

Composition-dependent phase separation of P3HT:PCBM composites for high performance organic solar cells

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ABSTRACT

Phase separation of the poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) active layer was investigated by varying its relative ratio in the bulk heterojunction (BHJ) organic solar cells (OSCs). The UV/visible absorption spectra of P3HT and PCBM were proportional to their compositions in the active layer. However, the crystallinity of P3HT, characterized by X-ray diffraction (XRD), improved with increasing composition up to 50 wt.%, but then degraded upon any further increase in its composition above 50 wt.%. This unique phenomenon corresponded to the microstructure of the layer, which was analyzed using transmission electron microscopy (TEM). The fraction of the highly ordered fiber structure of P3HT increased as the P3HT composition increased up to 50 wt.% and decreased as the composition increased further, which was in accordance with the XRD results. The microstructure of the P3HT:PCBM active layer, determined by the composition-dependent phase separation, supported the optimized performance of the OSCs with the active layer composition of 50% P3HT and 50% PCBM.

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1. Introduction

Bulk heterojunction (BHJ) based organic solar cells (OSCs) with composites made of a conjugated polymer and fullerene derivative active layer have considerable potential as renewable energy resources. From a material point of view, blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) are most widely used as an active layer and have the highest recorded power conversion efficiency (PCE) up to 5% thanks to the thermal and illuminative stability [1] and high electron mobility [2]. It can also be fabricated on a large area substrate using a simple solution process because of its high solubility in organic solvents [3,4]. The

microstructure of the donor and acceptor BHJ should have a large interface area with nanometer-scale dimensions in order to guarantee the efficient charge separation for highly efficient OSCs because the typical diffusion length range of exciton is 4–20 nm in polymers [5].

Since the performance of the OSCs is determined by the properties of the P3HT:PCBM active layer and its microstructure, there have been intensive studies on the optical absorption, chemical properties, phase separation and consequent microstructure of the P3HT:PCBM active layer [6–14]. The UV/visible absorption peak of P3HT red-shifts to a lower energy state and is broader and more vibronic as its structure becomes more ordered with a longer chain [6–9]. Additionally, reports have shown that the performance of the OSCs improved through the formation of a highly ordered nano-scale structure with a large interface area between P3HT and PCBM [10,11]. The effect of the processing conditions such as the kind of solvent, annealing time, and temperature has been investigated for phase separation of the active layer in order to form the highly

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ordered structure of the active layer [10–12]. The composition of the P3HT:PCBM active layer, i.e. the relative ratio of each polymer, also influences the microstructure of the active layer and consequently the performance of the OSCs [9,12]. Several research groups have reported that the optimized morphologies and photovoltaic (PV) performances occurred at a 1:1 ratio of the P3HT:PCBM (50 wt.% of P3HT) composites [11,13]. Recently, reports have shown that the use of a low composition (1:0.8–0.7 ratio of P3HT:PCBM) of PCBM resulted in a PCBM cluster free structure and thermally stable devices [1,14]. Although there have been several reports about the effect of the composite ratio on the performance of the OSCs mostly with the optical and electrical properties [9,12–14], further studies are required in order to understand the relationship between the properties and the microstructure of the active layer associated with phase separation depending on the ratio of P3HT:PCBM and the OSCs performance.

In this study, the effect of the P3HT:PCBM composition in the active layer was studied by varying the composite ratio of P3HT from 20 to 80 wt.%. The optical properties and microstructure of the active layer and the correlation with the device performance were explored.

2. Experimental

Regioregular P3HT (Rieke Metals, Inc.) and PCBM (Nano-C) were used for the active layer as purchased without any further purification. P3HT and PCBM were separately dissolved in chlorobenzene (30 mg/ml for each solution) and stirred at 60 °C for 1 h. These solutions were mixed with different weight ratios of: 20, 30, 40, 50, 60, 70, and 80 wt.% of P3HT. The substrate for the OSCs, the indium tin oxide (ITO; 10 Ω /square) coated glass substrate, was cleaned in an ultrasonic bath with deionized water, acetone and isopropyl alcohol for 15 min each, and then cleaned with UV-ozone for 10 min. The poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Baytron P VP Al 4083, H.C. Stark), used as an anodic buffer layer, was spin coated at 6000 rpm for 10 s and baked at 130 °C for 10 min. The P3HT:PCBM photoactive layer was spin coated on the PEDOT:PSS at 4000 rpm for 5 s. The thicknesses of the buffer and active layers were 30 nm and 70 nm, respectively, as measured using a surface profiler (alpha-step 500). The Al (100 nm) cathode was thermally evaporated through a shadow mask defining active area of 0.1 cm². Thermal annealing was conducted at 150 °C in an oven for 10 min under ambient N₂. The entire fabrication process was conducted in an air environment except for thermal annealing.

