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Optical and structural performance of polymer/fullerene thin film based on Poly (3-hexylthiophene)/1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C_{61} [(P3HT)/PCBM] after post-annealing

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The polymer solar cell is a promising candidate for the next-generation solar cells because of its light weight, flexibility and easy fabrication. Poly (3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C_{61} (PCBM) are, to date, the most-studied active materials around the world for bulk-heterojunction structure. Recent power-conversion efficiencies are reported up to approximately 13%. This research investigates the optical and morphological properties of P3HT, $PC_{61}BM$, and P3HT:$PC_{61}BM$ blend thin films deposited on glass substrate by spin-coating technique. Optical absorbance and transmittance measurements were recorded by using a single beam spectrophotometer. Morphological characterization was carried out with scanning electron microscope. Samples were pre-heated at 60°C for 30 min to evaporate the solvent. The samples deposited on the substrate were then annealed at 70 and 80°C for 30 min respectively. Optical properties of thin films were obtained. The sample annealed at 80°C has the highest absorption of photon energy in the visible region of the spectrum for the P3HT: PCBM blend thin film. Observation shows that as the annealing temperature increases, there is increase in absorption of photon energy for $PC_{61}BM$ and P3HT:$PC_{61}BM$ blend films and a reduction for P3HT thin film. Observation of surface morphology shows that: As the temperature increases the surface of the sample roughness increases. This is due to increase in grain size with increase in annealing temperature. It has been demonstrated in the study that gradual thermal annealing, in a controlled manner reveals a more stable and efficient control in tuning the P3HT-based thin film. Furthermore, this work has revealed the significance of employing thermal annealing strategies in the control of the bulk of active layer of organic thin film. The results of the study can be used to develop a guideline for improving the design and fabrication of organic solar cells. It is expected that this result will lead to improvement in performance and stability of organic solar cells.

Key words: Organic thin film, conjugated polymer, morphology, poly (3-hexylthiophene) (P3HT), 1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C_{61} (PCBM), post-annealing.

INTRODUCTION

Solar energy is a renewable energy source from the sunlight, and has attracted much attention in recent years as one of the most promising ways to tackle today's energy crises because it is renewable and eco-friendly. The first generations of solar cells fabricated are crystalline silicon solar cells and they are the major player

as far as current sales and commercialization is concerned. The second generations of solar cells are copper indium gallium selenide (CIGS) and cadmium telluride (CdTe), but are still costly and need special equipment and energy consuming processes for their production. The third generations are polymeric, quantum dot, dye-sensitized, and organic solar cells with potentials to allow for the fabrication of large area panels using less-complex processes and less-expensive materials and equipment, but still suffer from low efficiencies, stability, and durability. The third generation solar cells unlike inorganic solar cells usually employ solution-processed materials such as polymers, nanoparticles and additives which make them easier to manufacture using cheap processes and methods (Krebs, 2009). Efforts to improve the performance of solar cells which convert this abundant energy to electricity had been intensified lately. Polymer-Fullerene organic device are cheap electronics that can replace the widely used high cost silicon-based electronics for electricity generation. Organic solar cells (OSC) have strong advantages compared with conventional inorganic solar cells, which could expand the range of applications, including simple preparation, light weight, low cost, colorful, mechanically flexible and large area fabrication (Palgliaro et al., 2008; Jorgensen et al., 2008; Krebs et al., 2009). The recent power conversion efficiency of the organic solar cells is approximately 13% as reported by Berger and Kim (2018). Amongst the popular material used for the fabrication of OSCs is the combination of poly (3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C_{61}(PCBM) that form the interconnection of donor/acceptor components called bulk heterojunction. This blend system has been widely used for the study of OSCs and has been reported to have efficiency increase upon thermal annealing (Zhao et al., 2010; Kalonga et al., 2013; Wu et al., 2014; Bakar et al., 2014; Abdullah et al., 2015; Zhe et al., 2015). A number of research have been carried out on annealing treatment of P3HT:PCBM as a means of improving its performance (Cheng et al., 2015; Vinokur et al., 2015; Kadem et al., 2016). Polymer material can be deposited and fabricated at low temperature by spin-coating spray coating, and printing methods (Tang, 1986; Peumans et al., 2003; Reyes-Reyes et al., 2005; Eslamian and Joshua 2014; Sandeep and Dananjaya, 2015). Thin films were developed, characterized, and optimized for optical absorbance from blends of organic polymer poly (3-hexylthiophene-2, 5-diyl) (P3HT) and the fullerene derivative [6, 6] phenyl-C_{61}-butyric acid methyl ester (PCBM) as a means of improving its performance (Kalonga et al., 2013; Eslamian and Joshua, 2014; Oklobia, 2016) was studied in this work at low temperature using a spin-coating technique as a precursor for organic solar cells fabrication.

