Effect of composition ratio and illumination intensity on the internal parameters of ITO/PEDOT:PSS/ MEH-PPV:PCBM/Al polymer photovoltaics

FAHRU NUROSYID[a,b,*], RISA SURYANA[b], VISKA INDA VARIANI[c], KUWAT TRIYANA[a], YUSRIL YUSUF[a], KAMSUL ABRAHA[a]

[a]Department of Physics, Gadjah Mada University, Yogyakarta 55281, Indonesia
[b]Department of Physics, Sebelas Maret University, Surakarta 57126, Indonesia
[c]Department of Physics, Haluoleo University, Kendari, 93232, Indonesia

A comprehensive study of internal parameters of organic polymer solar cells is necessary to be carried out. This study aims to improve the power conversion efficiency (PCE) significantly. The analysis was made by fitting the current density - voltage (J-V) obtained from experiment and modeling. The experiment used material of MEH-PPV blended with PCBM with variation of composition. This modeling was made using a single diode with Linear Approximation Near Break-down Voltage. The modeling determines the parameters of diode ideality factor (n), photocurrent density (J_{ph}), diode saturation current (J_s), parallel resistance (R_p), and serial resistance (R_s). It was conducted by applying the best fitting to the experimental results. The efficiency of MEH-PPV: PCBM blended with ratio 1: 2 was 0.039 % and it was higher than the efficiency of 1: 1 and 1: 4 ratios was 0.001 % and 0.005 %, respectively. The modeling indicated that the addition of PCBM will decrease series resistance; in other words, the electron transport barriers in solar cells decreased. The results of the modeling also showed that the increase in the intensity of the illumination affected the photocurrent density increases (J_{ph}) and saturation current density (J_s). Series resistance (R_s) and parallel resistance (R_p) decreased as the light intensity increased.

1. Introduction

Polymer organic solar cells have been actively studied. Organic polymer solarcells have several advantages over organic solar cells, i.e., low fabrication cost, capable of being made into larger size, light and flexible. Many research conducted aimed to improve the power conversion efficiency (PCE) including materials synthesis and design of the device structure. Generally, researchers are attracted to investigate materials synthesis such as small organic molecules [1-2], a star–shaped oligomers [3], and conjugated polymers with low band gap [4-6]. They focused on design of device structure such as the influence of morphology on the performance of photovoltaic cells [4, 7, 8] especially on the heterojunctions.

Heterojunctions structure is where the acceptor and donor electrons are mixed in solution and deposited as a thin layer by spin-coating [9,10]. Materials MEH-PPV is a material having a local absorption at the wavelength of 450 to 600 nm of solar spectrum [11]. The absorbed solar energy may generate exciton thus it is expected that the more energy is absorbed correlating the more exciton is formed. The dissociation of exciton into electrons and holes are needed to increase mobility of charge carrier toward the electrodes. Thus, the efficiency of solar cell can be improved.

In fact, properties of MEH-PPV materials have low efficiency due to it has low mobility of the electrons thus the electrons are difficult to reach the electrodes. Improving the efficiency of MEH-PPV materials, commonly called donor materials, needs additional acceptor materials to increase electron mobility [12]. PCBM is one of materials that can be added as acceptor materials. As PCBM solvent is similar to MEH-PPV solvent, the blend of both polymers is expected to be a homogenous mixture. It is considered that electron transfer from donor to acceptor is faster than solid state of two layers.

In order to increase the PCE significantly, a comprehensive examination of internal parameters of polymer organic solar cells is required with assisting a modeling. In a previous publication [13], we reported a model to determine the internal parameters of organic solar cell with variation of illumination intensity on heterojunctions of copper-phthalocyanine (CuPc) and 3,4,9,10 - perylenetetracarboxylic bis-benzimidazole (PTCBI) materials. In this work, internal parameters of organic solar cell heterojunction structure which include the series resistance(R_s), parallel resistance (R_p), saturation current density (J_s), and the ideality factor (n) are performed with variation of mixed composition and variation of illumination intensity. To the best our knowledge this

modeling has not been invoked in the context of ratio variation between MEH-PPV and PCBM. The method employed in this work is by fitting the current density-voltage (*J-V*) obtained from the experiment and from modeling.