An UV/visible spectrophotometer (Shimadzu UV-1601) was used to characterize the absorption properties of the P3HT:PCBM layer. The crystallization of the active layer was analyzed using X-ray diffraction (XRD; Mac Science, Cu K α wavelength of 1.54056 Å). The phase separation and resulting microstructure were observed using optical microscopy and field-emission transmission electron microscopy (FE-TEM; JEM-2100F, JEOL). For the TEM analysis, the specimens were prepared by floating the active layers onto the deionized water and then picking them up with a Cu grid. The current density versus voltage

(*J*–*V*) characteristics were measured with a Keithley 236 source measurement unit and a solar simulator (Yamashita denso) under an AM 1.5 G (100 mW/cm²) irradiation intensity. The total incident light intensity was calibrated with a pyranometer (Eko MS-802) and a standard reference silicon solar cell.

3. Results and discussion

Fig. 1 shows the UV/visible absorption spectra of the P3HT:PCBM active layer with different concentration ratios. A previous reports showed that the maximum absorption wavelengths ($\lambda_{\max}$) of PCBM molecules are almost constant regardless of the amount of the PCBM composite or ordering of the active layer [9,15,16]. In this study, the intensity of the PCBM absorption spectra ($\sim$ 330 nm) increased without any shift in the wavelength as the composition of PCBM increased. On the other hand, as the composition of P3HT increased, the absorption spectra of P3HT between 450 and 650 nm gradually increased, was broader as well as more vibronic, and red-shifted. The $\lambda_{\max}$ of the P3HT peak were at 437, 461, 482, 495, 507, 512 and 515 nm for 20, 30, 40, 50, 60, 70 and 80% of P3HT, respectively. The shift of absorption peaks to higher energy indicates an increasing density of conformational defects, equivalent to non-planarity, and causes loss of conjugation [17]. Moreover, the absorption shoulder at $\sim$ 610 nm which is assigned to interchain interactions became bigger and more pronounced. Since the thickness of the active layer was kept the same ($\sim$ 70 nm) for the all of the samples, the increased, broadened, red-shifted and pronounced absorption peaks of P3HT were attributed not only to the increased composite ratio but also to the closer chain packing of P3HT which resulted from strong interchain interactions [9,12,17,18].

The XRD analysis in Fig. 2 depicted the crystallization of P3HT, which was represented by the peak intensity and the

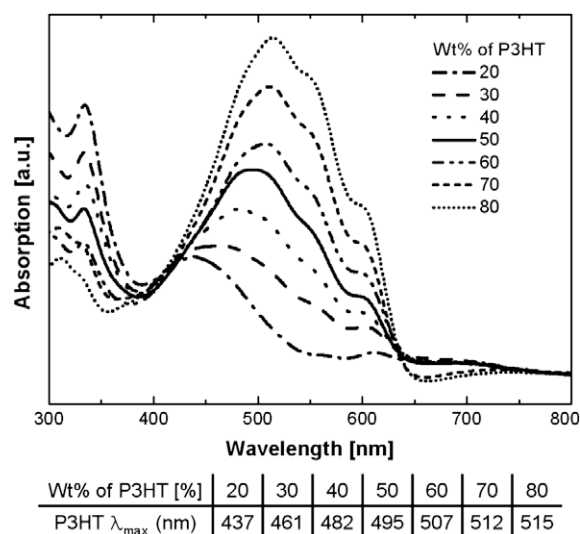


Fig. 1. UV/visible absorption spectra of the active layer with various composite ratios of P3HT:PCBM after thermal annealing at 150 °C for 10 min in a N₂ flow oven.