The impact of thermal annealing to the stability of P3HT, PC61BM, and P3HT:PC61BM blend thin films were investigated. This study reveals the significance of employing thermal annealing strategies in control of the bulk of active layer organic thin film. It has also been demonstrated in the work that gradual thermal annealing, in a controlled manner reveals a more stable and efficient control in tuning the P3HT – based thin film.

MATERIALS AND METHODS

The materials used for the research are Poly (3-hexylthiopene-2,5-diyl) regioregular (P3HT) product of USA, [6,6]-phenyl C_{61} butyric acid methyl ester>99.5% product of Nederlands ($PC_{61}BM$) which were supplied by Sigma–Aldrich. Also, the following experimental procedures were carried out.

Substrate preparation

Clean rectangular glass slides of dimension 25.4 mm by 76.2mm were used as substrates. The substrates were washed with detergent solution for 10 to 15 minutes in ultrasonic sonicator and rinsed in distilled water for 15 minutes at 30^0C. The substrate was cleaned with Isopropanol acid [IPA] in ultrasonic bath for 15 minutes at 30 ^{0}C and dried in a stream of nitrogen gas (N_2).

Sample solution preparation

1 ml of chloroform solvent was added into 15 mg of poly (3-hexylthiophene) (P3HT) and to 15 mg of [6,6] phenyl C-butyric acid methyl ester (PCBM) all from Sigma Aldrich to form P3HT and $PC_{61}BM$ solutions separately. The two solutions then underwent ageing process by using magnetic stirrer for 3 h without heat to allow the organic materials mixture to fully dilute into the solvent. Another solution was prepared by mixing P3HT solution with $PC_{61}BM$ solution in (1:3) volume ratio and stirred for another 3 h using magnetic stirrer for homogeneous mixture. The solutions were completely covered from light ray using an aluminum foil to avoid degradation of the materials.

Deposition of P3HT, $PC_{61}BM$ and P3HT: PCBM using spin–coater model laurel WS-650Hz-23NPP

To coat onto the substrate, cleaned substrate was placed on the stub of the spin-coater: setting the program, dispensing liquid, running the program. The researcher spin-coats the solution onto the pre-cleaned glass substrate at 4000 rpm for 30 s in ambient condition. The process of coating to drying was repeated to obtain the desired thickness of the film. The desired thickness of organic layer is between 85 to 100 nm. This technique is cheaper and easier to use because, it allows for uniform deposition unto flat substrate.

Annealing

Out of the three samples, two were annealed at temperature of 70

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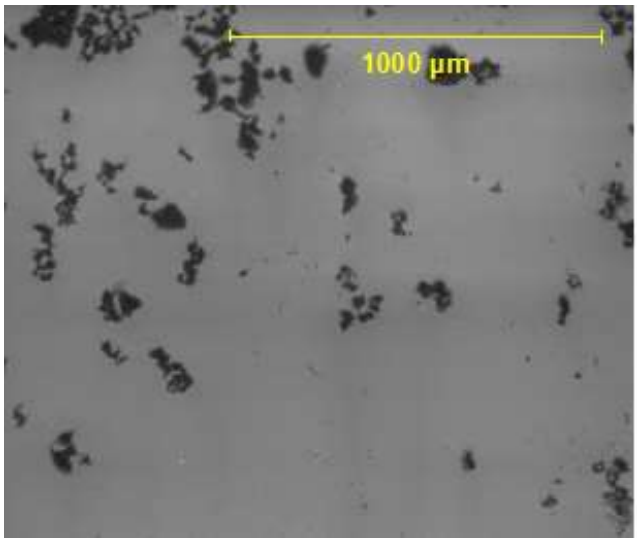

Figure 1. SEM image of P3HT unannealed (control).

