

PMMA/MEH-PPV Photoluminescent Polymer Blend as a Long Time Exposure Blue-light Dosimeter

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Abstract: In the present paper the photoemission intensity versus excitation exposure time of host/guest photoluminescent polymer blend has been investigated. The polymer blend was composed by poly(methyl methacrylate) (PMMA) as a host, and Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as a guest. The photoluminescent blend was characterized by optical absorbance and steady-state photoluminescence spectroscopy. The PMMA/MEH-PPV blend film presented high homogeneity and high photoemission intensity. Moreover, the PMMA/MEH-PPV blend film photodegradation in function of sample exposure time to the blue-light excitation curve presented long biexponential time decay. These results suggest that the PMMA/MEH-PPV blend film could be used as a long time exposure blue-light dosimeter.

1 INTRODUCTION

Conjugated polymers have received great scientific and technological attention due to its applications in the areas of light-emitting, photovoltaic and sensors devices (Yu, 1996, Hide, 1997, Leclerk, 2001, Silva, 2011, Ferreira, 2014). The biggest challenges in the development of polymer conjugated devices are increase the light emission efficiency and the life-time (Leclerk, 2001, Yan, 1994, Atreya, 1999, Yu, 2000, Jorgensen, 2008, Palacios-Lindon, 2013). In this system the macromolecular association is, generally, an undesired process, which decreases the efficiency of the light emission (Huser, 2001, Tozoni, 2009, Spano, 2014, Chou, 2005, Mirzov, 2006, Lin, 2010).

Moreover, the conjugated polymer photodegradation process cause changes in the polymers structures and physical properties and has lethal effects on efficiency of the devices (Silva, 2011, Ferreira, 2014, Yan, 1994, Atreya, 1999, Yu, 2000, Jorgensen, 2008, Palacios-Lindon, 2013). In contrast, the alteration in the structural, photoemission and the optical properties of solutions and films of conjugated polymers, produced due the photodegradation process, has been used in the

development of ionizing and non-ionizing radiation dosimeters (Silva, 2011, Ferreira, 2014).

The photodegradation process is oxygen dependent and has two possible pathways involving the generation of either singlet oxygen or superoxide radical anions (Atreya, 1999, Yu, 2000, Jorgensen, 2008, Palacios-Lindon, 2013, Soon, 2013). Furthermore, dosimeters based in conjugated polymers solutions, due the use of organic solvent, are not safe for medical utilization. In addition, due the macromolecular aggregation the films of conjugated polymers have low photoemission intensity and it is very difficult to obtain a structured film using a small amount of conjugated polymers.

Other problem to use the conjugated polymers as a long time irradiation exposure dosimeter is the fast exponential time decay of the photoemission intensity (Lee, 2011).

In a preceding paper, we have shown the de-aggregation of the poly(9,9-di-hexylfluorenediyl divinylene-alt-1,4-phenylenevinylene) (LaPPS16), an electroluminescent polymer which shows a high tendency to π -stacking aggregation, through the formation of photoluminescent polymers blends of the LaPPS16 with several members of a series of poly(n-alkyl methacrylate)s (Tozoni, 2009). The PnMA/LaPPS16 blends present high mechanical

properties and the photoluminescence spectra presented high intensity and efficiency emission (Tozoni, 2009).

Based on the above settings; in the fact of the photodegradation process is oxygen dependent that is dependent of the oxygen diffusion coefficient of the polymers (Yu, 2000, Jorgensen, 2008, Shoee, 2015, Rothberg, 1996), in the fact that the PMMA can works as a oxygen barrier (Yu, 2000, Jorgensen, 2008) and with the purpose to develop long time blue-light dosimeters with greater light emission efficiency, good mechanical properties and safer for medical applications, in this paper was studied the photodegradation of a photoluminescent polymer blend composed by poly(methyl methacrylate) (PMMA) as a host, and Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as a guest. The results show that the PMMA/MEH-PPV photoluminescent blend form a well structured film with high homogeneity and high photoemission intensity efficiency. Moreover, the PMMA/MEH-PPV blend photodegradation curve presented long biexponential time decay. These results suggest that the PMMA/MEH-PPV blend could be used as a long time blue-light dosimeter.