2. Material and methods

Materials used in the experiment included polymer MEH - PPV (poly {[2-[2'.5'-bis(2"- ethylhexyloxy) phenyl] -1.4- phenylenevinylene] - co-[2-methoxy-5(2'-thylhexyloxy)-1.4-phenylenevinylene]}) and PCBM which is the fullerene derivative ([6.6]-phenyl C61 butyric acid methyl ester) powders from Sigma Aldrich. The glass substrates coated indium tin oxide (ITO) with surface resistivity of 8-12 Ω/sq were cleaned respectively by acetone and ethanol in ultrasonic bath for each 15 min. PEDOT:PSS solution were deposited on those substrates using spin-coating method. PEDOT: PSS layers thickness obtained were about 1200-1600 Å. After deposition, sample was heated at 110º C for 15 min. In order to obtain a homogeneous solution, various composition ratios of MEH-PPV and PCBM (1:1, 1:2, and 1:4) were dissolved in chlorobenzene by stirring for 20 h. This blend polymer was then deposited on the PEDOT:PSS layer samples by spin-coating method. Then, this sample was heated at 60º C for 10 min. The obtained samples function as the active layer in solar cell devices. For the efficiency measurement purpose, this sample was coated by patterned aluminum as cathode in solar cell devices using thermal vacuum evaporation.

The absorption spectra measurements of samples were carried out using UV-VIS Spectrometer Lambda 25. The surface morphology of the active layer was characterized using AFM Park System. Current density-voltage (*J-V*) measurement of the devices was conducted on a computer-controlled Keithley 2602A source meter. Simulation to determine the internal parameters of solar cells was performed by fitting the *J-V* characterization between the experimental and modeling. This modeling approach was made using a single diode with Linear Approximation Near Break-down Voltage to determine the diode parameters of ideality factor (*n*), photocurrent density (J_{ph}), saturation current (J_s), parallel resistance (R_p), and serial resistance (R_s) [13].

3. Results and discussion

Fig. 1 shows the absorption coefficient of pure MEH-PPV, pure PCBM, MEH-PPV and PCBM blend layers with a ratio of 1:1, 1: 2 and1: 4, as a function of ultra-violet visible wavelength. It can be seen that the absorption spectra of the mixed layer is a superposition of spectra of the pure MEH-PPV and pure PCBM layer. As a donor material, MEH-PPV material has the absorption range at wavelengths of 400-600 nm. It can be observed that the donor layer spectra peak at about 500 nm, while the absorption range of the acceptor material appears at the UV region (<400 nm).

Curves of all MEH-PPV:PCBM ratio at 1:1, 1:2, and 1:4 indicate that curve peak at about 340 nm increase with the increasing of PCBM composition. While the curve peak at about 500 nm increase only at ratio of 1:1 and 1:2; and that peak decrease at 1:4 ratio. From the absorption spectra for all ratios as shown in Fig. 1, it is expected that the 1:1 and 1:2 ratio is good composition to polymer solar cell application because of that ratio have two regions of absorption of solar spectrum.
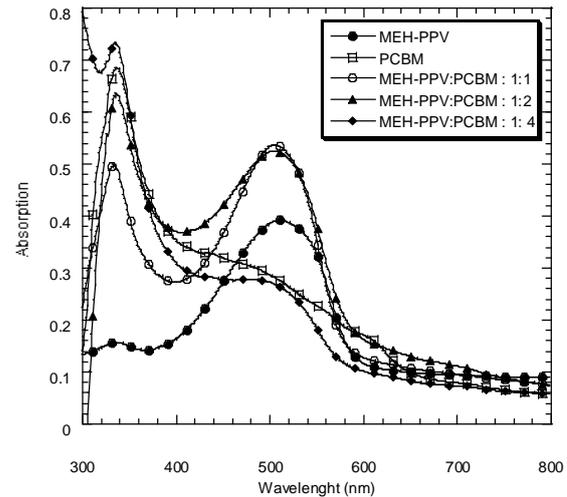

Fig. 1. Absorption spectra for MEH-PPV : PCBM films with different ratio including pure MEH-PPV and pure PCBM spectra.