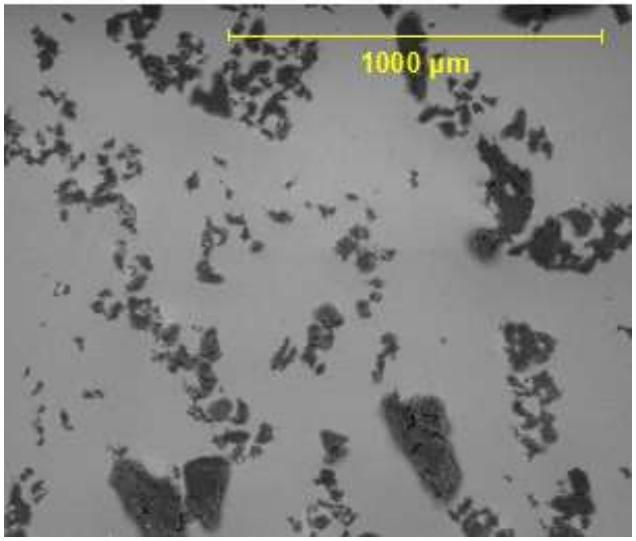

Figure 2. SEM image of P3HT at 70°C.

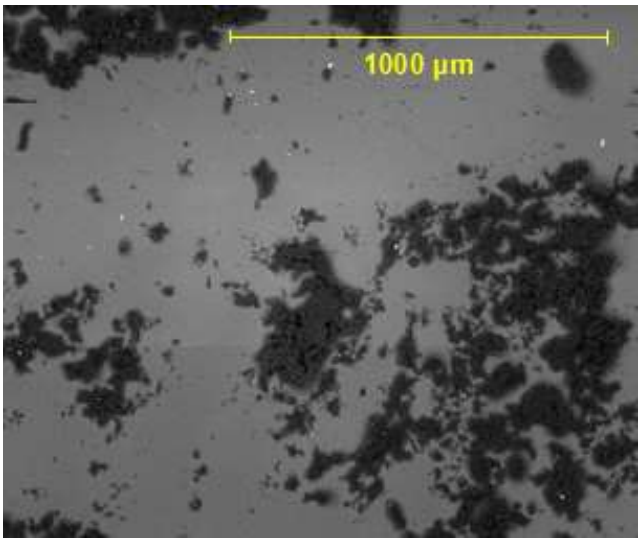

Figure 3. SEM image of P3HT at 80°C.

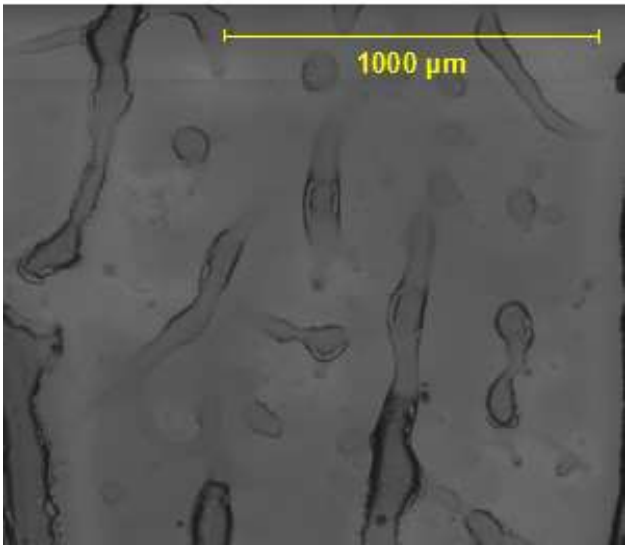

Figure 4. SEM image of $PC_{61}BM$ unannealed.

and 80°C for 30 min at step size of 10°C and then applied to slow cooling at room temperature. One sample was not heated, that is, the unannealed or control.

Samples characterization

The pre-heated deposited samples were annealed at temperature of 70 and 80°C for 30 min. Optical transmittance and reflectance was measured using UV-VIS Avantes spectrophotometer model Avalight-DH-5BAL. Samples were characterized to determine the optical spectrum at different annealing temperature. The surface morphology studies of the thin films were carried out using Scanning Electron Microscope (SEM) model ASPEX 3020. To convert between the absorbance and transmittance, Equation 1 was used.

$$\text{Absorbance (A)} = 2.00 - \log_{(\%T)} \quad (1)$$

Where, A is the Absorbance of the solution, T is the Transmittance; (%T) is the % Transmittance.

