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LUMINESCENT POLYMETHYL METHACRYLATE MODIFIED BY GAMMA RADIATION

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ABSTRACT

Thin films of PMMA (polymethyl methacrylate) doped with luminescent complexes have been studied and developed for applications in advanced technologies. The problem of stability of these films is focused in this study. Films stabilization by reaction with fluorinated monomers is a recent study that aims to increase its luminescence properties for long time. The films were prepared by dilution of PMMA in chloroform with addition of europium complex, at proportion of 5% by weight of polymer. The luminescent polymer films were obtained by casting. Thin layer slides of the film were separated in three parts. One was reacted with fluorinated monomers (C_2F_4) in closed reactor for 48 hours. A second part was reacted with C_2F_4 after irradiation in gamma source at 5 kGy in simultaneous process. The last part was used as obtained. The luminescent polymer matrices were characterized using the techniques of infrared (FTIR) and thermogravimetry (TGA/DTG). Samples of the films were, in presence of fluor monomers, exposed to ionizing radiation in dose of 5 kGy, for react with monomers in the doped polymer surface. In this case the effects of radiation were evaluated on the luminescent films.

1. INTRODUCTION

In recent years have grown significantly in research involving materials luminescent trivalent rare earth compounds (TR^{3+}) as emitting centers [1-2]. One of the biggest advantages of using rare earth complexes is due to its atomic behavior, derived from the effective shielding of the chemical environment on the 4f electrons by the electrons of the filled $5s^2$ and $5p^6$ sub shells. This shielding effect makes the TR^{3+} ions potentially applicable in luminescent systems, for showing luminescence in the presence of characteristic emission bands extremely thin and well defined. This fact gives character to the monochrome colors emitted by these ions. For example, compounds containing ions (Eu^{3+}) are excellent emitting red light, and their emission spectra typically display high-intensity bands arising from transitions hypersensitive $^5D_0 \rightarrow {}^7F_2$ (~ 612nm) [3].

However, characteristics of such as low thermal stability and photo - sensitivity and, along with mechanical properties, are inevitable challenges regarding the applicability of the complexes of rare earths in some areas, for example, lighting, sensors, display etc [4].

This work was developed polymer systems of PMMA (polymethyl methacrylate) doped with luminescent materials [5], and its stability was studied by reacting fluorinated monomers (C_2F_4) with ionizing radiation.

PMMA (polymethyl methacrylate) is a rigid thermoplastic, transparent, and synthetic, with excellent mechanical and chemical resistance, density 1.18, refractive index 1.49 and very low crystalline, so widely accepted in the market due to their intrinsic properties associated with lightness and moldability [6].

This work aims to improve the stability of films doped with europium complex. After doping the films were treated in an atmosphere of C_2F_4 and compared with films irradiated at 5 kGy also in C_2F_4 atmosphere. Evaluation using infrared (FTIR) and thermal analysis is reported in this work.

2. MATERIALS AND EQUIPMENT

2.1. Synthesis

PMMA (polymethyl methacrylate) used was provided by Resarbras, DLH line of medium molecular weight, distributed by Piramidal - SP. The europium complex $[Eu(tta)_3(H_2O)_2]$ was previously prepared [7] and doped into the PMMA matrix at concentration of 5% of the complex.

The luminescent polymer films were obtained by casting. Thin layer slides of the film were separated in three parts. One was reacted with fluorinated monomers (C_2F_4) in closed reactor for 48 hours. A second part was reacted with C_2F_4 after irradiation in gamma source at 5 kGy in simultaneous process. The last part was used as obtained.

2.2. Methods

Thermogravimetric Analysis (TGA/DTG) was recorded with a Mettler-Toledo TGA / SDTA 851thermo balance in nitrogen or oxygen atmosphere of 50 mL min^{-1}, in the range from 25 up to 600 °C at heating rate program of 10 °C min^{-1}. Samples about 5 mg were placed at alumina pans. This technique is used to obtain the initial decomposition temperature (T_{onset}).

