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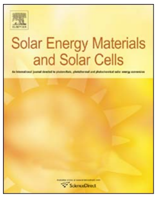

Effect of heat, UV radiation, and moisture on the decohesion kinetics of inverted organic solar cells

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ABSTRACT

Organic solar cells subjected to environmental stressors such as heat, moisture, and UV radiation can undergo significant mechanical degradation, leading to delamination of layers and device failure. This paper reports the effect these stressors have on the mechanical integrity of active layers and interfaces as measured by subcritical debonding tests, and the in situ evolution of defects and fracture processes is characterized. At elevated temperatures below 50 °C in inert conditions, significant device weakening was observed, an effect we attributed to a temperature-induced P3HT:PCBM delamination mechanism from the underlying ZnO. At 50 °C in ambient conditions with UV exposure—selected to better simulate real-world environments—devices were more resistant to fracture because of an interfacial strengthening effect from increased hydrogen bonding where UV-induced $Zn(OH)_2$ formation reinforced the interface with P3HT:PCBM. This photoinduced hydroxylation mechanism was determined from a decrease in the Zn/O ratio with increased UVA or UVB exposure, and hydroxylation was shown to directly correlate with the resistance to fracture in devices.

1. Introduction

Low-cost solar technologies such as organic photovoltaics are particularly susceptible to degradation from environmental stressors, limiting device stability and operational lifetimes to well below that of commercial silicon cells [1]. Although recent work has shown promise for improving the long-term reliability of organic photovoltaics with material design and encapsulation [2,3], thermomechanical degradation of the materials comprising solar cells and modules continues to be a ubiquitous challenge [4,5]. The synergistic contributions of mechanical, thermal, and chemical stresses, as well as ultraviolet (UV) radiation accelerate the evolution of internal defects—e.g., blistering, cracking, discoloration, and delamination—in devices [6–9]. These defects result in fracture processes leading to delamination either at the interfaces of adjacent device layers or cohesive fracture through a single layer, leading initially to decreasing performance through the loss of Ohmic contact—a pathway for accelerated diffusion of environmental species—and ultimately to device failure.

In organic semiconductors, the degradation of mechanical and electrical properties due to individual stressors has been well-characterized [10–14]. In particular, PEDOT:PSS has been shown to be highly sensitive to moisture-assisted decohesion, where water molecules react with strained hydrogen bonds and lead to weakening of the hygroscopic material [15]. However, the synergistic effects of these stressors on thermomechanical reliability is largely unknown. For example, the combined effect of UV light and heating on the kinetics of interface debonding or defect growth has never been directly characterized in any organic solar cell material. In this study, we characterized the synergistic effects of heat (up to 50 °C), UVA (315–400 nm) or UVB (280–315 nm) exposure, and inert (0% relative humidity in N_2) or ambient (45% relative humidity in air) atmospheric conditions on solution-processed organic solar cells. Our aim was to elucidate the mechanisms for degradation in devices subjected to stressors similar to the real-world conditions experienced when in service.

2. Background on subcritical debonding

In the absence of chemical or thermal stresses, crack growth through device layers does not occur below the critical fracture energy, G_c [16]. Real-world operational conditions are far from equilibrium, however, and solar cells are especially likely to endure environments

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where conditions are subject to rapid change. When debonding of device interfaces is initiated under these non-ideal conditions, molecular species (e.g., water) near the crack tip may break neighboring bonds, resulting in extension of the crack even if mechanical stresses on the device are below the critical fracture energy (i.e., $G < G_c$, where G is the amount of energy required for crack propagation in the presence of environmental species) [17]. This phenomenon refers to subcritical debonding, which has been characterized in a variety of thin-film device structures ranging from bulk glasses to microelectronic packages, and has recently been observed in organic photovoltaics [7,18–22].

Subcritical debonding measurements are useful in determining the effects of environmental stressors (e.g., moisture or heat) on the cohesion or adhesion of films [17]. The technique used for this work was similar to a double cantilever beam (DCB) experiment, which requires a test structure of the thin films of interest sandwiched between two beams (e.g., glass). On one end of the test structure, a uniaxial load is applied to each beam normal to the films. Unlike DCB testing, where displacement of the beams continues until the specimen undergoes critical fracture, subcritical testing halts the displacement immediately before critical fracture. The relaxation of the load over time is then monitored at a fixed displacement until the load becomes constant and crack growth ceases. The debond (or crack) growth rate, da/dt, is inferred directly from the change in load with time (see experimental details).

Plotting da/dt vs. G shows the behavior of the material system over a wide range of crack-growth rates, frequently spanning many orders of magnitude, from nearly 1 mm/s to below 1 Å/s. The crack-growth rate curve typically exhibits a sigmoidal shape with three distinct regimes of behavior corresponding to low, medium, and high growth rates (Fig. 1) [17,23,24]. At the beginning of the load-relaxation test, the crack-growth rate is high and approaches critical fracture, aligning closely with $G \approx G_c$. This initial crack propagation does not provide information about chemical reactions occurring at the crack tip. As the test progresses, a plateau is usually observed at medium growth rates (diffusion controlled), where the kinetics are controlled by the diffusion of reactive species to the crack tip [17]. At low growth rates (reaction controlled), a threshold value of G_{th} is eventually reached, indicating a limit in applied driving force below which no further crack extension is observed. This value is obtained as the load becomes constant, usually after several hours, and is an important metric with respect to material reliability because it indicates the level of resistance to fracture when a material is subjected to synergistic mechanical and environmental stresses.

