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Efficiency Dependency of MDMO-PPV Based Polymer Solar Cells on Surface Morphology and Molecular Weight

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Abstract : *In the scope of this study, polymer solar cells were fabricated by using poly [2-methoxy, 5-(30,70-dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV) with three different molecular weight (A:25000, B:85000, C:450000). Their efficiencies were investigated and the highest efficiency was obtained in organic solar cells, which were prepared with batch of B polymer. On the other hand, the least efficiency values were detected by group A polymer. Studied Solar Cells are solution processable and prepared by Spin Coating. Obtained Efficiencies and AFM profiles of prepared solar cells were compared. When AFM images of three groups of MDMO-PPV polymers were examined, it was seen that surfaces of high efficiency B batch solar cells were smoother than those of A and C groups and the cells of lowest efficiency (batch A cells) had been showing the worst roughness values in compared to the others. Obtained results constitute an optimization basis for organic solar cell applications, where MDMO-PPV based materials can propose an alternative perspective. We are also planning to improve the current efficiencies by doping tailored nanoparticles such as C_{60} to our optimized results.*

Keywords: *AFM images, efficiency, molecular weight, polymer, organic solar cells, organic bulk heterojunction solar cells.*

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I. Introduction

In recent years, investigation of solar cells using organic semiconductors have attracted much attention of the optoelectronics researchers due to their potential applications for the realization of flexible, light weight and cost effective energy conversion platforms [1]. Organic bulk heterojunction (BHJ) solar cells, in which photoactive layer are based on the blends of p-type and n-type organic semiconductors, have consistently been playing a leading role in this emerging area of photovoltaic. P-type and n-type organic semiconductors which are also called as Donor and Acceptor, respectively, from an interpenetrating network with a nanoscale phase separation in bulk volume of the organic layer. Processing of this layer is mostly carried out using vapour deposition approach for the case of low molecular weight organic species whereas solution processing is adopted for the case of polymer based systems [2]. During the past decade, Polymer fullerene blends were well investigated for bulk heterojunction solar cells due to their ease of processing and promising features [3, 4]. Thompson et al. [5] have explained general mechanisms of photoenergy conversion using polymer fullerene bulk heterojunction (BHJ) solar cells and discussed the effect of BHJ film morphology and polymer-fullerene interactions on the performance of these devices.

MDMO-PPV: PCBM blend is among the well-studied polymer fullerene combination for BHJ solar cells [6, 7]. Earlier studies on this typical polymer fullerene pair include the investigation of the effect of solvent type [8, 9], blend ratio [10, 11], photo and thermal degradation [12], electric field variation [13], etc. It has been shown that these variations significantly affect the performance of these devices by altering the morphology and structure of polymer fullerene films. Thus performance of a solar cell can be modified by tuning the morphology and transport properties of its BHJ photoactive layer.

In this work, we have studied the effect of polymer Molecular Weight on the performance of MDMO-PPV: PCBM blend based BHJ Solar Cells which is not previously investigated to our best knowledge. Three different batches of MDMO-PPV polymer with varying intrinsic properties were used for this study. Then surface morphology of polymer groups and their efficiencies were compared.

II. Experimental Details

Effect of polymer molecular weight on the performance of BHJ solar cells is investigated in this study using three different batches of MDMO-PPV polymer which will be denoted as batch A, B and C. Molecular weight and properties of the polymer batches are given in Table-1.

Table 1. Molecular Weights (M_w), Polydispersity (PDI) values, Charge Carrier Density (N_A), HOMO/LUMO Levels and Bandgap Energies (Eg) for three different batches of MDMO-PPV Polymers.

MDMO-PPV	M_w	PDI	N_A (cm^{-3})	HOMO(eV)	LUMO(eV)	E_g (eV)
Batch-A	25000	3.5	1.8×10^{-17}	4.97	2.85	2.12
Batch-B	85000	16.8	3.2×10^{-17}	4.93	2.85	2.08
Batch-C	450000	4.2	3.0×10^{-17}	4.90	2.84	2.06

Fabrication of the devices was started with the cleaning of Indium Tin Oxide (ITO) coated patterned glass substrates in an ultrasonic bath using detergent, deionised water, acetone and isopropyl alcohol. Drying of the substrates was carried out using nitrogen blow and thermal oven. Poly(3,4-ethylenedioxylenethiophene)-polystyrene sulfonate (PEDOT:PSS) film was coated on ITO substrates using spin coating technique. This hole conductive layer not only smoothes ITO surface but also used to increase the work of bottom electrode so that it can accept holes, and to decrease the work function of top electrode so that it can accept electrons from the active layer. PEDOT:PSS coated samples were annealed at 110 ºC for 30 minutes. MDMO-PPV:PCBM blends with 1:4 w/w ratio, were prepared in dichlorobenzene by the process of stirring at 50 ºC for 24 hours, using three different batches of polymer (MDMO-PPV). Spin coating technique was used to coat organic semiconducting layers on the samples using these MDMO-PPV:PCBM blends. Then samples were annealed in the Glove Box at 50 ºC for 10 minutes. Finally, around 50 nm thick top contact was made on the organic films by the evaporation of Aluminum in the vacuum chamber at 10^{-5} mbar pressure. Prior testing, samples were annealed again at 80 ºC for 10 minutes in the nitrogen environment. Fig. 1 schematically presents the structure of devices along with the molecular formulas of PEDOT:PSS, MDMO-PPV and PCBM.