Infrared spectroscopy was performed at Nexus 670 of Thermo Nicolet, FTIR with samples of the films cut into pieces and analyzed.

3. RESULTS AND DISCUSSION

3.1. Fourier Transformed Infrared Spectroscopy (FTIR).

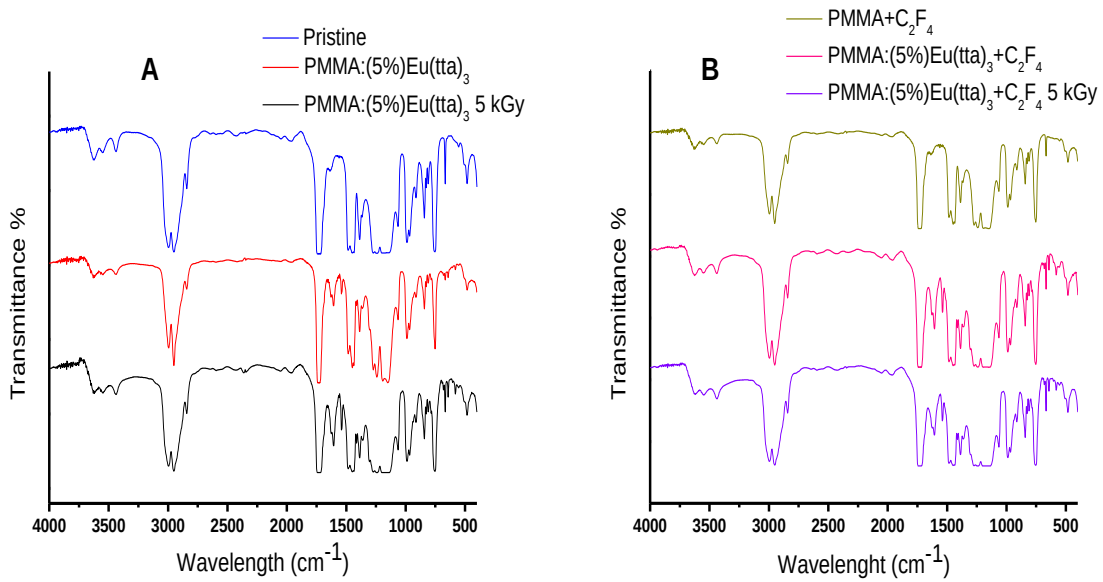

Figure 1. Infrared spectra of A (polymer pure and doped) and B (polymer with C_2F_4)

In the spectra of the doped polymer is observed bands in the wavelenght range from 1627 – 1527 cm^{-1}, typical from the beta- diketonate , CO groups. These peaks are stable after reaction with the monomers and irradiation. Peaks of the fluor-compond are not attributed unequivocally owing to the superposition of bands in the convulated spectra.