2 MATERIALS AND METHODS

The poly(methyl methacrylate) ($M_w=350,000$) was purchased from Scientific Polymer Products Inc. and was used as received. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and the chloroform was purchased from Sigma-Aldrich, and was used as received too. Solutions of PMMA/chloroform (262.5mg/15mL) and PMMA/MEH-PPV/ chloroform (262.5mg/0.216mg/15mL) and were prepared using three sequential cycles of sonication (5 minutes) and mechanically stirring (5 minutes) at 60°C. Then, each solution were cast in one Petri dish at ambient conditions and allowed to dry for a week, in the dark. After the solvent evaporation the PMMA and PMMA/MEH-PPV samples formed films with thicknesses of about 100 μm . Dried films of PMMA and PMMA/MEH-PPV with dimensions of $\sim 1.5 \times 1.5$ cm were separated for analyses.

AFM images were recorded using the Shimadzu Scanning Probe Microscope (SPM-9600). Optical absorption spectra were recorded using the spectrophotometer FEMTO 800 XI. The steady-state photoluminescence excitation (PLE) spectrum was recorded on a Hitachi U-2001 spectrofluorometer. The PMMA/MEH-PPV photoluminescence

emission spectra, over the entire band (500-800nm) in function of exposure time to the blue-light excitation and at ambient conditions, were obtained by exciting the samples with a low-pressure mercury vapour fluorescent lamp emitting light in the blue part of the visible spectrum (Philips TL 20W/52 emission spectra over the entire band 400-540nm with maxima at 450nm). This lamp is normally used in incubators for the treatment of Hyperbilirubinaemia in neonates. The PMMA/MEH-PPV photoluminescence emission spectra were acquired by Ocean Optics spectrometer USB2000. The blend film was put at 38 cm apart the lamp, the irradiance incident on the blend film region was $5\text{mW}/\text{cm}^2$. Figure 1 shows the scheme of the experimental setup.

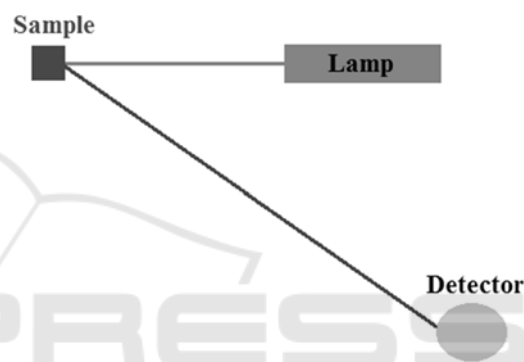


Figure 1: Scheme of the experimental setup used for the acquisition of the photoluminescence spectra versus time of exposure to the blue-light excitation.

3 RESULTS AND DISCUSSION

Figure 2 shows the PMMA/MEH-PPV blend film image after 45.50 hours of irradiation. Visually it is observed that the sample presents great homogeneity without presenting phase segregation.



Figure 2: PMMA/MEH-PPV blend image after 45.50 hours of irradiation exposure.

Moreover, due the reduction of absorption

(photobleaching in the central region), it is possible to differentiate the irradiated region from the non-irradiated region. Figure 3 shows the PMMA/MEH-PPV blend film AFM images of the regions non-irradiated and after 45.50 hours of irradiation exposure.

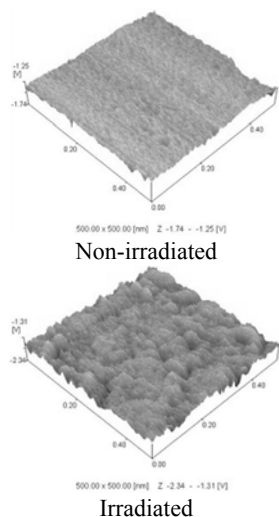


Figure 3: PMMA/MEH-PPV blend AFM images before and after 45.50 hours of irradiation exposure.

The AFM images show that the photo-oxidation changes the blends morphology favoring the formation of nanostructures increasing the roughness of the blend surface. Figure 4 shows the optical absorbance spectra of the PMMA and PMMA/MEH-PPV blend film in the UV-Vis range and the Lamp Emission region (gray region).

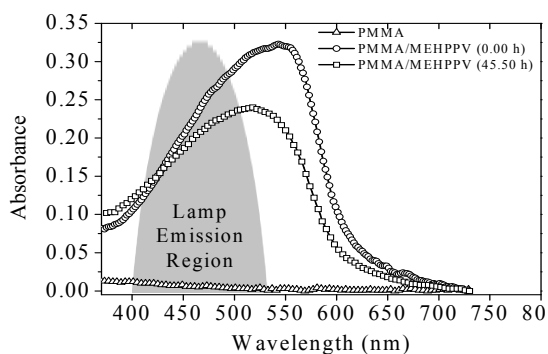


Figure 4: Absorbance spectra of the cast film of PMMA (open triangle), the PMMA/MEH-PPV blend film before irradiation exposure (open circle) and PMMA/MEH-PPV blend film after 45.50 hours of irradiation exposure (open square). The gray inset figure shows the Lamp Emission region.