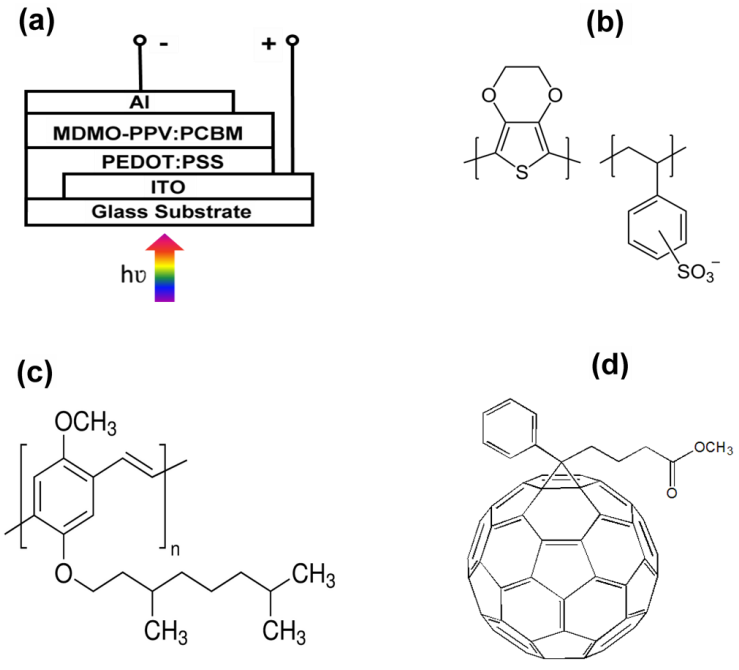

Fig. 1. (a) Schematic architecture of devices and with the molecular structure of (b) PEDOT:PSS, (c) MDMO-PPV and (d) $PC_{71}BM$.

Current-voltage (J–V) characteristics of the devices were studied under dark and UV-Vis illumination of 100mW/cm^2, using Semiconductor Characterization System, SCS-Keithley4200, and 150W Oriel Solar Simulator with AM1.5 filter. Solar Simulator was calibrated by a reference solar cell during the measurements. Structural properties of the semiconducting layers were studied using Nanoscope Multimode Atomic Force

Microscope (AFM). Absorption spectra were extracted using UV-Vis Spectrophotometer (S-3100). Thicknesses of the organic and electrode films were measured using DEKTAK-8 profiler. All the test and measurements were performed in the ambient conditions.

III. Results and Discussion

Fig. 2 shows 10×10 μm^2 surface and high resolution 3D AFM Profiles of Polymer:Fullerene BHJ based semiconducting layers developed using three different batches of MDMO-PPV polymers. Thin film casted from polymer batch-A exhibits the highest height variations. Root Mean Square (RMS) roughness values of the blend films cast from polymer batch A, B and C were found to be 3.104, 0.909 and 1.647 nm, respectively. Lowest surface roughness was found for the polymer batch with moderate molecular weights of batch-B. Phase separation of the composite film developed using polymer batch-B was found significantly larger as compared to the films prepared using other polymer batches. Differences in the Donor-Acceptor phase separations, feature sizes, roughness values and 3D profiles of the films developed using different polymer batches, indicates the clear effect of polymer intrinsic properties on the structural properties of organic films. Fig. 3 shows UV-Vis absorption spectra of Polymer:Fullerene bulk heterojunction based nanolayers prepared from three different batches of MDMO-PPV polymers. Thin films, prepared using polymer batch-B showed highest UV-Vis absorption with maximum absorption peak (λ_{max}) at 497 nm, and two shoulder peaks at 416 and 598 nm. Thin films prepared from polymer batch-A demonstrated the lowest absorption of photons. Further, no significant peaks were observed for polymer-fullerene blend based films prepared from batch-A and batch-C.