3.2. Termogravimetric Analysis (TGA/DTG).

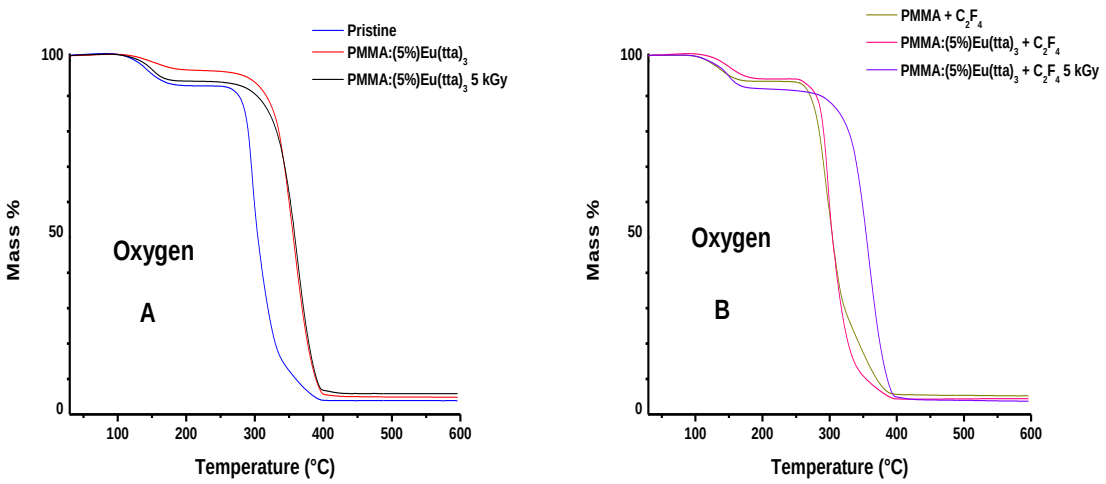

Figure 2. TGA curves of A (polymer pure and doped) and B (polymer with C_2F_4).

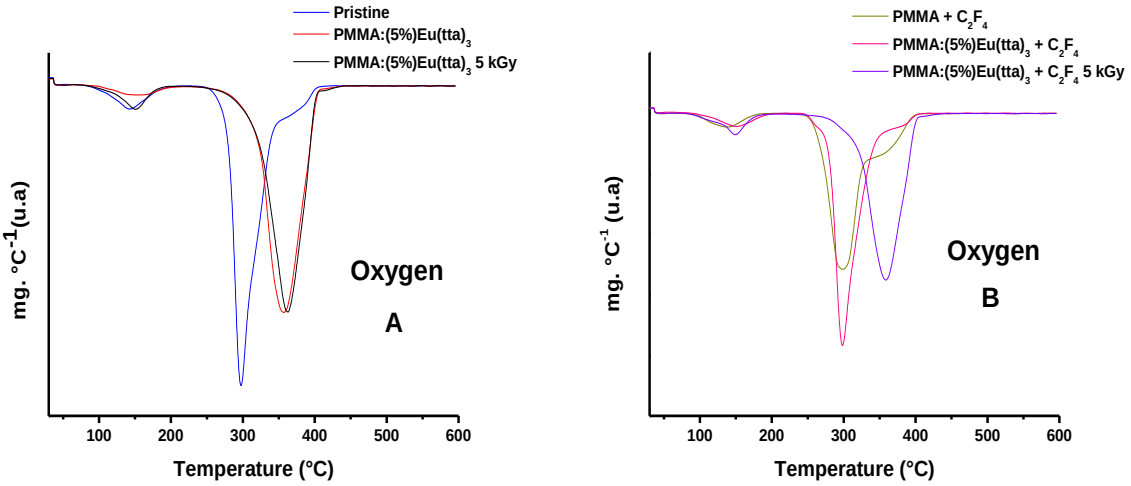

Figure 3. DTG curves of A (polymer pure and doped) and B (polymer doped with C_2F_4) in O_2 atmosphere.

As we noted in the TGA, Fig. 2 A and B and DTG curves, Fig. 3 A and B, of the pure polymer suffers a decomposition in loss mass in a temperature lower than that of the doped polymer, that is due to the addition of the europium complex [8], as is consistent with the literature. The doped polymer after reaction with the monomers remains stable as the doped polymer before the reaction, this condition not prove effective monomer addition. In the other hand, when the reaction occurs in presence of radiation, the doped film remains highest stable. Probably the radiation promotes the fixation of the monomer in the polymer surface.

