MONTE CARLO SIMULATION OF POLYMER SOLAR CELLS

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ABSTRACT

Monte Carlo method was successfully employed to study the mechanism inside a three dimensional bulk hetero-junction polymer solar cell using a model based on a novel architecture of adjustable structural parameters. The amorphous properties of the conjugated polymers were modelled to determine the operating conditions and structural properties and dimensions that maximize current generation efficiency. The dimensions of the best morphology of a polymer solar cell in terms of the charge carrier collection efficiency by the electrodes were found. The effect of applied external voltage, internal structural design and the simulated performance of polymer solar cell fabrication materials, MDMO-PPV:PCBM, M3EH-PPV:PCBM and P3HT:PCBM on efficiency were obtained. For polymer solar cells with practical dimensions, the charge carrier collection efficiency was almost governed by the strength of the applied electric field. For strong electric field, charge carrier efficiency in the range of 10%-20% was achieved. Reduction of the interfacial height from 30nm to 10nm resulted in a drop of almost 13% in the charge carrier generation efficiencies. The impact of the valance and conduction band energies of the three hole transporting materials on the charge carrier collection efficiencies was significant.
KEY WORDS: Monte Carlo simulation, polymer solar cell, excitons, morphology, charge carrier collection efficiency, applied external voltage, fabrication materials.

1. INTRODUCTION

Recognition of polymer solar cells as a potential and competitive alternative for the silicon or gallium arsenide based solar cells, attracted the attention as the fabrication of organic cells are much less expensive than their inorganic counterpart. In addition they have favourable characteristics like flexibility, lightweightness and integrability. Theoretical and practical researches on organic solar cells are motivated to come up with optimal structural properties and conditions for more efficient solar cells. Due to the restrictions governed by the nature of the polymer materials, the assistance of powerful computers are used to model the polymer solar cell structure in a virtual environment and to study the behavioural aspects and performance under various external and internal conditions. To deal with the motion of charge carriers within the regions dedicated for hole and electron transportation of a polymer solar cell, a model was developed by Meskers et al [1] considering the effect of charge carrier recombination at the interfacial regions between hole and electron transporting phases. A comprehensive analytic simulation involving theoretical solutions to the Poisson’s and continuity equations known as drift-diffusion methodology was implemented by Buxton et al [2] to obtain concentration of excitons and charge carries with respect to time. To investigate the effects of annealing time on the morphology of phase separation and charge transfer behaviour inside the active layers of two dimensional polymer solar cells employing Monte Carlo techniques was developed by Lie et al [3].

In the present study, Monte Carlo method was successfully employed to study the mechanism inside a three dimensional bulk conjugated hetero-junction polymer solar cells using a model based on adjustable parameters for
determining their structural appearances. The amorphous properties of the conjugated polymers were modelled to study the behaviour and the motion of excitons and charge carriers. The process of electric current generation was studied using simulating techniques. The modelled energy states of the active layer were considered to be normally distributed with a specific mean and a standard deviation. For a bulk hetero-junction structure, the three dimensional behaviour of the excitons and the charge carriers; the effect on efficiency due to internal structural design and applied external voltage; the simulated performance of a polymer solar cell for different practical dimensions and polymer solar cell fabrication materials were addressed. The results for three active layer blends, namely MDMO-PPV:PCBM, M3EH-PPV:PCBM and P3HT:PCBM are presented for analysis and in all three cases PCBM was used as the electron accepting or electron transporting material. Initially a polymer solar cell with minimum possible dimensions was modelled in order to capture the changes in the performance and the efficiency with the variation of parameters that determine the structural architecture of the device. Since the electric current generation inside a polymer solar cell takes place inside the active layer as exciton generation, exciton diffusion and dissociation, charge carrier generation and charge carrier motion, the modelling of this active layer inside a computationally executable environment was vital in accurately simulating the whole mechanism. The effect of recombination of charge carriers was not considered since the influence of the charge carrier recombination becomes insignificant for higher electric field strengths and can only take place if the oppositely charged carriers meet together within an interfacial region. The amorphous nature, a major influencing factor on exciton and charge carrier motion was addressed satisfactorily by the simulation to obtain reliable results agreeing with the experimental findings. The charge carrier generation efficiency for each morphology proved that the simulation results are in agreement with the experimental findings regarding the diffusion lengths of the
excitons. The effect of the externally applied electric field on the performance of the device was very significant. Monte Carlo simulations had to be averaged over many runs to come up with a reliable estimate. Even though the execution of this kind of a simulation is computationally expensive, the results obtained can be considered very accurate.

