SIGNIFICANCE OF SUBSTRATE TEMPERATURE ON ELECTRICAL CONDUCTIVITY, HALL EFFECT, AND THICKNESS OF BILAYER HETEROJUNCTION ORGANIC SOLAR CELL USING RHODOMYRTUS TOMENTOSA (AITON) HASSK AND IXORA COCCINEA L DYE

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Abstract

In this work, Indium Tin oxide (ITO) glass used was 27°C to 200°C as substrate. The polymer used was Poly (3-Dodecylthiophene) (P3DT) thin film, Ixora coccinea L and Rhodomyrtus tomentosa (Aiton) Hassk. as natural dye. The P3DT films were prepared using electrochemistry method at room temperature. Then, the natural dye was prepared layer by layer via spin coating method. Influence of heat treatment on the electrical properties and the efficiency of the system were investigated by Four Point Probes (FPP) under different light radiation (range of 0 Wm-2 to 200Wm-2). Hall Effect and thickness measurement. The electrical conductivity of the solar cell system increased with the increment of light radiations and the temperature of substrates. From Hall Effect measurement, the type of sample, Hall mobility, and highest charge carrier in the sample obtained. The thin film thickness was determined. The results show that the sample is suitable for further solar cell fabrications.

Keywords: Ixora coccinea L, Organic Solar Cell, Electrical Properties, Hall Effect, Efficiency, Heat treatment, Rhodomyrtus tomentosa (aiton) hassk

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1.0 INTRODUCTION

Fossil fuels become increasingly scarce, and the uses of fossil fuels harm the environment more and more seriously. People focus on solar energy for its inexhaustible, pure, cheap and flexible use [1]. Solar cell is one of the potential candidates for solving the present world’s energy crisis. In last years, organic photovoltaic technology has drawn attention as an alternative to traditional silicon or other inorganic technologies. It is based on polymers and small molecule materials [2-8]. The advantage of organic material is good processability with low cost deposition techniques, environmental, cost-effective, mechanical properties of the constituent materials, including the use of plastic-based substrates and encapsulants, opening the possibility of manufacturing flexible and low weight solar modules [9-13]. The best performance is currently achieved with bilayer, polymer:fullerene bulk heterojunction (BHJ) or tandem cells [14]. Organic solar cells could alleviate the stated drawbacks through the use of natural pigments for the conversion of solar energy into electrical energy. Foremost, the natural dyes abundantly available in plant parts, like flowers, seeds, barks, leaves, and stem can be extracted by simple procedure. Due to their cost efficiency, easily extractable using cheap organic solvents [15], non-toxicity, and eco-friendly [16-17], natural dyes are still a popular subject of research. In this study, we used natural dyes:Ixora coccinea L flower and Rhodomyrtus tomentosa (Aiton) Hassk fruits. Rhodomyrtus tomentosa (Ait.) Hassk, a member of the Myrtaeae family, known as rose myrtle, is an abundant evergreen shrub native to southeast Asia, with rose-pink flowers and dark purple edible bell-shaped fruits.

Among organic polymers, that have been used as the sensing materials, poly(3-dodecyl thiophene) (P3DT). P3DT with 12 carbon atoms in the side chain is rated as one of the most technologically promising good electrically conducting polymer due to its ease of synthesis, thermochromism, solubility [18], low cost, versatile processability and relatively stable electrical conductivity [19]. Figure 1 and Figure 2 shows the chemical structures of P3DT and Ixora coccinea Linn respectively.

2.0 EXPERIMENTAL

2.1 Sample Collection and Preparation

Rhodomyrtus tomentosa (Aiton) Hassk (Kemunting fruit) and Ixora coccinea L (Ixora flower) was hand-picked from three separate plants located in Kuala Abang, Dungun and Universiti Malaysia Terengganu (UMT), Terengganu respectively. P3DT was prepared through polymerization of the Dodecylthiophene.

