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Photo-degradation in air of spin-coated PC₆₀BM and PC₇₀BM films

Vanja Blazinic, *vanja.blazinic@kau.se*

Leif K.E. Ericsson, *leif.ericsson@kau.se*

Stela Andrea Muntean, *andrea.muntean@kau.se*

Ellen Moons (corresponding author), *ellen.moons@kau.se*

Department of Engineering and Physics, Karlstad University, 65188 Karlstad, Sweden

Abstract

The fullerene derivatives PC₆₀BM and PC₇₀BM 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 PC₆₀BM and PC₇₀BM to simulated sunlight in ambient air for up to 47 hours, 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 PC₆₀BM photodegrades faster than PC₇₀BM. 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 PC₆₀BM than of PC₇₀BM is in agreement with its slightly lower density and its higher reactivity. The use of PC₇₀BM in solar cells is advantageous not only because of its absorption spectrum, but also because of its higher stability.

Keywords: fullerene derivatives, photo-oxidation, UV-Vis spectroscopy, IR spectroscopy

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:PC₆₀BM solar cells with 0.5 cm² 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 (PC₆₀BM) and [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₀BM) 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 PC₆₀BM and PC₇₀BM have rather similar energy levels, slightly different absorption in the 400-700 nm region (higher for PC₇₀BM than for PC₆₀BM) [20], and different solution properties, such as solubility in common chlorinated solvents (higher for PC₇₀BM than for PC₆₀BM) [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 PC₆₀BM and the parent C₆₀ molecules, observing the changes occurring in the carbonyl region of the FT-IR spectra when thin films were illuminated in air. They showed that PC₆₀BM 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 PC₆₀BM 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 shown that PC₆₀BM 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 PC₆₀BM thin films exposed to simulated sunlight (AM1.5) and air. They showed that thin films of PC₆₀BM dispersed in polystyrene are photo-degrading faster than neat PC₆₀BM 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

PC₆₀BM leads to easier photo-oxidation of the fullerene derivative. Anselmo *et al* [19] studied the effect of photo-oxidation of PC₆₀BM and C₆₀ 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 PC₆₀BM and that the photo-degradation in PC₆₀BM is similar but faster than for C₆₀. 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 a matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry study on photo-oxidized PC₆₀BM and established a reaction schematic for photo-oxidation, that resulted in PC₆₀BM+O₄ being the most abundant product. Kettle *et al* [26] studied the photo-oxidation products of PC₇₀BM 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 C₇₀ 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 PC₆₀BM and PC₇₀BM are photo-chemically 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 C₆₀ and C₇₀ have been reported. Cox *et al* [28] have characterized thin C₆₀ and C₇₀ 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 C₆₀ and C₇₀ films in inert He atmosphere and in O₂ via UV-Vis, FT-IR and Raman spectroscopy and found that UV-visible

light exposure in O₂ can photo-chemically assist the diffusion of oxygen into the films. In a comparative study of the reaction of C₆₀ and C₇₀ 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 sp² 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 sp² 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 PC₆₀BM and PC₇₀BM by measuring the growth rates of oxidation products, as observed in FT-IR spectra. From these results we find that PC₆₀BM photodegrades faster than PC₇₀BM in air. We discuss possible explanations for the observed difference.

2. Materials and Methods

2.1 Materials

PC₆₀BM (purity > 99.5%) and PC₇₀BM (purity > 99%) were purchased from Solenne B. V. (The Netherlands). Chlorobenzene (purity 99%) was purchased from BDH Lab Supplies (UK). 15 mg/ml PC₆₀BM and PC₇₀BM solutions in chlorobenzene were prepared under yellow light in a N₂-filled (O₂ < 0.1 ppm, H₂O < 0.1 ppm) glove-box (MB200MOD, M. Braun Intergas-Systeme GmbH, Germany). Thin films of PC₆₀BM and PC₇₀BM 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 (25.4x25.4 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 PC₆₀BM and PC₇₀BM, and for cumulative exposure times of 15 minutes and 2, 10, 19, 30 and 47 hours 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 PC₆₀BM and PC₇₀BM after ~~for~~ different

exposure times. In Fig. 1a, characteristic absorption bands in the UV region around 217 nm, 265 nm and 337 nm are observed for PC₆₀BM, 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 C₆₀ 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 PC₆₀BM 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 PC₆₀BM photo-degraded in N₂ atmosphere. In Fig. 1b, UV-Vis spectra of PC₇₀BM 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 PC₆₀BM. The main loss in absorption occurs in the UV part of the spectra, where the first three absorption bands of PC₆₀BM decrease faster than the corresponding first three bands of PC₇₀BM. Additionally, a small decrease in absorption is observed in the visible part of the spectra, which is greater for PC₇₀BM than for PC₆₀BM. This observed decrease in absorption of PC₇₀BM in the visible spectrum is in agreement with results reported by Mateker *et al* [27].