2. EXCITON GENERATION AND DEFUSION

With the absorption of solar light, the conversion of solar energy into electric current inside a polymer solar cell takes place without significant delay [1]. This is unique and characteristic to the polymer, organic molecules composed of a large number of repeating structural units called monomers. Conjugate polymers consist of a chain of $sp^2$ hybridized carbon atoms bonded with $\sigma$ bonds and weak $\pi$ bonds. Energy of the weak $pi$ bonds, corresponding to the $\pi$ state forms the highest occupied molecular orbital (HOMO). When the atoms are in their most stable state, HOMO energy level corresponds to the maximum energy of $2p_z$ electrons or valence band of the molecule. The $\pi^*$ state or the lowest unoccupied molecular orbital (LUMO) energy level forms the conduction band (Figure 1). A typical polymer solar cell consists of two electrodes at either ends of the cell with an active layer sandwiched in between. Active layer is formed by conjugated polymer materials of two phases of hole and electron transportation, arranged so as to maximize the charge carrier generation. Their molecules take the form of repeating structural units of long chains, coiled and twisted, creating a disordered mess of polymer chain segments of different lengths, oriented in random directions. The lengths of these segments determine the extent to which the $pi$ cloud of electrons is allowed to delocalize. The longer chain segments possess a lower $pi$ to $pi^*$ energy gap and shorter segments are characterized by higher energy gaps. Due to this amorphous nature of the structure, energy states are unevenly distributed and the arrangement of energy levels inside the polymer material cannot be accurately predetermined. Therefore the energy states were assumed to be normally
distributed with only a small fraction of the energy states allowed to have energy values closer to the valance and conduction band energies. The Gaussian distribution of the density of states (DOS) is given by equation 1,

$$g(\varepsilon) = \frac{n}{\sqrt{2\pi}\sigma} e^{-\frac{(\varepsilon - \varepsilon_0)^2}{2\sigma^2}}$$  \hspace{1cm} (1)$$

where \( n \) is the normalization constant and \( \varepsilon \) is the mean energy value. The standard deviation value \( \sigma \) defines the extent to which the energy values are dispersed in the energy space. The two phases have distinct values for valence and conduction energy levels. Hence the mean energy values of the respective phases are characteristic to each phase. The standard deviation values used in each phase are also different as the degree of disorderedness of the electron donating materials tends to be generally greater than that of the electron accepting materials [4].

![Energy levels splitting](image)

Figure 1: Energy levels splitting. Top: Energy levels splitting in a conjugated polymer molecule. Bottom: Valence and conduction band in a conjugated polymer molecule.
When a solar photon is absorbed by the active layer, an electron hole pair called an exciton is created. These excitons exhibiting random motion are very unstable with an average lifetime of about 10 $\mu$s. To break the bond between the electron and the hole of an exciton, a considerable amount of energy is needed as the width of the band gaps of conjugated polymers lie around 1-4 eV. Since thermal energy is not sufficient for exciton dissociation, energy is supplemented with the aid of potential energy difference at the interfacial region between the two phases. The dissociated holes and electrons are transferred to the respective transporting mediums and will move towards the electrodes located at either ends, generating an electric current (Figure 2). An electron in the highest occupied molecular orbital, absorbing sufficient energy, jump to the lowest unoccupied molecular orbital (LUMO) generating an exciton and thereby creating a hole in HOMO. This electron hole pair is coulombically attracted to each other and behaves as a single unit (Figure 3). The exciton generation is directly related to the photon flux incident on the polymer solar cell by

$$G(r) = \phi_i(r)\alpha_i e^{-\alpha_i(L_y-r)}$$

(2)

where $\phi_i$ is the incident photon flux, $\alpha_i$ is a frequency dependant absorption coefficient, $L_y$ is the position of the topmost surface (location of the anode) and $r_y$ is the distance into the cell from the anode. The absorption coefficient is assumed to have a Gaussian distribution with specific mean and standard deviation values. According to this relationship, more excitons are generated closer to the topmost electrode.
Figure 2: Basic steps involved in electric current generation inside a polymer solar cell. (1) photon absorption (2) exciton generation (3) exciton diffusion (4) exciton dissociation (5) charge carrier motion.

