500 cm^{-1} attributed to the amine groups originated from scission of the peptide chain. The carbonyl group C=O of oxidized products are also observed, as effect of radiation, at around 1700 cm^{-1} in the irradiated samples.

Chain scission of structures are associated to the oxidative groups formation and it is related to the scission of the C-N amide, weaker bond of the polymeric macrochain as reported by Gupta e Pandey [17].

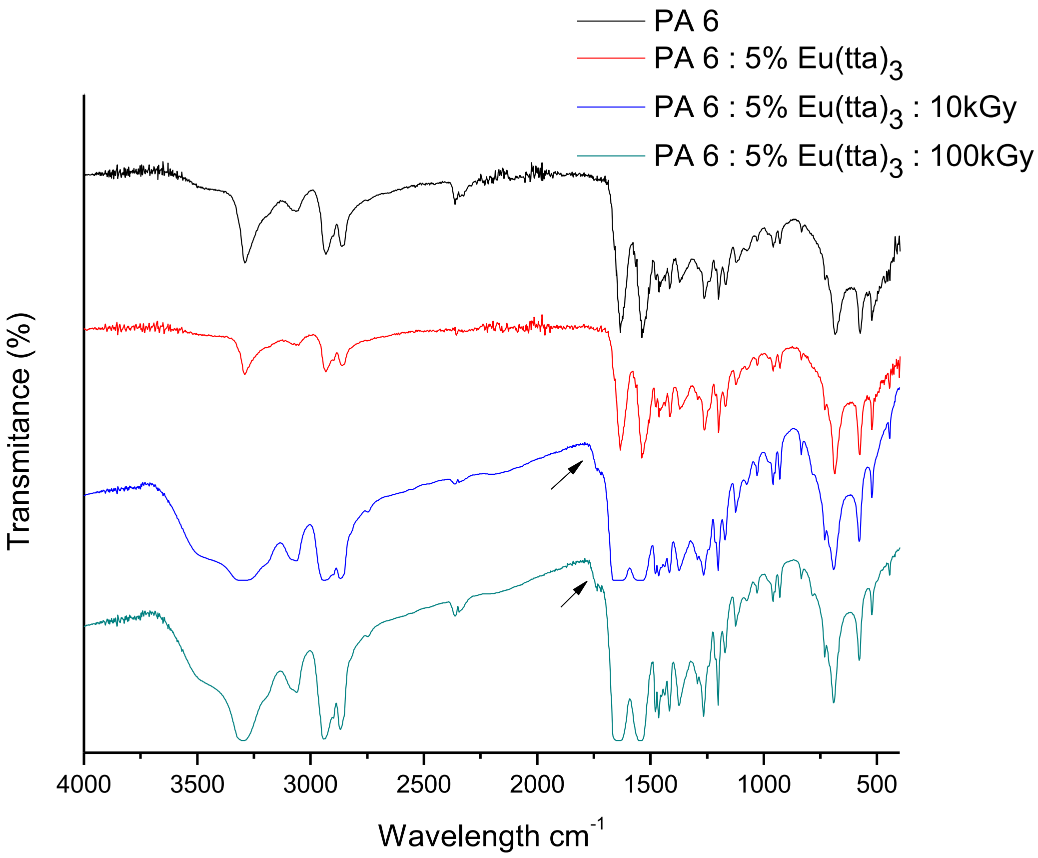

Figure 1. Infrared spectra of PA6 pure, PA6 with 5% $Eu(tta)_3$ complex, PA6 with 5% $Eu(tta)_3$ complex irradiated with 10kGy and PA6 with 5% $Eu(tta)_3$ complex irradiated with 100kGy. The arrow indicate the C=O group formation by oxidation.

3.2 Thermogravimetry

The TG curves in oxidative atmosphere are presented in figure 2 ((a) TG and (b) DTG). Under inert atmosphere the results are showed in figure 3 ((a) TG and (b) DTG). It is showed that sample PA 6 : 5% $Eu(tta)_3$ irradiated with 10 kGy has a small increase of thermal stability comparing with PA 6 : 5% $Eu(tta)_3$ non irradiated. The sample PA 6 : 5% $Eu(tta)_3$ irradiated with 100 kGy showed the worst thermal stability.

