Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

Enhanced lifetime of organic photovoltaic diodes utilizing a ternary blend including an insulating polymer

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ARTICLE INFO

ABSTRACT

We report on the lifetime of unencapsulated organic photovoltaic diodes (OPVs) based on a ternary blend of poly(3-hexylthiophene) (P3HT), phenyl-C_{61}-butyric acid methyl ester (PCBM) and a soft insulating polymer, poly(methyl methacrylate) (PMMA) as compared to reference binary P3HT:PCBM OPVs. The performance of ternary devices was shown to decay more slowly than that of their binary counterparts to an extent that depends on the relative humidity (RH). The power conversion efficiency of ternary OPVs when stored in a low humidity environment (1% RH) decayed to 80% of their initial value after 200 h, almost double that of the reference binary OPVs. AFM measurements suggest that the PMMA forms pillars within the P3HT:PCBM matrix. It is proposed that the PMMA absorbs water in the active layer, and in doing so, slows the rate of deep trap formation that would otherwise lead to enhanced Shockley-Read-Hall recombination.

1. Introduction

Organic photovoltaic diodes (OPVs) are a promising technology that has attracted considerable interest because of the possibility of fabricating large area, flexible, low-cost and lightweight devices [1–3]. However, the lifetime of OPVs is a key factor hindering commercialization [4,5]. Although the lifetime of poly(3-hexylthiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM) devices can be up to 1000 h [6], this still represents significantly worse performance than, for example, inorganic silicon photovoltaics, which have a lifetime approaching 25 years [7]. The degradation mechanisms in OPVs are not fully understood [8] and a considerable effort is needed to improve their lifetime. OPVs degrade due to both chemical and physical processes. Chemical degradation may result from light [9], temperature [10], oxygen and water [11,12], with water and oxygen being considered the principal factors [4,12]. These molecular species can cause oxidation of the OPV materials [13] and electrodes [14], in turn leading to electronic traps [15] and low performance. The rate of degradation due to water increases with relative humidity (RH) [16]. Deterioration in performance can also result from changes in the bulk heterojunction (BHJ) morphology [5]. For example, several studies have showed that BHJ materials aggregate over time, thereby reducing exciton dissociation and hence short circuit current [2,17].

The use of insulating polymers as a third component in OPV blends has been suggested as a strategy to improve their lifetime [4]. This approach, whereby the 'active' organic semiconductor is blended with an inert insulating polymer, has been used in organic field effect transistors (OFETs), where it has been shown to increase lifetime with minimal effect on electronic properties [18,19]. For example, blending high-density polyethylene (HDPE) with P3HT in an OFET results in a lifetime of around four months in air, as compared to a reference P3HT OFET which lasted only a few hours [20]. Arias et al. [21] added poly(methyl methacrylate) (PMMA) to poly[5,50-bis(3-dodecyl-2-thienyl)-2,20-bithiophene] (PQT-12) OFETs and stored these devices in air. The thin film structures with PMMA had an improved lifetime of 48 h as compared to PQT-12 OFETs, which had a lifetime of only 20 h. Notwithstanding this initial success in the use of insulating polymers to improve the lifetime of OFETs, there are relatively few studies on the application of this technique in OPVs. Ferenczi et al. [18] showed that adding up to 50 wt% of HDPE or isotactic polystyrene (i-PS) to P3HT:PCBM OPVs had minimal detrimental effect on initial device performance. Indeed, Wu et al. [22] have demonstrated that adding PMMA to a P3HT:PCBM blend can actually improve the initial fill factor and open circuit voltage of the resulting OPV. This was suggested to be due to a reduced number of vacancies and leakage pathways.

In this paper, we investigate the use of PMMA as a ternary component in P3HT:PCBM OPVs as a means to reduce degradation and increase lifetime. The PMMA has been selected because it is readily available and compatible with the solvents used for P3HT:PCBM OPVs (dichlorobenzene in this study). The performance of ternary

P3HT:PCBM:PMMA OPVs is measured over time in a variety of ambient conditions and compared to reference P3HT:PCBM OPVs. It is found that adding PMMA to the OPV blend improves lifetime to an extent that depends on RH, with larger RH leading to smaller improvements in lifetime. Atomic force microscopy (AFM) and conductive AFM measurements suggest that the PMMA forms columnar features dotted within an otherwise largely P3HT:PCBM matrix. It is proposed that the PMMA absorbs ambient water vapor, and in doing so, reduces the rate of trap formation in the active OPV materials.

2. Experimental

Indium tin oxide (ITO) coated glass substrates were patterned into stripes by etching the substrates using zinc powder and hydrochloric acid. The patterned substrates were sonicated in Decon 90 solution (2% aqueous), deionized water, acetone and then with propanol-2-ol for 15 min each followed by drying with N_2 gas. The cleaned substrates were exposed to oxygen plasma (Yield Engineering Systems Inc., YES-R3) for 5 min with a radio frequency (RF) power of 100 W. The conductive polymer poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) PEDOT:PSS (CLEVIOS P VP AI 4083) was filtered using a 0.2 µm poly(tetrafluoroethylene) (PTFE) syringe filter and spun-cast onto the clean ITO surface at 2500 rpm for 45 s prior to annealing at 140 °C for 10 min in ambient atmosphere.

