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Citation for published version (APA):

Conings, B. S. T., Bertho, S., Vandewal, K., Senes, A., D'Haen, J., Manca, J. V., & Janssen, R. A. J. (2010). Modelling the temperature induced degradation kinetics of the short circuit current in organic bulk heterojunction solar cells. *Applied Physics Letters*, 96(16), 163301-1/3. Article 163301. <https://doi.org/10.1063/1.3391669>

DOI:

[10.1063/1.3391669](https://doi.org/10.1063/1.3391669)

Document status and date:

Published: 01/01/2010

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Modeling the temperature induced degradation kinetics of the short circuit current in organic bulk heterojunction solar cells

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(Received 10 February 2010; accepted 24 March 2010; published online 20 April 2010)

In organic bulk heterojunction solar cells, the nanoscale morphology of interpenetrating donor-acceptor materials and the resulting photovoltaic parameters alter as a consequence of prolonged operation at temperatures above the glass transition temperature. Thermal annealing induces clustering of the acceptor material and a corresponding decrease in the short circuit current. A model based on the kinetics of Ostwald ripening is proposed to describe the thermally accelerated degradation of the short circuit current of solar cells with poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) as donor and (6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM) as acceptor. The activation energy for the degradation is determined by an Arrhenius model, allowing to perform shelf life prediction. © 2010 American Institute of Physics. [doi:10.1063/1.3391669]

In organic bulk heterojunction (BHJ) solar cells, charge dissociation and transport are enhanced by an intimate nanoscale mixing between a light absorbing donor polymer and a fullerene derivative acceptor.¹ Since the introduction of the BHJ solar cell,² many research groups have embraced this concept in the development of high efficiency organic photovoltaics. Today's top performing organic solar cells are still polymer:fullerene blends.^{3,4} Inherent to the incorporation of a fullerene derivative (mostly PCBM) in organic solar cells, though, is their tendency to degrade under the influence of temperature.⁵

MDMO-PPV has been a benchmark material for the development of present-day organic photovoltaics, combined with PCBM as acceptor.⁶ Within years, efficiencies obtained with this material, blended with PCBM, have evolved up to 2.9%.⁷ At present however, higher efficiencies of BHJ solar cells are obtained with poly(3-hexylthiophene) (P3HT) as absorbing polymer.⁸⁻¹¹ P3HT:PCBM blends respond to thermal treatment in a quite complex way, in the sense that there are two morphological processes occurring upon annealing. On the one hand, there is the enhanced crystallization of P3HT. On the other hand, there is diffusion of PCBM to form large (>μm) clusters consisting of single crystals.¹² MDMO-PPV is an amorphous polymer, and no crystallization will take place upon heating. Therefore, only clustering of PCBM is observed upon thermal annealing of MDMO-PPV:PCBM solar cells. For this, MDMO-PPV is a suitable material to investigate solely the influence of the clustering of PCBM on the photovoltaic properties of polymer:fullerene solar cells. In this paper, we present a method to model the temperature induced degradation of the short circuit current in MDMO-PPV:PCBM solar cells, to extract the corresponding activation energy, as well as to predict the shelf life of a device at a given temperature.

MDMO-PPV:PCBM (1:4 weight ratio) BHJ solar cells were prepared according to standard preparation guidelines. A 40 nm thick layer of poly(3,4-ethylenedioxythiophene-polystyrenesulfonate) [PEDOT-PSS, (H.C. Starck)] was spin-coated on cleaned ITO substrates. The substrates were dried for 15 min at 120 °C on a hot plate. The active layer blend was spincoated on top of the PEDOT-PSS layer with a thickness of 120 nm, from a 0.5 wt % solution (with respect to the polymer) in chlorobenzene. The top electrode consisted of 1 nm of lithium fluoride and 60 nm of aluminum and was evaporated at a pressure of 1×10^{-6} mbar. All devices have an active area of 25 mm².