RESULTS AND DISCUSSION

Surface morphology of the P3HT, $PC_{61}BM$, P3HT:$PC_{61}BM$ thin films

SEM images of the thin films of unannealed (unheated) and the annealed samples at 70 and 80°C are shown in Figures 1 to 9. Figures 1 to 9 revealed images at different

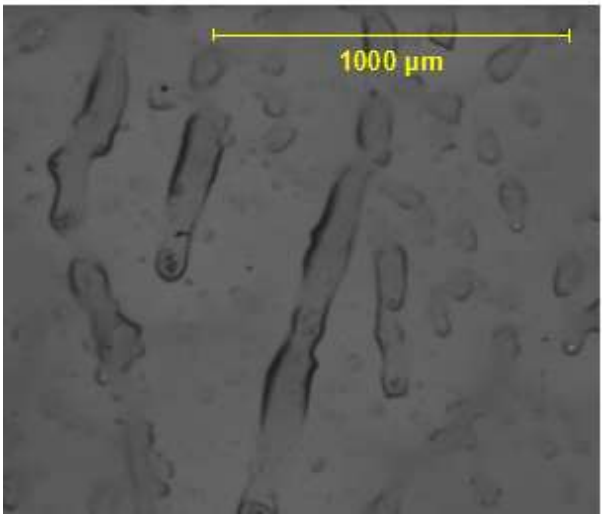

Figure 5. SEM image of $PC_{61}BM$ at 70°C.

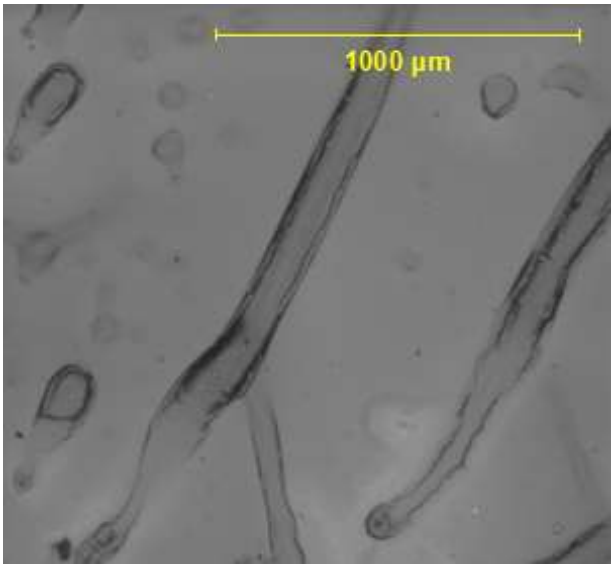

Figure 6. SEM image of $PC_{61}BM$ at 80°C.

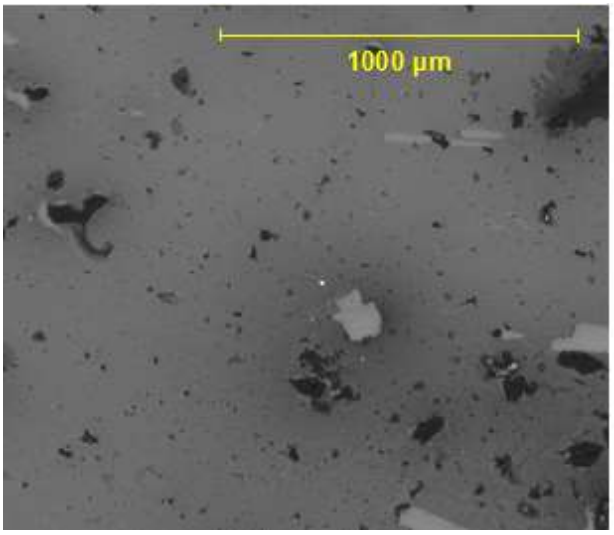

Figure 7. SEM image of P3HT:PCBM unannealed.

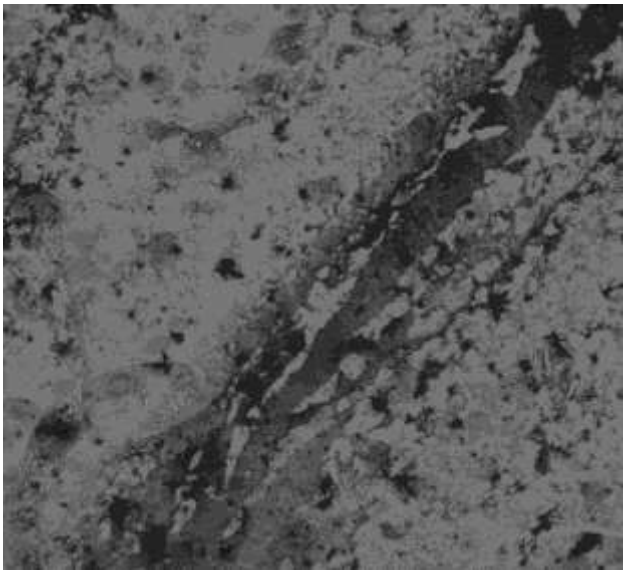

Figure 8. SEM image of P3HT: PCBM at 70°C.

temperatures in order to compare their surface morphologies with respect to the temperature variation. By comparing the image of thin films annealed at 70 and 80°C and the unannealed, it is observed that film roughness increases as increase in annealing temperature. This is attributed to increase in grain size with increase in annealing temperature.

