RESEARCH Revista Mexicana de Física **61** (2015) 323–329 SEPTEMBER-OCTOBER 2015

Luminescent polystyrene films, a novel way to reduce styrofoam residues

S. Carmona-Téllez[a,*], G. Alarcón-Flores[c], E. Zaleta-Alejandre[e], Z. Rivera-Alvarez[b], A. N. Meza-Rocha[b],
R. Martínez-Martínez[d], H. Murrieta S.[a], M. Aguilar-Frutis[c] and C. Falcony[b]
[a]*Instituto de Física, Universidad Nacional Autónoma de México,*
México D.F., 01000 México,
[*]*e-mail: s_carmona@fisica.unam.mx*
[b]*Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional,*
México D.F., 07360, México
[c]*Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del Instituto Politécnico Nacional,*
México D.F., 11500, México
[d]*Instituto de Física y Matemáticas de la Universidad Tecnológica de la Mixteca, Oaxaca, 69000, México*
[e]*Universidad Autónoma del Estado de Hidalgo de la Escuela Superior de Apan,*
Hidalgo, 43901, México.

Received 5 November 2014; accepted 5 June 2015

Polystyrene (PS) films doped with blue, yellow and red organic pigments have been deposited on glass and on commercial LED chips by spray pyrolysis using recycled PS as precursor, at deposition rates between 100 and 200 Å/s. Doped films have roughness between 100 and 2500 Å depending on the kind of pigment used; the surface morphology shows that the organic pigments incorporate into the polystyrene host forming globular particles of about 2 μm in diameter. The organic pigments used have luminescent emissions peaked at 440, 509 and 590 nm. The introduction of the proper combination of pigments on the PS film deposited on the LED chips renders a white light emission with (0.29, 0.37) and (0.30, 0.33) CIE (Commission international de l' éclairage) color coordinates. It was determined that the exposure to violet light degrades the luminescent characteristics, however, blue light is not energetic enough to cause a degradation of the luminescent layer over similar period of time.

Keywords: Spray pyrolysis; polymeric films; polystyrene; white light emission.

PACS: 78.60.Lc; 85.60.Jb; 81.05.Qk

1. Introduction

There is an active quest to develop white light emitting phosphors that could provide a way to convert the characteristic monochromatic light from light emitting devices (LED's) into a broader emission in the visible that could be used for ambient illumination. At present the most popular approach has been to partially convert the light of a blue light LED through a cerium doped yttrium oxide phosphor which produces a yellow emitting light that results in a bluish total emission [1-4]. To compensate the lack of red component in the light generated in this way, a red emitting component has to be added. Some approaches to solve this problem involve adding a red light emitting chip to be able to modulate the total light emission [4-7]. Other approaches involve the design of phosphors with the proper active elements in such way that the luminescence spectrum generated is already well balanced without the need of other chips. This is not an easy task since the blue light of the LED has to activate all the luminescent centers involved.

Polymeric films used as matrix on luminescent process are extensively studied and synthesized by many techniques like electrostatic fiber formation, spin-coating, plasma polymerization synthesis, Langmuir-Blodgett, spreading, dipping or solvent casting methods and more [8-11]. Spray pyrolysis technique is conveniently used to make a many kinds of thin films, metallic oxides films especially, since it operates at atmospheric pressure [12]. To our best knowledge, polymeric films have not been synthesized by this technique, mainly because spray pyrolysis frequently uses relatively high temperatures to operate (above 300°C).

In the present work, the use of styrofoam films doped with blue, yellow and red organic pigments (OP) is studied as a possible white light emitting phosphor. The OPs have luminescent emissions at 450, 510 and 590 nm respectively. PS films were made by spray pyrolysis technique on glass or LED chips (390 and 455 nm light emission) as substrates and the photo and electroluminescence emission of these films are reported. White light emission was achieved using an adequate combination of OP into the PS films.

2. Experimental

The PS films were prepared from recycled Styrofoam, dissolved in N,N-Dimethylformamide (N,N-DMF). The films were deposited at 240°C on corning glass and GaN based LED chips using the spray pyrolysis technique [12]. This is an atmospheric pressure deposition technique that has been used widely to obtain films or coatings of different materials, mainly metallic oxides and it is considered an inexpensive, versatile and scalable technique to obtain films and coatings with excellent properties. The technique consists in supplying an aerosol generated from a chemical solution which undergoes a pyrolytic chemical reaction on a hot substrate, leading to a solid film or coating on top of its surface.