Solutions of regioregular P3HT (Rieke Metals, M_w=50–70 kg mol^{-1}) and PCBM (Lumtec, M_w=0.91 kg mol^{-1}) were prepared by dissolving each material in anhydrous 1,2-dichlorobenzene (DCB) separately, and mixing in a weight ratio of (1:1). In order to make a ternary blend solution, a PMMA (M_w=97 kg mol^{-1}) solution was first prepared by dissolving in DCB and stirring for two days in a N_2 glovebox to achieve a clear solution. The P3HT:PCBM (1:1) solution was stirred for 3 h before 14 wt% of PMMA was added to achieve a solution with a concentration of 35 mg ml^{-1}. Both binary and ternary OPV blends were stirred for 24 h before spin-coating onto PEDOT:PSS films at 1000 rpm for 1 min. The active layers were kept under high vacuum for around 24 h prior to the deposition of 150 nm of Al through a shadow mask to result in 4 separate OPVs per substrate. Devices were annealed at 120 °C for 10 min in the glovebox prior to lifetime tests.

The performance of the OPVs was determined by using a Keithley 2400 SourceMeter, both in the dark and under AM 1.5 illumination from a solar simulator (Oriel Sol1A 94021 A). All solar simulator measurements used a mask to restrict illumination to an active area of 0.79 mm^2. Each set of experiments involved measurements on 20 nominally identical OPVs to ensure reliable statistics. Only the results from representative average devices are shown here. The devices were stored in a dark environment with ambient air at different humidities. An environmental chamber was used to provide high humidity (85%, 65% RH), while low humidity (1% RH) was achieved by storing devices in a desiccator containing silica gel. These are compared to a standard ambient (50% RH). In all cases, the RH was measured over the course of the aging process with a humidity sensor.

Conductive atomic force microscopy (C-AFM) was used to measure the distribution of conductivity in the active layer. The measurement was performed in a clean room environment using a Dimension 3100 microscope and Nanoscope IVa controller (Bruker). Gold–coated (with a Cr adhesion layer) contact − mode AFM probes (Budget Sensors ContGB-G, nominal spring constant=0.2 N m^{-1}) were used for all measurements under a forward bias of 1 V. The height and current images were taken simultaneously.

3. Results and discussion

Fig. 1 illustrates the effect of humidity on the power conversion efficiency (PCE) of the binary P3HT:PCBM and ternary P3HT:PCBM:PMMA OPVs, hereafter referred to as binary and ternary OPVs, respectively. It is clear that the rate of degradation increases with humidity. The PCE of both sets of devices is negligible or nil after 300 h of being stored at 50% RH, while at 1% RH, both sets of devices still show measurable performance after 800 h. Table 1 lists the lifetime of the cells at different humidity levels. Here, we quantify lifetime of the devices by T_{80} and T_{20}, which represent the time the device takes to degrade to 80% and 20% of its initial efficiency, respectively. Given that both sets of devices were stored in an environment with ambient oxygen, these data agree with previous findings that the principal degradation mechanism in P3HT:PCBM OPVs under normal operating conditions (i.e. ~40–50% RH) involves interaction with water [16,23]. However, we note that the quantitative relationship between RH and lifetime (i.e. T_{80}) shown in Table 1 is non-linear for both binary and ternary OPVs. This may indicate that the lifetime of OPVs is determined by a variety of mechanisms, only some of which involve water. We speculate that the lifetime of OPVs at 1% RH is only partly limited by water-based degradation, and that we may be probing a regime in which oxygen-based degradation is more prominent. Devices stored in dry N_2 show no measurable drop in PCE after more than 1400 h of aging, as illustrated in Fig. SI1 (see
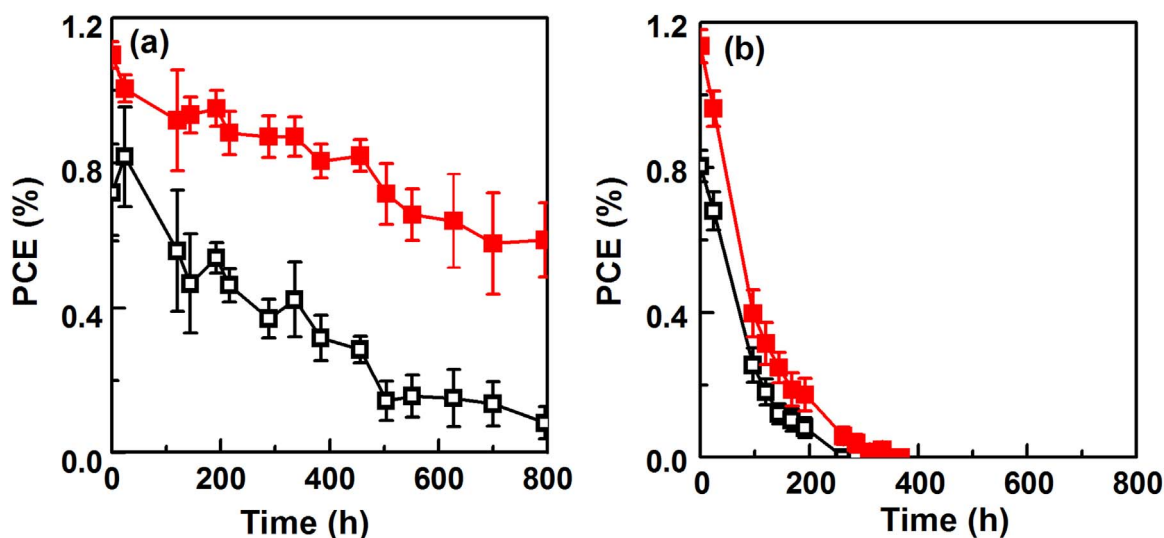

Fig. 1. Power conversion efficiency (PCE) as a function of time for P3HT:PCBM (1:1) blend, (open diamonds), and ternary (1:1:0.3) P3HT:PCBM:PMMA blend, (closed diamonds), stored at relative humidity levels of (a) 1% and (b) 50%.