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From spin coating to doctor blading: A systematic study on the photovoltaic performance of an isoindigo-based polymer

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ABSTRACT

Doctor blading is suitable to roll-to-roll process with much little solution wasting and is less studied compared with the mainstream spin coating. In this work, we used a novel polymer blended with two common fullerene derivatives as active solutions. To systemically understand the different coating methods and the different fullerene acceptors on the effect of polymer solar cells (PSCs) photovoltaic performance, the wet active solution physic-chemical properties and variations of the dried active layer characterizations were investigated. It was observed that it is much easier to obtain a homogeneous film from doctor blading compared with spin coating for the polymer: $PC_{71}BM$ solution due to the high surface tension and viscosity. Moreover, the high boiling point additive plays an important role in inhibiting the wet film shrinkage and forming a uniform film. The longer film drying time for the doctor-blading films leads to larger domains than spin coating, thus increases the geminate recombination and results in lower mobilities as well as power conversion efficiencies (PCE). Doctor-blading-processed PSCs with PCE of 4.46% were achieved for P3TI:$PC_{71}BM$ devices, which were comparable to those of spin-coating devices. This work provided valuable suggestions and solutions for the doctor-blading process, especially for crystalline D-A polymer-based devices.

1. Introduction

The energy crisis caused by the increasing demand for fossil fuels and the rapidly vanishing fossil fuel reserves, coupled with the threat of climate change from increasing carbon dioxide levels, have placed renewable energy firmly on the global agenda. As one of the emerging novel photovoltaic technologies, polymer solar cells (PSCs) have been intensively studied in recent years because they possess potential advantages in low-cost flexible large-area substrates via roll-to-roll (R2R) coating technology [1–6]. For PSCs based on the bulk hetero-junction (BHJ) of a blend of conjugated polymers and fullerene derivatives, power conversion efficiencies (PCE) over 9% on the laboratory scale have recently been achieved [7,8]. However, the high efficiencies were achieved in small-area devices processed using the spin-coating method, which is not compatible with the large-area R2R process. Another problem with the spin-coating process is that most of the solution is wasted [9]. As an attractive alternative to spin coating, doctor blading, which is compatible with the R2R process on a large scale with little coating solution wasting, has been much less investigated [10,11]. Moreover, most of the studies on the doctor-blading process are based on the poly(3-hexylthiophene) (P3HT): (6,6)-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) material system, which can yield an unimpressive efficiency of approximately 3.8% [12–15]. The newly emerged high-efficiency donor–acceptor (D–A) polymers have been rarely investigated using the doctor-blading process, and the drying kinetics of the films during the spin-coating and doctor-blading processes have not been systematically investigated.

Therefore, we selected a representative high-efficiency D–A polymer, poly[N, N′-bis(2-hexyldecyl)isoindigo-6,6′-diyl-*alt*-3,3′′-dioctyl-2,2′:5′,2′′-terthiophene-5,5′′-diyl] (P3TI), for a comparison study of the spin-coating and doctor-blading processes with a focus on the correlation between the drying kinetics and the device photovoltaic performance. This polymer is easy to synthesize, which grants the possibility of scaling up for mass production. An efficiency over 6% can be achieved based on this polymer in laboratory-scale devices processed using spin coating [16,17]. It is difficult to obtain a uniform film of P3TI: (6,6)-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$)

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by spin coating. Holes often appear in the film when spin-coated on top of the poly(ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) hole transport layer, which motivated us to explore other process methods such as doctor blading. In this study, we observed that the effect of two widely used acceptors $PC_{61}BM$ and $PC_{71}BM$ have quite different behaviors during different processing methods. Additives were observed to be important in forming a homogeneous film in the doctor-blading process. It was also demonstrated that the solution viscosity has a great effect on the quality of spin-coated films but much less of an effect on that of doctor-blading films [18,19]. Furthermore, we present the device performance results associated with the solution properties, transient drying process and film morphology. The PSCs fabricated using the doctor-blading method can achieve a comparable PCE compared with those fabricated using the spin-coating method for the P3TI:$PC_{71}BM$ system.