Optical properties of P3HT, PC 61BM, and P3HT:$PC_{61}BM$ thin films

Figure 10 shows the Plot of Transmittance vs Wavelength of P3HT thin film. P3HT transmittance reduces with increase in annealing temperature. The transmittance value of the thin film is about 35% at 80°C and maintains a stable state in the visible region. Figure 11 indicates the Plot of Transmittance vs Wavelength of $PC_{61}BM$ thin film. Transmittance at 80°C annealing temperature is the least. The transmission of the film is above 40% at 70°C in the visible spectrum. Figure 12 shows Transmittance vs Wavelength of P3HT:$PC_{61}BM$ blend thin film. The transmission of the thin film shows that the unannealed sample has the highest transmission at 400 to 600 nm and steady rise at 600 nm upward in the visible spectrum, whereas the sample annealed at 80°C has the least transmission at 400 to 600 nm in the visible region. In the absorbance versus wavelength graph of polymer P3HT

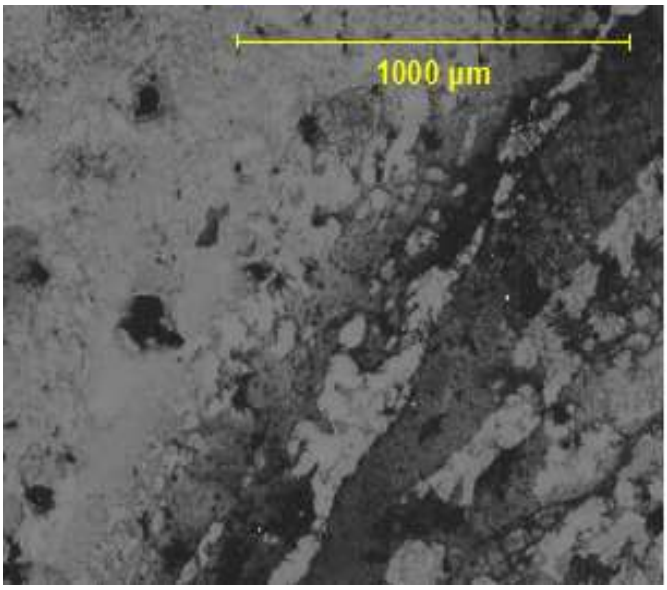

Figure 9. SEM image of P3HT: PCBM at 80°C.

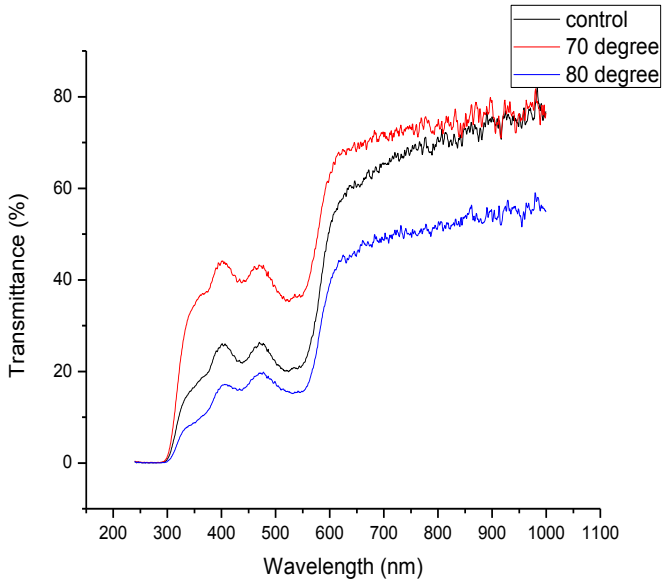

Figure 11. Plot of transmittance vs. wavelength of $PC_{61}BM$ graph.

