Luminescence Characteristics of Hybridized Polyfluorene

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Abstract. This study was to investigate luminescence characteristics of polyfluorene (PF) hybridized with silicone (agar sample) in term of the potential application in optoelectronic. The hybridization was accomplished by preparing silicone mixture comprising of epoxy and resin into different quantities (0.625 mg, 1.25 mg, 2.5 mg) of poly [(9, 9-diocyl-fluorenyl-2, 7-diyl)-co-(1, 4-phenylene)] end capped with dimethylphenyl dissolved in toluene solution, followed by heating at 40°C and stirring process for 5 min. In a proof of concept phase, luminescence properties of the hybridized samples were examined by using spectroscopic techniques UV-Visible (UV-VIS), photoluminescence (PL) and electroluminescence (EL). Changes in term of the peak intensity happened with respect to the quantities of PF being hybridized. Corresponding results have been systematically presented and discussed in this work.

1. Introduction
Light emitting diodes (LEDs) have been generally used in the industry nowadays as the solid-state lighting (SSL) sources used for display and lighting applications [1,3]. Several advantages of LEDs, for example eco-friendliness, dependability, and high efficiency have been reported overcome the outdated illumination sources [4]. In order to achieve high quality white emission in LEDs, silicone has been the material-of-choice for the dispersion of yellow phosphor over the blue LEDs [5]. It has been reported that silicone was generally used because of its flexible behaviour, good thermal stability, low surface energy, and biocompatibility [6]. Likewise, blue emission could be attained in organic-based LEDs via the utilization of polyfluorene (PF) as a class of polymeric resources, which can be dissolved in solvents, allowing low-cost large-area device manufacture through solution deposition methods, for instance spin coating and inkjet printing [7]. Polyfluorene consists of two advantages that are widely used in molecular engineering, such as cross-linking by dissimilar monomers to produce copolymers, by substituting the side chains and accumulating combined polymer linkages to their material properties, which include luminescence efficiency and wavelength [8]. Therefore, a well-organized light production ended the completely visible spectrum could be attained.

A preliminary work has been carried out in this project by hybridizing the blue emitting PF with silicone to study luminescence characteristics of the polymer. Hybridization of PF solution have been involved in LEDs industry to enhance emission efficiency of the LEDs and the method has been found suitable for interior design and cars [9]. Consequently, researchers have stated the use of the hybrid polymer to get the good optical characteristic [10-12]. To the best of our knowledge, there are only a few researcher reports on hybrid material composed of emitting polymer and silicone. Drop-casting technique, known as low cost and suitability, has been usually used in research area for dispensing of the hybridized PF onto substrates. Hence, it is significant in this work to incorporate this technique to decrease the excess and deliberate device characteristic of LEDs. Photoluminescence (PL) and
Electroluminescence (EL) have been employed to investigate the emission wavelength from the hybridized PF (agar sample) while ultraviolet-visible (UV-VIS) spectroscopy was used to access transmittance and reflectance behaviours of the agar samples.

2. Experimental Procedure

Figure 1 presents the chemical structure used in this experiment, which is the poly [(9, 9-dioctyl-fluorenyl-2, 7-diyl)-co-(1, 4-phenylene)] end capped with dimethylphenyl group purchased from American Dye Source Inc (ADS148BE) as well as toluene (99.8%) from Sigma-Aldrich. Distilled water was used in these experiments. Different amount (0.625 mg, 1.25 mg, 2.5 mg) of PF was dissolved in colourless liquid of toluene solution (formula C7H8, molecular weight, M = 92.141g/mol, refractive index, n= 1.497), followed by heating at 40°C and stirring process for 5 min. On the other hand, silicone was prepared by mixing part A (epoxy) and part B (resin) at 3:2 volume ratio. The PF solution was mixed together with silicone by continuous stirring before being poured into a mould. After preparation, the samples were subjected to a post mixing treatment in an oven at 100°C for 15 min to dry the mixture. Agar samples were taken out from the oven and applied on top of a commercial purchased blue LED chip (10 W, 460 nm - 465 nm) to study EL characteristics of the LED using EL spectrometer measured at 0.05A. Similarly, the PF solution was also deposited on top of cleaned raw glass slides via a simple drop-casting technique. The raw glass slides were cleaned in acetone solution for 30 min before rinsing with plenty of de-ionized water and drying with nitrogen air gun. The samples were subjected to oven heating at 100°C for 15 min to transform the wet film to dry film through the removal of excess water composition before characterization [13].

