CHAPTER III

POLYMER: MODIFIED FULLERENE BULK HETEROJUNCTION MORPHOLOGY CONTROL DURING SPIN COATING: MODELLING DIFFUSION ASSISTED PHASE SEPARATION
Summary

In this chapter, results of the study to control the Polymer:Modified fullerene blend morphology, by controlling the ambient in spin coating chamber has been discussed. It has been shown that this method can be used to influence the solvent evaporation rate, and obtain the desired nanoscale phase separation and crystallinity of the polymer: modified fullerene blend films. As a typical case, polymer and modified fullerene used are P3HT and PCBM respectively, and the solvent used is chlorobenzene (CB). The ambient is controlled by purging dry inert gas and by introducing CB in the coating chamber to affect the evaporation rate during spin coating. Blend morphology has been characterized by UV-Visible absorption spectroscopy, small angle X-ray diffraction, atomic force microscopy and time resolved photoluminescence study. To understand the mechanism driving the phase separation, we modeled the phase separation process, assuming the diffusion of PCBM initiated due to finite solubility of PCBM in the solution. Spin coating process has been modeled using the model proposed by Meyerhofer. Stokes-Einstein equation has been used, to quantify the diffusion process. For the first time, we predicted the PCBM phase dimensions based on the number of molecules that can nucleate, before complete drying of the film. Obtained results confirm our assumption.
III-1: INTRODUCTION

As discussed in earlier chapters the performance of PSC is critically decided by the nanometer scale morphology of the donor and acceptor blend. The nanomorphology of polymer: modified fullerene blend films depends on volume percent of the donor and acceptor, evaporation rate of solvent, solvent vapor annealing, deposition method, post deposition thermal annealing, addition of poor solvent into good solvent, etc. [1-5]. Besides controlling morphology by different experimental techniques, it is important to understand the basic phenomenon leading to phase separation, which ultimately decides the bulk-heterojunction morphology.

III-2: LITERATURE REVIEW

III-2.1: REVIEW OF MORPHOLOGY CONTROL IN BULK-HETEROJUNCTION

X. Yang and others [6] showed that, crystallization and demixing induced by thermal annealing controls the nanoscale organization of P3HT and PCBM in the photoactive layer, toward a morphology in which, both components have a large interfacial area, for efficient charge generation, and have attained crystalline order, that improves charge transport. Nelson et al. [7] showed that initial efficiency improvement to 3.64 % upon thermal annealing, was due to P3HT crystallization, and PCBM diffusion, while further improvement to 3.92 % was due to PCBM diffusion only as P3HT crystallization was complete upon annealing for 5 minutes only. Chih Cheng Lin and his coworker [8] demonstrated, the use of electric field assisted annealing method, for self-organization of a poly (3-hexylthiophene) (P3HT): [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM) blends, without any thermal post-treatment. By applying dc electric field during film drying process, fibrous P3HT crystalline domains, and phase-separated domains of bulk heterojunctions can be achieved, which could lead to over 4 % power conversion efficiency. Yoshikawa et al. [9] showed that, PSC efficiency can also be increased by microwave irradiation, due to morphology control under mild conditions, enabling less damage on active layer membrane of the cell, than that by thermal annealing method. Flügge et al. [10] has also studied the effect of microwave annealing of polymer solar cells with various transparent anode materials. Effect of annealing photoactive layer in different solvent vapor has been studied by various groups. Park et al. found that for films annealed with good solvents, P3HT nanofibrils and PCBM aggregates are well
developed. P3HT can self-organize, even at the non-solvent (acetone) annealing case, but the overall crystallinity is more when annealed in good solvent vapor [11]. Yang Yang and others showed that, the π-conjugated structure of RR-P3HT in P3HT:PCBM blend films is optimally developed when the solvent annealing time is greater than 1 minute [12]. Fanchini et al. [13] found that, solvent vapor annealing of P3HT:PCBM at room temperature leads to a marked increase in the photovoltaic efficiency, due to the more ordered structure formed due to demixing of PCBM from P3HT. Kim et al. [14] found that, by controlling the solvent vapor pressure during thermal annealing, nanowires of highly conjugated polymer P3HT can be formed. The nanowire length can be easily adjusted (from several nanometers to several micrometers), by controlling the solvent vapor pressure in the coating chamber. The P3HT:PCBM blend morphology has also been controlled by using an unfriendly solvent in the good solvent [15-17]. The principle of using an unfriendly/dipolar solvent is interesting in order to control the aggregation of P3HT, in mixed polymer–fullerene device layers. As has been shown by Zhang et al., a dopant solvent can have a large effect on the final morphology of a polymer–fullerene blend at very low concentrations, if the dopant has a higher boiling point than the main solvent.