J-V characterization under illumination 1000 W/m^2 is shown in Fig. 2. Based on Fig. 2, the equation of $\eta = \dfrac{P_{max}}{P_{in}} = \dfrac{I_{sc}V_{oc}FF}{P_{in}}$ with $FF = \dfrac{I_{mpp}V_{mpp}}{J_{sc} \times V_{oc}}$ [14] is used to determine the power efficiency as shown in Table 1. The efficiency of blended MEH-PPV: PCBM with ratio of 1: 2 has an efficiency of 0.039% which is higher than 1: 4 and 1: 1 ratio with efficiency of 0.005% and 0.001%. Power conversion efficiency of solar cells is directly related to the three parameters, namely short-circuit current (J_{sc}), open circuit voltage (V_{oc}), and fill factor (*FF*). It is clear that the 1:2 ratio has optimum parameters. The J_{sc} is affected by several factors including generation, dissociation rates of the charge and free charge carrier mobility [15]. The J_{sc} value of the 1:1 and 1:4 ratios is almost similar. We assumed that the amount of PCBM correlated with the dissociation rate of exiton. At 1:1 ratio, exiton can be generated after absorbed the solar spectrum at two regions (<400nm and range of 400-600nm) but dissociation rate of exiton into electrons and holes are not as fast as at 1:2 ratio. On the contrary, at 1:4 ratio, dissociation rate of exiton into electrons and holes are faster than that of 1:1 ratio even with 1:2 ratio but exiton which can be generated at 1:4 ratio lower than 1:1 and 1:2 ratios. This is confirmed by absorption spectra as shown in Fig. 1 whose dominant absorption region at UV only.
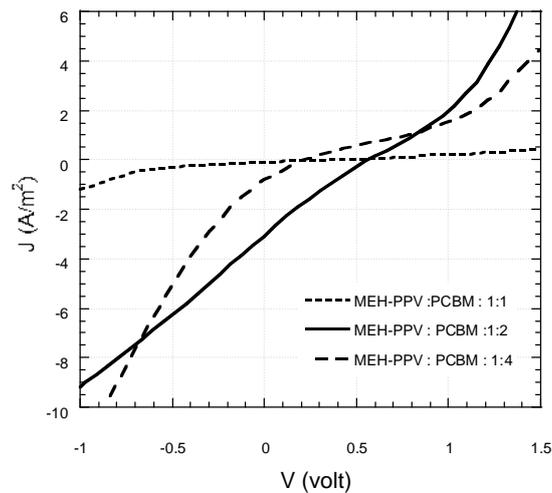
Fig. 2. J-V characteristics for polymer solar cell devices with   different ratio of MEH-PPV : PCBM under illumination of 1000 W/m².

Table 1. The calculated efficiency.

Polymer ratio	V_{oc} (volt)	J_{sc} (A/m²)	V_{max} (volt)	J_{max} (A/m²)	FF	PCE (%)
MEH-PPV: PCBM : 1:1	0.15	-0.2	0.1	-0.09	0.26	0.001
MEH-PPV: PCBM : 1:2	0.50	-3.0	0.3	-1.3	0.26	0.039
MEH-PPV: PCBM : 1:4	0.20	-0.7	0.1	-0.5	0.36	0.005

From the AFM results as shown in Fig. 3, it can be seen that by adding PCBM, the layer morphology is increasing the roughness. This is understood, the PCBM $(C_{72}H_{14}O_2)_n$ molecules are larger than the MEH-PPV $(C_{18}H_{28}O_2)$ molecules [16]. The surface roughness of blended MEH-PPV and PCBM layer at 1:4 ratio is about 0.02 μm as shown in Fig. 3 (right side). Thus the absorption of solar spectrum is dominated by PCBM material.

