AFM Studies of Pristine PCBM Changes Under Light Exposure

Erin Chambers

Faculty of health, science, and technology
Department of engineering and physics

15 cr

Krister Svensson
Lars Johansson

28 March 2013
Abstract

Organic solar cells promise a cheap and easy alternative to silicon photovoltaics, but there are many problems that must be solved before they can be a stable and efficient substitute. One such problem is the degradation of solar cells under exposure to light and oxygen. In response to evidence of change in electronic properties of polymer:PCBM solar cells, the mechanical properties of pristine PCBM films are investigated for analogous development using atomic force microscopy. Although no significant change in the elastic modulus is detected, differences in material response indicate a skin effect which is beyond measurement sensitivity. Presence of a hard skin is verified in tapping phase imaging and spectroscopy.

1 Introduction

Organic photovoltaic devices constitute a field of intense research in materials science. Though polymer solar cells have many advantages over existing silicon solar cell technology, namely reduced cost and increased ease of production, their use is plagued with many disadvantages. The most major of these are the low power conversion efficiencies in comparison to inorganic solar cells (the best results giving 5%) and short lifetime due to degradation under light exposure [1]. Investigation into these problems is essential in creating a commercially viable organic solar cell. Previous research into poly(3-hexylthiophene)(P3HT):[6,6]-phenyl-C_{61}-butyric acid methyl ester(PCBM) solar cells has demonstrated a dependence of the efficiency on
given mechanical properties of the cell. Notably, as the elastic modulus of the blended film is increased, the efficiency decreases [2]. The electronic properties of pure PCBM films has also been demonstrated to change in response to as little as thirty minutes of light exposure [3].

In this paper, the possibility of changes to mechanical properties of pristine PCBM films in response to light exposure is investigated by atomic force microscopy measurements of the elastic modulus. While no change is able to be detected, the measurements suggest the formation of a thin hard skin on the film surface, which is verified by tapping mode images and point spectroscopy.

2 Theory

2.1 Hertz Theory

The simplest of models used in indentation studies of elastic moduli results from Heinrich Hertz’s 1881 work on the problem of colliding elastic spheres [4]. In this model, spheres which would only touch at a single point exert forces on each other which increase the area of contact to a circle of radius \( a \) and bring the spheres’ centers together by the indentation depth \( \delta \), as indicated in Figure 1. The Hertz model assumes that the spheres are homogeneous and isotropic, that strains are small \((a < R_t \text{ and } a < R_s)\), that adhesion and friction are not present, and that the force is applied along the axis of contact symmetry [5].

![Figure 1: Variables in Hertz’s model of colliding spheres.](image-url)
Under these constraints, the force as a function of indentation depth is given by the following:

\[ F = \frac{4}{3} E^* R^{1/2} \delta^{3/2} \]  

(1)

\( R \) is the relative curvature, which is the inverse sum of the radii of both spheres:

\[ \frac{1}{R} = \frac{1}{R_t} + \frac{1}{R_s} \]  

(2)

\( E^* \) is the relative elastic modulus of the spheres given by:

\[ \frac{1}{E^*} = \frac{1 - \nu_t^2}{E_t} + \frac{1 - \nu_s^2}{E_s} \]  

(3)

\( \nu \) and \( E \) are Poisson’s ratio and the elastic modulus for each material. Under the conditions of this experiment, the Hertz model can be simplified further. For a silicon cantilever tip on a soft polymer surface such as PCBM, \( E_t \gg E_s \). The surface can be considered an infinite plane. Therefore, \( E_t \) and \( R_s \) approach infinity, and the force equation becomes dependent only upon the elastic modulus and Poisson’s ratio of the sample, the tip radius, and indentation depth:

\[ F = \frac{4}{3} \frac{E_s}{1 - \nu^2} R_t^{1/2} \delta^{3/2} \]  

(4)

### 2.2 Sneddon Theory

Ian Sneddon extended Hertz theory to include the interaction of conical and flat-ended cylindrical tips with planes of infinite thickness [6][7]. Assumptions made for Hertz theory also apply to Sneddon theory.