For this work, PS films were prepared with a 0.0005 mol/L chemical solution formed with recycled PS dissolved in N,N-DMF and doped with 2% of Organic Pigments (OPs); all OPs were supplied by DayGlo, according to company's catalog, OP codes are: MP-BL6182 for blue OP, AX-16N Arc for yellow OP and AX-13 Roc for the red one. A YUEHUA WH-802 ultrasonic mist generator that operates at 1 MHz was used to generate an aerosol from these chemical solutions.The generated mist is carried out to a nozzle placed about 30 mm above the hot substrate. A molten tin bath was used as thermal energy source for the substrate to achieve the pyrolytic reaction, nitrogen (N_2) at a flow rate of 5 L/min was used as carrier gas. In order to regulate the deposition rate, a mist of deionized H_2O was supplied simultaneously during deposition; because it was observed that the presence of water helps to achieve PS thin films faster.

PS doped films were deposited onto either glass slides or GaN chips pasted on a glass slide. Once the doped-PS layer was deposited, the chips were biased to observe the effect on the electroluminescence color produced as the emitted light from the LED passed through the doped-PS layer. Theoriginal LED emission was at either 390 or 450 nm (violet and blue light LED's).

The UV-vis optical transmittance spectra for the films were obtained by a Perkin Elmer Lambda 25 spectro-photometer in a wavelength range of 200-1100 nm, and a Thermo Scientific Nicolet 6700 FT-IR spectro-photometer in a wavelength range of 500-40000 nm was used to achieve infrared analysis. Roughness and morphology were measured with an Atomic Force Microscope Veeco CP Research. SEM images were measured in a Scanning Electron Microscope JEOL using an acceleration voltage of 2 KV. Finally photoluminescence (PL) and electroluminescence (EL) measurements were carried out using a Jobin-YvoneFluoro-Max-P spectro-photometer. All measurements were made out at room temperature.

3. Results and Discussion

Figure 1 show two IR absorbance spectra images: image A corresponds to the reported infrared spectra of PS [13], image B: is for the undoped PS films deposited at a temperature of 240°C. Both spectra present the same bands, only the intensity of them is different (because of difference on samples thickness). Table I lists the principal absorbance bands of PS.