Figure 3: Exciton generation. (a) Exciton generation and diffusion, (b) First step of exciton dissociation, (c) Second step of exciton dissociation (d) charge carrier motion, (e) Exciton decay and (f) charge carrier recombination. ET and HT correspond to electron and hole transporting phases respectively.
Exciton diffusion is explained in terms of the Förster transfer mechanism, which suggests that the exciton motion is due to hopping from one energy state to a lower energy state [1]. The hopping rate is given by,

\[ w_i = w_e \left( \frac{R_j}{R_i} \right)^6 e^{-\left( E_j - E_i \right) \hbar \omega T} \quad E_j > E_i \]

\[ w_i = w_e \left( \frac{R_j}{R_i} \right)^6 \quad E_j < E_i \]

where \( w_e \) is a frequency factor, \( R_i \) is the hopping distance which generally takes the value of 1 nm and \( R_j \) is the Förster radius. \( E_i \) is the value of the energy state currently occupied by the exciton and \( E_j \) is the energy state to which the exciton hops. Once an exciton reaches an interface between hole transporting and electron transporting phases, the electron in the LUMO energy level of the hole transporting phase is transferred to the LUMO energy level of the electron transporting phase (Figure 3 (b)). This effectively occurs, when the LUMO and HOMO energy levels of the electron transporting region is located sufficiently below the respective energy levels of the hole transporting phase. The electron and the hole are still coulombically bound. This bond is broken (Figure 3(c)) with the assistance of an externally applied electric field of magnitude in the range 2x10^6 V/m to 5x10^6 V/m. After the exciton is dissociated, electrons and holes are free to move inside their respective phases. The charge carrier motion is also a hopping process following a path of subsequently lower energy from the initial position to the electrode. The charge carrier hopping rate between two energy sites derived from the Miller-Abrahams expression [1] is given by,

\[ v_i (r_i, \Delta E_i, T) = v_0 e^{-\gamma T} e^{-\Delta E_i / \hbar \omega T} \quad E_j > E_i \]

\[ v_i (r_i, \Delta E_i, T) = v_0 e^{-\gamma T} \quad E_j < E_i \]

\[ \Delta E_i = E_j - E_i \]

where, \( v_0 \) is a term governed by the hopping frequency and \( \gamma \) is the wave function decay rate. \( T \) is the temperature and \( k_B \) is the Boltzmann constant.
3. MONTE CARLO SIMULATION

The electric current produced inside a polymer solar cell was investigated by dividing the total time duration of the process into discrete time steps. Within a given time step, a particular event can take place in several possible ways. Monte Carlo simulation technique was used to choose a particular option from several possibilities. The most probable possibility out of all these alternatives was determined by first evaluating the rates that govern the event or the action which is to be simulated. These rates were derived theoretically by considering all the influencing factors and with this rates, probability values for each of the possibility were decided. These probabilities were then compared against a random number between zero and one. For a particular possibility when this random number was less than the calculated probability, the action suggested by the respective possibility was executed. The hopping distance \( r_{ij} \) of charge carriers was fixed at 1 nm. The effect of an externally applied electric field was modelled by modifying the term given by equation (4)

\[
\Delta E_{ij} = E_j - E_i - q \varepsilon d
\]

where, \( q \) is the carrier charge, \( \varepsilon \) is the magnitude of the electric field and \( d \) is the hopping distance.

The whole cell structure was divided into small cells of dimension 1 nm x 1 nm x 1 nm. Two tags, plus one or minus one was assigned to each unit cell depending on whether it is in the hole or electron transporting phase respectively. Another tag was assigned to the energy corresponding to that particular unit cell, chosen randomly from a set of normally distributed values lying between the conduction and valence band energies. The mean and the standard deviation values of this distribution function are characteristic and unique properties of the polymer material. Hence, the energy values of the hole-transporting and electron transporting regions were picked from two Gaussian distributions with different
mean and standard deviation values. The cell structure depicted in figure 4 was modelled as a two dimensional matrix. The three dimensional nature of the cell was realized by creating a three dimensional matrix by appending identical two dimensional matrices in parallel. The dimensions (length, depth and breadth) of the polymer solar cell were alterable so that the morphological effects on the current generation efficiency can be quantitatively analysed for different internal architectural designs.