Overall, UV-Vis spectra indicate that amorphous PC₆₀BM thin films are more affected by exposure to light and air than PC₇₀BM thin films for the same exposure times. To gain more insight on the light- and air-induced changes in the PC₆₀BM and PC₇₀BM thin films, we investigate these films by means of FT-IR.

3.2 FTIR

Fig. 2 shows the FT-IR spectra of unexposed PC₆₀BM and PC₇₀BM films in the 2000 cm⁻¹ – 1000 cm⁻¹ region. Both spectra show a high intensity band around 1737 cm⁻¹, assigned to the C=O stretch of the ester bond of the side-chain, and two bands at 1428 cm⁻¹ and 1249 cm⁻¹. The peaks around 1737 cm⁻¹ and 1249 cm⁻¹ are both of similar intensity in the two spectra. However, the spectra of the two fullerene derivatives differ significantly in peak intensities around 1428 cm⁻¹ and 1182 cm⁻¹. Both features are characteristic for the fullerene cages C₆₀ and C₇₀ [28,29,36]. The 1428 cm⁻¹ feature is much larger in the PC₇₀BM spectrum, while 1182 cm⁻¹ is somewhat larger in PC₆₀BM.

Fig. 3 shows the carbonyl region in the FT-IR spectra of PC₆₀BM and PC₇₀BM films in detail. After exposure of the films to light and ambient air, the characteristic peak around 1737 cm⁻¹ of the side-chain ester C=O bond does not significantly change in intensity. However, in both spectra two new features appear simultaneously: one at higher wavenumber than the ester peak, with its maximum at 1780 cm⁻¹, and one at lower wavenumber, which partly overlaps with the ester peak. By fitting the 1737 cm⁻¹ peak together with two broader Gaussian features on each side, the center of the lower wavenumber component is found at 1720 cm⁻¹. Both features grow as the exposure time increases. Our observations are in line with results reported by Chambon *et al* [18] and by Speller *et al* [23] upon photo-oxidation of PC₆₀BM in air, and by Dettinger *et al* upon photo-oxidation of PC₆₀BM in O₂ [37]. Two features, around 1785 cm⁻¹ and 1730 cm⁻¹, have also been reported by Wohlers *et al* [38] for thermally oxidized C₆₀ and C₇₀ thin films in the absence of light, as well as for photo-oxidation in air of the fullerene derivatives 1',4'-dihydro-naphtho[2',3':1,2][5,6]fullereneC₆₀ (ICMA) and 1',1'',4',4''-tetrahydro-di[1,4]methanonaphthaleno[1,2:2',3',56,60:2'',3''] [5,6]fullerene-C₆₀ (ICBA) by Yamane *et al* [39], thus indicating that our observed changes are occurring on the fullerene cage, regardless of how it is functionalized. Both the 1780 cm⁻¹ peak and the 1720 cm⁻¹ shoulder observed in this study can, in analogy with earlier assignments for C₆₀, be attributed either to the formation

of dicarbonyls or cyclic anhydrides on the fullerene cages [40–42].

Growing of the aforementioned features at the same position in the spectra of both PC₆₀BM and PC₇₀BM indicates that these fullerene derivatives have similar oxidation products. Different intensities indicate different rates of production. Already at a first inspection of spectra we see that the growth of both features is faster in PC₆₀BM (Fig. 3a) than in PC₇₀BM (Fig. 3b). We analyze in more detail the peak heights in the 1780 cm⁻¹ region of the FT-IR spectra, as shown in Fig. 4. We can see that after an initial strong increase, the peak intensities grow monotonously as a function of exposure time. The data points below 2 hours of exposure are less accurate due to lower signal-to-noise ratio. Without claiming to describe the actual photo-degradation process, we choose to use a power law as a guide to the eye for the 2-47 hours exposure time. The exponents obtained from this fitting for PC₆₀BM and PC₇₀BM are (0.8±0.1) and (0.7±0.1), respectively. This means that in the time window 2-47 hours PC₇₀BM degrades 10-15% slower than PC₆₀BM.

To understand the reasons for this difference in the photo-degradation rate between PC₆₀BM and PC₇₀BM we note that the shape of the molecules is different. This may imply both a difference in reactivity of the individual fullerenes with O₂ and a difference in packing of the molecules in the film. We discuss these two factors separately.