#### 2.2.1 Conical Indenter

The force versus indentation depth for a conical indenter is given by [6]. The relevant variables are defined in Figure 2. Applying the same considerations as for the Hertz model, it becomes:

\[ F = \frac{2E_s \tan \alpha}{\pi (1 - \nu^2)} \delta^2 \]  

(5)
2.2.2 Cylindrical Indenter

The force versus indentation depth for a cylindrical indenter is given by [7]. The relevant variables are defined in Figure 3. Applying the same considerations as for the Hertz model, it becomes:

\[ F = \frac{2E_s R \delta}{1 - \nu^2} \]  

(6)

2.3 Application to Experiment

Each theoretical model covered here reflects a slightly different tip-sample interaction. The Hertz indenting spheres portray the smallest total deformation of the surface. The Sneddon cone instead implies a deeper penetration into the material, and the Sneddon cylinder indicates a lack of penetration. It was found that the Hertz model fits best for short indentation depths and the Sneddon cylindrical model dominates in the long range.
3 Experimental

3.1 Introduction to the Instrument

The primary apparatus used in this experiment was the Veeco Innova atomic force microscope. By measuring the interaction between a sample and a sharp tip, force microscopy is accurate to forces much smaller than the forces between atoms in a lattice, offering the possibility of true atomic precision measurement. Detection of the force is accomplished using multiple methods. The Veeco Innova uses a beam-deflection setup (Figure 4). In this method, a four-segmented photodiode is used to detect changes in the deflection of a laser from the surface of a cantilever, attaining a signal limited only by the thermal noise of the cantilever [8].

![Figure 4: Schematic of the beam deflection method of force detection.](image)

Measurements were made in both contact and tapping modes. In contact mode, the cantilever is held fixed, and deflections from that position due to changes in the tip-sample interaction are detected by the photodiode and translated into sample topography. This type of measurement, while easy to understand, must be taken with care to avoid altering the sample during a scan. A major example of alteration via contact scanning is shown in Figure 5. In tapping mode, the cantilever is made to oscillate at its natural frequency. In a more complex process, changes in oscillation amplitude and tapping phase are used to map the sample.
3.2 Force Calibration

As measurements of the surface are detected as voltage changes in the photodiode in response to cantilever deflection, significant measures must be taken to calibrate for a measurement of force. In particular, the spring constant of the cantilever must be experimentally determined. There are multiple approaches to calibration of AFM cantilever spring constants, investigated in [9], [10], [11], and many others. In this experiment, the cantilever-on-cantilever method was used. In this method, a cantilever with unknown spring constant $k_u$ is used to push against a reference cantilever with known constant $k_k$. The total displacement $z$ of the AFM is the sum of individual cantilever deflections $s_u$ and $s_k$, where $s_k$ is the measured deflection (Figure 6). From Newton’s third law, the forces exerted by the cantilevers on each other are equal in magnitude, so by plotting $s_u$ versus $(z - s_u)$, an expression for $k_u$ is attained in terms of the slope $m$ and $k_k$.

$$(z - s_u)k_k = s_u k_u \Rightarrow k_u = \frac{k_k}{m}$$

(7)
Figure 6: Schematic of variables in the cantilever-on-cantilever method of spring constant calibration.

For a dependable measurement, the unknown cantilever was used to push at multiple points along the known cantilever length. Using the known spring constant and the geometric equation for the spring constant of a rectangular cantilever, the spring constant for several points along the reference cantilever was calculated. These values are tabulated in Figure 7, along with images for a select few positions.

Figure 7: (a) (b) (c) Position images for points three, five, and seven, respectively. (d) Table of positions, calculated reference spring constants, and experimentally found unknown cantilever constants.

Olympus Standard Silicon tapping mode cantilevers used in this experiment have a nominal spring constant of 26 N/m and resonance frequency
of 300 kHz. As the cantilever-on-cantilever method is time-consuming, the decision was made to use it for the first two cantilevers and plot the relation between the spring constant and the actual resonance frequency of cantilever, which was easily determined with the AFM apparatus. This relation was assumed to be linear. All further cantilevers were calibrated using this relation. The graph and fit are displayed in Figure 8.

![Graph showing Cantilever spring constant vs cantilever resonance frequency.](image)

Figure 8: Cantilever spring constant vs cantilever resonance frequency.

### 3.3 Tip Characterization

As all theoretical models used to analyze the tip-surface interaction are highly dependent on the geometry of the probing tip, significant importance was placed on precise characterization of the cantilever tip. Olympus Standard Silicon Cantilevers are rated at a nominal tip radius of 7 nm. Being tetrahedral, there is no nominal value of cone angle. Additionally, interaction with the sample can change both radius and cone angle, notably by picking up particles. To ameliorate this, tips were periodically used to run a tapping mode scan of a Porous Aluminium PA01 Ultrasharp Cantilevers & Gratings sample. The sample topology data was transferred into the SPIP 5.1.5 software, where an in-built tip characterization procedure was used to find radii and cone angles for the tip’s x- and y-axes. One such tip characterization is shown in Figure 9.
Figure 9: The output of SPIP 5.1.5 Tip Characterization algorithm is dependent upon a provided tapping mode image shown in the Main Window. The scanning sample is required to have extremely fine texture for the software to render correct radii for extremely sharp tips like the one in this image.

