Photo-degradation in air of spin-coated PC$_{60}$BM and PC$_{70}$BM films

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ABSTRACT

The fullerene derivatives PC$_{60}$BM and PC$_{70}$BM are widely used as electron accepting components in the active layer of polymer solar cells. Here we compare their photochemical stability by exposing thin films of PC$_{60}$BM and PC$_{70}$BM to simulated sunlight in ambient air for up to 47 h, and study changes in their UV–vis and FT-IR spectra. We quantify the photo-degradation by tracking the development of oxidation products in the transmission FT-IR spectra. Results indicate that PC$_{60}$BM photodegrades faster than PC$_{70}$BM. The rate of photo-oxidation of the thin films is dependent on the rate of oxygen diffusion in to the film and on the photo-oxidation rate of a single molecule. Both factors are dependent on the nature of the fullerene cage. The faster photo-oxidation of PC$_{60}$BM than of PC$_{70}$BM is in agreement with its slightly lower density and its higher reactivity. The use of PC$_{70}$BM in solar cells is advantageous not only because of its absorption spectrum, but also because of its higher stability.

1. Introduction

Polymer solar cells (PSC), consisting of a thin photoactive layer sandwiched between an anode and a cathode, offer an inexpensive way for converting light to electrical energy. They are versatile devices due to their light weight, mechanical flexibility, and low-cost processing [1,2]. While record power conversion efficiencies have passed the limit of 10% [3–5], the operational lifetime of PSC devices needs to be improved before the technology is commercially viable for large energy-harvesting applications.

The limited operational lifetime has been assigned to degradation processes in the different device components, such as electrode material degradation, chemical and morphological changes in the active layer [6]. Degradation can be initiated by heat, light, diffusion of oxygen and water vapor into the device, for instance through pinholes in the metal electrode, as well as the hygroscopic nature of the commonly used hole transporting material PEDOT:PSS [7–10]. Device encapsulation [11,12], inverted device architecture [13], and the use of more stable interfacial layers to replace PEDOT:PSS have all significantly improved solar cell stability. So far, record extrapolated lifetimes of 15 years, defined by the "T80" value, have been predicted for sealed PCDTBT:PC$_{60}$BM solar cells with 0.5 cm^2 device area, after a 1500 h burn-in period, by Roesch et al. [14].

Light-induced chemical changes are intrinsic for conjugated molecules, such as the conjugated polymer and the fullerene derivatives that together make up the active layer. These changes are particularly pronounced in the presence of oxygen. Beside the photo-oxidation of the donor polymer, which leads to decreased light absorption, so-called photo-bleaching [15,16], and decreased charge carrier mobility [17], it has also been shown that the fullerene-based electron-acceptor is highly susceptible to photo-oxidation [18,19].

The fullerene derivatives [6,6]-phenyl C61-butyric acid methyl ester (PC$_{60}$BM) and [6,6]-phenyl C71-butyric acid methyl ester (PC$_{70}$BM) are the most commonly used electron acceptor materials in PSC. The dependence of the photovoltaic performance of polymer:PCBM devices on the choice of fullerene electron acceptor is most commonly explained by differences in the fullerenes' contributions to light absorption or morphology differences. Indeed, fullerene derivatives PC$_{60}$BM and PC$_{70}$BM have rather similar energy levels, slightly different absorption in the 400–700 nm region (higher for PC$_{70}$BM than for PC$_{60}$BM) [20], and different solution properties, such as solubility in common chlorinated solvents (higher for PC$_{70}$BM than for PC$_{60}$BM) [21]. Not many arguments for an up-front choice for fullerene acceptor are mentioned in the literature, apart from absorption spectrum and price. In our study, we shed light on another difference that can affect this choice, namely their photochemical stability in air.