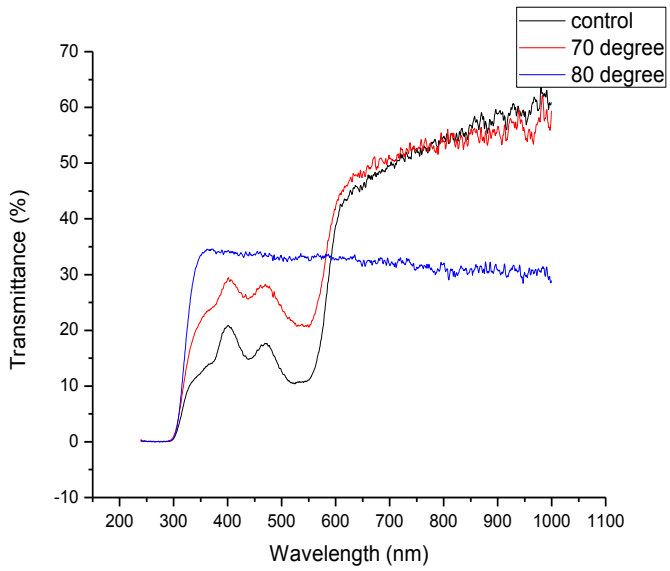

Figure 10. Plot of transmittance vs. wavelength of P3HT graph.

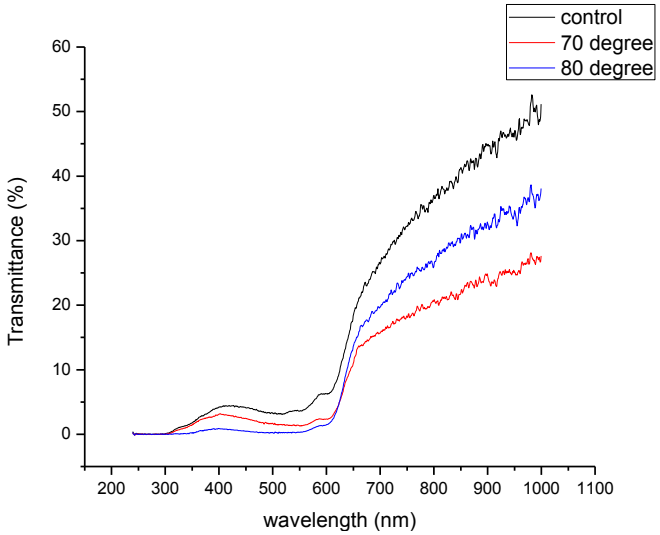

Figure 12. transmittance vs. wavelength of P3HT:$PC_{61}BM$ graph.

in Figure 13, unannealed (unheated) sample has the highest absorption of photon energy from 400 to 580 nm in the visible region whereas the sample heated at 80°C has its peak at 600 to 700 nm in the visible range and Near infrared region. For the fullerene $PC_{61}BM$ in Figure 14, the sample heated at 80°C has the highest absorption of photon energy from 400 to 450 nm and second peak from 500 to 560 nm in the visible spectrum and in NIR region. The blend thin film of P3HT:$PC_{61}BM$ in Figure 15 in the Absorbance versus Wavelength graph, the sample annealed or heated at 80°C have the highest absorption of photon energy from 400 to 550 nm in the visible region.

The wavelength absorption spectra of P3HT, $PC_{61}BM$ and blend P3HT:$PC_{61}BM$ (1:3) thin films at 70°C are shown in Figure 16, the blend of both materials (P3HT:$PC_{61}BM$) absorption peak exists at 550 nm with a shoulder at 600 nm in the visible range.

The wavelength absorption spectra of P3HT, $PC_{61}BM$ and blend P3HT:$PC_{61}BM$ (1:3) thin films annealed at 80^0C are shown in Figure 17, the blend system P3HT:$PC_{61}BM$ has highest absorption range from 400 nm to 800 nm in the visible spectrum.

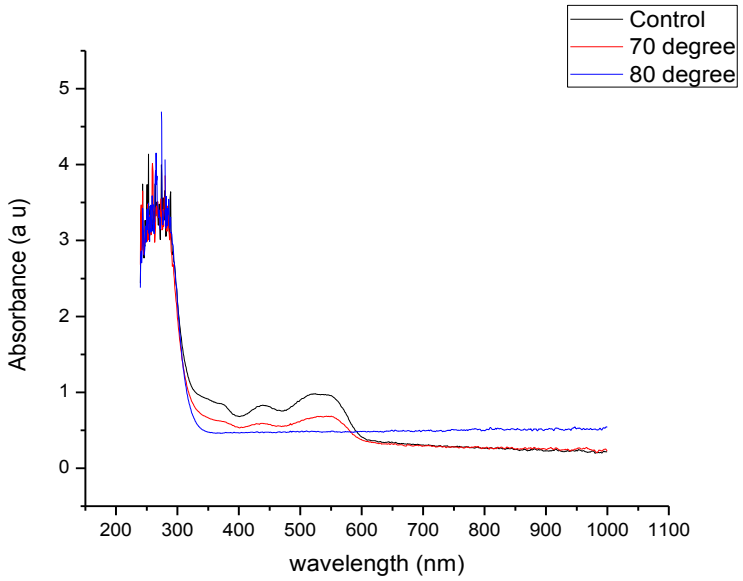

Figure 13. Plot of absorbance vs. wavelength graph of P3HT.