The absorbance spectrum of PMMA shows that the

PMMA/MEH-PPV absorbance was independent of the PMMA matrix. Furthermore, the absorbance spectra of PMMA/MEH-PPV blend film are broader, with maxima at ~ 542 nm before irradiation, and ~ 517 nm after 45.50 hours of irradiation exposure. Figure 5 shows the normalized PLE spectrum of the PMMA/MEH-PPV before irradiation at wavelength detection of 590 nm ($\lambda_{\text{Det}}=590$ nm) and the normalized absorbance spectra of the PMMA/MEH-PPV before and after 45.50 hours of irradiation exposure. These results show that the absorbance spectra line shapes were dependent of the film exposure time to the excitation. After 45.50 hours of irradiation exposure the PMMA/MEH-PPV blend film absorbance spectrum was broadened, presents a significant blue-shift (~ 25 nm) and intensity decrease. The optical absorbance spectrum modifications in function of the film exposure time are due the photo-oxidation that promotes changes in the chemical structure of the PMMA/MEH-PPV blend film. These results show that the photo-oxidation changes the distribution of effective conjugation length to shorter chains and increase the microscopic disorder (Yan, 1994, Rothberg, 1996, Atreya, 1999). The PLE spectrum presents two maxima, one around ~ 566 nm (maximum of efficiency) and other around ~ 480 nm.

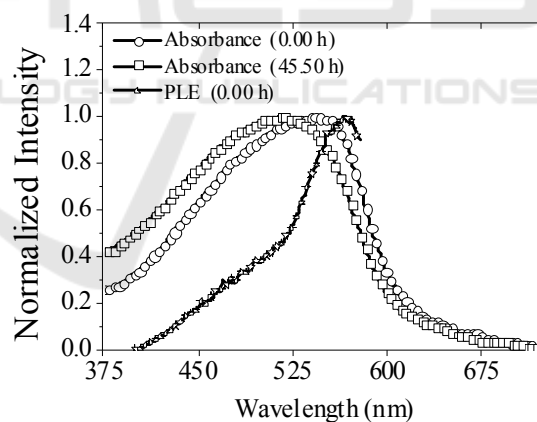


Figure 5: Normalized PLE spectrum of the PMMA/MEH-PPV before irradiation exposure at wavelength detection of 590 nm (open star), the normalized absorbance spectra of the PMMA/MEH-PPV blend film before irradiation exposure (open circle) and after 45.50 hours of irradiation exposure (open square).

The PLE spectrum maximum was red shifted approximately 24 nm as compared to the optical absorbance spectra. The difference between the absorbance and PLE normalized spectra of the PMMA/MEH-PPV blend (before irradiation) suggests that, due the presence of aggregated

species, the exciton diffusion is very efficiently.

Due to the fact that MEH-PPV photo-oxidation results in the creation of carbonyl groups that quench the photoluminescence intensity (Rothberg, 1996; Yu, 2000; Jorgensen, 2008), and in order to quantify and correlate this effect with the film exposure time to the lamp light excitation measures of the photoluminescence spectra of the PMMA/MEH-PPV blend film in function of the irradiation exposure time have been done. Figure 6 shows the PMMA/MEH-PPV blend film Integrated PL intensity (over the entire band 580-800nm) in function of sample time of exposure to the lamp light excitation curve (0.00 to 45.50 hours in intervals of 0.25 hours, open square) and the bi-exponential fitting equation 1 (solid line).

$$I(t) = I_0 + I_1e^{-t/t_1} + I_2e^{-t/t_2} \quad (1)$$

The curve present a bi-exponential time decay behavior with a long time $t_1=16.67$ hours and a fast time $t_2=1.40$ hours). Since the MEH-PPV photo-oxidation depends on the oxygen diffusion in to the sample (Yu, 2000, Jorgensen, 2008, Shoee, 2015, Rothberg, 1996) and the PMMA can works at a oxygen barrier (Yu, 2000, Jorgensen, 2008), probably the fast decay time t_2 was due the photo-oxidation of the superficial MEH-PPV and the long decay time t_1 was due the bulk MEH-PPV photo-oxidation.