The concept of a bulk heterojunction (BHJ) solar cell structure with graded composition could lead to improved transport and extraction of electrons near the cathode, and hence overall efficiency improvement has been demonstrated by Kumar et al. and Chen et al. [18, 19]. B. S. Hansberg et al. [16] showed that P3HT:PCBM film morphology depends on the drying process related to the drying time and temperature. Interface morphology and the physical properties of bulk heterojunction layers can be manipulated by applying specific drying conditions. A longer drying time causes bigger domains at the interface at a constant temperature. Furthermore, the surface topography features showed bigger structures at lower temperatures at comparative drying kinetics. They also found that temperature dependent solubility of the organic semiconductors can modify the time at which phase separation and crystallization initiates during drying, which in turn affects the overall bulk heterojunction morphology [16].

III-2.2: REVIEW OF MODELLING STUDY

Various models have been proposed, to describe the phase separation process in blend films. The phase segregation of blend components has been explained by Flory-Huggins
mean field theory, coupled with Cahn-Hilliard equation [20-23]. Ray et al. has described the physics of phase segregation during fabrication as well as during operating/stress conditions. This model is based on the kinetics of the temperature induced diffusion, and Ostwald ripening driven clustering of PCBM. Xue et al. [21] has combined the atomistic simulation with mesoscale to predict the morphology of bulk-heterojunction and conclude the optimal parameters including composition, ratio, temperature, and Flory-Huggins parameters. The evolution of crystal structure has also been explained by considering the P3HT paracrystallinity [24]. The structure evolutions in polymer mixture during the spin coating process have been explained by Heriot et al. and Jones by using the concept of Marangoni instability [25, 26]. The authors speculated that, instability at the polymer-polymer interface arose because of a solvent concentration gradient through the film. Such phase separated domains have also been attributed to the induced capillary effects along the solution radial flow and the unsteady air flow field above the film during spin coating [27-29].

III-3: CHALLENGES, OPEN AREAS FOR STUDY, AND OBJECTIVES OF PRESENT WORK

As described in preceding sections, the bulk-heterojunction morphology can be controlled by using solvents of varying evaporation rates. However, solvent choice of different evaporation rates is limited, and moreover by using high boiling point (BP) solvent like dichlorobenzene (BP = 180°C) excess solvent trace remains in the film even after annealing at 150°C, compared to solvent of low boiling point like chlorobenzene (BP = 131°C) [30, 31]. During normal operation under 1 sun condition, device temperature can mount to 80°C [32]. Under this condition, trace solvent can affect the blend morphology, which is detrimental for device performance. Use of low BP solvent is therefore desirable. Furthermore several groups have studied the effect of slow film drying during spin coating, by employing different solvents of varying evaporation rates [33, 34]. However, such an approach is not an ideal way of studying the effect of evaporation rate during spin-coating because, the effect of viscosity, different affinities and solubility must also be accounted.