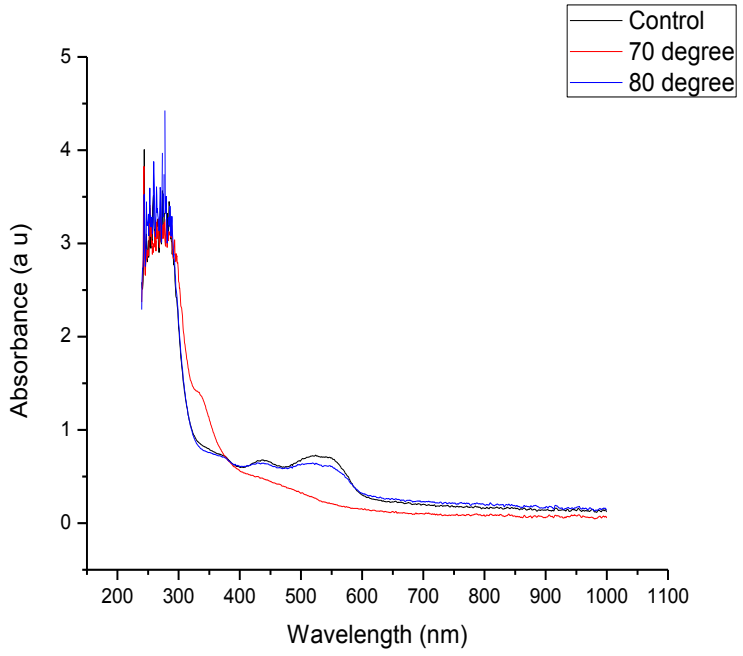

Figure 14. Plot of absorbance vs. wavelength graph of $PC_{61}BM$.

Conclusion

The thin films based on P3HT, $PC_{61}BM$, and P3HT:PC_{61}BM blend have been deposited and annealed at 70 and 80°C, respectively. UV/Visible/NIR characterization was carried out with the UV Spectrophotometer. SEM was used to study the surface morphology. The result of the study shows that annealing the sample improves the absorption of photon energy. Thermal annealing of the sample increases the surface roughness of the material due to increase in grain size. P3HT absorbance reduces with increases in annealing temperature in Figure 13 while the absorbance of PCBM increases with increased annealing temperatures. This work has shown the significance of employing thermal annealing strategies in control of the bulk of active layer of organic thin film.

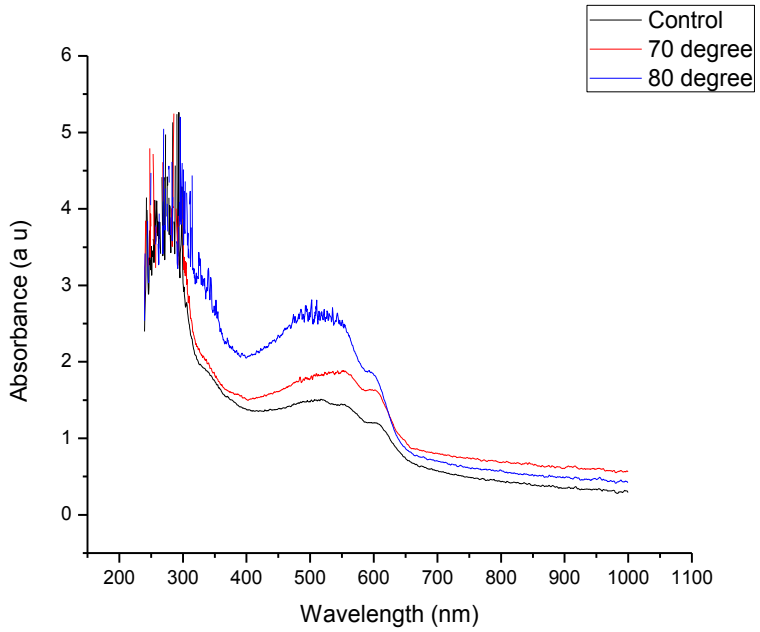

Figure 15. Plot of absorbance vs. wavelength graph of P3HT:$PC_{61}BM$.

