Self-Healing Polymer Sealant for Encapsulating Flexible Solar Cells

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Abstract

Herein we demonstrate the utility of polyisobutylene (PIB) as a fully printable self-healing sealant for protecting organic photovoltaic devices from degradation under ambient conditions. These sealants can be applied on flexible substrates using drop casting, spin coating or blade coating. PIB-based crosslinked sealants show excellent device stability, especially the low molecular weight PIB.

Keywords: polyisobutylene, self-healing, sealants, organic photovoltaic devices, device stability

1. Introduction

The power conversion efficiencies of organic photovoltaic (OPV) devices continue to increase for single junction [1] and tandem cells [2]. Low cost large area fabrication process on flexible substrates [3] makes this technology more exciting and attractive to the solar cell community. There are three major areas of research in OPVs; (1) improving device efficiency by tuning absorption spectra [4,5], (2) device architecture and processing [6,7] and (3) encapsulation for long-term stability [8,9]. Although in last two decades, tremendous efforts have been made to increase the efficiency by synthesizing low band-gap polymers [10,11] and engineering various processing conditions [12,13] for large area roll-to-roll (R2R) printing, there are only very few reports (less than 5% of the total published work on OPVs) on the device stability [9]. The stability of OPVs can be broadly classified into two categories; chemical stability [14] and mechanical stability [15]. Active layers of OPVs such as polymers and small molecular semiconductors and electrode materials such as calcium and aluminium are susceptible to oxidation due to presence of oxygen and moisture in air. Reducing the oxygen and moisture penetration into the active layer can improve the chemical stability of these OPVs. It has previously been shown that oxygen and moisture can diffuse through the electrodes into the polymer active layers [16]. There have been some reports on device architecture where inverted type geometry containing oxide from both sides of the active layers show higher chemical stability over conventional architecture due to less diffusion of oxygen [17]. But the most common practice to prevent oxygen and moisture diffusion into the active layer is by encapsulating the device active area with gas impermeable materials [18]. Though transparent glass is almost impermeable and can be used as encapsulating materials [19],

it is incompatible with large-scale R2R printing. There are polymers such as polyvinyl alcohol (PVA) [20], polyurethane [21], poly(methyl methacrylate) PMMA or PMMA-polyolefin which have been used as a coating materials to protect organic active layers from degradation. However these polymers are also susceptible to degradation and crack formation upon prolonged exposure to unfavourable weather condition [22]. Therefore there is a need for new encapsulating materials, with high flexibility and excellent barrier properties to oxygen and moisture to realize stable and flexible OPVs for commercial applications. Polyisobutylene (PIB) based networks have good flexibility and strong adherence to the substrates, excellent damping and barrier properties, thermal stability and also high chemical and solvent resistance [23]. Kim et al. recently reported desiccant-filled linear PIB edge sealant for organic electronics. But the sealant has to be dissolved in a solvent before applying on organic electronics. Furthermore, the sealant is susceptible to damage caused by the harsh environment, as it is not self-healing [24]. Recently, Banerjee *et. al.* has reported a PIB-based self-healing polymer based on reversible [2+2] cycloaddition of coumarin [25] demonstrating light-induced self-healing properties, but the device stability is not studied.

Herein, we demonstrate the use of a new class of UV curable “solventless” PIB-based self-healing sealant from coumarin functionalized tri-arm star PIB to improve the stability of OPVs under environmental conditions. These sealants are compatible to R2R printing [26,27] for fabrication of stable and flexible OPVs for commercial applications. We also studied the impact of the molecular weight of PIB on the gas permeability and hence device stability.

2. Experimental detail

2.1. Synthesis of UV curable Tri-arm Star PIBs

Coumarin functionalized tri-arm star PIBs (PIB-MUMB)₃ with number average molecular weight (M_n) = 2000 g mol⁻¹ [(PIB-MUMB)₃-2k], 5000 g mol⁻¹ [(PIB-MUMB)₃-5k] and 10000 g mol⁻¹ [(PIB-MUMB)₃-10k] were synthesized (Scheme S1 in the Supporting Information) following a procedure reported earlier [25]. Table S1 and Figure S1 depict the molecular characterization data and SEC chromatograms of the (PIB-MUMB)₃ samples, respectively. ¹H NMR spectrum of a representative (PIB-MUMB)₃-2k sample (see SI Figure S2) revealed the characteristic peaks of coumarin moiety at 2.39 and at 6.82 and 7.48 ppm (for -OCOCH- and for aromatic signals) suggesting efficient functionalization of PIB.