Besides controlling morphology by different experimental techniques, it is important to understand the basic phenomenon leading to phase separation which ultimately decides
bulk morphology. However, a thorough study to quantitatively predict the phase separation between polymer and small molecule, during film drying in spin coating process is not available. The inherent complexity of spin coating process and the need for material specific thermodynamic and kinetic parameters are the main modelling challenges [29, 30]. Therefore, a simple model, which can provide quantitative information about the phase separated domains, can have immense technological importance, for rational design of processing conditions, to achieve desirable morphology for various applications.

On the above ground, we have discussed the following in the present chapter:

1) Use of controlling the ambient, in spin coating chamber, to influence the solvent evaporation rate, and obtain the desired nanoscale phase separation, and crystallinity of the polymer: modified fullerene blend. As a typical case polymer and modified fullerene used are P3HT (poly(3-hexylthiophene)) and PCBM ([6,6]-phenyl-C61 butyric acid methyl ester) respectively and the solvent used is chlorobenzene (CB). The ambient was controlled by purging dry inert gas (nitrogen in the present study) and by introducing CB in the coating chamber to affect the evaporation rate during spin coating.

2) To understand the mechanism driving the phase separation, we modelled the phase separation process, by assuming the diffusion of PCBM once it’s solubility limit is crossed during film drying process. Obtained results confirm our assumption.

III-4: EXPERIMENTAL DETAILS

A spin coating chamber of volume 300 cm$^3$ with effective opening 0.6 cm$^2$ for gas outlet was used for coating the films. A schematic diagram of the coating chamber and the solar cell structure is shown in figure 1. The direction of gas flow in the chamber was such that, it does not fall directly on the film during drying. For the present study, films with gas flow rates 3 liters per minute (lpm), 0.5 lpm, 0 lpm and by introducing chlorobenzene vapor in the coating chamber were prepared. The chlorobenzene vapor was introduced by adding chlorobenzene (with spread area 3.0 cm$^2$) in the coating chamber, prior to film deposition. Devices were prepared on thoroughly cleaned and oxygen plasma treated Indium Tin Oxide (ITO, 10 Ω/□) coated glass substrates. A 30 nm thin layer of PEDOT:PSS
from Baytron P, was first spin coated and dried at 140°C for 15 minutes. Subsequently, the P3HT:PCBM (1:1 wt %, 10 mg/ml) solutions in CB was spin casted at 1000 rpm at different nitrogen flow rates and by introducing CB vapor in the coating chamber. An aluminum top contact (200 nm) was finally evaporated at 10⁻⁶ mbar pressure to define devices of area 0.09 cm².

![Schematic diagram of (a) The spin coating chamber used, (b) Device architecture](figure1)

**Figure 1: Schematic diagram of (a) The spin coating chamber used, (b) Device architecture**

### III-5: RESULTS AND DISCUSSION
#### III-5.1: MORPHOLOGY CONTROL BY SPIN COATING

The UV-Visible absorption spectra for P3HT solution in CB, PCBM film and that of blend films is shown in the figure 2. Absorption due to P3HT in solution show a maxima at ~450 nm due to $\pi-\pi^*$ transition, and that of PCBM film shows a broad peak around 450 nm while sharp and prominent peak at ~ 335 nm. It is known that the absorption spectra of P3HT red-shifts by ~ 70 nm and appears at ~ 520 nm [35, 36]. Blend films prepared under 3 lpm (liters per minute), 0.5 lpm, 0 lpm nitrogen flow, and by introducing CB vapor, were labeled as film $a$, $b$, $c$, and $d$ respectively. The idea was that, dry nitrogen gas would take out the CB vapor during the film drying process, from the spin coating chamber. Therefore, film $d$, $c$, $b$, and $a$ represents film prepared at decreasing CB vapor concentration in the chamber during spin coating. Film $a$ has maxima at 480 nm, which red-shifts to ~ 490, ~ 510, and ~ 520 nm, for films $b$, $c$ and $d$ respectively along with a little shift in the onset of absorption. Such behavior of P3HT absorption spectra is broadly due to highly interchain-delocalized excitation, due to improvement of local order in aggregated P3HT mass. This indicates that with increased CB vapor concentration in the
chamber, blend films with increased P3HT aggregation and improved crystallinity are obtained.