Figure 4: A cross section of the cell model. Hole and electron transporting phases are tagged with +1 and -1 respectively

Figure 5: Hopping destinations of an exciton. Shows the six possible hoping directions of the exciton
In three dimensional simulation used, a given charge carrier has the option to hop to six lattice points around its current location (Figure 5). The possibility for each of these hops was assessed by calculating hopping rate and thereby the probability of a jump to each location was obtained. The new lattice point of the charge carrier was determined for the highest hopping probability. Excitons were allowed to generate throughout the active layer, where the number of photo generated excitons was governed by the relationship given by equation (2). Using this equation, a value for the number of excitons generated was calculated for each unit distance into the depth. At each time step, the probabilities for a hop to the nearest neighbours in six directions were derived from the respective hopping rates according to the equation,

$$P_{ij}^{k} \text{(exciton)} = w_{ij}^{k} \sum_{k=1,2,3,...,6} w_{ij}^{k}$$

where $i$ and $j$ are the initial and final positions of the exciton. The direction with the highest hopping probability was chosen and the exciton was moved to the respective lattice point in this particular direction. This operation was executed when the highest probability was greater than a machine generated random number between zero and one. Hopping rates to each of the possible lattice points were calculated to determine the most probable subsequent (or new) location of the charge carrier by equation 4. These rates were also weighted depending on the hopping direction. The rates corresponding to downward jumps were weighted with one and the rates corresponding to other directions were weighted with 1/8. The charge carrier motion is similar to that of the excitons (figure 5). At the electrodes the holes and the electrons were collected and the number of the holes and the electrons accumulated within each of the time steps was calculated to determine the efficiency of the cell.
4. MOTION OF EXCITONS, ELECTRONS AND HOLES IN A MDMO-PPV: PCBM SOLAR CELL

Excitons were allowed to generate anywhere inside the active layer during their lifetime and to move in random directions. Figures 7(a), 7(b) and 7(c) depict the three dimensional behaviour of excitons in “y”, “x” and “z” directions for a polymer solar cell of MDMO-PPV hole transporting phase and PCBM electron transporting phase. These plots reveal two types of motion. In figure 7(a), the excitons 1, 3, 4 depict, ideal random motions and exciton 2 a long time \((8.5 \mu s)\) occupation of a lattice cite after a very short random motion. The latter kind of situation occurs when the excitons get trapped in stable or low energy sites, where all the surrounding energy sites have higher energy values than that of its current location.

![Figure 6](image1.png)

**Figure 6:** Monte Carlo simulation of charge carrier motion

![Figure 7(a)](image2.png)

**Figure 7(a) : y Position of Excitons**
Figure 7(b) : x Position of Excitons

Figure 7(c) : z of the excitons

The influence of the externally applied electric field on the motion of the electrons were studied. The initial “y” positions of the electrons reaching the cathode within $100\,\text{ns}$ were plotted in Figures 8(a) and 8(b) for electric fields of 0 and $0.05\,\text{V/}nm^2$ respectively. The influence of the externally applied electric field on the motion of the electrons was very significant. In the absence of an electric field, only a small number of electrons generated very close to the cathode reached the cathode within $100\,\text{ns}$. These electrons starting between 40-45 nm distances approximately had a maximum distant of 10 nm to travel to the
cathode. When the applied electric field is $0.005 \text{Vnm}^{-1}$, the electrons generated around 30nm have a higher ability to reach the cathode. With the further increase of the electric field to $0.05 \text{Vnm}^{-1}$ even electrons generated at higher interfacial regions (10 -20 nm) were assisted to move by this electric field.

![Figure 8: Initial Position of the Electrons Reaching the Cathode in y Direction. Show the for the initial “y” positions in nm, the number of electrons collected by the cathode for the applied electric field (a) 0 Vnm$^{-1}$, (b) 0.05Vnm$^{-1}$](image)

Figure 9(a) illustrates the “y” directional position of five electrons chosen randomly from about hundred electrons. Most of the electrons generated at the interfacial regions tend to relax in lower energy states for a very long time. This is a direct consequence of the disordered nature of the energy states. The newly generated electrons initially start moving towards the cathode with the assistance of the external electric filed. For most of these electrons the probability of finding a lower subsequent energy state reduces with the time. Infact, majority of these electrons get trapped in low energy states without making any contribution to the electric current. Figures 9(b) and 9(c) depict respectively the change in the “x” and “z” directional positions of the electrons with respect to the time. For the “z” position only three electrons were plotted as they represent all the z directional behavioural patterns of the electrons. These two plots further
prove the concept of charge carriers being trapped in lower energy sites for long periods of time. This is a significant effect that limits the current generation not only in polymer solar cells but also in other organic photovoltaic devices.