2.2. Device fabrication

Poly[3-hexylthiophene-2,5-diyl] (P3HT) (M_w = 36 kDa, rr = 96%, D = 2.7) from Rieke Metals, Inc. and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) from Nano-C Inc. were used as received for the fabrication of bulk hetero-junction (BHJ) polymer solar cell for this stability study. Devices were fabricated following a standard protocol reported in the literature [28]. A hole-transporting buffer layer, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was spin coated at 3000 r.p.m. for 35 second on pre-cleaned Indium tin oxide (ITO) substrates. A P3HT/PCBM blend (1:1 by weight) from chlorobenzene (20 mg mL⁻¹ concentration) was spin coated on a PEDOT:PSS coated ITO substrates at 1000 r.p.m. for 60 second. As cast samples were then annealed under chlorobenzene solvent vapour (solvent assisted annealing) for 5 minutes in air. Polymer film was removed from the edges of the substrate to prevent oxygen and moisture

penetration through the active layer after encapsulation as shown in Figure 1. A thin layer of Ca (5 nm) at $0.5 \text{ \AA s}^{-1}$ followed by a thick layer of Al (100 nm) at $3 \text{ \AA s}^{-1}$ was deposited thermally in a physical vapour deposition chamber attached to a N_2 filled glove box at a chamber pressure of 1×10^{-6} mbar. Devices were then encapsulated with the polymers by drop coating onto the substrates inside a glove box and kept in vacuum for 10 minutes for degassing (Figure 1). Encapsulated devices were then exposed to 365 nm UV light ($\sim 3 \text{ mW cm}^{-2}$) for 20 hours for photo-crosslinking in air. Device efficiency was studied periodically under AM1.5G solar simulator at 100 mW cm^{-2} light intensity and stored in ambient conditions over 20 days.

3. Results and discussion

3.1. Photo-crosslinking of Tri-arm Star PIBs

Coumarin functionalized tri-arm star PIB was used as the base material to develop the sealant. Photoreversible dimerization of coumarin led to self-healing property of the network, as described in our earlier publication [25]. UV light ($\lambda_{\text{max}} = 365 \text{ nm}$) induced crosslinking ability of the of coumarin functionalized tri-arm star (PIB-MUMB)₃-2k, (PIB-MUMB)₃-5k and (PIB-MUMB)₃-10k samples was measured by UV-vis spectroscopy (see Supporting Information for the detailed procedure). The cross-linking percentage of the polymer (%D) (Figure S3) was estimated from the A_{320} value using the following equation

$$\%D = [\{ (A_{320})_o - (A_{320})_t \} / (A_{320})_o] \times 100 \dots \dots \dots (1)$$

where, $(A_{320})_o$ and $(A_{320})_t$ are the absorbance of polymers at 320 nm before and after irradiation for t min respectively [25]. Low molecular weight (PIB-MUMB)₃-2k exhibited

highest crosslinking compared to the higher molecular weight PIB-MUMB)₃-5k and (PIB-MUMB)₃-10k. This is probably due to the easy availability of the coumarin end groups in case of 2k polymer compared to 5k and 10k polymer.

3.2. *Device stability*

To test the efficacy of PIB as an encapsulant, we chose P3HT/PCBM system as it has been widely studied and serves as a bench mark system [29]. We have chosen calcium as cathode electrode to study the degradation caused by the oxygen and moisture diffusion through the polymers and aluminium electrodes. As calcium is more prone to oxidation in ambient condition compared to the active polymer materials, any penetration of oxygen or moisture will lead to rapid degradation of the device leading to lower PCEs. We have used three different molecular weight polymers (PIB-MUMB)₃-2k, (PIB-MUMB)₃-5k and (PIB-MUMB)₃-10k) for this study. Initially it was important to show that these UV-curable polymers do not damage (physically and/or chemically) the active layers and electrodes. Again, UV illumination during the photo-crosslinking [25] of the polymer does not adversely affect the active layer materials. From Figure 2 only 5% drop in efficiency is observed from ‘as prepared’ device to ‘encapsulated’ device. PIBs before photo-crosslinking and after photo-crosslinking in air are shown In Fig. 3a. P3HT/PCBM solar cells having Ca-Al cathode electrode with no encapsulation (reference cell) degrades to 10% of its maximum efficiency within two days whereas encapsulated devices retain their efficiency up to 85% even after 20 days as shown in Figure 3b (also see SI Figure S4a). Slight drop in efficiency is mostly from the reduced short circuit current density (J_{sc}) as shown in Figure 4, whereas open circuit voltage (V_{oc}) and device fill factor (FF) remain unaffected as shown in Figure 5a & 5b. A stable efficiency of 1.3% is extrapolated from