Fill factor will increase significantly at 1:4 ratio. It is considered that the addition of PCBM can increase the rate of electron transfer [17,18] and thus increases the current density. Modeling results (Table 2) show that the addition of PCBM decreases series resistance (R_s). As the existence of resistance will decrease the electron transport towards the electrode, the addition of PCBM increases the charge-carrier mobility thus at the same time increase the current density. However, the addition of PCBM causes reduction on the absorption of solar cell which then decreases the exciton amount and eventually also decreases the photocurrent generation.
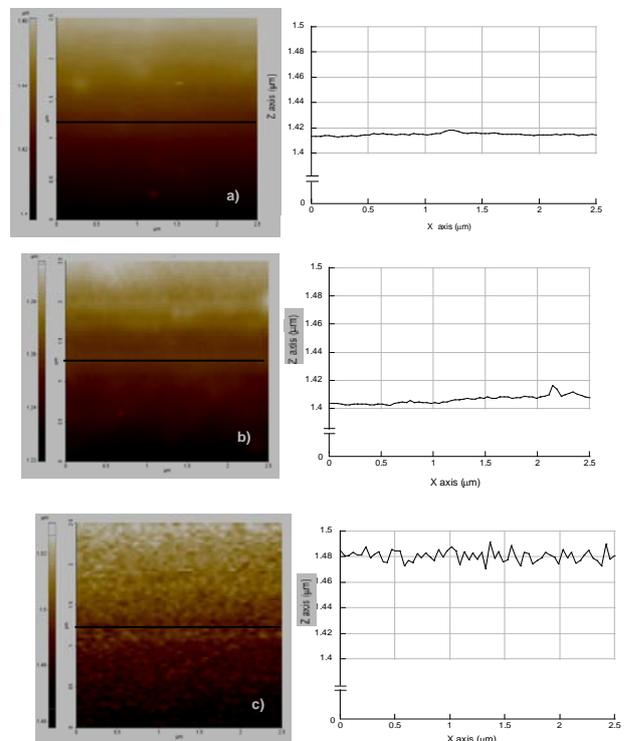

Fig. 3. AFM images showing the surface morphology of blended MEH-PPV:PCBM films at a) 1:1, b) 1:2 and c)1:4 ratio. The surface profiles (right side) are obtained from line scan along the black line on surface morphology (left side).

Table 2. Internal parameter values (n,J_{ph}, J_s, R_s, and R_{sh}) for variations polymer ratio.

Polymer composition	n	J_{ph} (A/m^2)	J_s (A/m^2)	R_{sh} (KΩ)	R_s (Ω)
MEH-PPV : PCBM : 1 :1	1.5	3.09	1.73	71.9	153.3
MEH-PPV : PCBM : 1:2	1.5	43.36	2.58	0.9	8.2
MEH-PPV : PCBM : 1:4	1.5	5.46	0.07	14.5	6.5

As the 1:2 ratio have higher efficiency than 1:1 and 1:4 ratios, 1:2 ratio is chosen at modeling. Fig. 4 shows the suitability of the current density-voltage (*J-V*) experimental and the modeling of solar cells with a structure of glass/ITO/PEDOT:PSS/MEH-PPV:PCBM/Al with variations in light intensity. Based on the fitting curve between experimental and modeling, it is concluded that modeling using single diode with Linear Approximation Near Break-down Voltage which have been developed by Triyana et al [13] can also be applied in this work.

The modeling internal parameter results of solar cells with the variations of light intensity are presented in Table 3. Correlation between the internal parameters and the illumination intensity is discussed in this paper. Influence of the illumination intensity to photocurrent (J_{ph}) is shown in Fig. 5 while Fig. 6 presents correlation between parallel (R_{sh}) and series (R_s) resistances and the illumination intensity.
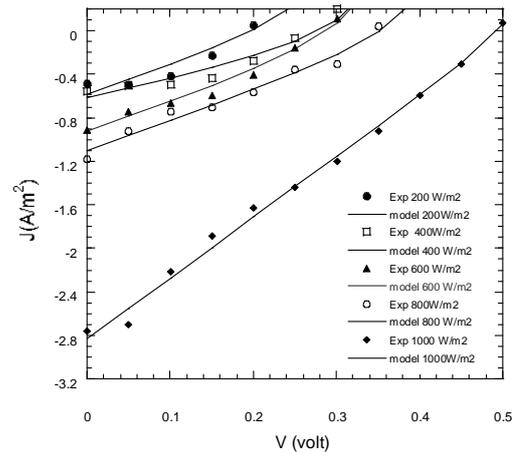

Fig. 4. J-V characterization curve of experimental and modeling results of solar cells with the structure of glass/ITO/PEDOT:PSS/MEH-PPV:PCBM/Al with variations of light intensity. Ratio of MEH-PPV:PCBM is chosen at 1:2.