The 2cm x 2cm ITO glass were used as a substrate. The cleaning process of substrates was done using ultrasonic vibrator (JEIOTECH model). The tank in ultrasonic vibrator was rinsed using distilled water to make sure it is cleaned [22]. 50ml beaker filled with distilled water and ITO substrates was putted into the ultrasonic vibrator. Then, ITO substrates were thoroughly cleaned by distilled water, the detergent. It was followed by acetone in order to remove any contaminations that might have been formed on the substrates [23] and distilled water, respectively. The time was set for 20 minutes, 30°C and mode vibration was set as medium for each cleaning. ITO substrates were dried using the dryer before kept into a Petri dish. Then, ITO substrate used was in different temperature (room temperature, 50°C, 100°C, 150°C, 200°C).

2.2 Extraction of Dye

In the laboratory, the fresh flowers was washed under tapwater and then rinsed in distilled water three times on the same day. This is to remove the contamination and to maintain the freshness in order to yield the best plant pigment. Fresh flower were crushed into small size and shade dried. 20g of flower was put into a beaker, then 100 mL absolute ethanol was added and the mixture was immersed for 48 hours and lastly, it was vibrated into the ultrasonic vibrator for 24 hours. It is for maximizing the efficiency of natural colorant extraction [24]. Later, the solid residues were subjected to repeated filtration with filter paper to yield a pure natural dye.

Figure 1 Chemical structure of P3DT [20]

Figure 2 Chemical structure of Ixora coccinea Linn [21]
solution. This extraction was protected from direct sunlight exposure and stored at about 5°C and used for further characterization. The same method was repeated for Kemunting fruit. Figure 3 and 4 show Rhodomyrtus tomentosa (Aiton) Hassk (Kemunting fruit) and Ixora coccinea Linn (Ixora flower) respectively.

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Figure 3 Plant (A, B), and fruits (C, D, E) of Rhodomyrtus tomentosa (Aiton) Hassk

Figure 4 Plant (A), and flower (B) of Ixora coccinea Linn

2.3 Fabrication of Organic Solar Cells

The bilayer heterojunction organic solar cell of P3DT/kemunting/Aurum (ITO/P3DT/KE/AU) and P3DT/ixora/Aurum (ITO/P3DT/IX/AU) were deposited on heated substrates by electrochemistry method using electrochemical Impedance spectroscopy (EIS) PGSTAT302 for first layer (P3DT thin film). EIS located in Department of Physical sciences, school of ocean engineering, Universiti Malaysia Terengganu. In the EIS method, it is based on the concentration of the solution. The less concentration of the solution will generate more cyclic in order to ensure the desired thickness is formed [25]. During EIS thin film coating, the liquid was heated at 50°C and stirred continuously on magnetic stirrer.

The second layer of thin film was deposited by spin Coater Model Laurell WS-400/500 - Lite Series via the spin coating technique. The spin coating is a procedure used to apply uniform thin films to flat substrates. In short, an excess amount of the solvent is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. The higher the angular speed of spinning, the thinner the film will be form. In this study the spinning speed was fixed. Natural dye film was deposited on ITO using spin coating with 4 rates of spin; 500 rpm for 10 s, 1000 rpm for 15 s, 1500 rpm for 20 s and 2000 rpm for 30 s to complete one cycle. The procedure was repeated the same way to complete with 10 cycles for each samples. Figure 5 show the structure of bilayer heterojunction of organic solar cell.

Figure 5 The structure of bilayer heterojunction of organic solar cell

2.4 Characterization

2.4.1 Electrical Conductivity

The samples were measured in two conditions. They were; in the dark condition and under illumination of light. The sheet resistivity produced by films was measured using FPP (Jandel RM3 Test Unit) and calculated using:

\[ R_s = \frac{4.532 \times V}{I} \]  

where, \( R_s \) is the sheet resistance, 4.532 is the correction factor, \( V \) is the voltage measured and \( I \) is the current applied from the test unit. Thus, electrical conductivity (EC or \( \sigma \)) can be determined using:

\[ \sigma = \frac{1}{R_s} \]

2.4.2 Hall Effect Measurement (HEM)

In HEM, the samples should have well-defined geometries and good ohmic contacts in order to obtain the accurate results. The samples must have van der Pauw (vdP) geometry. For this vdp shape, the error in the measurement can be minimized if the following conditions are met; that the contacts are on the circumference of the sample, the contacts are sufficiently small, sample is of uniform thickness,
and the sample is singly connected which contains no isolated holes; all four ohmic contacts should be of the same material, any leads from the contacts should be constructed from the same batch of wire to minimize thermoelectric effects. The advantages of square vdP shape is only four contacts are required. The sample on the holder system is then connected to contacts 1, 2, 3 and 4, using the silver paint on four edges as shown in Figure 6. The connection to the contact is then tested using a multimeter to ensure proper contact.