3.4 Sample Preparation

The samples studied in this work were produced by dissolving PCBM in chloroform at a ratio of 20 mg/ml and heating at 60°C for 20 minutes before spin-coating on silicon. All preparation was done in darkness, and samples were covered in aluminium foil when not in use.
4 Results and Discussion

4.1 Elastic Modulus of Pristine Samples

Figure 10: Values for elastic modulus of pristine PCBM, taken in darkness and analyzed in the small $\delta$ (Hertz) and large $\delta$ (Sneddon, cylindrical indenter) regimes.

<table>
<thead>
<tr>
<th>Hertz S1</th>
<th>Cylinder S1</th>
<th>Hertz S2</th>
<th>Cylinder S2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>4.5</td>
<td>2.6</td>
<td>1.7</td>
</tr>
<tr>
<td>2.9</td>
<td>4.6</td>
<td>2.5</td>
<td>1.7</td>
</tr>
<tr>
<td>3.0</td>
<td>4.0</td>
<td>2.5</td>
<td>1.7</td>
</tr>
<tr>
<td>2.8</td>
<td>4.2</td>
<td>2.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The first objective of this work was to determine by AFM the elastic modulus of pure PCBM. This was done under darkness for samples one and two, and the result are summarized in Figure 10. For sample one, this gave an average result of $E = 3.0$ GPa (Hertz) and $E = 4.3$ GPa (Sneddon, cylinder); for sample two, it gave $E = 2.6$ GPa (Hertz) and $E = 1.7$ GPa (Sneddon, cylinder). These are in good agreement with the value published by Awartani et al [12]. The error is dominated by systematic error in the cantilever force measurements of up to twenty percent.
4.2 Development Under Light Exposure

![Graph: Elastic Modulus vs Illumination Time](image)

Figure 11: Time evolution of the elastic modulus exhibits no statistically significant change, even up to twenty hours of illumination.

Following the measurements of the pristine unlit PCBM, the sample was illuminated to 0.5, 1, 3, 5, 10, and 20 total hours using a solar simulator. Data was taken and the elastic modulus was calculated for each interval. As seen in Figure 11, changes in the elastic modulus were found to be negligible.
Figure 12: (a) The force vs depth profile of an unlit sample shows distinct nonlinear behavior for small indentations. (b) After 20 hours of illumination, the nonlinear zone has virtually disappeared, indicating that Hertz is no longer applicable.

However, changes in the force versus indentation depth behavior of the sample at small $\delta$ during spectroscopic measurements indicated possibility of a surface effect on the sample that measurements were not sensitive enough to detect. After exposure to light, the curvature in the Hertz regime becomes linear. An example is shown in Figure 12. To investigate this, sample one was frozen in liquid nitrogen and then cracked for the purpose of making a cross-sectional scan in tapping mode. This scan, shown in Figure 13 along with a height profile, spanned the entire depth of the PCBM film, including sharp lines where it met the silicon substrate and the void. As expected, bordering the void was a bright surface layer of hardened PCBM on top of a darker layer of unexposed film.
Figure 13: (a) Broken sample 1, mounted upright on side for cross-section imaging. Photo was taken after measurements were completed. (b) Height image from tapping mode scan. Drastic falloff in lower right quadrant constitutes tip imaging from moving off the edge of the sample. (c) Phase image from tapping mode scan. Silicon and a hard skin sandwich a softer layer of unexposed PCBM. Dots indicate points where spectroscopy data was taken.
Point spectroscopy was performed on each layer, shown in Figure 14. As the tapping phase image contrast is dependent on designated voltage setpoint, this served to quantify the differences in phase between the silicon substrate and exposed and unexposed PCBM. The unexposed layer is shown to behave much differently than the surface layer, which closely resembles silicon.

![Phase vs Position](image)

Figure 14: Point spectroscopy at different points shows a distinct shift towards Si behavior at the surface of the PCBM sample.

5 Conclusions

In this experiment, the Veeco Innova atomic force microscope was used to study the mechanical properties of pristine films of [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM). In particular, changes undergone by the elastic modulus as the film was exposed to illumination were followed. Efforts to capture a time evolution of the elastic modulus were thought to be unsuccess-
ful due to the creation of a hard skin that could not be probed, and tapping phase imaging and spectroscopy of a broken and side-mounted sample cross-section verify the presence of a surface layer of modified PCBM shown to behave similarly to silicon in energy dissipation.

This research could be continued using AFM to investigate how the adhesion between tip and sample changes with illumination and hard skin formation. Otherwise, further studies would require a change to another technique, one with greater sensitivity to surface effects to achieve the hoped-for time evolution of the elastic modulus. Finally, one could test how dependent surface effects and stiffness are to different preparation methods, including heating times and solvent choice.

References