Chambon et al. [18] have reported on photo-oxidation experiments on PC$_{60}$BM and the parent C$_{60}$ molecules, observing the changes occurring in the carbonyl region of the FT-IR spectra when thin films were illuminated in air. They showed that PC$_{60}$BM significantly reduces the degradation kinetics of the polymer MDMO-PPV when the two are in a blend film. Reese et al. [17] have shown that PC$_{60}$BM slows down the photo-oxidation of poly (3-hexylthiophene) (P3HT) assigning this to the fullerene's role as oxygen scavenger, and Hansson et al. [22] have

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shown that $PC_{60}BM$ exhibits similar behavior when blended with thiophene-quinoxaline (TQ1) polymer. Speller et al. [23] have investigated the impact of nano-morphology on photo-chemistry and stability of $PC_{60}BM$ thin films exposed to simulated sunlight (AM1.5) and air. They showed that thin films of $PC_{60}BM$ dispersed in polystyrene are photo-degrading faster than neat $PC_{60}BM$ films by observing films' ultraviolet-visible (UV–vis) absorption spectra and attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra for different exposure times. They concluded that a lesser degree of aggregation of polystyrene-dispersed $PC_{60}BM$ leads to easier photo-oxidation of the fullerene derivative. Anselmo et al. [19] studied the effect of photo-oxidation of $PC_{60}BM$ and C_{60} when exposed to simulated sunlight (AM1.5) on the electronic structure by ultraviolet photoelectron spectroscopy (UPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. They showed that even a short exposure to ambient laboratory light affects the shape of the lowest unoccupied molecular orbit (LUMO) of $PC_{60}BM$ and that the photo-degradation in $PC_{60}BM$ is similar but faster than for C_{60}. In an attempt to identify possible oxidation products, Brumboiu et al. [24] conducted density functional theory (DFT) calculations of different geometric configurations (i.e. oxygen adsorption site on the fullerene cage) and corresponding X-ray photoelectron and NEXAFS spectra. Yamane et al. [25] performed matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry study on photo-oxidized $PC_{60}BM$ and established a reaction schematic for photo-oxidation, that resulted in $PC_{60}BM + O4$ being the most abundant product. Kettle et al. [26] studied the photo-oxidation products of $PC_{70}BM$ by means of C1s XPS and O1s XPS and noted a decrease of C−C feature and simultaneous increase of C−O and C=O components, attributing the observed changes to the breakage of the C_{70} cage and the oxidation of carbon atoms. Mateker et al. [27] studied the photochemical stability of commonly used active layer materials and found that it increases as the crystalline content and material density increase. Specifically, they have shown that both amorphous $PC_{60}BM$ and $PC_{70}BM$ are photochemically less stable than their respective crystalline counterparts and photo-bleach four times faster, most likely due to geometric constraints in the molecular packing of ordered films.

Several comparative studies on parent molecules C_{60} and C_{70} have been reported. Cox et al. [28] have characterized thin C_{60} and C_{70} films by UV–vis absorption spectroscopy, Fourier Transform Infrared (FT-IR) spectroscopy, cyclic voltammetry and electric spin resonance. Eklund et al. [29] studied the photochemical transformation of C_{60} and C_{70} films in inert He atmosphere and in O_2 via UV–vis, FT-IR and Raman spectroscopy and found that UV–vis light exposure in O_2 can photochemically assist the diffusion of oxygen into the films. In a comparative study of the reaction of C_{60} and C_{70} with molecular oxygen at atmospheric pressure in the absence of light, Wohlers et al. [30] concluded that the chemical reaction pathway for both fullerenes is the same, but with different rates which they attributed to the different curvatures of the fullerene cages, i.e. to the different deviation of sp^2 bond angles (C=C bonds) from the planar geometry. In a theoretical study on stability of carbon structures, Silva et al. [31] have shown that the angular deviation (curvature) from equilibrium sp^2 angles of graphene-like planar structure will enhance the oxidation of a given carbon-based molecule.

In this work, we determine the photo-oxidation rates of $PC_{60}BM$ and $PC_{70}BM$ by measuring the growth rates of oxidation products, as observed in FT-IR spectra. From these results we find that $PC_{60}BM$ photodegrades faster than $PC_{70}BM$ in air. We discuss possible explanations for the observed difference.