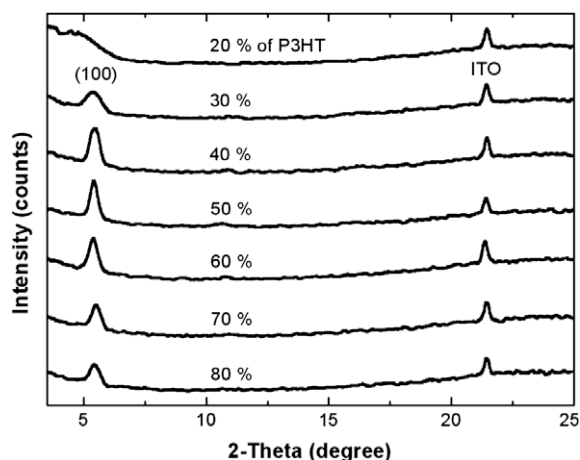


Fig. 2. XRD pattern of the active layer with various composite ratios of P3HT:PCBM.

full width at the half maximum (FWHM) intensity of the peak. The peak intensity of P3HT (100) gradually increased with increasing P3HT composition from 20% to 50%. One remarkable observation was that further increase of the P3HT composition exceeding 60% results in a gradually reduced peak intensity. The size of the crystallites was calculated from the broadening of a peak in the diffraction pattern with Scherrer's equation;

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

From the XRD peak intensity results, the calculated sizes of the crystallites gradually increased with increasing P3HT composition from 20% to 50%, and further increasing the P3HT composition above 60% reduced the crystallite size.

Comparing the absorption and XRD data, the absorption of P3HT continually increased and red-shifted with increasing P3HT composition which indicated closer chain packing at higher compositions. On the other hand, the dif-

fraction peak of the P3HT (100) phase increased until 50 wt.% of P3HT and then decreased upon further increase of the P3HT composition. The results of the XRD denote the volume fraction of the π -conjugated planes of P3HT (100) with lamella oriented normal to the substrate [12,18]. Therefore, both results can be summarized as follows. The interchain packing of P3HT within the crystallized phase improved with increasing P3HT composition, but the volume fraction of the P3HT (100) phase normal to substrate increased until a P3HT composition of 50% and decreased at higher compositions.

The phase separation and microstructure of the active layer was directly characterized by optical microscopy and TEM. The phase contrast optical microscopy images in Fig. 3 show the macroscopic morphology of the active layer. Overgrown clusters resulting from local diffusion and crystallization of PCBM were observed in the active layers with P3HT compositions of 20, 30, and 40%, and their size and density reduced as the composition of P3HT increased. No PCBM clusters were found at higher P3HT compositions. Previous reports showed that the thermal annealing of the P3HT and PCBM composite film leads to the formation of overgrown PCBM clusters when the PCBM composition exceeds 50% [16,19,20].

Fig. 4 shows the FE-TEM images of various ratios of the P3HT:PCBM layer. For 20% of P3HT in Fig. 4(a), the P3HT rich (bright domains) and PCBM rich (dark domains) regions were barely distinctive compared to the higher compositions of the layer. For the layer with 30–50% of P3HT in Fig. 4(b–d), the phase separation was clear, and P3HT formed a fiber structure embedded in the PCBM matrix. The difference in the microstructures of the phase separated P3HT and PCBM was minimal though the composition varies from 30 to 50% in these TEM images. The TEM images were believed to be obtained in the regions without any PCBM overgrown clusters as shown in the optical micrographs. Therefore it was concluded that almost the same fraction of P3HT and PCBM formed the similar phase separated morphologies and the remaining PCBM formed overgrown clusters. The phase separated microstructure noticeably became blurred and eventually randomized

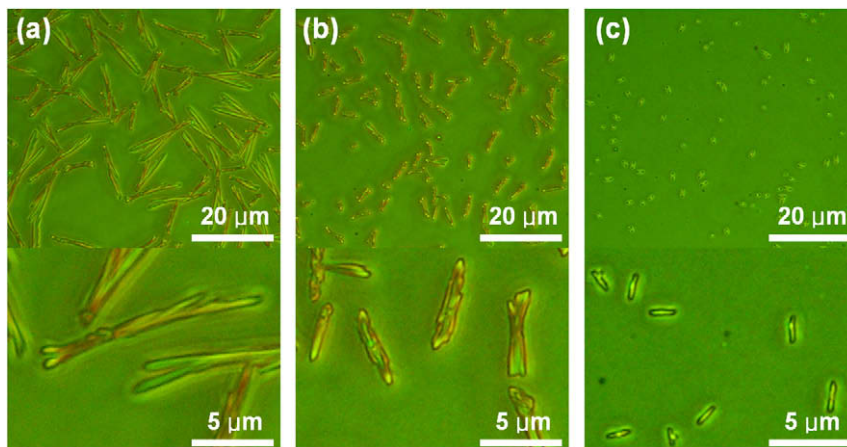


Fig. 3. Phase contrast optical microscope images of the active layer with various composite ratios of P3HT:PCBM; (a) 20%, (b) 30%, (c) 40% of P3HT.