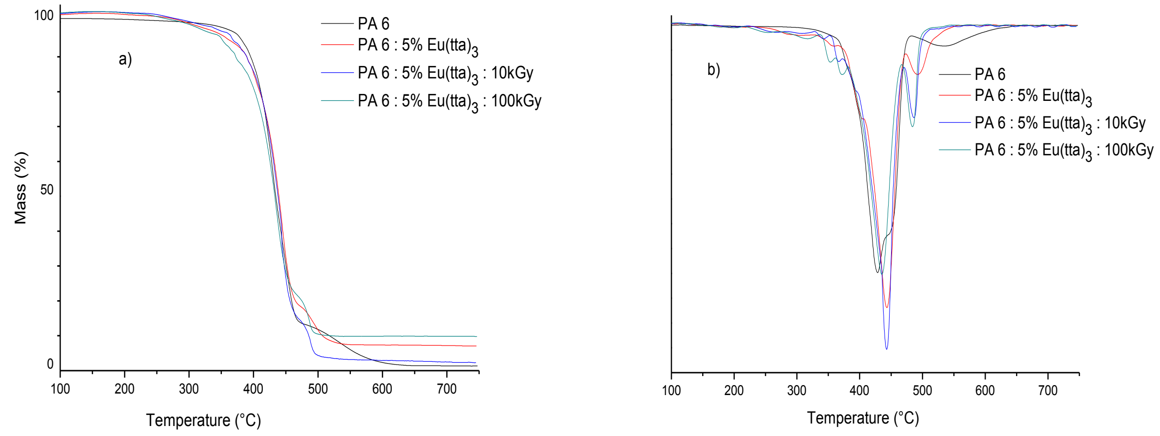

Figure 2. The TG (a) and DTG (b) curves of PA6 pure, PA6 : 5% $Eu(TTA)_3$, PA6 : 5% $Eu(TTA)_3$ at 10kGy and PA6 : 5% $Eu(TTA)_3$ at 100kGy in oxygen atmosphere.

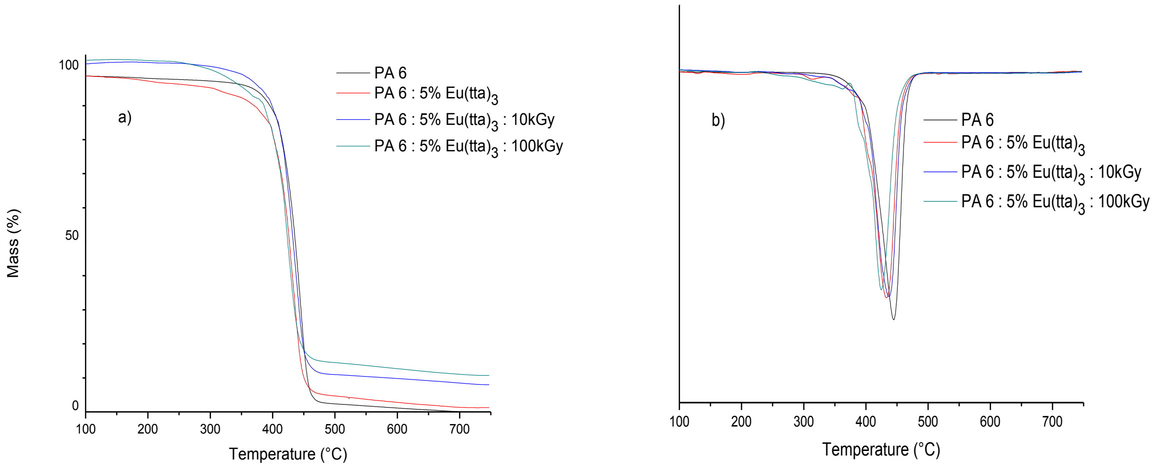

Figure 3. The TG (a) and DTG (b) curves of PA6 pure, PA6 : 5% $Eu(TTA)_3$, PA6 : 5% $Eu(TTA)_3$ at 10kGy and PA6 : 5% $Eu(TTA)_3$ at 100kGy in nitrogen atmosphere.