In their recent work, Silva *et al* [31] showed that the larger the angular deviation (curvature) from equilibrium sp² angles of graphene-like planar structure, the more prone to oxidation a given carbon-based molecule is. The spherical cage of PC₆₀BM has greater curvature compared to the ellipsoid cage of PC₇₀BM, thus making the former more susceptible to chemical reaction with an oxygen molecule. Due to the asymmetric structure of the C₇₀ cage, not all sites on the cage may be equally prone to oxidation. From their DFT calculations, Silva *et al* have shown that the (so-called) polar regions of C₇₀ cage are equally reactive to oxidation as the C₆₀ cage

as a whole [31], whereas the (so-called) equatorial regions of C₇₀ cage are less prone to oxidation. These calculations support our assumption that the difference in photo-oxidation rate, as observed by our UV-Vis and FT-IR results, can explain the different chemical reactivity due to curvature of individual fullerene molecules.

The different shape of molecules also implies difference in molecular packing in the thin films. The thin films in this study have not been annealed and are likely to be amorphous [43,44], i.e. random-close packed with fullerene derivative molecules, and thereby similarly structured as fullerene derivative domains in the active layer of a low temperature processed PSC. The shape of the fullerene cages, with PC₆₀BM being close to spherical and PC₇₀BM being ellipsoidal, could influence the random packing. It has been shown that the volume fraction in the case of random-close packing of spheres is ~0.64, while for ellipsoids it is in the range 0.64-0.74, depending on the aspect ratio [45]. Difference in the packing in thin films could contribute to the observed differences in photo-oxidation rate since smaller packing coefficient, i.e. larger free volume ratio, would allow easier diffusion of molecular oxygen into the thin film. Mateker *et al* [27] reported the same photo-bleaching rate of amorphous PC₆₀BM and PC₇₀BM thin films, despite the small difference in densities between the two (1.60 g/cm³ for PC₆₀BM, 1.63 g/cm³ for PC₇₀BM). This density difference (e.g. due to molecular packing difference between PC₆₀BM and PC₇₀BM thin films) is too small for the oxygen diffusion to account for 10-15% difference in growth of oxidation products that we observe in our FTIR results.

Therefore, we conclude that the dominant factor responsible for the observed difference of the oxidation products' growth rate is the difference in chemical reactivity of single molecules, which is due to the curvature of the individual fullerene derivatives.

4. Conclusions

We have studied the photo-oxidation in air of spin-coated amorphous thin films of PC₆₀BM and PC₇₀BM by UV-Vis and FT-IR spectroscopy. In the UV-region of the UV-Vis spectra, the absorption is more affected in PC₆₀BM than in PC₇₀BM, while a much weaker and opposite effect is observed in the visible region. UV-Vis measurements on PC₆₀BM and PC₇₀BM thin films indicate that amorphous thin films of PC₆₀BM are less stable than the ones of PC₇₀BM. The growth of new features in the carbonyl region with exposure time in both fullerene derivatives, as shown by FT-IR, shows that photo-oxidation occurs faster in PC₆₀BM than in PC₇₀BM thin films. We conclude that individual chemical reactivity of the molecules has a stronger influence on the photo-oxidation of PC₆₀BM and PC₇₀BM thin films than the materials' density and, subsequently, the oxygen diffusion.

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Figures

FIG. 1. UV-Vis spectra of spin-coated films of PC₆₀BM (a) and PC₇₀BM (b), unexposed and exposed to AM1.5 simulated sunlight in ambient air for a selection of different lengths of time. The UV region of PC₆₀BM is more affected than that of PC₇₀BM.

FIG. 2. FT-IR transmission spectra of spin-coated films of pristine PC₆₀BM (green) and PC₇₀BM (red). Insets represent the chemical structure of the fullerene derivatives. The fullerene derivatives are distinguished clearly by the difference in peaks at 1428 cm⁻¹ (stronger in PC₇₀BM) and 1182 cm⁻¹ (stronger in PC₆₀BM).

FIG. 3. The carbonyl region of the FT-IR transmission spectra of spin-coated films of PC₆₀BM (a) and PC₇₀BM (b), unexposed and exposed to AM1.5 simulated sunlight in ambient air for different lengths of time. Photo-oxidation products are developing faster in PC₆₀BM thin film than in PC₇₀BM thin film.

FIG. 4. Time development of 1780 cm⁻¹ peak of PC₆₀BM (green) and PC₇₀BM (red). Triangles represent the measured points and dotted (···) lines serve as a guide to the eye.