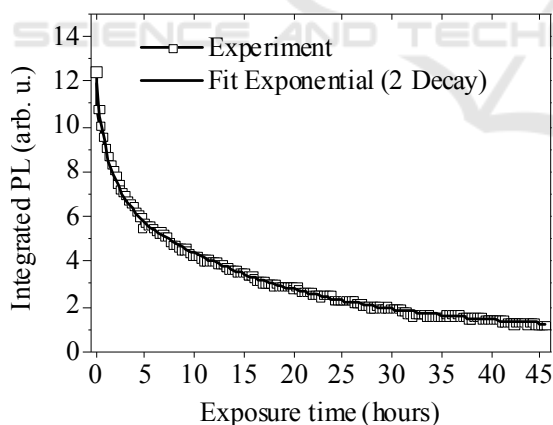


Figure 6: PMMA/MEH-PPV blend film Integrated PL intensity in function of the irradiation exposure time (open square) and the bi-exponential fitting curve (solid line).

Figure 7 shows some PMMA/MEH-PPV blend film PL spectra in function of sample irradiation exposure time. The PL spectra present two well defined maxima, one around ~600nm (0-0 transition) and other around ~640nm (0-1 transition).

Figure 8 shows some PMMA/MEH-PPV blend film PL normalized spectra in function of sample

irradiation exposure time. No significant changes in the MEH-PPV PL spectra line shapes were observed, probably there was no formation of aggregates and the PL intensity decrease is basically due the carbonyl formations that work as a PL and excitons quenchers (Atreya, 1999; Yu, 2000, Jorgensen, 2008; Rothberg, 1996).

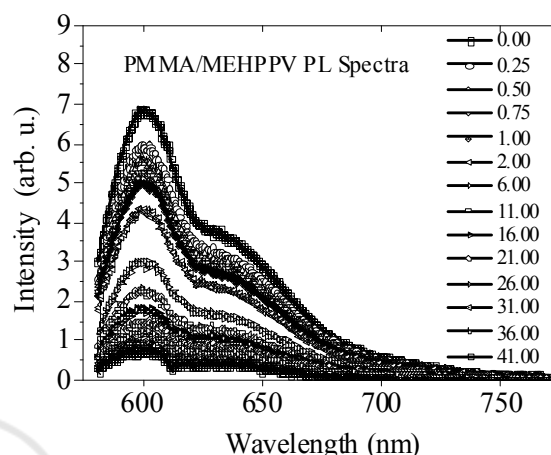


Figure 7: Various PMMA/MEH-PPV blend film PL spectra in function of sample irradiation exposure time.

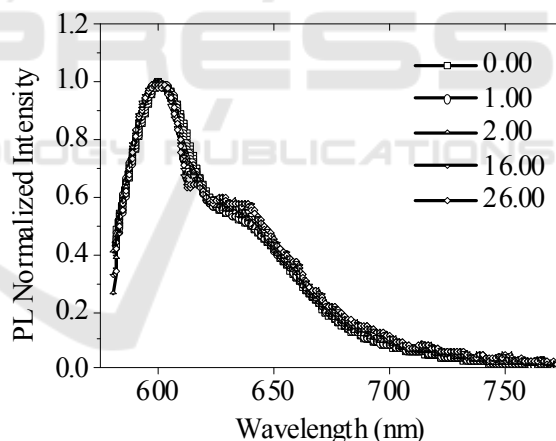


Figure 8: Some PMMA/MEH-PPV blend film PL normalized spectra in function of sample irradiation exposure time.

Moreover, like in the Rothberg et al. work the rapid decrease of the PL intensity, while the absorption decrease slowly, shows that the PL intensity is extinguished by the photochemically induced defects (Rothberg, 1996). Perhaps FT-IR experiments in function of irradiation exposure time corroborate this supposition.

4 CONCLUSIONS

With the intention to develop long time irradiation exposure blue-light dosimeters with greater light emission efficiency, good mechanical properties and safer for medical applications, in this paper was studied the photodegradation of a photoluminescent polymer blend composed by poly(methyl methacrylate) (PMMA) as a host and Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as a guest.

The results show that the PMMA/MEH-PPV photoluminescent blend form a well structured film with high homogeneity and high photoemission intensity efficiency. Additionally, the PMMA/MEH-PPV blend film photodegradation curve present a biexponential time decay behavior with a long time $t_1 = 16.67$ hours and a fast time $t_2 = 1.40$ hours. These results suggest that the PMMA/MEH-PPV blend could be used as a long time irradiation exposure blue-light dosimeter in the neonates treatment of Hyperbilirubinaemia.

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