2. Experimental details

The molecular structures of P3TI, $PC_{61}BM$ and $PC_{71}BM$ are shown in Fig. 1a. Widely used acceptors, $PC_{61}BM$ and $PC_{71}BM$, were employed in this study for comparison. The optimal weight ratio of P3TI:$PC_{61}BM$ and P3TI:$PC_{71}BM$ is 1:1.5 (w/w) [16,20]. For comparison, the other copolymer poly[2,3-bis-(3-octyloxyphenyl) quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl] (TQ1) blended with $PC_{61}BM$ or $PC_{71}BM$ was used with the same weight ratio. The number-average molecular weight (M_n) of P3TI is 101 000 with a polydispersity index (PDI) of 3.3, and the M_n for TQ1 is 71 000 with a PDI of 3.7. As a method of film-forming process, the working principle of doctor blading is described in Fig. 1b, in which the active solution is placed in front of the blade, and the blade is moved across the substrate in a uniform linear motion to produce a wet film behind the blade. The additive of high-boiling-point 1-chloronaphthalene (CN) was mixed with chlorobenzene (CB) as the processing solvent. The doctor-blading film thickness can be well controlled by changing the fabrication parameters, including the solution concentration, the gap between the blade and the substrate and substrate temperature [14,21,22]. In this study, the optimal substrate temperature was 50 °C, and the gap height was 20 μm with a 4 cm/s blading speed and 6 mg/mL active solution concentration (see Table. S1). For comparison, the active layers were also produced by spin coating, while the active solution concentrations were as high as 20 mg/mL for P3TI:$PC_{61}BM$ and 10 mg/mL for P3TI:$PC_{71}BM$.

2.1. Solution characterization

The viscosity of the solution was measured using a DV-I digital viscometer (Brookfield). The surface tension value of the solution was calculated using the pendant-drop method.

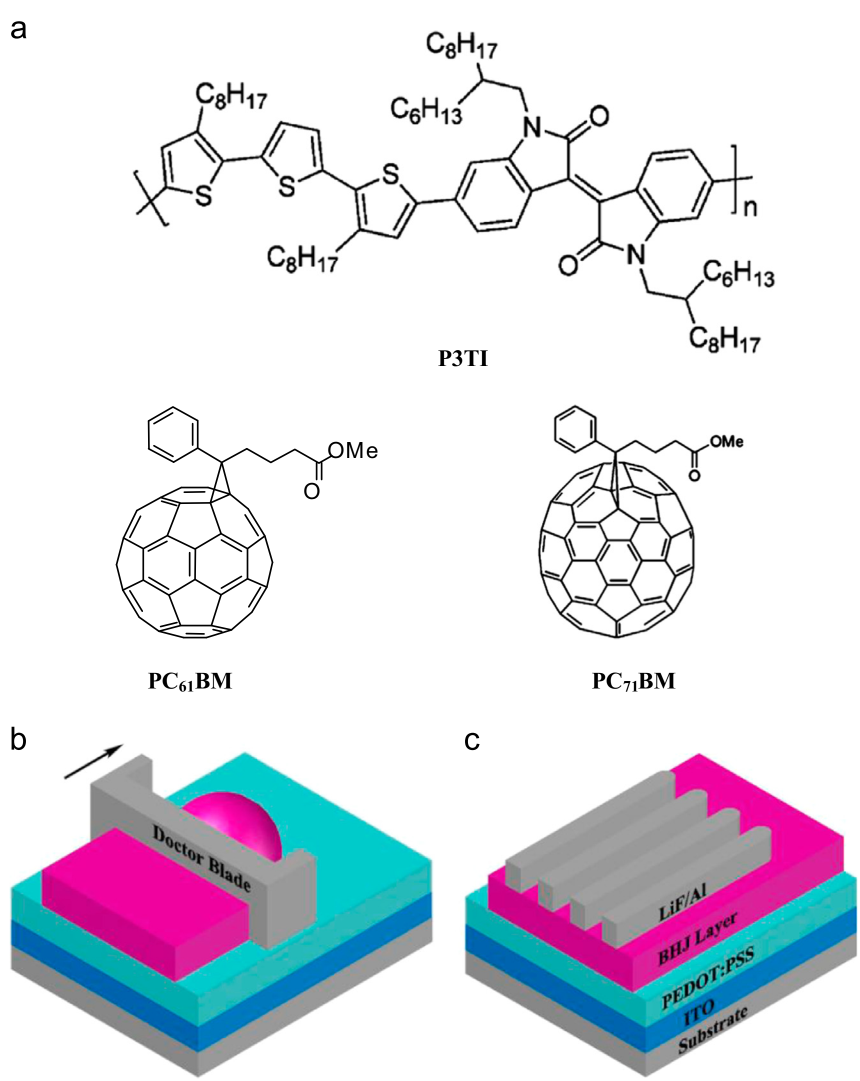

Fig. 1. The molecular structure of P3TI, $PC_{61}BM$ and $PC_{71}BM$ (a), doctor-blading process (b), and the schematic of the device structure (c).