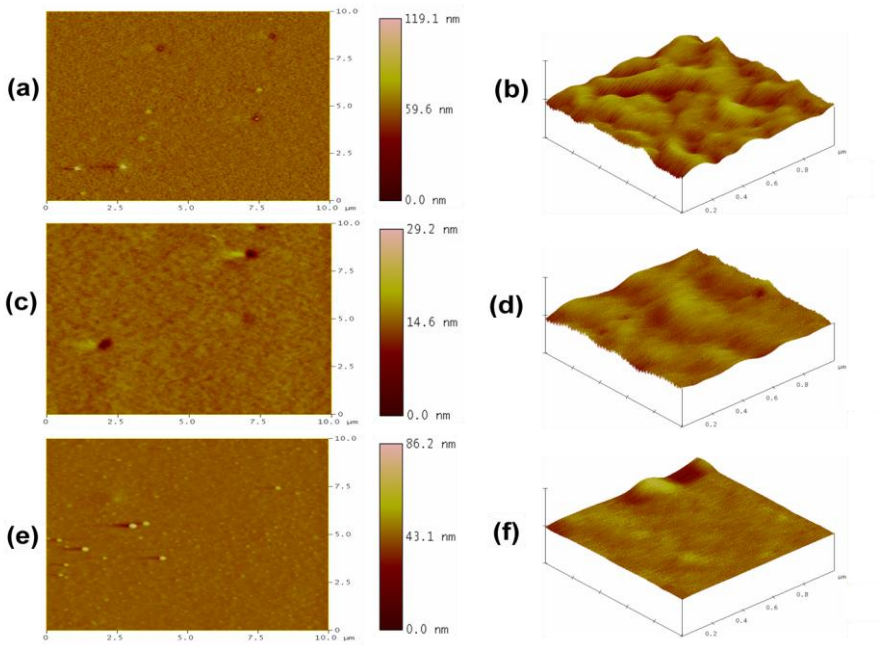

Fig. 2. 10×10 μm^2 surface and high resolution 3D AFM profiles of Polymer:Fullerene BHJ based semiconducting layers for three different batches of MDMO-PPV: A[(a,b)], B[(c,d)] and C [(e,f)]

Formation of excitons, their diffusion towards Donor and Acceptor (D-A) interface and dissociation into free carriers (electrons and holes) at D-A interface, and transportation of these carriers towards electrodes are among the basic steps which are essentially followed in BHJ solar cells during the process of solar energy conversion into electrical power [14]. Therefore, role of the organic film morphology and D-A interface is of primary importance in these devices. The ideal film architecture is the one which supports the excessive generation of excitons, minimizes the chances of exciton and carrier recombination simultaneously enhancing charge carrier generation and their transportation towards electrodes.

Basic characterization parameters of an organic solar cell are Open Circuit Voltage (V_{oc}), Short Circuit Current Density (J_{sc}), Maximum Power Point (MPP), Fill Factor (FF) and Power Conversion Efficiency (η). V_{oc} is the maximum possible voltage across the illuminated cell when no current is flowing, J_{sc} specifies current per unit area that flows through the cell under light when both electrodes of the cell are short-circuited and MPP is the point on the J-V characteristics of the solar cell at which the product of voltage and current results into

maximum value. That is why voltage and current density values at MPP are denoted as V_m and J_m, respectively. Fill Factor (FF) and Power Conversion Efficiency (η) of a solar cell can found using following relations:

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (1)$$

$$\eta = \frac{J_m V_m}{P_{in}} = \frac{J_{sc} V_{oc} FF}{P_{in}} \quad (2)$$

Where P_{in} is the power of incident illumination which was fixed to 100 mW/cm^2 for our experiments.

Table 2. Fill Factor (FF), Short Circuit Current Density (J_{sc}), Open Circuit Voltage (V_{oc}) and efficiency (η) of polymer fullerene BHJ based solar cells realized using three different batches of MDMO-PPV Polymers

MDMO-PPV	J_{sc} (mA/cm^2)	V_{oc}(V)	FF	% η
Batch-A	2.78	0.84	0.30	0.70
Batch-B	5.16	0.80	0.51	2.10
Batch-C	4.61	0.78	0.49	1.76

The performance of the devices developed using three different batches of MDMO-PPV were compared using their Current Density-Voltage (J-V) curves, shown in Fig. 4. Current Density (J_{sc}), Open Circuit Voltage (V_{oc}), Fill Factor (FF) and Efficiency (η) values of devices, under an illumination intensity of 100 mW/cm^2, are summarized in Table 2. Results showed that polymer intrinsic properties have significantly influenced on the J_{sc} and FF values of the devices. In earlier investigations, these parameters of BHJ solar cells have been shown to be sensitive to the type of solvents [15, 16], annealing conditions [17, 18] evaporation rate [19], doping species [20], molecular weights of polymers [21] etc. In most of these reports, variation in the FF and J_{sc} parameters of the devices was suggested due to differences in the morphology of their organic films. BHJ solar cell developed using polymer batch-B with moderate molecular weights and highest PDI and N_A value, among the investigated polymer batches, has shown highest efficiency which was attributed due to higher photon absorption capability (Fig. 3) and favourable morphology of its photoactive layer. Furthermore, proper separation of Donor and Acceptor phases for the case of polymer batch-B (Fig. 2), may also be the reason of its enlarged efficiency. Thus based on the earlier investigations [14, 22] and current study, we suggest that the performance of a polymer fullerene BHJ solar cell can enhanced by using polymer having higher PDI values. In short, in this work an effort was made to highligt the importance of polymer intrinsic properties for MDMO-PPV:PCBM blend based solar cells.