![Graphs showing electron position with time](image)

**Figure 9:** Position of Electrons with Time 9(a), 9(b) and 9(c) show the y, x and z position of electrons with respect to time respectively

The three dimensional behaviour of the holes are presented in Figures 10(a), 10(b) and 10(c) for “y”, “x” and “z” directions respectively. For the “z” position only four holes were plotted since these represent all the z directional behavioural patterns of the holes. The behaviour of the holes are very similar to that of the electrons, except that due to higher mobility characterized by the holes, the number of holes reaching the anode within 100ns was comparatively higher. The holes are also affected by the relaxing effect at stable energy sites. The external electric field applied normal to the surface of the cell directly affect the “y” directional position of holes. This argument is also valid for the electrons.
The three dimensional behaviour of the holes are presented in Figures 10(a), 10(b) and 10(c) for “y”, “x” and “z” directions respectively. For the “z” position only four holes were plotted since these represent all the z directional behavioural patterns of the holes. The behaviour of the holes are very similar to that of the electrons, except that due to higher mobility characterized by the holes, the number of holes reaching the anode within 100 ns was comparatively higher. The holes are also affected by the relaxing effect at stable energy sites. The external electric field applied normal to the surface of the cell directly affect the “y” directional position of holes. This argument is also valid for the electrons.
In Figures 11, the number of charge carriers collected with respect to time for holes (a1, a2, and a3) and for electrons (b1, b2, and b3) under electric fields 0.00, 0.05 and 0.20V/nm for 100ns are shown. The number of holes collected was always greater than the corresponding value for electrons. When the external electric field strength was increased, the number of charge carriers collected toward the latter part of the time scale gradually diminished as most of the charge carriers were assisted by the high electric field to jump out of their trapped energy sites and move towards the respective electrodes quickly.

Figure 11(a1): Number of holes collected for electric field 0.00V/nm

Figure 11(a2): Number of holes collected for electric field 0.05V/nm

Figure 11(a3): Number of holes collected for electric field 0.2V/nm
Figure 11(b1): Number of electrons collected for electric field 0.00 Vnm⁻¹

Figure 11(b2): Number of electrons collected for electric field 0.05 Vnm⁻¹

Figure 11(b3): Number of electrons collected for electric field 0.2 Vnm⁻¹

5. MORPHOLOGICAL EFFECT OF A MDMO-PPV: PCBM SOLAR CELL

The effect of morphological properties on the current generation efficiency of the solar cell was analysed to determine the optimum morphological condition
and material properties of an efficient polymer solar cell. The breadth of the cells simulated was kept constant at 7nm. Each morphology was tested under the same illumination conditions and the number of excitons generated was changed as a function of the surface area and the depth of the polymer solar cell. The hole transporting phase of these morphologies was composed of MDMO-PPV and the electron transporting phase with PCBM. Valence (HOMO) and conduction (LUMO) band energy levels of MDMO-PPV were -3.0eV and -5.2eV respectively and for PCBM the corresponding values were -4.1eV and -6.1eV respectively [6]. The structure of the morphology 1 is depicted in Figure 12.

![Figure 12: Morphology 1](image)

The number of charge carriers collected by the electrodes was analysed by changing the applied external voltage within 100ns. Figure 13 shows the increase of the number of charges collected at the electrodes with respect to the applied external electric field. It is evident that the charge carrier collections are negligible at the beginning. They start to increase form about 10nm onwards. This is a quite predictable result as most of the charge carriers generated at the interfacial regions take a considerable amount of time to reach the electrodes. At higher electric fields like 0.2Vnm\(^{-1}\) almost all the charge carriers are drifted towards and collected by the electrodes within approximately 50-60ns. The number of holes collected is observed to be greater than the number of electrons collected by the cathode for each electric field value. This is a direct
consequence of the mobility values of the each type of charge carrier. The energy states of the hole transporting material are more dispersed than that of the electron transporting materials and the standard deviation value of the energy states of the hole transporting phase is greater than the standard deviation value used to construct the electron transporting phase. So a hole moving in its transporting phase has a higher probability of finding subsequent lower energy sites to complete its journey to the anode by hopping from one site to another. On the other hand, the chances are high for an electron in a particular energy site to remain immobile for relatively long time periods or to oscillate between two energy sites as the energy values of its neighbouring sites are almost similar to the value of its current location, due to the less dispersion characterized by the energy sites in the electron transporting medium. The charge carrier generation efficiency given by

\[ \text{efficiency} = \frac{\text{number of charge carriers generated}}{\text{number of photons absorbed}} \times 100 \]  

