



Fatigue in organic semiconductors: Spectroscopic evolution of microstructure due to cyclic loading in poly(3-heptylthiophene)



Adam D. Printz, Andrew S.-C. Chiang, Suchol Savagatrup, Darren J. Lipomi*

Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive, Mail Code 0448, La Jolla, CA 92093-0448, USA

ARTICLE INFO

Article history:

Received 7 November 2015
Received in revised form 25 February 2016
Accepted 23 March 2016
Available online 1 April 2016

Keywords:

P3HpT
Stretchable electronics
Stretchable solar cells
Conjugated polymer
Mechanical properties
Organic semiconductor

ABSTRACT

Organic electronic materials have many characteristics that make them attractive for applications in which mechanical deformability—i.e., flexibility and stretchability—are required. While deformation often degrades the performance of these devices, very little is known about the effects of cyclic loading—i.e., mechanical fatigue—on the microstructure and mechanical properties of the active materials. This paper examines the evolution of microstructure, stiffness, and ductility of thin films of poly(3-heptylthiophene) (P3HpT) as the film undergoes cyclic straining using ultraviolet-visible (UV-vis) spectroscopy and film-on-elastomer techniques. Thin films of P3HpT are cyclically stretched by 5, 10, or 25 percent (i.e., below, at, and above the yield point—the point at which the polymer plastically deforms with strain) up to 10000 cycles. UV-vis absorption spectroscopy is taken in intervals and the weakly interacting H-aggregate model is used to determine the aggregate quantity (from the vibronic progression) and quality (from the exciton bandwidth) in the films. Films cyclically strained at 5 and 10 percent (below and at the yield point) do not undergo significant reduction in the aggregated fraction of polymer chains, while films strained to 25% (above the yield point) undergo a reduction in aggregated fraction of over 10% by the 2000th cycle. At 25% strain, a significant reduction in the buckling wavelength from $3.4 \pm 0.4 \mu\text{m}$ to $2.4 \pm 0.3 \mu\text{m}$ is observed within the first 100 strain cycles suggesting a significant reduction in the stiffness and resilience of the films. A significant decrease in ductility is observed in films cyclically strained, and the effect is found to increase with increasing levels of strain. These results suggest that materials cyclically strained below their yield point will retain a microstructure that is their most electronically favorable, and that the mechanical properties of materials strained above their yield point will evolve significantly under repeated deformation. This information can be used to inform design where accommodation of repetitive strain is required, such as outdoor, portable, and wearable devices.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Organic electronic devices have several key advantages over their inorganic counterparts, including low cost [1–3], manufacturability by roll-to-roll processes [4–6], molecular customizability [7,8], and their flexibility or stretchability—qualities that (though often assumed) are not always present [9–11]. These properties could enable devices in a new range of new applications including wearable [12–14] and implantable biosensors [15,16], electronic skins [17,18], and mechanically robust organic photovoltaics that can handle harsh outdoor environments [11,19,20]. Many of these applications require materials capable of handling repetitive strains. For example, as part of the “Lighting Africa” initiative,

lamps powered by flexible OPVs were deployed to rural Africa; these lamps and flexible organic photovoltaic (OPV) devices were subjected to the repeated mechanical stresses of everyday use [21]. After only three weeks of testing, it was found that 40% of the devices suffered catastrophic mechanical failure, attributed to contact failure [21]. While it is expected that the failure due to contacts will be resolved, it highlights an area of the field that requires further understanding: how devices behave when repeatedly strained. It is thus important to understand how the microstructure of semiconducting layers of devices evolves under cyclic loading. Ideally, the semiconducting materials selected for a device will be able to accommodate the strain elastically so that no permanent deformation of the active components of the device occurs. However, under cyclic strain, even devices that accommodate the strain elastically might deform irreversibly with continued cycling. Prior to catastrophic failure of devices such as organic solar cells and thin-film transistors due to cracking, changes in the

* Corresponding author.

E-mail address: dlipomi@eng.ucsd.edu (D.J. Lipomi).

morphology of the active materials could produce changes in the electronic structure of the material, which may be deleterious to the performance of devices.

Fatigue is a phenomenon in materials science whose effects are well known to be deleterious. In metals, strain hardening due to the accumulation of dislocations causes embrittlement and eventual structural failure. In conventional polymers, accommodation of cyclic strains dissipates heat that can produce chain scission and the rearrangement of microstructure that both have the effect of reducing the load-bearing capacity of a structure. In the context of semiconducting polymers, the effect of repetitive loading has not been explored but should almost certainly have an effect on the microstructure and thus the electronic structure. We thus explored the effect of the repetitive strain on the microstructure of thin films of the polymer poly(3-heptylthiophene) (P3HpT) (Fig. 1). We measured the absorption of relaxed films after straining and used the weakly interacting H-aggregate model developed by Spano and others to evaluate the evolution of the fraction of polymer aggregates and the order within these aggregates, as manifested in the exciton bandwidth [22–25]. We expected that as the number of cycles of strain increased, the aggregation would decrease, which would be concomitant with a decrease in the amount of energy needed to deform the film (i.e., reduced modulus and resilience). We observed different behavior for films cycled below, at, and above the yield point of P3HpT (using a value of yield point previously measured by our group) [26].