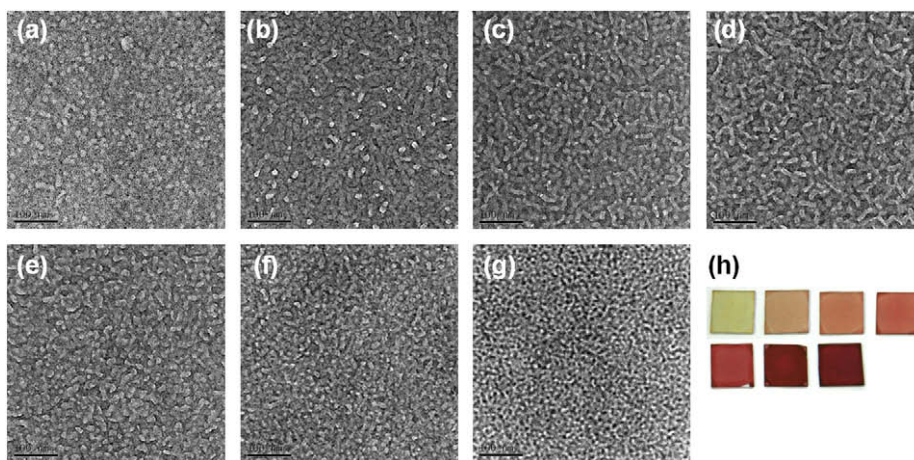


Fig. 4. Bright field TEM images of the active layer with various composite ratios of P3HT:PCBM; (a) 20%, (b) 30%, (c) 40%, (d) 50%, (e) 60%, (f) 70%, (g) 80% of P3HT; scale bar; 100 nm. (h) Photographs of the films with a sample size 20 mm × 20 mm; from the left 20, 30, 40, and 50% on the top and 60, 70, and 80% of P3HT on the bottom.

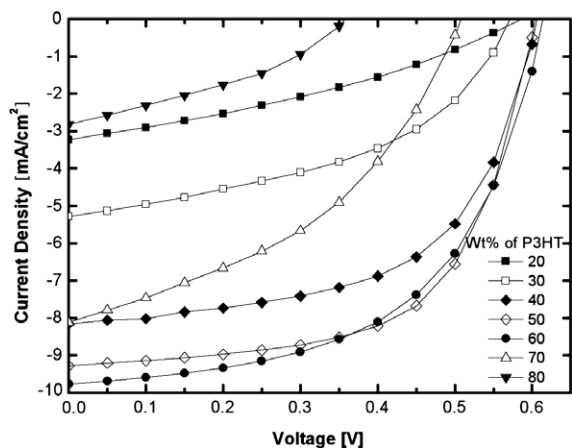


Fig. 5. The characteristics of the OSCs with various composite ratios of the P3HT:PCBM active layer; J - V curve for the best efficiency devices.

without clear fiber phases when increasing the P3HT composition above 60% in Fig. 4(e–g), which was in accordance with the XRD results. A previous report showed that the pure P3HT molecules form fibrillar structures even at room temperature [4]. Therefore, the disordering of P3HT in Fig. 4(e–g) was evidently caused by the small amount of PCBM molecules added to the P3HT matrix. Yang et al. suggested that the PCBM molecules deteriorate the ordering of P3HT by disrupting the chain packing and also by reducing the conjugation length of the polymer [12]. For the high P3HT composition regime in Fig. 4(e–g), the PCBM molecules did not likely crystallize because of the small amount of them present, which led to a lower probability of the molecules meeting for crystallization to take place in the given annealing conditions. Rather, the PCBM molecules hindered the crystallization of the P3HT phases because they were dispersed in the P3HT phases. As a result, a less ordered phase separated structure formed in the high P3HT composition layer.