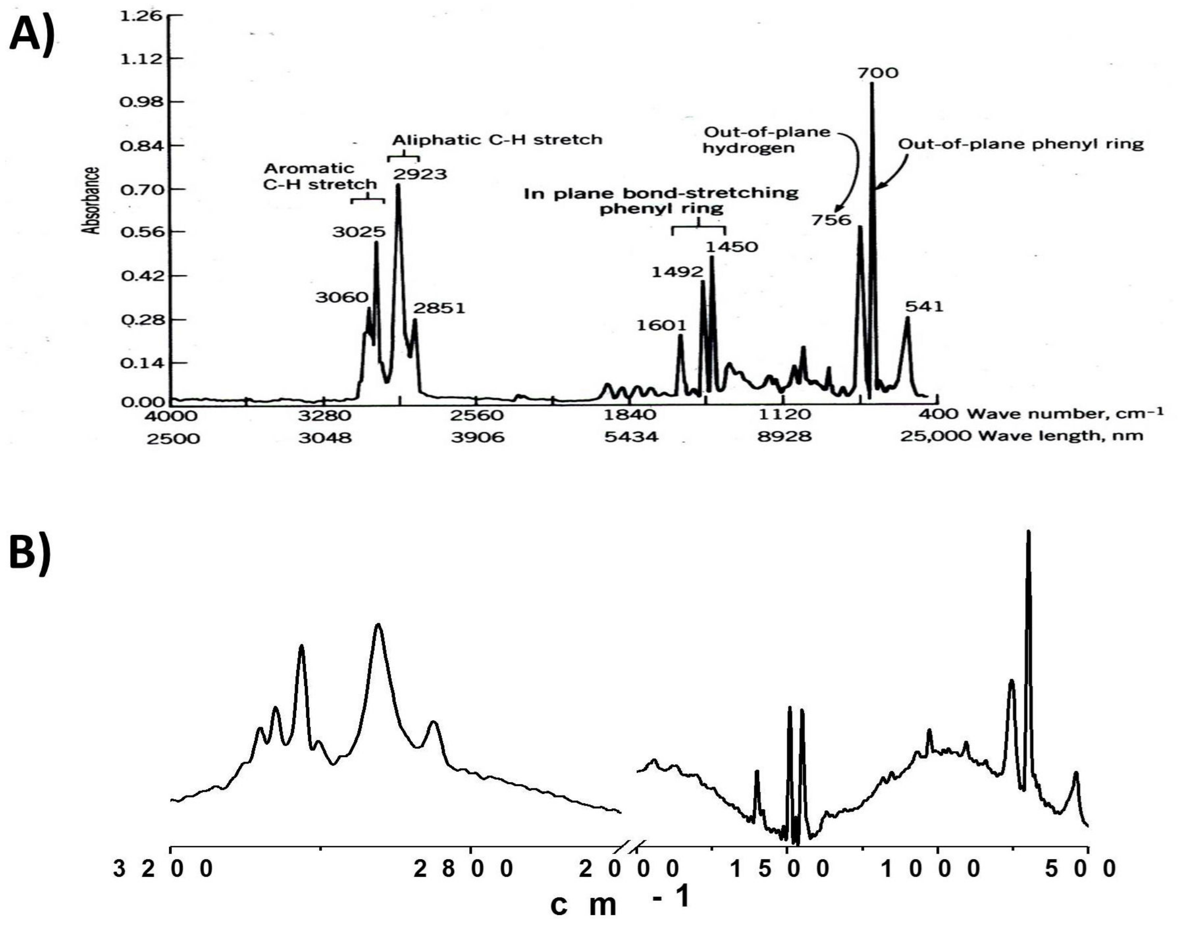

FIGURE 1. Infrared spectra (A) bulk PS, (B) PS thin film.

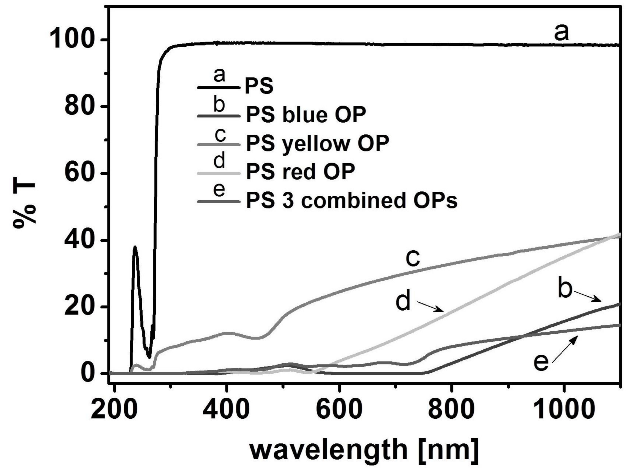

FIGURE 2. UV Vis percent transmittance characteristics for (a) PS thin film, (b) PS with blue OP, (c) PS with yellow OP, (d) PS with red OP and (e) PS with 3 OPs.

Figure 2 shows the UV-Vis percent transmittance characteristics for PS films deposited at 240°C by ultrasonic spray pyrolysis. It is observed that films without any dopant, are transparent (close to 100%) in the whole visible range, and comparable to the best quality bulk PS [14]. Meantime, blue, red and combined OPs doped films, are opaque and have low transparency, lower than 10%. Only the yellow OP doped films are semi transparent (∼40% T).

TABLE I. IR bonds of PS thin films deposited at 240°C.

Band (cm^{-1})	Type of bond
700	out of plane phenyl ring
756	out of plane hydrogen
1450 - 1600	in plane bond-stretching phenyl ring
2850 - 2925	aliphatic C-H stretch
3025 - 3060	aromatic C-H stretch

SEM images for the PS films are shown in Fig. 3; they were measured with accelerating voltages of 20 KV (Fig. 3A, 3B and 3D) and 15 KV (Fig. 3C) and × 5000 as magnification. Image A) is a SEM image of a non-doped PS film, it is observed that PS films deposited by overlapping drops that coated on the substrate surface to form a solid layer; this films are transparent, with low roughness. Images B, C and D show the surface morphology of films doped with blue, yellow and red Organic Pigments, respectively. It is possible to observe the presence of spherical OPs particles embedded in the PS films; it seems that these particles are conformed with to the OPs drops trapped within the PS film during pyrolytic deposition process.