It was already shown that elevated temperatures induce a large-scale phase separation in these solar cells.⁵⁻¹³ Temperatures above the glass transition temperature of MDMO-PPV (~45 °C) cause the polymer to become softer, so the PCBM turns more mobile and starts forming clusters. Figure 1 shows a transmission electron microscopy (TEM) image of

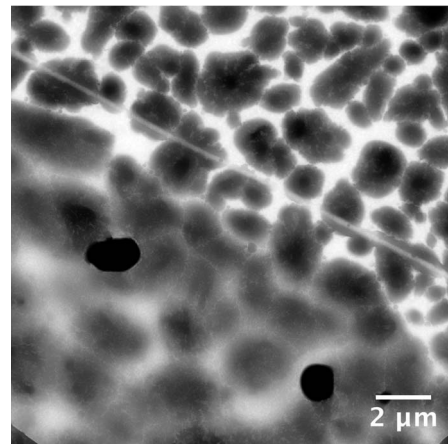


FIG. 1. TEM image of an annealed MDMO-PPV:PCBM (1:4 weight ratio) active layer (4 h at 110 °C): transition under(bottom left)/beside(upper right) electrode.

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the morphology of such an annealed device, under the electrode (bottom left) and beside the electrode (upper right). This image confirms that the same process is occurring beside and under the electrode, though the extra confinement of the active layer due to the top contact causes the clusters to be blurrier.¹⁴ It was checked that the time scale of the clustering process under and beside the electrode is the same.

A fresh device already exhibits a small-scale phase separation (50–100 nm): it is fine enough to guarantee a large interfacial area between donor and acceptor, but at the same time it allows the separated charge carriers to easily move toward the electrodes without too much chance of recombination in transit.¹⁵ After a short annealing time, small nuclei of PCBM are formed. Each nucleus is surrounded by a PCBM-depleted zone.¹³ Once nuclei are formed, they grow by incorporating molecules that are drawn from the PCBM network that is originally dispersed throughout the polymer matrix. After some time, the clusters touch each other because of their growing number and size, and they grow into each other due to lack of space. In this process, the larger clusters do not move as a whole.¹⁶ The smallest particles (with high surface energy) diffuse toward larger clusters (with low surface energy), to form compounds with even lower surface energy. Finally, when the polymer matrix is depleted of PCBM, the clusters stop growing. This clustering behavior, that starts from nuclei (that can form under the presumption that the system is sufficiently saturated with its dispersed phase) and grows clusters by adsorbing very small particles that diffuse toward them, fits into the theory of Ostwald ripening, which is an act of lowering the overall energy in the system.¹⁷ Analysis of TEM images of MDMO-PPV:PCBM samples as in Fig. 1 showed that the average radius of the two-dimensionally growing clusters upon annealing increases proportional to the square root of the time. This is exactly what is expected for an Ostwald type growth.¹⁸

The major consequence of annealing BHJ devices is the reduced interfacial area between the donor polymer and the acceptor fullerene. Electrically, this means that the current drawn from the device under illumination at short circuit drops.¹⁵ This effect occurs consistently and, imposing equal experimental conditions, in a quantitatively reproducible fashion. This makes it an attractive parameter to monitor in the thermal degradation investigation of organic solar cells.^{5,19,20} To that end, a homemade degradation chamber was used inside a glovebox with nitrogen atmosphere, to avoid degradation due to oxygen and UV radiation. Devices were degraded at temperatures from 50 to 90 °C. White light illumination was only switched on when an IV-characteristic was measured. Figure 2 shows the normalized short circuit current I_{sc} as a function of time for different annealing temperatures. To correlate the accelerating stress (temperature) to the measured device parameter (I_{sc}), a life test model is needed. This model should be as simple as possible, yet physically meaningful enough to describe the occurring degradation kinetics in the device. First, a mathematical model for the time dependence of I_{sc} has to be found. Recent reports use linear and first order exponential models.^{19,21} The curves in Fig. 2 indicate an exponential decay, and I_{sc} seems to stagnate at a fixed value $I_{sc}(\infty)$, independent of the imposed temperature, which yields the following formula:

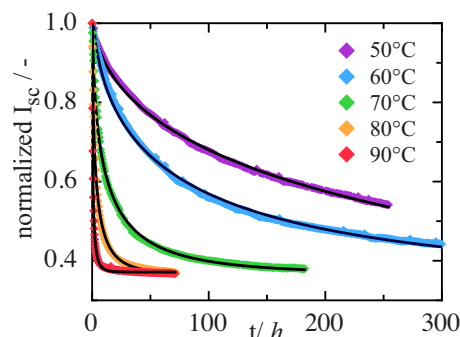


FIG. 2. (Color online) I_{sc} data at different annealing temperatures (symbols) and fitted curves (solid lines).

$$I_{sc}(t) = I_{sc}(\infty) + I_{sc}(0)\exp(-k_{deg}t), \quad (1)$$

where k_{deg} is a rate constant that characterizes how fast the degradation is evolving.