During film solidification, the solvent is removed from the wet film by evaporation from the surface. With a larger flow of N\textsubscript{2} through the coating chamber, the evaporated solvent vapor is quickly removed, thereby preventing the saturation of overlying gas with CB vapor. With no N\textsubscript{2} flow in the coating chamber, the overlying gas is partially saturated with solvent vapor, during film drying by evaporation. This creates an internal resistance to solvent evaporation from the wet film, thereby increasing the drying time of the film. This allows longer diffusion times and a higher degree of domain-coarsening during the spin coating procedure. By introducing CB vapor into the coating chamber the film drying time increases further and it is expected that increased drying time shall lead to greater phase separation, and more ordered structure of P3HT and PCBM phases. Due to the increase in drying time, more liquid is thrown away due to centrifugal force during spinning, and the final film thickness decreases. The thickness measured experimentally was 65 nm, 76 nm, 85 nm and 102 nm for film d, c, b, and a respectively.

It was now expected that, increase in domain size of the P3HT and PCBM phases would result in reduction in time of charge transfer, from P3HT to PCBM phase or increase in exciton lifetime upon photoexciton. The charge transfer study of the blend films was performed using time resolved photoluminescence spectroscopy (femto upconversion spectrophotometer). Figure 3 shows the time resolved photoluminescence (TRPL) spectra for pristine P3HT film as well as for film a, b, c, and d recorded at 650 nm. The
fluorescence decay measurements were well fitted by using a two-exponential function. One lifetime in the sub-picosecond range and other in few picoseconds was observed. Details are listed in Table 1.

![Time resolved photoluminescence spectra of pristine P3HT film and that of films a, b, c and d](image)

In film a the photoluminescence lifetime is shortest, while that for pristine P3HT film it is maximum. This suggests less intersegment and interchain interaction of polymer in film a, as P3HT is more homogeneously mixed with PCBM [37-39]. A time scale of less than 400 fs i.e. 227.5 fs is obtained in film a, which suggests ultrafast charge transfer in the blend. In the pristine P3HT film however, there is ignorable charge transfer and no exciton quenching in the sub picosecond time scale. The fluorescence decay with a time scale of 1016.4 fs was attributed to the downhill relaxation of self trapped excitons.

**Table 1: Decay parameters of fluorescence dynamics of the Pristine P3HT and P3HT/PCBM films**

<table>
<thead>
<tr>
<th>Film</th>
<th>$\tau_1$ (fs)</th>
<th>$A_1$</th>
<th>$\tau_2$ (ps)</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine P3HT</td>
<td>1016.4</td>
<td>0.14</td>
<td>11.3</td>
<td>0.85</td>
</tr>
<tr>
<td>Film a</td>
<td>227.5</td>
<td>0.25</td>
<td>2.9</td>
<td>0.74</td>
</tr>
<tr>
<td>Film b</td>
<td>298.3</td>
<td>0.23</td>
<td>4.2</td>
<td>0.77</td>
</tr>
<tr>
<td>Film c</td>
<td>448.0</td>
<td>0.18</td>
<td>5.3</td>
<td>0.82</td>
</tr>
<tr>
<td>Film d</td>
<td>530.0</td>
<td>0.17</td>
<td>6.3</td>
<td>0.83</td>
</tr>
</tbody>
</table>

In film b, c and d the PL lifetime increased compared to film a. This is due to the improvement of packing order of nanostructures in the films b and c and further in film d. A characteristics life time of 448.0 fs and 530.0 fs in film c and d respectively was
observed. Lifetime greater than 400 fs suggests charge transfer and the relaxation of self trapped exciton are competitive processes in these films. This also suggested a loss of charge separation at the blend interface, but such losses are compensated by the increase in component crystallinity and carrier mobility. The time scale with several ps in the fluorescence decay emission at 650 nm is attributed to the excitation energy transfer between conjugated segments.