AFM microscopy was also used to observe surface morphology and to measure the films roughness. Figure 4 shows

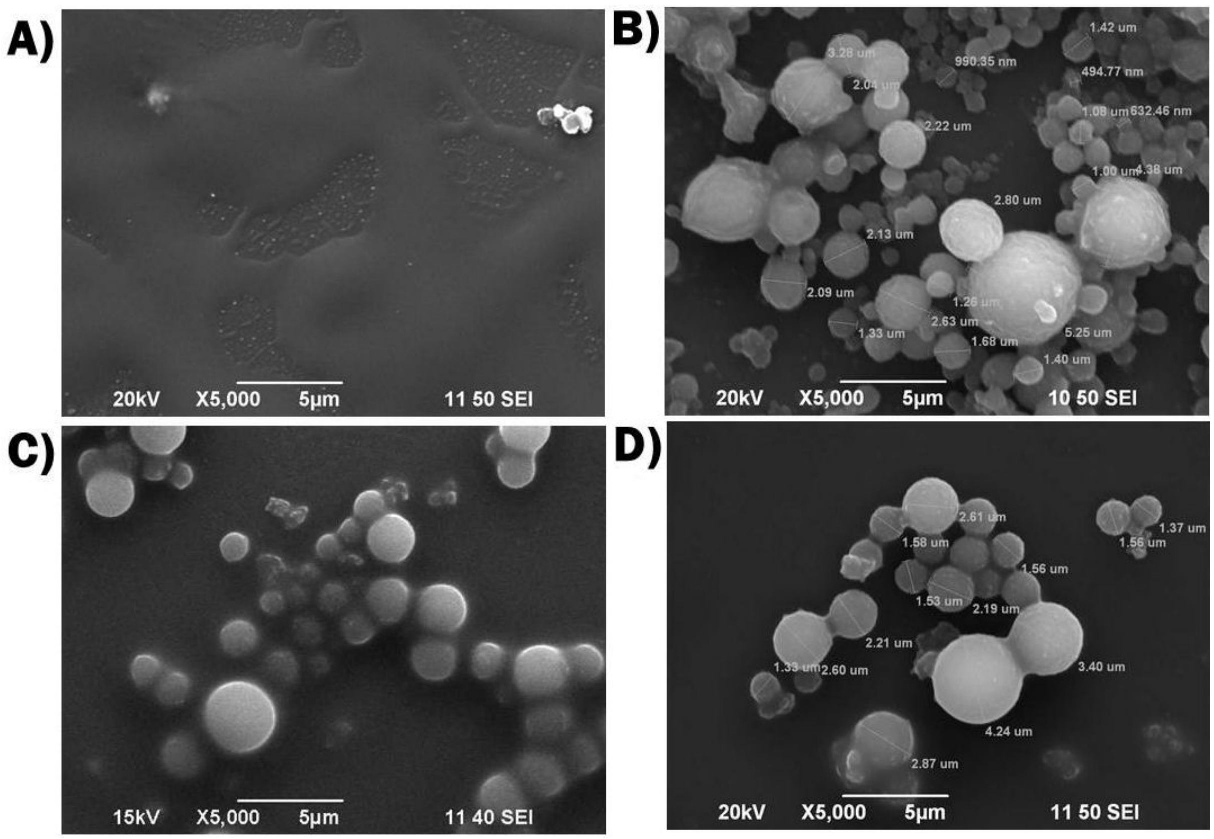

FIGURE 3. SEM images for (A) non doped PS thin film, (B, C and D) doped PS thin films.