(8)

Figure 13: Charge Carriers Collected vs Electric Field. Change in the number of charge carriers collected with respect to the externally applied electric field gave an average of 19.8%. In Table 1 and 2 the number of charge carriers collected at the electrodes for different external electric field values are presented. These results were obtained for five runs of the simulation. Each new
execution of the simulating program corresponds to a distinct energetic disorder. This is the reason for the significant deviation that can be observed in the charge carrier counts corresponding to different runs, even though the cell is initially populated with the same amount of excitons. Charge carrier counts of Table were obtained for an average initial exciton population of 8750 which is about 70% of the total number of excitons.

Table 1: Number of electrons collected

<table>
<thead>
<tr>
<th>Electric field ($V_{nm}^{-1}$)</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Trial 5</th>
<th>average</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42</td>
<td>60</td>
<td>50</td>
<td>61</td>
<td>69</td>
<td>56±5</td>
<td>0.65±0.05</td>
</tr>
<tr>
<td>0.001</td>
<td>62</td>
<td>128</td>
<td>105</td>
<td>116</td>
<td>129</td>
<td>108±12</td>
<td>1.2±0.1</td>
</tr>
<tr>
<td>0.002</td>
<td>91</td>
<td>185</td>
<td>141</td>
<td>154</td>
<td>168</td>
<td>148±16</td>
<td>1.7±0.2</td>
</tr>
<tr>
<td>0.003</td>
<td>111</td>
<td>165</td>
<td>163</td>
<td>169</td>
<td>203</td>
<td>162±15</td>
<td>1.9±0.2</td>
</tr>
<tr>
<td>0.004</td>
<td>123</td>
<td>186</td>
<td>256</td>
<td>271</td>
<td>225</td>
<td>212±27</td>
<td>2.4±0.3</td>
</tr>
<tr>
<td>0.005</td>
<td>148</td>
<td>205</td>
<td>241</td>
<td>281</td>
<td>253</td>
<td>226±23</td>
<td>2.6±0.3</td>
</tr>
</tbody>
</table>

Table 2: Number of holes collected

<table>
<thead>
<tr>
<th>Electric field ($V_{nm}^{-1}$)</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Trial 5</th>
<th>average</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84</td>
<td>80</td>
<td>58</td>
<td>152</td>
<td>161</td>
<td>107±21</td>
<td>1.2±0.2</td>
</tr>
<tr>
<td>0.001</td>
<td>194</td>
<td>147</td>
<td>143</td>
<td>259</td>
<td>272</td>
<td>203±27</td>
<td>2.3±0.3</td>
</tr>
<tr>
<td>0.002</td>
<td>245</td>
<td>162</td>
<td>162</td>
<td>332</td>
<td>402</td>
<td>207±47</td>
<td>3.0±0.5</td>
</tr>
<tr>
<td>0.003</td>
<td>324</td>
<td>202</td>
<td>195</td>
<td>435</td>
<td>477</td>
<td>327±58</td>
<td>3.7±0.7</td>
</tr>
<tr>
<td>0.004</td>
<td>380</td>
<td>253</td>
<td>215</td>
<td>478</td>
<td>488</td>
<td>362±56</td>
<td>4.2±0.6</td>
</tr>
<tr>
<td>0.005</td>
<td>413</td>
<td>274</td>
<td>267</td>
<td>529</td>
<td>519</td>
<td>400±57</td>
<td>4.6±0.7</td>
</tr>
</tbody>
</table>