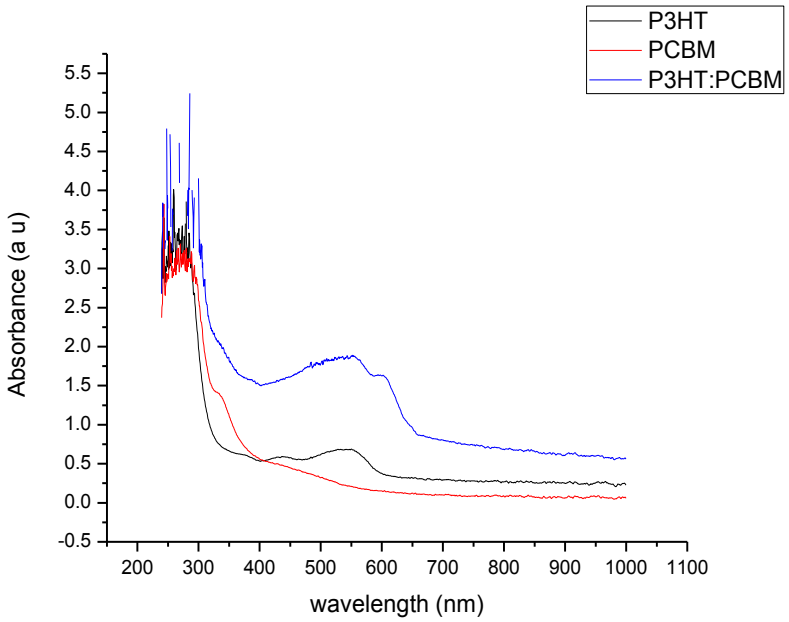

Figure 16. Absorbance of P3HT, $PC_{61}BM$, and P3HT:$PC_{61}BM$ thin films at 70°C graph.

It has also been demonstrated in the work that gradual thermal annealing, in a controlled manner revealed a more stable and efficient control in tuning the P3HT - based thin film. The results can be used to develop a guideline for improving the design and fabrication of organic solar cells. It is expected that the result could lead to improvement in performance and stability of organic solar cells. Further study on the annealing temperature rise is the next focus.

The research was chosen to study the effect of thermal annealing on the optical properties and surface morphology of polymer/fullerene based materials at low temperature, a precursor towards an improved organic solar cells fabrication.

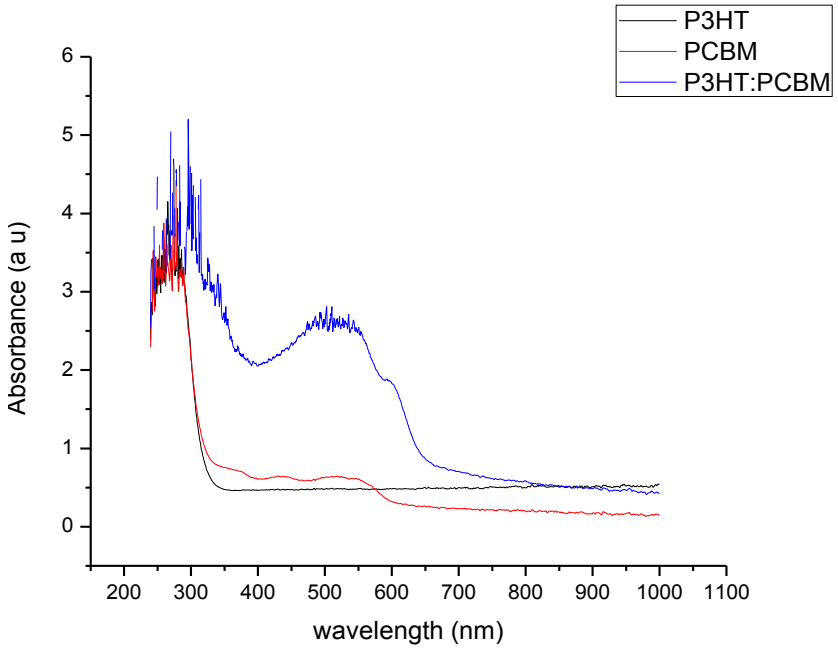

Figure 17. Absorbance of P3HT, $PC_{61}BM$, and P3HT:$PC_{61}BM$ thin films at 80°C graph.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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