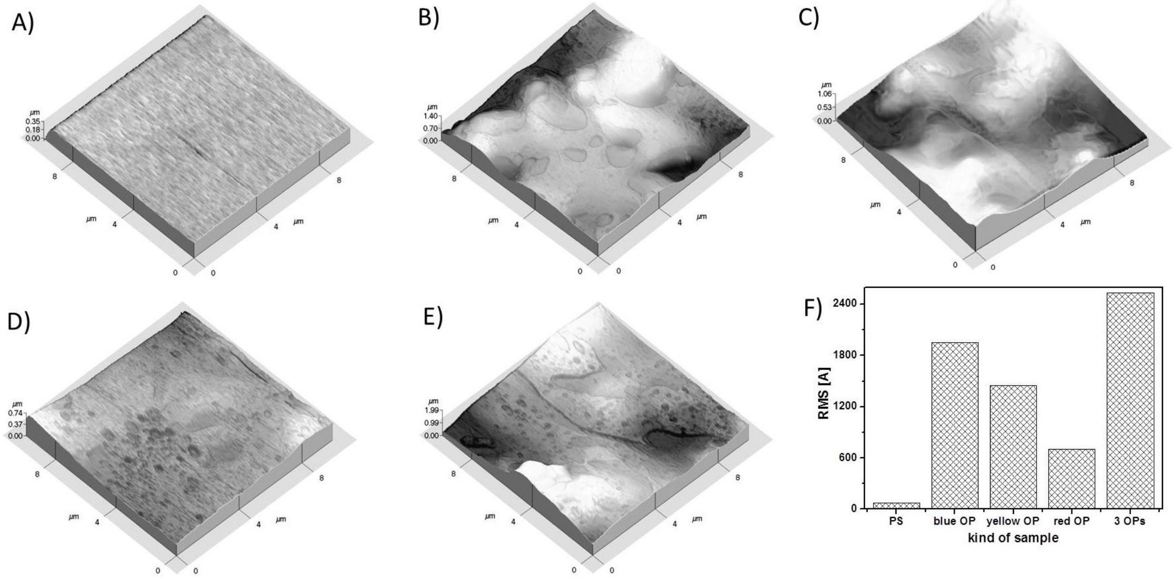

FIGURE 4. AFM Images for (A) PS thin film, (B) PS with blue OP, (C) PS with yellow OP, (D) PS with red OP and (E) PS with 3 OPs. (F) RMS Roughness as function kind of sample.

TABLE II. Thickness, deposition rate and RMS roughness for PS thin films deposited at 240°C.

Sample	Thickness [μm]	Deposition rate [Å/s]	Roughness RMS [Å]
PS	5.0	84	73 ± 20
PS - blue OP	8.7	144	1950 ± 820
PS - yellow OP	5.9	99	1450 ± 644
PS - red OP	11.1	183	702 ± 168
PS - 3 OPs	5.9	142	2530 ± 1283

AFM images and a roughness histogram. Image A) corresponds to a non doped PS sample, it is observed that the surface is pretty smooth (RMS roughness is $\sim 73 \pm 20$ Å). These samples have the same characteristics of bulk PS, they are transparent and its roughness is like commercial PS [15]. Images B to D) show the blue, yellow and red OP doped PS surface images, and image E) corresponds to a sample that was doped with the three OP at the same time. A significant increase in roughness is observed with respect to undoped PS sample, the increase in roughness is due surface morphology observed in the SEM images and are probably related to the

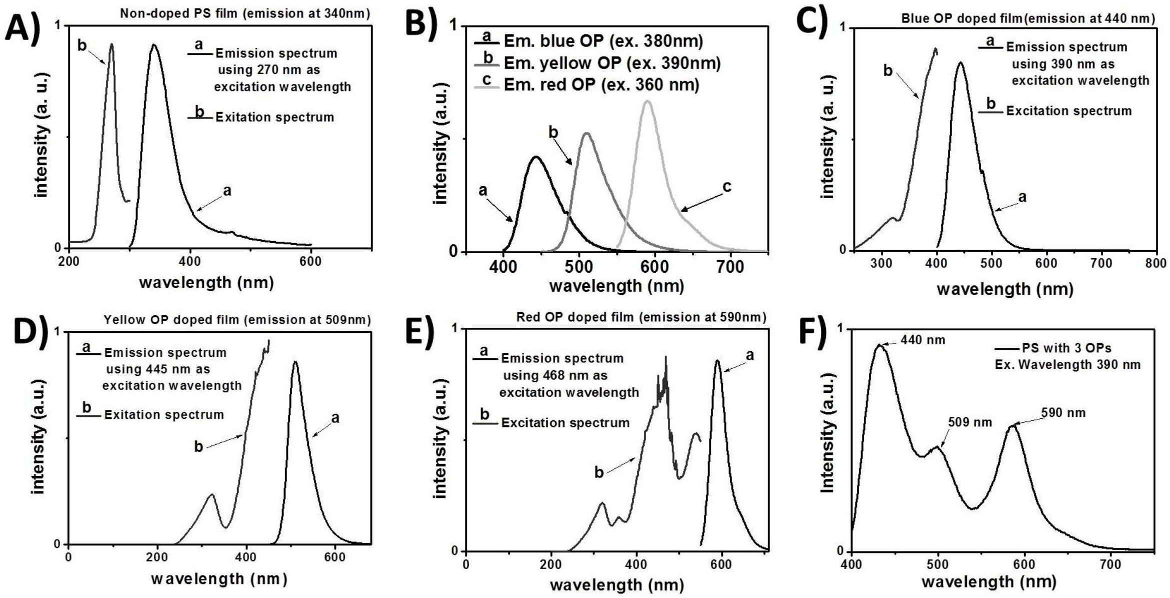

FIGURE 5. PL spectra for (A) non doped PS thin film,(B) three OPs on powder shape (C) PS with blue OP, (D) PS with yellow OP, (E) PS with red OP and (F) PS with a mix of 3 OPs.