![Figure 1. Chemical structure of poly [(9, 9-dioctyl-fluorenyl-2, 7-diyl)-co-(1, 4-phenylene)] end capped with dimethylphenyl group.](image)

The EL characteristic of the agar coated blue LED chip was measured at a dark environment using United Power Research Technology Corporation (UPRtek) model: MK350N PLUS spectrometer, with spectral responses ranging from 380 nm to 780 nm at a constant current (0.05 A). In order to study emission wavelength of the agar sample, PL measurement was performed at room temperature using Mini PL Raman 5.0 Photon Systems Inc, operated at 224 nm wavelength using a solid-state laser. In addition, a Cary 5000 UV-Vis spectrophotometer has been used to investigate reflectance and transmission characteristics agar samples.

3. Results and Discussion

The electroluminescent properties of the invented LED were explored by determining their intensity and wavelength characteristics as well as the emission spectra. Electroluminescence (EL) spectra agar samples are plotted in Figure2. The detection blue emission consists of main peak at 463nm and a long tail extending beyond 780nm could be attributed to PF present in the agar samples. As the amount of PF was increased from 0.625 to 2.5 mg, an increase in the peak intensity was obtained. One can see that the amount 2.5mg had good effect on the performance of the LEDs. The results showed that the coating of
increasing quantity of blue emitting PF over the blue LED chip has led to an improvement in the blue emission wavelength of the LED.

![EL spectra of agar samples.](image)

**Figure 2.** EL spectra of agar samples.

Room temperature mini PL spectra was performed to determine emission characteristics of the agar samples, as being illustrated in Figure 3. The agar sample demonstrated three emission peaks, respectively. In comparison, a stronger PL emission peak was attained by agar sample with 1.25 mg of PF at 4320 Å when compared with the other two samples. The obtained broad emission wavelength for the investigated samples were in agreement with the previous reported result of broad emission wavelength in the range of 400 to 700 nm for P99-toluene solution [13]. In addition, it could be seen that the emission wavelength obtained from PL measurement was blue shift as compared to the EL emission wavelength. The acquisition of a higher wavelength from EL (Figure2) was because of the existence of blue emission originating from the 460 nm -465 nm blue LED chip. In Figure 3., It was therefore plausible that the emission wavelength coming from the PF itself was within the PL emission region (4290Å – 4320Å).

![PL spectra of agar samples.](image)

**Figure 3.** PL spectra of agar samples.
According to UV-Vis characterization, it was found that the value of reflectance become greater with the decreasing of PF amount (0.625 mg, 1.25 mg, 2.5 mg) shown in Figure 4. Single peak in the range of 400-500 nm was due to the blue color emission of PF. It could be seen that the agar samples having 2.5 mg and 0.625 mg of PF have demonstrated reflectance characteristics of approximately 18% and 23%, respectively at the peak wavelength of 440 nm. The highest reflectance value (28%) was shown by the agar sample having 1.25 mg of PF because of higher amount of PF to react through the optical properties of sample.

Figure 4. UV-Visible Reflectance spectra of agar samples.

Transmittance spectra of various samples of PF solution deposited on glass substrates are illustrated in Figure 5 (a). The transmittance was increasing from 0.625 mg to 1.25 mg. The lowest transmission around 50-60% on 425nm was obtained by the 0.625 mg sample. The increase of PF quantity to 1.25 mg has increased the transmittance value to approximately 60-70%. Nonetheless, subsequent increase for PF to 2.5 mg has degraded the transmittance properties of the sample [14].

Figure 5. Transmittance single layer PF solution on raw glass slides from 300 nm to 750 nm.
4. Summary
In summary, luminescence characteristics of different amount (0.625 mg, 1.25 mg, and 2.5 mg) of polyfluorene (PF) hybridized with silicone (agar sample) have been successfully investigated using photoluminescence (PL), electroluminescence (EL), and UV-Visible spectroscopy. Emission wavelength originating from PF has been determined from PL measurement, located in the range of 429 nm – 432 nm. A larger emission wavelength (~463 nm) was obtained via EL measurement for all the samples because of the coating of the agar samples over the 460 nm – 465 nm blue LED chips. This finding suggested that the PF quantity did not contribute much to the emission wavelength of the LED, but did enhance the peak intensity, showing stronger emission. In comparison, the highest peak intensity was obtained for the sample having 2.5 mg of PF, followed by 1.25 mg and 0.625 mg. The trend was not in agreement with that obtained from PL measurement because the highest PL intensity was obtained by the 1.25 mg sample, followed by 2.5 mg and 0.625 mg. Further investigation was needed to deliver an understanding about this discrepancy.

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