The improvement in crystalline P3HT phases was then confirmed by small angle x-ray diffraction study. Figure 4 shows the small angle X-ray diffraction result of the films. The increase in (100) diffraction intensity (2θ between 5.0° to 5.4°) indicates increased size or/and number of P3HT crystallites in the film due to enhanced head to tail arrangement, where, main chains are parallel and side chains perpendicular to substrate (Inset in Figure 4), with increasing CB vapor inside the coating chamber [40]. In film a, peak corresponding to (100) reflection was observed at 5.0° which shifts to 5.4° for film d. This indicates reduction in d spacing (2d sinθ = nλ, where λ = 0.154 nm ) from 1.76 nm to 1.64 nm. Shifting of P3HT d-spacing, along with increase in peak intensity, is attributed to the diffusion of PCBM molecules out of the P3HT chains and the formation of larger crystalline regions of P3HT [41, 42].

![Figure 4: X-ray diffraction pattern of the films. Inset show schematic preferred orientation of P3HT chains](image)

To elucidate the nanoscale morphology of P3HT:PCBM blend films, AFM images were recorded (See figure 5). For film a, the two phases are separated by ~15-20 nm. The domain size increases to 30-40 nm by introducing CB in the coating chamber. The
contrast between P3HT and PCBM in film $a$ is much less compared to film $d$. This indicates that, in addition to the small phase separation, PCBM molecules are embedded within the P3HT chains. The comparatively greater contrast in film $d$ again confirms that PCBM has diffused out of the P3HT regions and pure phases are formed. Film solidification in all the present cases, is non-equilibrium process and therefore concentration gradient is established across the grains giving rise to mixed phases at the boundary. The non-equilibrium condition is more pronounced in film $a$ due to rapid solidification compared to film $d$. The topography images show that rms roughness for film $a$ is 0.35 nm which increases to 0.42 nm, 0.50 nm and 0.65 nm for film $b$, $c$ and $d$ respectively, primarily due to the domain coarsening. All the films can be considered fairly smooth, compared to the reported roughness values for annealed films [11]. Due to the small phase separation in film $a$, the components do not have a clear height difference and the film appears flat over large areas compared to the actual phase separation. However film $d$ has greater phase separation and therefore height difference between the phases is clearer, but still there are exceptions.

![Figure 5](image_url)

**Figure 5:** Atomic Force Microscopy phase images of film $a$, $b$, $c$, and $d$ (above) and corresponding topography images (below)

On the basis of above discussion, it is clear that by controlling the ambient in spin coating chamber, domain dimensions of the individual phases and polymer crystallinity can be controlled in blend films. Phase separation of polymer blends depends on various factors...
viz. miscibility of the components in a common solvent, entropy of mixing, enthalpy of formation and surface tension effects \([41, 43]\). However the actual mechanism through which phase separation between the components takes place in P3HT:PCBM mixtures is by diffusion of PCBM through the P3HT matrix \([11, 40, 43]\). Earlier the structure evolution in polymer mixture during spin coating has been explained through various simulation studies \([40]\). For the first time, we explain the PCBM aggregate formation in the blend films during spin coating by considering the diffusion of PCBM in the solution towards a nucleation site once the solubility limit of PCBM is crossed in the drying film.

### III-5.2: MODEL FOR PHASE SEPARATION PROCESS

It is known that, during spin coating, the solvent is removed from the drying film, and simultaneously solute concentration and solution viscosity increases until film dries completely. At a particular stage during this process, solute concentration increases to a level where solubility of PCBM is crossed. In the proposed model, we consider that, at this stage PCBM aggregation initiates due to diffusion towards a nucleation centre.