A second morphology shown in Figure 14 was constructed by reducing the height of the interface by 10 nm. The average charge carrier generation efficiency
for this morphology was 6.48%. For an external electric field of $0.005 \ V nm^{-1}$, the efficiency of the electrons collected was $0.31 \pm 0.4\%$ and of the holes collected was $1.3 \pm 0.1\%$. Even though the purpose of reducing the interfacial height was to provide charge carriers an undisturbed path towards the respective electrodes, the obtained results showed that this strategy is ineffective. This fact was also clearly reflected by the reduced efficiencies for both holes and electrons. A third morphology shown in Figure 15 characterized by broad regions of $10 nm$ between the interfaces was considered. Since the maximum diffusion length of the excitons is about $10 nm$, the number of excitons that could reach an interfacial region within their lifetime of $10 \mu s$ is evidently much less than in the cases of morphology 1 and 2. Due to this reason, the number of charge carriers generated was also reduced. This was well justified by the charge carrier generation efficiency for this morphology which amounted to $10.7\%$. This fact was also clearly reflected by the reduced efficiencies for both holes and electrons. For the external electric field of $0.005 \ V nm^{-1}$, the average efficiency of the electrons collected was $1.35 \pm 0.08\%$ and of the holes collected was $1.3 \pm 0.3\%$. A fourth, hypothetical morphology as shown in Figure 16 was considered. This is a structure that optimizes the charge carrier generation as the interfacial area is maximized. In fact the average charge carrier generation efficiency of this morphology estimated using this simulation was $21.1\%$. The major drawback of this morphology is that the recombination effect of charge carriers could reduce the number of charge carriers that reach the respective electrodes which is not modelled into this simulation. The above four morphologies were tested to determine the best morphological structure in terms of the current generation efficiency. These results revealed that, as the dimensions of a morphology increases, higher electric fields were required to move the charge carriers towards the respective electrodes. The best morphological parameters were then applied to a polymer solar cell with practical dimensions.
As the morphology 1 was the most efficient, when the amount of charge carriers collected within a definite time period was concerned, morphology 5 was constructed using morphology 1 with practical dimensions (Figure 17). In this device, the number of lower and stable energy sites that is available for the charges to get trapped is higher. To jump out of more stable energy sites and to
travel long distances, the assistance of a strong external electric field is required. The number of charge carriers collected at the electrodes for different external electric field values for morphology 5 are presented in Tables 3 and 4.

**Table 3: Number of Electrons**

<table>
<thead>
<tr>
<th>Electric field ($V\text{nm}^{-1}$)</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Trial 5</th>
<th>Average Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>4</td>
<td>0</td>
<td>19</td>
<td>7</td>
<td>7</td>
<td>7 ±3 0.03 ±0.01</td>
</tr>
<tr>
<td>0.005</td>
<td>11</td>
<td>3</td>
<td>43</td>
<td>29</td>
<td>6</td>
<td>18 ±8 0.06 ±0.03</td>
</tr>
<tr>
<td>0.200</td>
<td>3304</td>
<td>3481</td>
<td>3281</td>
<td>3032</td>
<td>2931</td>
<td>3206 ±99 10.7 ±0.3</td>
</tr>
</tbody>
</table>

**Table 4: Number of Holes**

<table>
<thead>
<tr>
<th>Electric field ($V\text{nm}^{-1}$)</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Trial 5</th>
<th>Average Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>128</td>
<td>67</td>
<td>165</td>
<td>81</td>
<td>150</td>
<td>118 ±19 0.39 ±0.06</td>
</tr>
<tr>
<td>0.005</td>
<td>265</td>
<td>157</td>
<td>269</td>
<td>166</td>
<td>299</td>
<td>231 ±29 0.8 ±0.1</td>
</tr>
<tr>
<td>0.200</td>
<td>6948</td>
<td>4880</td>
<td>5828</td>
<td>6052</td>
<td>5315</td>
<td>5804 ±351 19.4 ±1.2</td>
</tr>
</tbody>
</table>