As the decrease in the I_{sc} is a direct consequence of the clustering of the PBCM,⁵ the time scale of the Ostwald ripening must have its reflection in the behavior of I_{sc} . For that reason, the typical $t^{1/2}$ kinetics was introduced into Eq. (1):

$$I_{sc}(t) = I_{sc}(\infty) + I_{sc}(0)\exp(-k'_{deg}\sqrt{t}). \quad (2)$$

All curves were fitted simultaneously to Eq. (2) (Fig. 2), and the fit results agree nicely with the measurements. Each fitted curve from Fig. 2 possesses a different value for the degradation constant k'_{deg} . When this constant is plotted on a logarithmic scale against $k_B^{-1} T^{-1}$, the slope reveals the corresponding activation energy E_a of the occurring degradation mechanism. The result is in Fig. 3, yielding an activation energy of $E_a=0.85$ eV ($R^2=0.9986$). Herein, Eq. (3) was used, which is referred to as the Arrhenius model, one of the traditionally used models for temperature dependent life tests. For this model, k'_{deg} is defined by

$$k'_{deg} = A \exp(-E_a/k_B T), \quad (3)$$

where E_a is the activation energy in eV, k_B the Boltzmann constant (8.62×10^{-5} eV K⁻¹), and A is a constant that depends on the degradation mechanisms and the experimental conditions. A higher E_a means a higher barrier to overcome for the system to degrade, so this characterizes a more stable device. Once the value of E_a is known, the degradation constant k'_{deg} can be calculated for any temperature to predict the device's shelf life at that temperature. After one year storage at room temperature, MDMO-PPV:PCBM solar cells will have retained at least 90% of their original I_{sc} . The simple

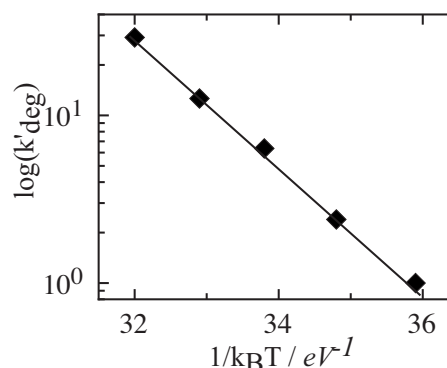


FIG. 3. Fit of k'_{deg} as function of the reciprocal temperature.

Arrhenius model can be extended to account for additional stresses, though this is unnecessary here as these were prevented in the experimental setup. The nitrogen atmosphere avoided oxygen contamination, and the light source was only switched on when an IV-characteristic was measured, so the only stress was the temperature. Notice that because of the $t^{1/2}$ utilized in Eq. (2), the unit of k'_{deg} is different compared to k_{deg} in Eq. (1), but this is absorbed by the constant A and the activation energy maintains its significance. The exact origin of E_a is hard to specify. Considering the nature of the degradation, it is plausible that E_a is related to the diffusion energy needed for a PCBM molecule to move across a polymer strand upon diffusion.

In summary, measurements of the short circuit current of MDMO-PPV:PCBM solar cells at different temperatures as a function of time were modeled using a customized exponential model with an Arrhenius-type degradation constant. This model was based on the kinetics of the temperature induced diffusion and Ostwald ripening driven clustering of PCBM. Using this model, a shelf life prediction is possible for any given temperature above the glass transition temperature of the donor polymer. Bearing in mind that the current highest performing organic solar cells are still a blend of a polymer and a fullerene derivative (PCBM or likewise), this work highlights that in the development of light absorbing polymers, special attention should be paid to their rigidity. The most evident methods therein are crosslinking polymer chains^{22,23} or trying to obtain a high T_g .^{5,24,25} The presented approach in this work can be used to investigate the morphology related degradation kinetics of material combinations.

We acknowledge the institute for the promotion of science and technology in Flanders (IWT Vlaanderen) for funding via the IWT-SBO project Polyspec, the Fund for Scientific Research, Flanders (Belgium) (F.W.O.) in the framework of project G.0252.04 and the Special Research Fund (B.O.F.).

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