![Figure 6: PCBM molecule separation](image)

In the initial stages of film drying process PCBM molecules move closer due to reduced solvent content. However, they still remain distributed uniformly. After the solubility limit is crossed, motion due to diffusion superimposes on the earlier one and aggregation of PCBM starts. Figure 6 (a) show the PCBM molecule separation in the solution before spin coating, (b) in the dry film considering infinite solubility, and (c) in the dry film considering finite solubility of PCBM. If we consider infinite solubility, PCBM aggregation does not take place and they remain uniformly separated due to the presence of P3HT in the resultant solid film. However, if a finite solubility is considered, PCBM aggregation will take place due to diffusion, once the solubility limit is crossed in the drying film. If a
particular molecule is considered as the nucleation centre, neighbouring PCBM molecules diffuse simultaneously towards it. Once the nearest molecule attaches to the nucleation centre its dimension increases and the next diffusing molecule has to travel a distance less than the original distance due to the already attached mediator molecule. Due to such diffusion process, molecules from certain distance $x$ from the nucleation centre are able to join the aggregated PCBM mass. The mean square displacement $<x^2>$ of the diffusing particles in time $t$ was calculated using the relation:

$$<x^2> = q_iDt,$$  

Where $q_i = 2, 4, or 6$ for 1, 2, or 3 dimensional diffusion.

The Einstein-Stokes relation for diffusion of spherical particles of radius $r$ through a liquid is used to calculate the diffusion coefficient $D$ [45].

$$D = \frac{K_BT}{6\pi\eta r},$$

Where $K_B$ and $T$ are the Boltzmann constant and absolute temperature respectively, $\eta$ is the liquid viscosity which varies with time during the spinodal decomposition. For simplicity radius $r$ of the PCBM molecule was taken equal to that of C60, i.e. 0.35 nm. Due to the large molecular weight (50,000/mole) of polymer chains, diffusion of P3HT was neglected. We estimated the time $t_{diff}$ for which PCBM molecules diffuse in drying film as the difference between the total drying time $t_{dry}$ and the time $t_s$ at which solubility limit of PCBM is exceeded. $t_{dry}$ was determined experimentally, by visual observation. After the first fraction of second of dispensing the solution, the surface appeared completely flat, but color changes as the film dries. After the film is completely dried, color changes to purple and remains so thereafter. The drying time was taken as the point where the color stops changing. To estimate $t_s$ the time varying solid concentration in the drying film was calculated by modelling the spin coating process by using the Meyerhofer model [46]. Recently R. A. L. Jones et al. [43] have used a simpler form of above model to establish a quantitative relationship between the process variables and evaporation rate during spin coating. Related equations are given below,

$$\frac{dl}{dt} = [1 - c(t)]\frac{2\rho(t)\omega^2}{3\eta(t)}h^3(t) - e_r$$  

$$\frac{ds}{dt} = -c(t)\frac{2\rho(t)\omega^2}{3\eta(t)}h^3(t)$$

Here $l$ is the volume of solvent and $S$ is that of solids in the drying film. $e_r$ is the solvent evaporation rate during spin coating. Solution of this model gives an equation for the
evolution of the film thickness $h(t)$ with time. $L$ and $S$ are defined per unit area and therefore, solid content in the drying film at any time $t$ is given by,

$$
c(t) = \frac{S(t)}{S(t) + L(t)}
$$

The concentration $c(t)$ was found by evaluating $L$ and $S$ at every 0.01 msec. To the best of our knowledge concentration dependent viscosity $\eta(t)$ of P3HT:PCBM/CB solution is not yet reported. We therefore experimentally determined the viscosity of P3HT:PCBM/CB solution at various concentrations and fitted the data with power law function,