Table 3. Internal parameters of solar cells ITO / PEDOT: PSS / MEH-PPV: PCBM / Al with variations in light intensity.

Intensity (W/m^2)	n	J_{ph} (A/m^2)	J_s (A/m^2)	R_{sh} (KΩ)	R_s (Ω)
200	1.134	12.906	0.5188	7.192	28.969
400	1.294	13.194	0.5728	6.461	28.192
600	1.249	29.953	0.6842	2.283	20.359
800	1.632	36.644	1.8407	1. 682	11.792
1000	1.545	43.362	2.5847	0.914	8.228

Fig. 5 shows the curve of photocurrent density (J_{ph}) to illumination intensity. The J_{ph} increases with increasing the illumination intensity which indicates that the exiton is more generated. It is expected that the more electrons move toward the electrode.
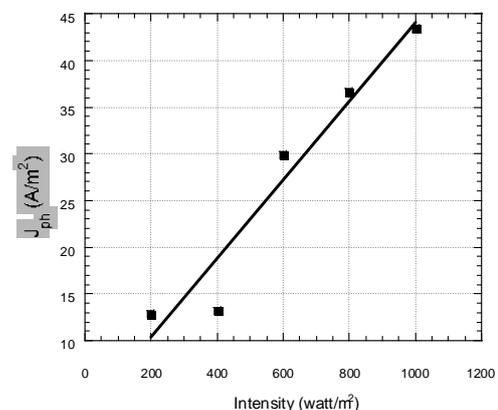

Fig. 5. Curve of photocurrent density and illumination intensity.

The higher illumination intensity causes the decrease in the series resistance (Fig. 6) because it encourages more exciton to be formed around electrode thus electron flows easily to electrode. Series resistance is a barrier that prevents electron flowing into electrode. The decrease of series resistance is expected to increase the efficiency whilst parallel resistance drops within the increase of light intensity. In addition parallel resistance is a barrier that prevents recombination of electrons and holes. In a higher illumination intensity, exciton are mostly formed in the area of electrode causing recombination often occurs thus the parallel resistance decreases. The modelling result shows that the illumination intensity directly effects on the series and parallel resistance. These also affect the power conversion efficiency of polymer solar cells.
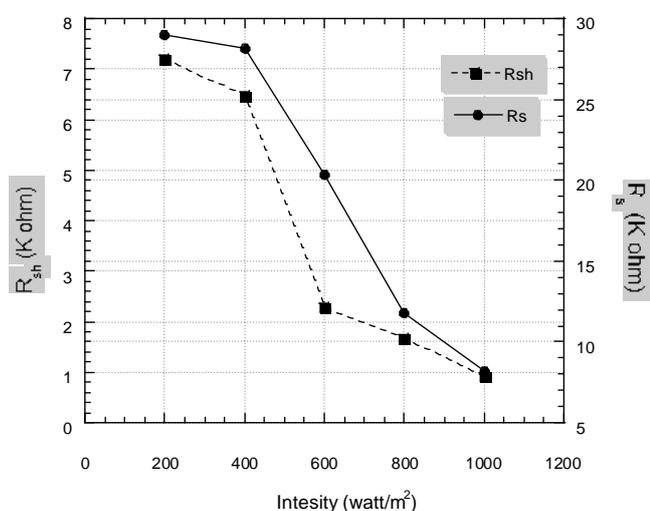

Fig. 6. Effect of the illumination intensity on parallel and series resistances.

4. Conclusion

The absorption spectra of the blended film are basically formed by a superposition of pure MEH-PPV and pure PCBM absorption spectra. The efficiency of blended-MEH-PPV:PCBM with ratio of 1: 2 had an efficiency of 0.039 % which was higher than the efficiency of 1: 4 and 1: 1 ratio. In addition, modeling results of internal parameters showed that the optimum of current density (J_{ph} and J_s) could be reached at ratio of 1:2. Furthermore, from the fitting results on the *J-V* characterization curves of the *glass/ITO/PEDOT:PSS/MEH-PPV:PCBM/Al* structure as function of the illumination intensity at MEH-PPV:PCBM ratio of 1:2 confirmed that modeling using single diode with Linear Approximation Near Break-down Voltage can be applied in this work.

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[*]Corresponding author: nurosyid@yahoo.com