the exponential fit to the efficiency curve for (PIB-MUMB)₃-2k and (PIB-MUMB)₃-5k polymer sealant (see in SI Figure S5). Device parameters such as series resistance (R_S) and recombination or shunt resistance (R_{SH}) are plotted in Figure 5c & 5d. Slight increase in R_{SH} is observed for (PIB-MUMB)₃-2k and (PIB-MUMB)₃-5k polymers. This result is counterintuitive as we expect to see more recombination losses due to chemical/morphological degradation of the active layer of the BHJ-OPVs. Therefore we argue that the chemical/morphological degradation of BHJ-OPVs is negligible compare to the degradation of the cathode electrode when the devices are encapsulated with low molecular weight (PIB-MUMB)₃. We observed that the device active area decreases (see in SI Fig S4b) as the major degradation is due to the oxidation of cathode electrode that hinders the charge transfer process at the polymer/cathode interface. However efficiency drop is more pronounced for a device encapsulated high molecular weight polymer, (PIB-MUMB)₃-10k. The increase in series resistance (R_S) and decrease in shunt resistance (R_{SH}) result in decreasing fill factor (FF) as shown in Fig. 5b. This observation indicates the chemical/morphological degradation of the active layer itself. Therefore the overall device – encapsulated with high molecular weight polymer sealant – performance decreases more rapidly than the devices encapsulated with low molecular weight (PIB-MUMB)₃ polymers. Microscopic images reveal the oxidation of Ca electrode at polymer/cathode interface reducing the effective active area of the devices. This could be due to oxygen and moisture present in the film during device fabrication (spin coating of PEDOT:PSS and active layer in air) and encapsulation. Oxygen and moisture can also diffuse through sealant or through the exposed Ca/Al electrode. Further device engineering is thus needed to improve the overall device stability. During UV induced

crosslinking study we observed that the percentage cross-linking for high molecular weight polymer is lower than the low molecular weight polymer (see SI Figure S3). These high molecular weight polymers ((PIB-MUMB)3-5k and (PIB-MUMB)3-10k) provides lower device stability compared to the low molecular weight (PIB-MUMB)3-2k (Figure 3).

4. Conclusions

In summary, we have demonstrated that PIB-based cross-linked self-healing polymer network can be used as an encapsulant for fabrication of fully printable and flexible solar cells. Devices are stable over twenty days in ambient. Observed degradation is due to partially from the diffusion of oxygen and moisture through the exposed Al electrode. Low molecular weight polymers show better stability due to higher percentage of crosslinking during photo-dimerization compared to high molecular weight polymers.

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Appendix A. Supplementary data.

Additional analytical analysis including spectral data. This material may be found in the online version of this article.

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Figure Captions

Figure 1. Schematic diagram of an encapsulated polymer solar cell.

Figure 2. P3HT/PCBM BHJ solar cell light J-V characteristics before and after encapsulation with PIB-based polymer sealant and photo-crosslinking under 365 nm UV lamp inside a glove box. Measurements were carried out under AM1.5G solar simulator at 100 mW cm⁻² light intensity.

Figure 3. (a) Encapsulated device before and after photo-crosslinking. (b) Device stability in air. Error was calculated based on 4 devices data from the same substrate.

Figure 4. Device short circuit current density (J_{SC}) as a function of device exposure time. Each data point on the graph represents an average value over four devices from the same batch. Error bars represent the deviation from the average value.

Figure 5. Device performance parameters as a function of exposure time. (a) V_{OC} (b) FF (c) R_S and (d) R_{SH} . Each data point represents average value over four devices while error bars represent deviation from the average value recorded for each devices. Black dotted lines are guide to the eyes and blue dotted lines represent the deviation from the expected values.

Figure 1. Schematic diagram of an encapsulated polymer solar cell.

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Graphical abstract

Self-Healing Polymer Sealant for Encapsulating Flexible Solar Cells

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PIB-based polymer sealant materials have been successfully coated on polymer photovoltaic devices to improve the environmental stability. Low molecular weight polymer shows higher percentage of crosslinking and hence better stability.