$$
\eta(t) = \eta_{\text{solvent}} + \eta_{\text{solid}} c^\gamma(t)
$$

### III-5.2.1: RESULTS AND DISCUSSION

The total drying time $t_{\text{dry}}$ of the film $a$, $b$, $c$, and $d$ is 6.2 second, 8.6 second, 10.8 second, and 16.0 second respectively. As described above, to calculate $t_s$ the spin coating process was modelled by Meyerhofer model. In order to do this concentration dependent viscosity is required. Viscosity of CB and that of P3HT:PCBM solution in CB, for various concentrations are determined experimentally. Experimentally determined values of viscosity are given in Table 2.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure chlorobenzene (CB)</td>
<td>0.79</td>
</tr>
<tr>
<td>5 mg/ml P3HT + 5 mg/ml PCBM solution</td>
<td>0.86</td>
</tr>
<tr>
<td>10 mg/ml P3HT + 10 mg/ml PCBM solution</td>
<td>0.97</td>
</tr>
<tr>
<td>15 mg/ml P3HT + 15 mg/ml PCBM solution</td>
<td>1.12</td>
</tr>
<tr>
<td>20 mg/ml P3HT + 20 mg/ml PCBM solution</td>
<td>1.20</td>
</tr>
<tr>
<td>25 mg/ml P3HT + 25 mg/ml PCBM solution</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Above viscosity values were fitted with the power-law function. The obtained value of $\eta_{\text{solid}}$ and $\gamma$ are 221 cP and 1.47 respectively. Due to the slight difference in the density of CB and PCBM the density of the film during solidification also varies. To include density variation, the following density values were considered.

- Density of CB = 1.1 mg/ml
- Density of P3HT = 1.1 mg/cm³
- Density of PCBM = 1.4 mg/cm³
Figure 7 shows the viscosity and density variation of the drying film as a function of solid fraction $c(t)$.

![Graph (a)](image1)

![Graph (b)](image2)

**Figure 7:** (a) Viscosity and (b) density variation of the drying film as a function of solid fraction

Figure 8 shows the liquid thickness $L$ and solid thickness $S$ in the drying film as a function of time. It shows that during the 1st second, after dispensing the liquid, thickness decreases rapidly due to convective outflow resulting from rapid centrifugation. After this initial period, hydrodynamic thinning of the film ceases, and the film thinning is dominantly due to solvent evaporation from the film. Average evaporation rate of the film, obtained from modelling is given in the figure.

The solid content variation in the liquid film during spin coating along with $t_{diff}$, $t_{dry}$ and $t_s$ values are shown in Figure 9. Typical values for film $d$ have been illustrated. Due to the slow evaporation rate of solvent in film $d$, the total drying time $t_{dry}$ along with $t_{diff}$ and $t_s$ values are considerably greater than that in film $a$. During the film solidification process,
solid content increases exponentially, and at \( c(t) = 0.075 \), as indicated by dotted arrows, the concentration of PCBM in the spinning film rises to its solubility limit (50 mg/ml) [47]. At this point PCBM diffusion initiates. Greater \( t_{diff} \) value in film \( d \) indicates that, PCBM diffusion will occur for a longer time and therefore larger PCBM aggregate size is expected in film \( d \). However, in all cases, \( t_{diff} \) is considerably smaller than the total drying time \( t_{dry} \).

**Figure 8: Variation of (a) liquid thickness and (b) solid thickness as a function of time during spin coating**

This is in agreement with earlier study where it has been shown that phase separated morphologies in polymer mixtures appear over the last fraction of seconds [19]. The calculations show that each molecule can diffuse to 10.3 nm, 12.2 nm, 13.6 nm, and 16.6 nm in film \( a, b, c, \) and \( d \) respectively during the film drying process. This leads to the formation of one dimensional structures of size 20.3 nm, 24.1 nm, 27.3 nm, and 34.3 nm for films \( a, b, c, \) and \( d \) respectively. These results agree very well with the aggregate sizes obtained with AFM images (See figure 5).
Figure 9: Variation of solid fraction in the wet film during spin coating for films a, b, c and d. The values of $t_{\text{dry}}$, $t_s$ and $t_{\text{diff}}$ values are also stated in the figure.