2. Materials and methods

2.1. Materials

$PC_{60}BM$ (purity > 99.5%) and $PC_{70}BM$ (purity > 99%) were purchased from Solenne B. V. (The Netherlands). Chlorobenzene (purity 99%) was purchased from BDH Lab Supplies (UK). 15 mg/ml $PC_{60}BM$ and $PC_{70}BM$ solutions in chlorobenzene were prepared under yellow light in a N_2-filled ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) glove-box (MB200MOD, M. Braun Intergas-Systeme GmbH, Germany). Thin films of $PC_{60}BM$ and $PC_{70}BM$ were spin-coated at 750 rpm for 100 s, inside the glove-box. For FT-IR spectroscopy, the films were prepared on KBr plates (Φ13 mm, 2 mm thick, Thermo Fisher Scientific (USA), used as received) and for UV–vis spectroscopy on quartz glass substrates (25.4 × 25.4 mm, 1 mm thick; Ted Pella Inc. (USA)). Prior to spin coating, the quartz glass substrates were cleaned in isopropanol in an ultrasonic bath for 60 min and UV-ozone treated for 20 min.

The photo-degradation of the samples was performed by exposing the thin films in air to simulated sunlight (AM 1.5) from a solar simulator (Sol2A, model 94022A, Oriel Instruments (USA)), intensity-calibrated by means of a silicon photodiode reference cell (model 91150V, Oriel Instruments).

2.2. Methods

Infrared spectra were recorded in transmission mode using a Nexus 470-FTIR spectrometer (Thermo Nicolet (USA)), working with OMNIC 6.0a software. The 2000–1000 cm^{-1} spectra were recorded using 50 scans and 4 cm^{-1} step size, while the carbonyl region between 1900–1650 cm^{-1} was recorded using 60 scans and 2 cm^{-1} step size. UV–vis absorption spectra were collected in transmission mode, range 200–800 nm and step size 1 nm, using a Cary 5000 UV–vis-NIR spectrophotometer (Agilent Technologies (USA)), equipped with Cary WinUV 6.1 software. Spectra were recorded for unexposed $PC_{60}BM$ and $PC_{70}BM$, and for cumulative exposure times of 15 min and 2, 10, 19, 30 and 47 h in air. All samples were exposed simultaneously.

3. Results and discussion

3.1. UV–vis

UV–vis absorption spectroscopy is frequently used to investigate the effects of photo-bleaching in conjugated polymers and polymer:fullerene blends and how the presence of fullerene affects the degradation rate of polymer within the blend. Here we used this method to observe the rate of changes in electronic structure of two fullerene derivatives.

Fig. 1 shows the UV–vis absorption spectra of $PC_{60}BM$ and $PC_{70}BM$ after different exposure times. In Fig. 1a, characteristic absorption bands in the UV region around 217 nm, 265 nm and 337 nm are observed for $PC_{60}BM$, in agreement with Zhang et al. [32]. On the long absorption tail throughout the visible region of the spectrum, an additional broad absorption band with slightly increased absorption in the 420–520 nm region can be observed. The first three bands decrease significantly and blue-shift with increasing exposure time to light and air. For example, the absorption band at 337 nm shifts to 332 nm, which corresponds to an energy shift of ~0.05 eV. This type of spectral changes can have two possible causes – photo-polymerization, as reported by Wang et al. [33] for C_{60} thin films in the absence of oxygen, and oxidation. We can rule out photo-polymerization in our study, since it is hindered in the presence of oxygen, as shown by Eklund et al. [34]. We can exclude the possibility of $PC_{60}BM$ dimerization also, due to the fact that we do not observe the appearance of a 320 nm absorption band which was reported by Distler et al. [35] for $PC_{60}BM$ photo-degraded in N_2 atmosphere. In Fig. 1b, UV–vis spectra of $PC_{70}BM$ show three bands around 217 nm, 245 nm and 380 nm. There is also a broad absorption feature, extending through most of the visible part of the spectrum (420–750 nm), which is larger than the corresponding absorption in $PC_{60}BM$. The main loss in absorption occurs in the UV part of the spectra, where the first three absorption bands of $PC_{60}BM$ decrease faster than the corresponding first three bands of $PC_{70}BM$. Additionally,