2. Experimental design

2.1. Selection of materials

Poly(3-heptylthiophene) was selected as the conjugated polymer to be analyzed because of its favorable electronic and mechanical properties [27,28]. We previously reported that, when mixed with [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) in organic photovoltaic devices with all stretchable components, the power conversion efficiency (PCE) of devices made from P3HpT was $2.16 \pm 0.17\%$, similar to that of P3HT devices ($2.04 \pm 0.27\%$) [27]. In addition to good photovoltaic performance, P3HpT had a tensile (or Young's) modulus of 0.07 ± 0.01 GPa, which was an order of magnitude lower than P3HT (1.09 ± 0.15 GPa). Moreover, the crack-onset strain of the films on elastic substrates was significantly greater for P3HpT (58%) than for P3HT (10%) [27]. Conveniently, all members of the family of poly(3-alkylthiophene)s (P3ATs) form thin films with aggregates that can be modeled by the weakly interacting H-aggregate model [22,25].

Polydimethylsiloxane (PDMS) was selected as the elastomeric substrate because it is transparent to visible light and therefore allowed measurement of the absorption spectra of our films over the wavelengths of interest (300–850 nm).

2.2. Weakly interacting H-aggregate model

The stiffness of thin films of the poly(3-alkylthiophene) (P3AT), poly(3-hexylthiophene) (P3HT) has been correlated to the order present in the films [25,29]. In the aggregated state, the coupled electron-vibrational (vibronic) transitions determine the absorption of weakly interacting H-aggregates. Spano and others developed the weakly interacting H-aggregate model, which models the absorption by aggregated states in polymer films that form H-aggregates as Gaussian fits by: [22–25]

$$A(E) \propto \sum_{m=0}^{\infty} \left(\frac{S^m}{m!} \right) \times \left(1 - \frac{W e^{-S}}{2E_p} \sum_{n \neq m} \frac{S^n}{n!(n-m)} \right)^2 \times \exp \left(\frac{-(E - E_{00} - mE_p - \frac{1}{2}WS^m e^{-S})^2}{2\sigma^2} \right) \quad (1)$$

where A is the absorption by an aggregate as a function of the photon energy (E). W is the free exciton bandwidth, which is related to the nearest neighbor interchain excitonic coupling. Upon coupling, a dispersion of the energies occurs, the width of which is equal to W (which is four times the nearest neighbor coupling) [30]. E_{00} is the energy of the $0 \rightarrow 0$ vibronic transition, which is allowed assuming some disorder in the aggregates [22]. S is the Huang–Rhys factor, which is calculated from absorption and emission spectra, and is set to 1 for P3ATs [22,23]. E_p is the intermolecular vibration energy, which (in the case where $S = 1$) is set to 0.179 eV as determined by Raman spectroscopy [31]. The terms m and n are the ground- and excited- state vibrational levels, and σ is the Gaussian line width. The Gaussian line width, σ , E_p , W , and the scaling factor for the calculated absorption were found by a least-squares fit to the experimental absorption in the region of 550–620 nm (2.25–2.00 eV) [24,25,32]. This range was selected because in it the absorption is dominated by the polymer aggregates, while above 540 nm (2.30 eV), the amorphous polymer dominates absorption [23,32].

2.3. Cyclic loading of P3HpT

To understand the evolution of the microstructure of thin films of P3HpT as they are strained cyclically, we measured the absorption spectra before straining, as well as after 1, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000, and 10000 strain cycles while the

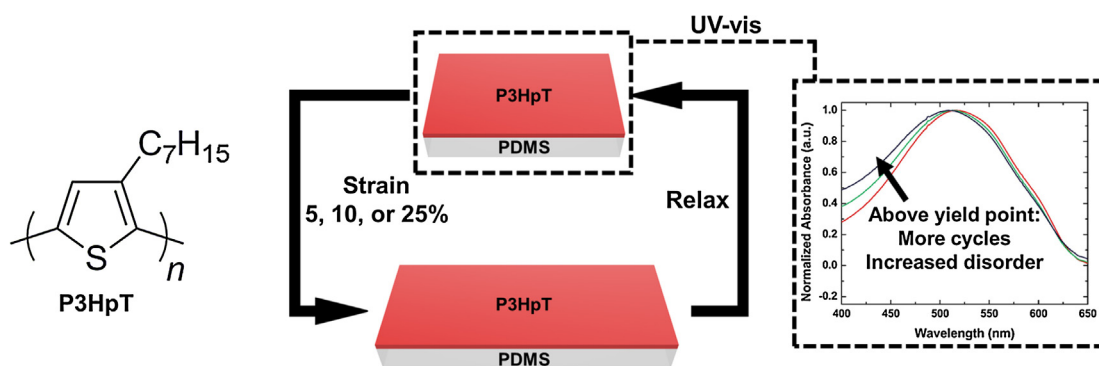


Fig. 1. Thin films of poly(3-heptylthiophene) (P3HpT) were transferred to elastomeric substrates of polydimethylsiloxane (PDMS) and strained cyclically 5%, 10%, or 25%. To evaluate the evolution of their microstructure, absorption spectra were taken periodically and the weakly interacting H-aggregate model was fit to the data.

Download English Version:

<https://daneshyari.com/en/article/1440184>

Download Persian Version:

<https://daneshyari.com/article/1440184>

[Daneshyari.com](https://daneshyari.com)