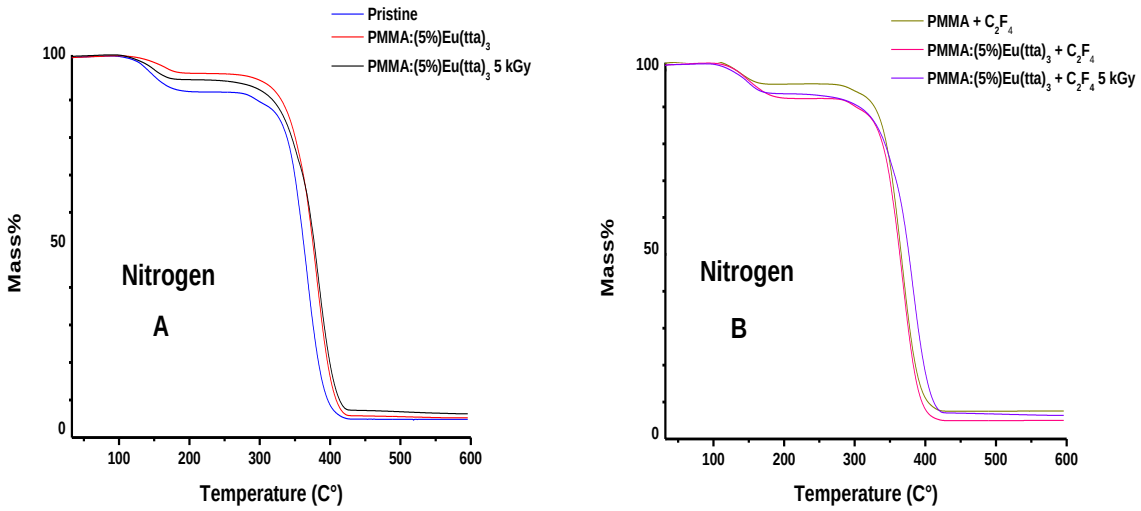

Figure 4. TGA curves of A (polymer pure and doped) and B (polymer with C_2F_4).

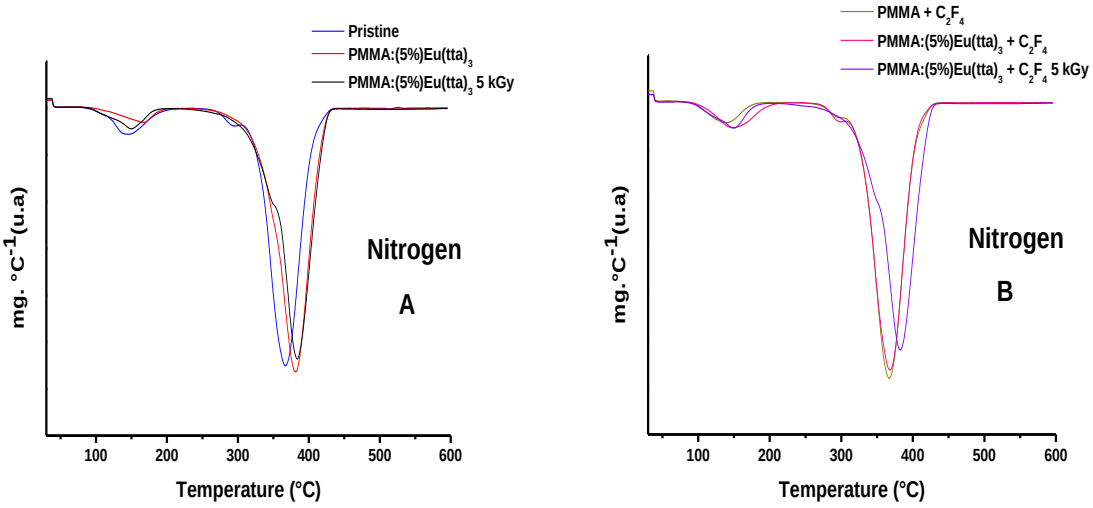

Figure 5. DTG curves of A (polymer pure and doped) and B (polymer doped with C_2F_4) in N_2 atmosphere.

In inert atmosphere the same evidence was observed concerning the maximum temperature of decomposition. The T_{onset} of thermal degradation has no significant difference. The thermal decomposition of the doped film obtained under irradiation is slower than the others, corroborating with the suggestion that reaction with the monomers in this condition.

4. CONCLUSION

When doped films are irradiated in presence of fluor monomer (C_2F_4), the reaction occurs in presence of radiation, the doped film remains higher stable compared with the original doped

film, as analised by thermal oxidation. Probably the radiation promotes the fixation of the monomer in the polymer surface. The thermal decomposition of the doped film obtained in reaction with the monomers, under irradiation, is slower than the original film, corroborating with the suggestion that reaction with the monomers occurs under irradiation.

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