6. **M3EH-PPV:PCBM AND P3HT:PCBM SOLAR CELLS**

There are other conjugated polymer materials which are being researched and used to fabricate polymer solar cells. Since morphology 1 has been proven to be the most efficient structure, the dimensions of morphology 1 have been used in these simulations. In M3EH-PPV:PCBM solar cell, hole transporting phase is fabricated using M3EH-PPV and the electron transporting phase with PCBM. The LUMO and HOMO energy levels of M3EH-PPV are -3eV and -5.3eV respectively[8]. For the external electric field of 0.005$V\text{nm}^{-1}$, the efficiency of the electrons was 2.6 ±0.4% and of the holes collected was 4.2 ±0.5%. M3EH-PPV can be considered as an efficient hole transporting material. On the other hand, when it is blended with PCBM the overall
efficiency of the cell is reduced since the electron collection efficiency of PCBM is observed to be much lower than the hole collection efficiency of M3EH-PPV. In P3HT:PCBM solar cell, hole transporting phase is fabricated with P3HT and the electron transporting phase with PCBM. The LUMO and HOMO energy levels of P3HT are $-3.3 \text{ eV}$ and $-5.2 \text{ eV}$ respectively. For the external electric field of $0.005 \text{ Vnm}^{-1}$, the efficiency of the electrons collected was $3.0\pm0.7\%$ and of the holes was $3.7\pm0.5\%$. This material has almost same hole and electron collection efficiencies. In Figures 18 and 19 electron and hole collection efficiencies for the three blends are presented respectively. Among the three fabricating materials, P3HT:PCBM has the highest electron collection efficiency and MDMO-PPV:PCBM has the highest hole collection efficiency.

![Figure 18: Electron Collection Efficiencies with respect to Applied Electric Field](image)

The percentage of electron collection efficiency for the three are shown as a function of applied electric field in mVnm$^{-1}$. 
Figure 19: Hole Collection Efficiencies with respect to Applied Electric Field. The percentage of hole collection efficiency for the three are shown as a function of applied electric field in mVnm\(^{-1}\).

7. CONCLUSION

As the main processes involved in electric current generation inside a polymer solar cell take place inside the active layer, the modelling of this layer inside a computationally executable environment was vital in accurately simulating the whole mechanism. The main factor that limited the exciton diffusion to an interface was the presence of stable energy sites in the active layer, which can be perceived as trapping sites for both excitons and charge carriers. This situation was well depicted by the plots obtained under the three dimensional behaviour of excitons. The composition of the active layer also played a decisive role in exciton diffusion, dissociation and charge carrier motion, and suitable electron transporting and hole transporting polymer materials had to be blended together so that the number of trap energy sites dispersed throughout the active layer was minimized.

The charge carrier generation efficiency obtained for different morphologies from the simulation was in agreement with the experimental findings regarding
the diffusion length of the excitons. The maximum reported current generation efficiency of the bulk heterojunction polymer solar cells to date is approximately 4.5%. The effect of the externally applied electric field on the performance of the device was very significant. At low electric fields, the charge carrier collection efficiencies were almost governed by the exciton dissociation rate. Even if the charge carriers get trapped in very low energy sites, with the assistance of high electric fields, they were able to jump out and move toward the respective electrodes. The effect of these external electric fields becomes material when the polymer solar cells with higher dimensions were considered. For strong electric field values like $0.2Vnm^{-1}$ charge carrier efficiencies in the range of 10%-20% could be achieved. For polymer solar cells with practical dimensions, the charge carrier collection efficiency was almost governed by the strength of this field. The charge carrier generation efficiency was reduced when the distance between two interfacial regions were increased. This clearly proved that the diffusion lengths of the excitons are very low and they are also vulnerable to be trapped in stable energy sites within short time periods after their generation. Reducing the height of the interfacial region also had a decisive and significant impact on the charge carrier generation efficiencies. Reduction of the interfacial height from 30 nm to 10 nm with all the other dimensions fixed, resulted in a drop of almost 13% in the charge carrier generation efficiency.

The results for the three active layer blends (MDMO-PPV:PCBM, M3EH-PPV:PCBM and P3HT:PCBM) showed that even though the valence and conduction band energies of the three hole transporting materials change by very slight amounts, the ultimate impact they have on charge carrier collection efficiencies, when blended with the same electron accepting material was significant. Since the three active layer blends are characterized with three different arrangements of energy sites, the availability and the dispersion of the trap sites also vary accordingly. This can be considered as the main reason to have different values for electron collection efficiencies. Another possibility is to
detect the performance of these devices by changing the chemical parameters that govern the degree of dispersion of the energy states in the hole and electron transporting phase fabricating materials. This has to be done by experimentally identifying most of the chemical properties of these conjugated polymers, so as to come up with more precise computationally executable representations. This could ultimately lead to the invention of very detailed morphologies, which capture, to a great extent the unpredictable disordered nature of the active layers of not only the polymer solar cells but also of the other organic photovoltaic devices.

REFERENCES