Few molecules just beyond the distance $x$, which are not able to join the aggregated mass, contributes to the formation of mixed phases, and beyond the mixed phase lies the pure P3HT phase. Thus, the simple model is able to explain the phase separated domains of P3HT:PCBM blends, by considering the diffusion of PCBM towards a nucleation site initiated due to its finite solubility limit.

**III-5.3: DEVICE PERFORMANCE**

Figure 10 show the $J$-$V$ characteristics of devices under 100 mW/cm$^2$ illuminations. Obtained device parameters have been tabulated in Table 3. The overall power conversion efficiency (PCE) in devices using film $d$ amounts to 2.4 %, compared to 0.74 % using film $a$. Considering the less thickness of film $d$ and the large phase separation, efficiency obtained is respectable one.

Figure 10: $J$-$V$ characteristics of devices using film a, b, c and d.
Due to the large domain sizes in film \( d \), loss of created excitons takes place. The increase in \( J_{sc} \) using slowly dried film is due to the enhanced charge mobility and improved charge transport in the highly crystalline and pure P3HT and PCBM domains, as discussed earlier. Improved FF is attributed to decreased series resistance and high shunt resistance due to balance of charge transport by reduction in defect sites on the charge transport route. This is due to enlarged growth of PCBM as a result of slow growth. However, high \( V_{oc} \) values in fast grown films were a surprise. In film \( a \), P3HT is intimately mixed with PCBM phases and most of the P3HT is amorphous as already revealed from UV and AFM results. The shift in absorption onset shows greater optical band gap for P3HT in film \( a \). It is widely accepted that the energy difference (\( \Delta E \)) between the highest occupied molecular orbital of the donor and the lowest occupied molecular orbital of the acceptor determines \( V_{oc} \) value of P3HT:PCBM bulk heterojunction solar cell [48, 49]. The red shift in the absorption peak of film \( d \) shows lower energy state of delocalized excitons in the highly \( \pi \)-conjugated P3HT domains. Due to this decrease in effective optical band gap of P3HT in film \( d \), it is expected that \( \Delta E \) would decrease and therefore \( V_{oc} \) is expected to be less compared to that using film \( a \). Also the formation of aggregated PCBM clusters near the contacts of the device as shown in AFM phase images can also reduce \( V_{oc} \). Decrease in \( V_{oc} \) has earlier been obtained by Chirvase et al. [50] due to the formation of large PCBM clusters upon thermal annealing. It has been earlier shown that traces of even CB can remain in the blend films prepared in excess CB environment. However, it is logical that CB traces can be removed in a lesser time with high convective air flow compared to ODCB which has a higher boiling point, to avoid degradation in device performance [50].

<table>
<thead>
<tr>
<th>Active layer</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>( V_{oc} ) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film a</td>
<td>3.2</td>
<td>0.68</td>
<td>33</td>
<td>0.74</td>
</tr>
<tr>
<td>Film b</td>
<td>5.0</td>
<td>0.65</td>
<td>39</td>
<td>1.26</td>
</tr>
<tr>
<td>Film c</td>
<td>6.6</td>
<td>0.62</td>
<td>46</td>
<td>1.88</td>
</tr>
<tr>
<td>Film d</td>
<td>7.3</td>
<td>0.61</td>
<td>54</td>
<td>2.40</td>
</tr>
</tbody>
</table>
CONCLUSIONS:
We have shown that the solvent evaporation rate and hence the nanoscale morphology of P3HT:PCBM blend films can be finely controlled by controlling the ambient during spin coating in order to improve the solar cell performance. We have also proposed a model to explain the process of phase separation during spin coating. Modelling results supported by the experimental evidences clearly show that the phase separation in P3HT:PCBM blends is due to diffusion of PCBM (initiated due to the finite solubility limit of PCBM in the solvent) towards a nucleation site in the drying film during spin coating.
REFERENCES:


