



# Solvent effect on the thin film formation of polymeric solar cells

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## ABSTRACT

This research work investigates the influence of the solvent used upon the formation of polymeric photoactive layer. This photoactive layer consists of a blend of poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), to produce P3HT:PCBM (at 1:1 ratio) blend thin films, in which the material solutions are deposited onto clean substrates via spin-coating technique. Three types of solvents were used namely: 100% dichlorobenzene (DCB), 100% chloroform (CH) and 50%:50% mixture of DCB and chloroform. The results reveal that the mixture of solvent produces a better solubility of the polymeric materials compared to that of the pure single solvent.

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## 1. Introduction

Converting solar energy into a form of electrical energy is one of the utilization of the natural energy resources. Solar energy converter based on silicon has become dominant in solar cell technology for the past few decades. However the high production cost and sophisticated fabrication process have aroused interest from researchers to venture for environment-friendly, cost-effective and simpler fabrication process based on polymeric materials [1–5].

Many approaches have been carried out and studied to enhance the efficiency of the photovoltaic devices based on polymeric photoactive thin films. By controlling and altering the processing conditions such as spin speed, spin time, thermal annealing temperature, types of solvents used and so on, the optical, physical as well as morphological properties of the photoactive polymeric thin films can be modified, and therefore enhance device performance [1,2]. In this study, we examine the effect of solvent used upon the formation of the P3HT:PCBM photoactive layers. If the solvent used for film formation possesses a high-volatility temperature, phase separation may occur during the solvent evaporation process. Thus, the interfacial area between the blend of photoactive materials increases, leading to an enhancement of exciton dissociation in the devices [6–8]. Furthermore, the solvent evaporation rate has a significant effect upon the surface morphology of polymeric thin films [9]. Most of the reported data in the literature of the P3HT:PCBM films were prepared from

chlorine based solvents such as chloroform and dichlorobenzene [3,5,8,9]. The solubility of P3HT:PCBM in the nonchlorinated solvents such as toluene or xylene is not as good as the chlorinated based solvents. Hence, chloroform and dichlorobenzene were used as solvents in our study.

## 2. Experimental

The photoactive polymeric layer consists of a blend of regioregular poly(3-hexylthiophene) (P3HT), purchased from Sigma-Aldrich and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), purchased from American Dye Source, Inc. The chemical structures of P3HT and PCBM molecules are shown in the inset of Fig. 1. The solution of P3HT:PCBM was prepared by blending both materials and dissolving in solvent of 100% 1,2-dichlorobenzene (DCB), 100% chloroform (CH) and also a cosolvent consisted of 50% chloroform and 50% 1,2-dichlorobenzene (DCB:CH). The concentration of P3HT:PCBM was set to 60 mg/ml at 1:1 weight ratio.

The design of the solar cell device was in the form of a sandwich structure of the photoactive polymeric layer between an anode electrode of indium tin oxide (ITO) and a metal cathode of aluminium (Al). The ITO glass substrates were ultrasonically cleaned in DECON™ foam solution for 15 min, and then were rinsed using deionised water, acetone solution, and ethanol solution sequentially. A buffer layer of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was spin-coated on top the ITO electrode. Then the photoactive layer was formed by spin-coating the blended P3HT:PCBM solution to produce a thin film of about 100 nm thick, which was then annealed at 100 °C for 10 min. Finally, the top electrode of aluminium was by a thermal evaporator under high vacuum. The final device construction of

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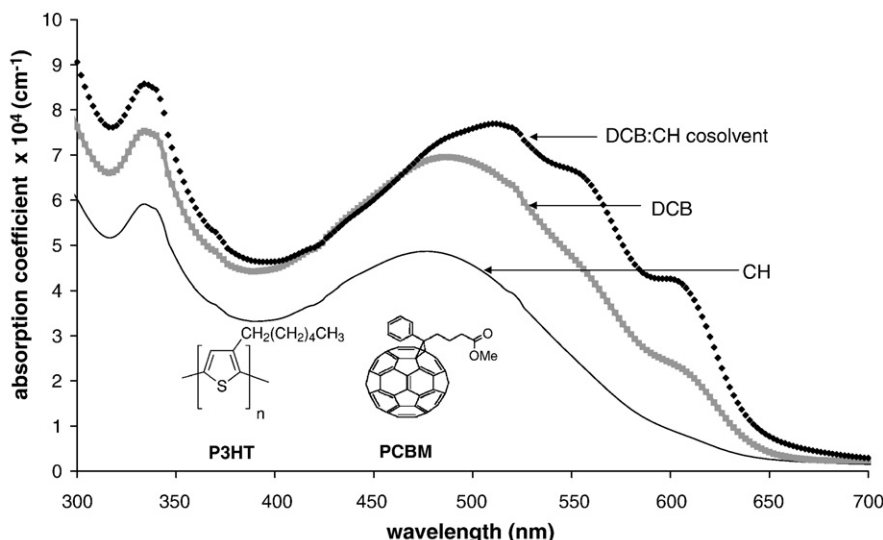


Fig. 1. Absorption coefficient spectra of P3HT:PCBM which were dissolved in pure DCB solvent, pure CH solvent and DCB:CH cosolvent. The inset shows the chemical structures of P3HT and PCBM.

ITO/PEDOT:PSS/P3HT:PCBM/Al is illustrated in the inset of Fig. 4. Absorption spectra measurements for P3HT:PCBM blend thin films were carried out using a Jasco V-570 UV/VIS/NIR spectrophotometer. A Siemens D5000 X-ray diffractometer was used to record the X-ray diffraction (XRD) patterns, whereas Veeco D300 Atomic force microscopy was used to visualize the surface morphology of the samples. Besides, the current–voltage characteristics of the devices were measured using a Keithley 2400 sourcemeeter under the AM1.5G-filtered irradiation ( $100 \text{ mW/cm}^2$ ) from a Newport 67005 solar simulator.

### 3. Result and discussion

The effect of the solvents on the absorption coefficient spectra of the P3HT:PCBM blend thin films is shown in Fig. 1. It can be obviously seen that the blend film prepared from DCB:CH cosolvent shows the highest value of absorption coefficient ( $\sim 8 \times 10^4 \text{ cm}^{-1}$ ) in the visible wavelength range from 450 nm to 650 nm compared to that of pure DCB and pure CH solvent. This indicates that a large number of photons are absorbed in the photoactive layer prepared from the DCB:CH cosolvent. Besides, the peak is red-shifted for the film prepared in cosolvent compared to that of pure DCB and pure CH. This indicates a significant increment in the conjugation length of the polymer chains. The formation of thin film using DCB:CH cosolvent is strongly influenced by the solubility of the blend components of P3HT:PCBM. The addition of a moderate amount of CH into the DCB solvent may reduce the surface tension, and the solvent can vaporize very fast, hence forming the uniform thin film [10].

Fig. 2 shows the XRD spectra of P3HT:PCBM blend films prepared in pure DCB, pure CH and DCB:CH cosolvent. For spin-coated P3HT:PCBM blend thin film, a crystalline peak at  $2\theta \approx 5.4^\circ$  in the diffractogram, which corresponds to the first-order reflection is observed [1]. This peak may be attributed to the partial crystallinity that was possessed by P3HT chains which dispersed within the amorphous domains of PCBM matrix. The XRD spectra indicate that the film prepared from DCB:CH cosolvent shows the highest value of intensity peak. The results of XRD are consistent with the absorption spectra in which the ordering and crystallinity of the polymer can be enhanced significantly by using DCB:CH cosolvent rather than using merely pure DCB or CH solvent.

The effect of solvent used on the surface morphology of the AFM images of the P3HT:PCBM films is shown in Fig. 3. The root-mean-square (rms) roughnesses of the blend layers dissolved in pure DCB

solvent, CH solvent and DCB:CH cosolvent are 11.062 nm, 12.623 nm and 14.2777 nm, respectively. This indicates that the film prepared from DCB:CH cosolvent has a coarser surface morphology compared to that of pure DCB and CH since it shows a higher rms roughness value. This may attribute to a stronger, better solubility of the mixture components of DCB:CH cosolvent that leads to the increase in phase separation upon the films. It is noted that the solvent evaporation rates can affect the surface morphological properties of the polymer films. Pure CH can aid in improving surface affinity, but it possesses a higher solvent evaporation rate than the pure DCB solvent, leading to a reduction in interfacial area of the blend films. However, by mixing both solvents together, the resulting solvent evaporation rate of the cosolvent can thus be modified. Besides, the solvating power also significantly influences the morphology of the films, since a good solvent can result in the better extension of a polymer chain in the solid state of thin film. Hence phase separation increases leading to the development of continuous pathways for charge carriers and increases the interfacial area that enhances the exciton dissociation [11].

Fig. 4 shows the current density–voltage ( $J$ – $V$ ) characteristic curves and device parameters of the short-circuit current density ( $J_{sc}$ ),

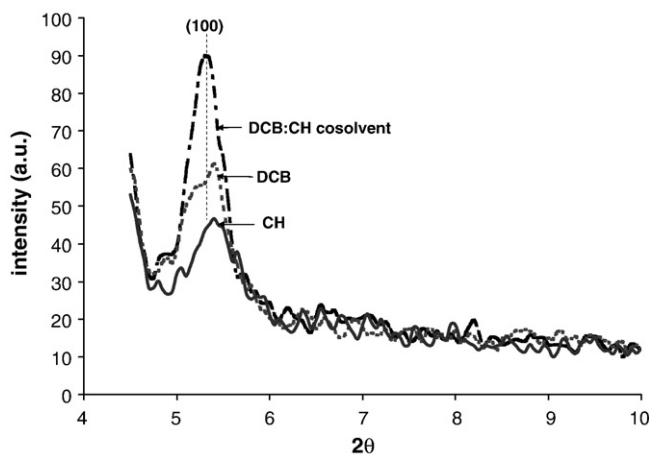


Fig. 2. X-ray diffraction of P3HT:PCBM blend films prepared in pure DCB, CH and DCB:CH cosolvent.

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