The measurements were performed using the Leois-JSF software. The Hardware system called Hall Effect measurement system model 7600 is supplied by Lakeshore Ltd. The important part of this HEM system is ensuring that the room temperature and set temperature was equivalent (20°C) in order to prevent the power supply from breakdown. The measurement consists of two parts. The first parts are called the IV curve traces measurement and the second part is variable magnetic field measurement. The purpose of IV curve traces measurement is to make sure that all the contacts are in good connections. In this work, the magnetic field fixed was 10 kG (1 Tesla) and the current was 0.1 A [28]. In addition, Figure 7 shows the numbering of sample for Hall calculations which used in this work.

Referring to Figure 7, the Hall voltage $V_{+31,42 \ (+B)}$ is measured between contact point 4 and 2 when a current $I_{+31}$ is passed from points 3 and 1. With field and current reversal, there will be eight voltages can be measured. HEM can be calculated according to our previous paper [28].

1. $V_{+31,42 \ (+B)} = \text{The current is passed from point 3 to 1, and the Hall voltage measured between 4 and 2.}$
2. $V_{-31,42 \ (+B)} = \text{The current is passed from point 1 to 3, and the Hall voltage measured between 4 and 2.}$
3. $V_{+42,13 \ (+B)} = \text{The current is passed from point 4 to 2, and the Hall voltage measured between 1 and 3.}$
4. $V_{-42,13 \ (+B)} = \text{The current is passed from point 2 to 4, and the Hall voltage measured between 1 and 3.}$
5. $V_{+31,42 \ (-B)} = \text{The current is passed from point 3 to 1, and the Hall voltage measured between 4 and 2 in negative field.}$
6. $V_{-31,42 \ (-B)} = \text{The current is passed from point 1 to 3, and the Hall voltage measured between 4 and 2 in negative field.}$
7. $V_{+42,13 \ (-B)} = \text{The current is passed from point 4 to 2, and the Hall voltage measured between 1 and 3 in negative field.}$
8. $V_{-42,13 \ (-B)} = \text{The current is passed from point 2 to 4, and the Hall voltage measured between 1 and 3 in negative field.}$

Lastly, types of charge carrier. It is determined by the polarity sign of $V_{H \ \text{avg}}$ and polarity sign of $R_{H \ \text{avg}}$. If the polarity sign is positive, the type of charge carrier is holes and called P-type. In contrast, if negative sign, it is electrons and called N-type.

### 2.4.3 Thickness Measurement

The thickness measurement was measured for different natural dyes using Dektak 150 Stylus Surface Profiler at Research center, Universiti Kebangsaan Malaysia (UKM). In this experiment, the concentration, the scan number, scan rate of the system was fixed.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Electrical Conductivity

Figure 8 and 9 represent the electrical conductivity measured in different light illumination. The electrical conductivity for ITO/P3DT/IX and ITO/P3DT/KE sample is rises with the increment of light intensity and substrate temperature. This happen as the samples were absorbed the light energy and converted to the electrical energy [29].
In Figure 8, under dark condition, ITO/P3DT/IX samples show an upward trend as substrate temperature rises. The same trend happened for samples measured in 20, 50, 100, 150 and 200 Wm$^{-2}$ of light intensity. In Figure 9, the small changes shown for samples ITO/P3DT/KE measured under dark condition as substrate temperature increase. But, the electrical conductivity was progressively rises as light intensity increased. The bottommost mark detected was using 27°C substrate temperature (unheated substrate) while the highest point was using 200°C substrate temperature for both sample when exposed to light illumination. This is due to natural phenolic compound namely anthocyanin. Anthocyanin (Figure 10) is involved in photo system assembly and contributes to light harvesting by absorbing light energy in a region of the visible spectrum [22]. ITO/P3DT/KE exhibit the highest electrical conductivity compared to ITO/P3DT/IX. This is due to plant pigments of anthocyanins and flavonoid (Figure 11) which contain in Kemunting dye [30]. The electronic structure of pigments reacting with sunlight by the plant tissue to change the wavelengths of Kemunting dyes [31]. In flavonoids, a broad absorption band in the visible region due to the charge transfer transitions from HOMO to LUMO require lesser energy which energizing the pigment molecules by visible light [32]. This flavonoid gets rapidly adsorbed to the surface of ITO. In addition, the carbonyl and hydroxyl groups from anthocyanin molecules bounded to the surface of ITO Substrates, which helps in excitation and transfer of electrons from the anthocyanin molecules to the conduction band of ITO substrate [33]. The anthocyanin pigments are exhibiting higher stability [33] and P3DT plays important role in improving electrical conductivity of OSCs. Thus, the range of electrical conductivity of ITO/P3DT/IX detected was between 0.200 Sm$^{-1}$ to 0.230 Sm$^{-1}$ and for ITO/P3DT/KE detected was between 0.195 Sm$^{-1}$ to 0.260 Sm$^{-1}$.

The electrical conductivity was higher as substrate temperature increase. This is due after heat treatment, the particle size becomes larger, and the particle shape becomes more regular. Then, the film atoms more energetic at higher temperature to migrate and more un-perfect crystal nucleuses sufficiently grow, leading to the reconfiguration of the grains and the formation of particles with perfect crystal structure [35]. As a result, higher substrate temperature was led to the formation of lower resistance films, then causes a rises on electrical conductivity. This is basically due to the increase of the mobility and/or carrier concentration at higher substrate temperature. The increase in substrate temperature may have led to oxygen deficient films,
resulting in an increase in carrier concentration as illustrated in figure 12.

3.2 Hall Effect Study

The Hall effect is a useful technique for making some electrical property measurements related to transport, such as the carrier concentration, Hall mobility, resistivity, and conduction type. The Hall measurements were performed under room temperature.

Figure below shows how carrier concentration ($n_s$), Hall Voltage ($V_{H}$), Hall Mobility ($\mu_{H}$), and Hall Coefficient ($R_{H}$) are related with the substrate temperature for the ITO/P3DT/KE and ITO/P3DT/IX thin film samples. Hall Effect measurements revealed that all the films exhibited N-type carrier. On increasing the substrate temperature from 0 to 200°C, the carrier concentration increased from $-1.70 \times 10^{20}$ cm$^{-3}$ to $-1.53 \times 10^{20}$ cm$^{-3}$, while Hall voltage and Hall coefficient decrease from $-1.67 \times 10^{-3}$ cm$^2$V$^{-1}$S$^{-1}$ to $-3.3 \times 10^{-3}$ cm$^2$V$^{-1}$S$^{-1}$. The Hall mobility also underwent a change from 1.76 to 3.97 mV.

Figure 12 clearly shows the growth of Hall Mobility as substrate temperature increases. Hall mobility is lower for unheated substrate (27°C) compared to heated substrate (50°C to 200°C) for both natural dyes bilayer with P3DT samples. For unheated substrate, ITO/P3DT/IX exhibited the lowest Hall mobility with 1.76 mV and increased as substrate temperature increase (heated substrate). ITO/P3DT/KE was increased gradually as substrate temperature increase. The maximum point for ITO/P3DT/IX and ITO/P3DT/KE was 200°C of substrate temperature. The Hall mobility for ITO/P3DT/IX (at 200°C) was higher than ITO/P3DT/KE (at 200°C) with 3.97mV and 3.50mV respectively.

From Figure 13, the carrier concentration increases with increasing temperature of substrate for both samples. This can be explained by the lack of Oxygen to compensate possible divacancies and so, to an enhancement on the bulk defects [36]. Furthermore, Oxygen vacancies induce free electrons as conduction carriers [37]. The Hall mobility and carrier concentration increased with increasing temperature [38]. Free charge carriers are easily activated at relatively high temperature. This relationship is found to be in good agreement reported by [39] and [40]. ITO/P3DT/KE samples reached a peak were $-1.53 \times 10^{20}$ cm$^{-3}$ (at 200°C). The carrier concentration for heated ITO substrate was higher compared to samples deposited on unheated ITO substrate for all samples.

Figure 14 Variation of Hall coefficient with temperature of substrate for Bilayer Heterojunction OSCs

The highest point of Hall coefficient in Figure 14 observed was $-1.67 \times 10^{-3}$ cm$^2$V$^{-1}$S$^{-1}$ and $-1.80 \times 10^{-3}$ cm$^2$V$^{-1}$S$^{-1}$ for ITO/P3DT/IX and ITO/P3DT/KE respectively. The Hall coefficient was decline as substrate temperature incline for all samples. This is revealed that, the heat treatment of substrate was affecting the Hall coefficient.

Figure 15, clearly shows that the Hall voltage is decreasing with the temperature of substrate. The unheated substrate (27°C) deposited exhibited the
maximum point. The lowest Hall voltage detected for ITO/P3DT/KE was -3.5 mV (at 200 °C). The range of Hall voltage obtained for these samples was between -1.9 mV to -3.5 mV. This graph clearly shows that the Hall mobility of heated substrate was lower than unheated substrate for both dye samples. This phenomenon could be attributed to the increase of charge carrier concentration, ns [28].

![Graph showing variation of Hall voltage with temperature of substrate for Bilayer Heterojunction OSCs](image)

Figure 15 Variation of Hall voltage with temperature of substrate for Bilayer Heterojunction OSCs

The charge carrier type can be determined by the polarity of the Hall voltage and Hall coefficient. If negative, the charge carriers are electrons and the material is of the N-type. In this work, it was found that, the Hall coefficient and Hall voltage was negative for all samples. This finding indicates that the majority carriers are electron. The ITO/P3DT/KE thin film shows higher electrical properties. The presence of carbonyl and hydroxyl groups in the anthocyanin molecules bound to the surface of ITO is in favor to facilitate the photoelectric conversion effect. From results obtained, we conclude that our samples deposited on ITO substrate are successfully investigated and improve the electrical properties of the commercial ITO substrate. Furthermore, the study of these dyes is promising and can promote additional studies oriented to educate people on renewable energy sources, and disseminate knowledge for the optimization of solar cell components compatible with such dyes.

### 3.3 Thickness Measurement

The thickness for ITO/P3DT/IX was thicker than ITO/P3DT/KE samples with 135.194 nm and 96.883 nm respectively. The thickness measurement was recorded in Table 1.

<table>
<thead>
<tr>
<th>Bilayer samples</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ixora</td>
<td>135.194</td>
</tr>
<tr>
<td>Kemunting</td>
<td>96.883</td>
</tr>
</tbody>
</table>

### 4.0 CONCLUSION

The ITO/P3DT/IX, ITO/P3DT/KE dye as Bulk Heterojunction Organic Solar Cell deposited on the different substrate temperature was successfully prepared by electrochemistry method and spin coating technique. The effect of substrate temperature on electrical conductivity, and Hall Effect of bilayer thin film was studied. The highest electrical conductivity at 200°C of temperature substrate was 2.60 × 10⁻¹⁵ Sm⁻¹ for ITO/P3DT/KE. For Hall Effect study it was found that, the polarity sign of Hall coefficient and polarity of Hall Voltage obtained were negative for all samples. This finding indicates that the majority carriers are electron. The ITO/P3DT/KE thin film shows higher electrical properties. The presence of carbonyl and hydroxyl groups in the anthocyanin molecules bound to the surface of ITO is in favor to facilitate the photoelectric conversion effect. From results obtained, we conclude that our samples deposited on ITO substrate are successfully investigated and improve the electrical properties of the commercial ITO substrate. Furthermore, the study of these dyes is promising and can promote additional studies oriented to educate people on renewable energy sources, and disseminate knowledge for the optimization of solar cell components compatible with such dyes.

### Acknowledgement

The authors would like to convey the deepest acknowledgement to the Minister of Higher Education, Malaysia for the scholarship under MyBrain15 and Research Acculturation Grant Scheme (RAGS) grant vote number: 57114 for the financial supports. The authors also would like to thank Physical Sciences Department, under School of Ocean Engineering, Universiti Malaysia Terengganu.

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