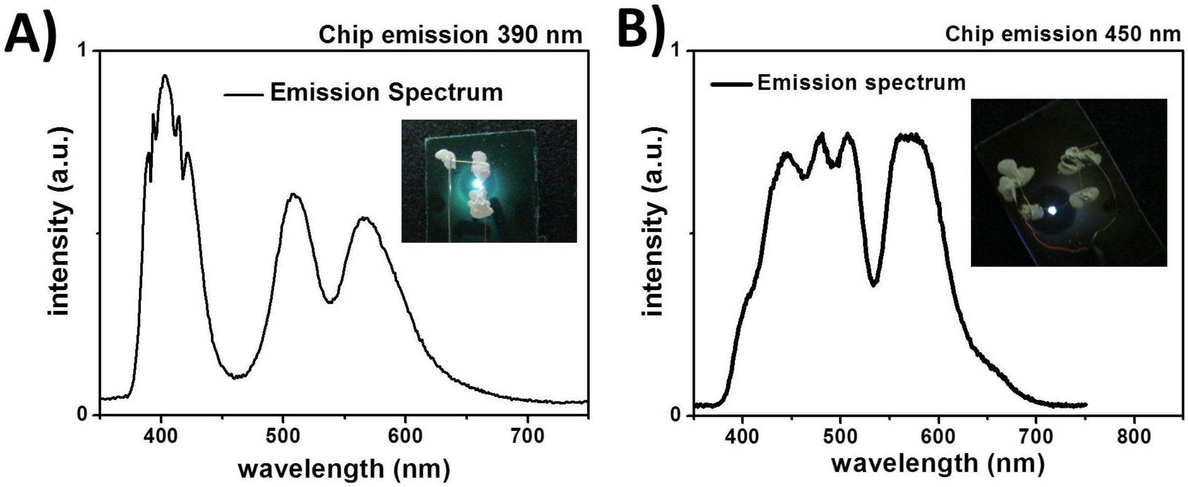

FIGURE 6. EL spectra for (A) PS thin film with a mix of 3 OPs on a violet (390 nm) LED chip, (B) PS thin film with a mix of 2 OPs on a blue (450 nm) LED chip.

OP powder size that was used for their synthesis. Image F) shows a roughness histogram for each type of sample, the blue dopant has the largest particle size, but the triply doped films present the largest roughness without being thicker than the others. The deposition rate was achieved as a function of thickness divided between the time deposition of samples; in Table II presents experimental values of thickness, deposition rate and roughness (measured by profilometry) for all types of samples studied.

Figure 5 shows the PL excitation and emission spectra for all samples studied; A) spectra for non doped PS samples, B) spectra for the three OPs powders studied, C, D and E) spectra for PS films doped with blue, yellow and red OPs respectively, F) spectrum for PS films doped with the three OPs simultaneously. The undoped PS films presented a broad photoluminescence emission band at 340 nm, the excitation wavelength used was 270 nm. The spectra for the three OP powders studied presented bands at 440 nm (obtained a 380 nm excitation wavelength), at 509 nm (excited using a 390 nm wavelength), and 590 nm (obtained with a 360 nm excitation wavelength) for the blue, yellow and red OPs respectively. Doped PS films using blue, yellow and red OPs respectively presented photoluminescence emission spectra similar to those of the OPs incorporated into the PS film (blue = 440 nm, yellow = 509 nm and red = 590 nm). In the case of excitation spectra, only the one for the blue OP doped PS film remained unchanged, but for the yellow and red OPs the main excitation peaks have a displacement to lower energies (445 nm and 468 nm respectively). It is possible that for these cases, the PS matrix participates in the excitation through an energy transfer process, yielding its energy to yellow and red OPs. This shift is convenient since it is now possible to use commercial blue and violet LED chips to excite the yellow and red doped PS films. Fig. 5F) shows the spectrum for a PS film doped with the three OPs at once, this kind of samples were obtained by a mix of the three OPs in a proportion; 50% blue, 30% yellow and 20% red within the PS in the spraying solution. 390 nm wavelength light was used as excitation light to obtain this spectrum; this wavelength is capable to excite all three OPs dopants at the same time, but at different intensity values. Thus, the OPs proportion in the mix was chosen to excite all OPs at an adequate intensity to achieve a white light emission.

Films doped with a similar mix of OPs were deposited on commercial LED chips, with an emission wavelength of 390 nm. A modified mixture of yellow and red OPs (50% and 50%) was used for PS films deposited on blue (450 nm) LED chips. Figure 6A and B, shows the modified emission spectra from both violet and blue chips screened by the multi-doped PS layer respectively. The emission of the violet chip covered by the multi doped film (mix above mentioned) when it was forward biased (3 volts) presents 3 bands; the first one at 400 nm, corresponding to the light emitted by the chip overlapped with the 440 nm OP emission, the second one centered

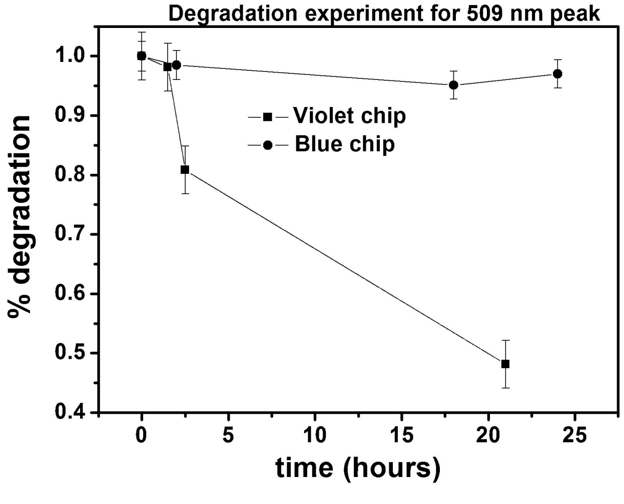

FIGURE 7. Luminescent degradation for polymeric films on violet and blue emitting LED chips (for the 509 nm band).

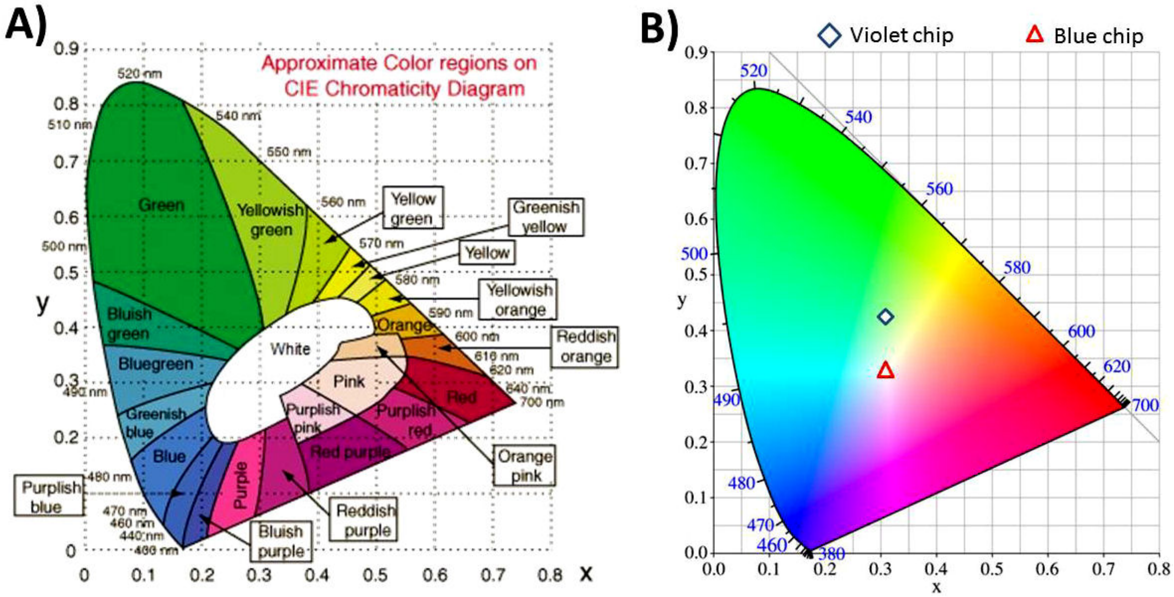

FIGURE 8. CIE diagram; (A) well known CIE, (B) Rhombus; global emission generated from 3 OPs doped PS thin film on a violet LED chip and triangle, global emission generated from 2 OPs doped PS thin film on a blue LED chip.

at 509 nm came from yellow OP and finally at 575 nm the one corresponding to the red OP. The inset shows the photograph of the modified LED's violet emitting white light. The emission spectra of a blue chip covered by a multi doped film without the blue OP shows just 2 bands; the first one starts at 400 nm and is quite broad, extending until 510 nm, this suggests an overlap of the blue emission (from the LED chip) and the yellow emission (from yellow OP). The second starts at 550 nm and is also extended until 610 nm and it is originated at the red OP. The inset photographic image shows the modified blue LED emitting white light.

In order to estimate the degradation induced by the exposure to the LED's emission of the final luminescent characteristic of the PS layer, the luminescence emission intensity of the yellow emission peak (509 nm) was monitored for up to 25 hrs for both types of LEDÂ´s considered. Figure 7 shows the luminescence degradation behavior of these polymeric films. In this case the devices were set into operation, applying 3 volts forward bias in both cases. In the case of the violet chip, the degradation of the luminescent emission at 509 nm was evident after 2hours of continuous operation and more than 50% after 20 hrs. The 390 nm wavelength light from the chip degraded both the OPs and the PS matrix after this time. In contrast, the blue chip shows little degradation if any (less than 5%) after 24 hours of continuous operation, it is likely that the blue emission from chip is not energetic enough to promote the degradation of OPs or PS matrix.

Figure 8 shows the diagram CIE (*Commission international de l'éclairage*) [16], in which the(x,y) coordinate for the global emission generated from the triply doped films deposited on a violet chip (operation voltage = 3 V) and that for the double doped films deposited on a blue chip [17].

Their corresponding coordinates are presented in Table III. According to the CIE diagram they fall in the "white" area, however, it is fair to indicate that in the violet chip case there is a tendency towards green. In the blue chips case the coordinate point falls in the "white" area, and no appreciable degradation is observed with exposure time.

TABLE III. CIE (X and Y) coordinates, for PS thin films deposited on violet and blue chips.

Operation time	X	Y
	Violet Chip	
0 sec.	0.2984	0.3785
90 min	0.3103	0.4042
150 min	0.3095	0.4038
21 hr.	0.2952	0.3842
	Blue Chip	
0 sec.	0.3030	0.3325
5 min.	0.3033	0.3323
20 min.	0.3035	0.3309
2 hr.	0.3038	0.3290
18 hr.	0.2846	0.3217
24 hr.	0.3023	0.3228

4. Conclusions

Polymeric luminescent PS films were deposited by spray pyrolysis technique for the first time up to our best knowledge. These films were doped using commercial organic pigments (OPs) in order to achieve photoluminescent characteristics. Non-doped films are very transparent and smooth; on the other hand, doped films are opaque and rough. The OPs luminescent emission wavelengths were preserved when they were incorporated in the PS films. Using an appropriate mix of OPs it was possible to obtain films that have white light emission. These multi doped films were deposited on violet and blue light emitting LED chips, achieving a complete white light source device. It was determined that the exposure to the violet light from the LED degrades the luminescent characteristics, however, the blue light is not energetic enough to cause a degradation of the luminescent layer over similar period of time.

Acknowledgments

The authors wish to acknowledge the technical assistance of R. Fragoso, M. Guerrero and A. Soto from physics department of CINVESTAV-IPN, and E. Yescas-Mendoza from UTM. The authors also thank CONACyT and SECITI (before ICyTDF) project # PICSO 12-119 to financial support.

---

1. Yuexiao Pan, *Materials Science and Engineering B* **106** (2004).
2. Mingmei Wu, *Journal of Physics and Chemistry of Solids* **65** (2004).
3. Joung Kyu Park, *Applied Physics Letters* **82** (2003) 683.
4. U. Kaufmann, *physics state solid A*, **192** (2002)2.
5. S. Nakamura, *Applied Physics Letters*, **64** (1994) 1687.
6. P. Schlotter, *Applied Physics A*, **64** (1997) 417.
7. G. Fasol, *The Blue Laser Diode*, Springer-Verlag, Berlin (1997).
8. Christopher J. Buchko, *Polymer*, **40** (1999).
9. F. Frank, *Surface and Coatings Technology*, **82** (1996).
10. R. Hernandez, *Journal of the American Chemistry Society*, **123** (2001).
11. O.K.C. Tsui, *Macromolecules*, **34** (2001).
12. S. Pramod Patil, *Materials Chemistry and Physics* **59** (1999).
13. H.F. Marck, *Encyclopedia of polymer science and engineering*, 2nd ed. 16, (John Wiley & Sons).
14. K.G. McGuigan, *Journal of Applied Microbiology* **84** (1998) 1138-1148.
15. BinZhao, *et.al*. *Macromolecules*, **33** (2000) 8821-8827.
16. D.B. Judd and David L. Macadam, *Journal of Optical Society of America*, **54** (1964) 1031.
17. S. Carmona-Téllez *et al*., *Métodos de obtención de películas luminiscentes a partir de poliestireno y polietilentereftalato mediante rocío pirolítico ultrasónico, procedimientos y aplicaciones*, México, MX/E/2013/095122, (19 Dec 2013).