3.3 Differential Scanning Calorimetry

The DSC curves in figure 4 showed that increasing the dose of radiation the melting temperature decreases, table 1. This agrees with the occurrence of chain scission mechanism, effect of the irradiation.

Table 1. Melting temperature of the second heating= 2^a T_m.

	2^a T_m(°C)
PA6 puro	220,2
PA 6 : 5% Eu(tta)$_3$	218,6
PA 6 : 5% Eu(tta)$_3$: 10kGy	218,0
PA 6 : 5% Eu(tta)$_3$: 100kGy	212,9

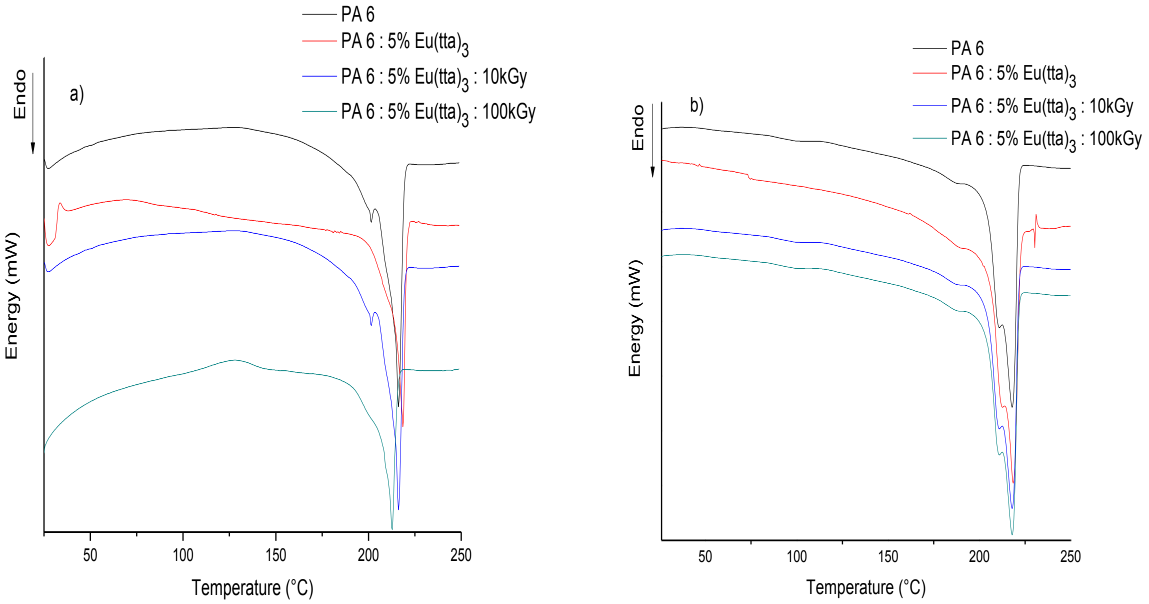

Figure 4. A) first and B) second DSC scanning curves of PA6 pure, PA6 : 5% Eu(TTA)$_3$, PA6 : 5% Eu(TTA)$_3$ at 10kGy and PA6 : 5% Eu(TTA)$_3$ at 100kGy systems obtained at a heating rate of 10 °C min^{-1}.

4. CONCLUSIONS

The thermal stability of PA 6 : 5% Eu(tta)$_3$, in both oxygen and nitrogen atmospheres showed a small increase of thermal stability of the irradiated sample at 10 kGy comparing to PA 6 : 5% Eu(tta)$_3$ non irradiated. The sample PA 6 : 5% Eu(tta)$_3$ irradiated with 100 kGy showed the worst thermal stability in consequence of degradation by radiation. When irradiation dose increases from 10 to 100 kGy the melting temperature of these films decreases owing to chain scission mechanism.

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