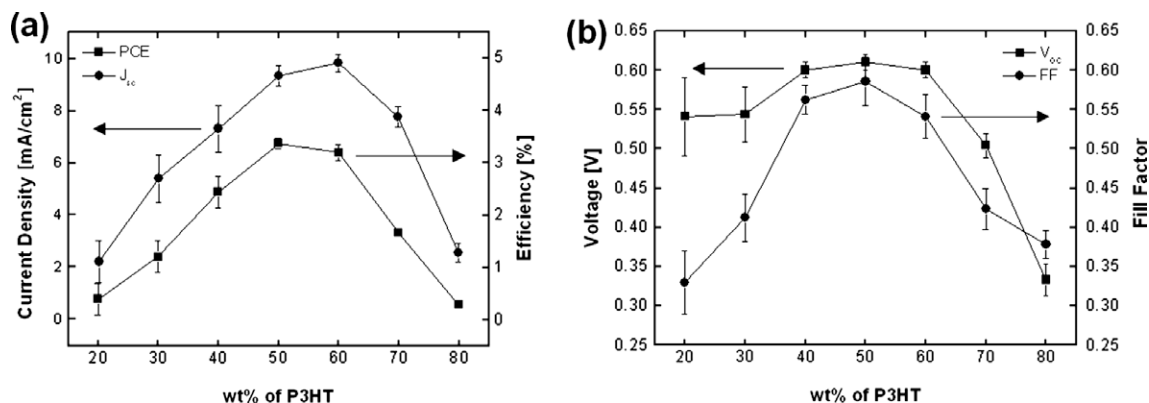


Fig. 6. Statistical data for the device parameters derived from each type of device with various composite ratios of the P3HT:PCBM active layer; (a) J_{sc} and PCE, (b) V_{oc} and FF.

Table 1

Summary of the statistical data for the device parameters derived from each type of device with various composite ratios of the P3HT:PCBM active layer.

Wt% of P3HT	20	30	40	50	60	70	80
J_{sc} (mA/cm ²)	2.21	5.40	7.33	9.35	9.84	7.78	2.56
V_{oc} (V)	0.54	0.54	0.6	0.61	0.60	0.50	0.33
FF	0.33	0.41	0.56	0.59	0.54	0.42	0.38
PCE (%)	0.40	1.20	2.44	3.37	3.20	1.66	0.29

Fig. 5 shows the current density–voltage (J – V) characteristics of the OSCs with various composite ratios of the P3HT:PCBM active layer. More than ten individual devices were fabricated and measured at each P3HT:PCBM composition. Fig. 6 and Table 1 show the statistical data of the device parameters. The device with 20% of P3HT exhibited very poor PV performances with a short circuit current density (J_{sc}) of 3.23 mA/cm², fill factor (FF) of 0.34, open circuit voltage (V_{oc}) of 0.58 V, and PCE of 0.63%. Moreover, the devices at this composition had a large variation in the device-to-device performance due to the large amount of PCBM overgrown clusters present (see Fig. 3). The PV performances depending on the P3HT:PCBM composition agreed well with the ordering of the P3HT phase and the phase separation as discussed in the XRD and TEM results. The J_{sc} , FF, PCE, and V_{oc} all remarkably increased as the composition of P3HT increased from 20% to 50% because of the improved absorption of the incident light and the charge transportation property of the highly ordered P3HT fibers. Further increasing the P3HT composition from 60% to 80% degraded the PV performances even with the increased absorption at the high P3HT composition layer. This degradation in the PV performance was caused by degraded ordering of P3HT, the deficient PCBM molecules that accepted the generated electrons, and the deteriorated phase separation of the blurred heterojunction. Finally, the best PCE of 3.4% was obtained with reproducible performances from the device with the 50% P3HT composition layer.

4. Conclusion

The effect of the composite ratio of P3HT and PCBM on the PV performance of the OSCs was investigated in the BHJ structure. The UV/visible absorption and XRD results denoted that the interchain packing of crystallized P3HT improved with increasing P3HT composition, while the volume fraction of the P3HT (1 0 0) phase that was normal to the substrate increased until a P3HT composition of 50% and decreased at higher compositions. From the TEM analysis, P3HT and PCBM formed a heterojunction with the

P3HT fiber structures as well as the PCBM overgrown clusters through phase separation when the PCBM composition exceeds 50 wt.%. Uniform phase separation, which formed P3HT fibers in the PCBM matrix without overgrown clusters, was obtained at a 50% P3HT and 50% PCBM composition. As the P3HT composition exceeded 50%, the fibril structures of P3HT were collapsed by the PCBM molecules, which hindered the crystallization of the P3HT phase. The optimized PV performance of the OSCs was achieved at an active layer composition of 50% P3HT and 50% PCBM with a maximum PCE of 3.4%.

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