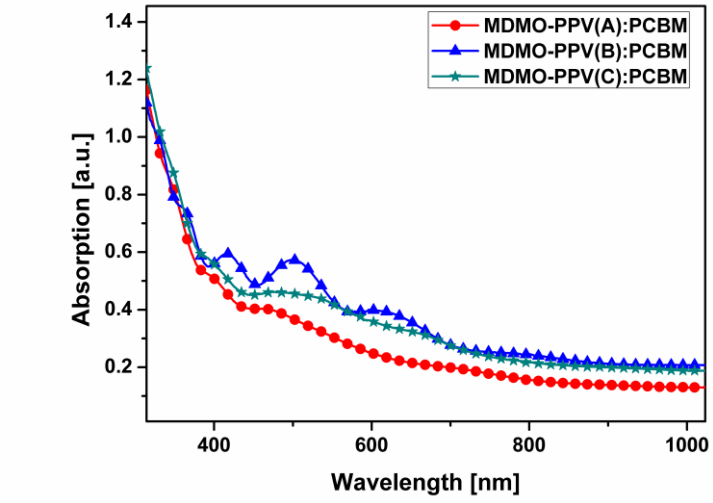

Fig. 3. Absorption Spectra of MDMO-PPV:PCBM nanolayers (with 1:4 w/w ratio) prepared using three different batches of MDMO-PPV Polymer

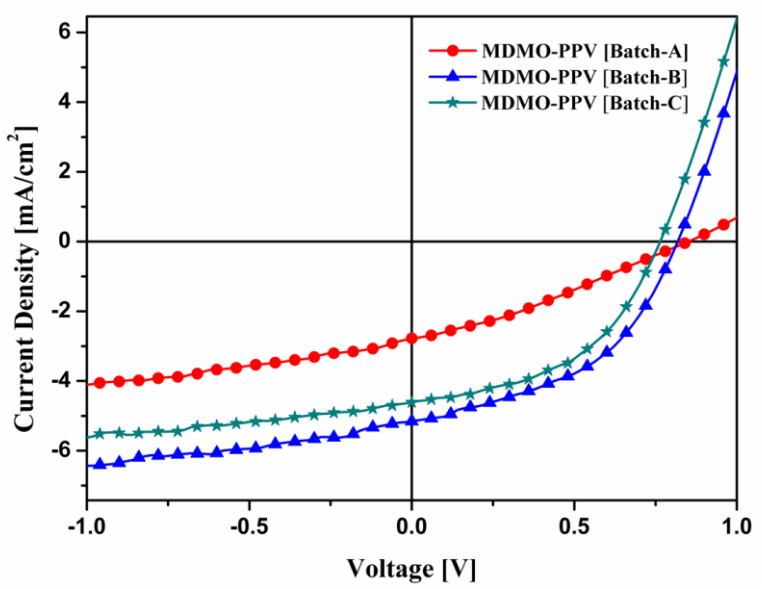

Fig. 4. Current Density-Voltage (J-V) Curves of BHJ solar cells developed using three different batches of MDMO-PPV Polymers under an illumination intensity of 100mW/cm^2.

IV. Conclusion

Polymer-Fullerene BHJ based organic solar cells were fabricated using three different batches of MDMO-PPV polymer with a motivation to investigate the effect of polymer intrinsic properties on the performance of these devices. Polymer batches with significant varying intrinsic properties such as Molecular Weights, Polydispersity values and HOMO/LUMO Levels were used for this investigation. Structural and optical properties of MDMO-PPV:PCBM blends based nanolayers developed using three different batches of polymer, were studies using Atomic Force Microscopic and UV-Vis absorption spectroscopic techniques, respectively. Current Density-Voltage (J-V) characteristics of the devices were investigated under an UV-Vis illumination intensity of 100mW/cm^2 and their results were compared. Differences in the nano morphology of organic films, casted using three different batches of polymers were observed which have significantly influenced on J_{sc} and FF parameters of the devices. Efficiency of the solar cell, realized using polymer with moderate Molecular Weights (M_n= 85 kg/mol and M_w= 1400 kg/mol), and highest Polydispersity (16.8) and Charge Carrier Density (3.2×10^{-17} cm^{-3}) values, was found maximum, which was attributed due to higher photon absorption capability and favourable morphology of its photoactive layer.

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