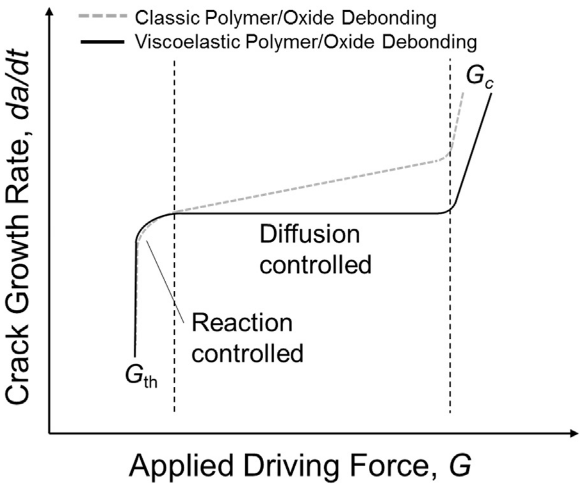

Fig. 1. Possible subcritical debond curves for an organic solar cell, showing three distinct regions based on the crack growth rate. The test is initiated near G_c at high growth rates and plateaus at medium growth rates where diffusion of reactive species to the crack tip controls the growth rate. Crack growth eventually ceases at the cohesive threshold, G_{th}. A decreasing slope in the diffusion controlled debonding region indicates viscoelastic behavior.

3. Experimental details

3.1. Solar cell preparation

Inverted polymer solar cell devices with an ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag architecture were fabricated on 30 mm × 30 mm square glass substrates. The details of the device preparation have been reported previously [25]. First, a 10 nm ZnO film was spun from a solution of zinc acetate dihydrate dissolved in 2-ethoxyethanol, ethanolamine, and ethanol onto an ITO-coated glass substrate (Kintec, Kowloon, Hong Kong). A 140 nm thick layer of P3HT:PCBM (2.5 wt%) was then deposited from a 1:1 wt% mixture of P3HT (Rieke Metals, Lincoln, USA) and [60]PCBM (Solenne B.V., Groningen, Netherlands) dissolved in ortho-dichlorobenzene. After deposition, all films were annealed at 130 °C for 10 min in an inert atmosphere. The devices were briefly exposed to O_2 plasma to improve wetting, and a 30 nm PEDOT:PSS layer was then deposited from a commercially available water-based dispersion (Clevios P VP Al 4083, Heraeus) prior to thermal evaporation of the 100 nm Ag electrode. Finally, the solar cells were encapsulated by bonding an identical glass substrate on top of the Ag electrode using a thin layer of epoxy, resulting in a square glass sandwich.

3.2. Decohesion testing

Double cantilever beam adhesion specimens 5 mm wide, 30 mm long, and 1.5 mm thick were diced from the encapsulated solar cells using a high-speed wafer saw with a resin blade. Rather than cutting entirely through the sandwich structure, trenches were cut on the top and bottom of the sandwich to prevent water from diffusing into the device structure and damaging the solar cell. These trenches were then easily cleaved, resulting in individual DCB specimens. The specimens were subsequently loaded into a thin-film cohesion testing system (Delaminator DTS, Menlo Park, CA) to create an initial crack of about 10 mm long as measured from the elastic compliance, $d\Delta/dP$, using the compliance relationship in Eq. (1): [26]

$$a = \left(\frac{d\Delta}{dP} * \frac{BE'h^3}{8}\right)^{1/3} - 0.\,64 * h \tag{1}$$

where a is the crack length, E' the plane strain elastic modulus of the substrates, B the specimen width, and h the specimen half-thickness.

The DTS system was placed in a glovebox purged with N_2 gas with an inert atmosphere of $O_2 < 1$ ppm and relative humidity (R.H) < 0.1% or into an environmental chamber at constant temperature of 50 °C (± 1 °C) and R.H. 45% (± 2%). In both cases, a series of in situ UV exposures were performed with UVA or UVB lamps with varying intensity, calibrated with a Stellar Net C-100 UV–Vis–NIR Spectrophotometer. The DCB specimens were held at a fixed displacement at a load just below critical fracture, from which a load, P, versus time curve was recorded. The load relaxation that occurred over time resulted from crack extension, which allowed for the calculation of the crack-growth rate, da/dt, from Eq. (2): [16,26]

$$\frac{da}{dt} = \frac{-a_i P_i^{1/3}}{P^{4/3}} * \frac{dP}{dt} \tag{2}$$

Where a_i and P_i are the initial crack length and loads, and da/dt was measured over several orders of magnitude from $\sim 10^{-4}$ m/s to below 10^{-10} m/s.

3.3. Characterization of the debond path

Following decohesion testing, an X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe) survey scan (0–1000 eV) was made of each of the fractured specimens using monochromatic Al K_α x-ray radiation at 1487 eV to characterize the surface chemistry and precisely locate