# LIFETIME STUDY ON MULIPLE ORGANIC PHOTOVOLTAIC MATERIALS THROUGH OUTDOOR TESTS

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4.2 – Tecnologias e ensaios de módulos fotovoltaicos

***Abstract.*** *Organic photovoltaics (OPV) have undergone a significant development in recent years, with companies reaching efficiencies above 13%. Its unique features of transparency, light weight and flexibility allow the OPV application where conventional photovoltaics reach their limits, such as building integrated photovoltaics (BIPV). Many projects are emerging for this type of application, such as façade integration, and it is important to guarantee that the lifetime of the OPV devices is similar to what it is being integrated to. As a relatively recent technology, there are not many studies focusing on the stability and lifetime of OPV and even though standard tests have been defined for means of comparison of technology development, there are no appropriate qualification tests to assure the durability of the modules. As accelerated tests are not yet correlated to real operational conditions either, outdoor tests are a must to study degradation behavior and pathways to improve the lifetime. In this paper, outdoor tests have been conducted for a period over a year to compare different photoactive materials and assess their stability under operational conditions. By the use of an in-house built software, the current-voltage measurements performed along the day hours were used to build degradation curves and model the energy generated over time. Differences in degradation rate were observed for the three polymers tested, as well as a relation between irradiance levels and the performance and stability of the devices.*

***Key words:*** *Organic photovoltaics, lifetime, outdoor test*

## 1. INTRODUCTION

Organic photovoltaic (OPV) technology offers a variety of applications due to its characteristics of transparency, lightweight and flexibility. While recent development has brought efficiencies up to 13.2%, the stability and lifetime of these devices still remains a concern. Although standard test protocols were defined by the International Summit of OPV Stability (ISOS) (Reese, et al., 2011), they only provide a means of comparison between the various institutes working with this technology, not serving to the purpose of defining qualification tests. Furthermore, due to the complexity and multitude of degradation mechanisms acting at the same time, it is hard to correlate accelerated tests and real life operation, which prevents a quick estimation of the lifetime of these devices. Thus, outdoor tests, although long, are still the most reliable source of data on the performance of OPV over time. They combine all important stressing factors known to affect the OPV stability - light exposure, temperature, oxygen and water (Giannouli, et al., 2015) , as well as their variation during the day and seasons. As the photoactive layer plays an important role in the stability of OPV devices (Gevorgyan, et al., 2015), in this paper, different photoactive materials had their degradation behaviour studied through outdoor tests run for a period over a year.

## 2. METHODS

The OPV devices used in this study follow the inverted structure, as depicted in Figure 1. The layers are coated through a slot die process on top of a PET substrate in the following order: Bottom electrode: IMI/Electron transport layer (ETL): polymer based/Active layer/Hole transport layer (HTL): PEDOT:PSS/Top electrode: Ag grid. Three different active layer materials were tested in this study, in the colors of red, green and blue, and will be referred as Polymers A, B and C, respectively. Polymer A is based on the well-studied Poly(3-hexylthiophene-2,5-diyl) (P3HT) and polymers B and C are based on low band gap materials under development. In all cases, fullerene (C60) based materials are used as acceptors.

The modules are processed in a single station roll-to-roll process on a flexible substrate, using non-chlorinated solvents and in air, in order to allow scaling up the process. The top electrode of silver is applied through a screen printing process. The resulting devices have 6 cells of 3.6cm² each, resulting on a total active area of 21.6 cm². As Polymer A is a well-known material and, by the time of the beginning of the experiment, was already optimized, bigger samples of 288cm² active area were used.

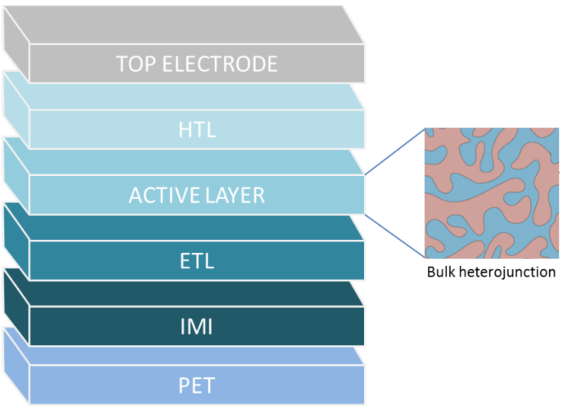


**Figure 1 - Stack structure of the samples.**

The samples are further laminated with a transparent flexible barrier film with a water vapor transmission rate (WVTR) in the order of $10^{-3}$ g/cm²day and a UV barrier (cut-off at 380nm). The modules are sandwiched between the barrier film by using an UV-curable adhesive with barrier properties, applied on the top and bottom surfaces, which passes through a nip pressure in a R2R process to achieve a thin and homogeneous layer of adhesive.

The samples were subjected to an outdoor test following the protocol of ISOS-O-2 (Kettle, et al., 2017). The conditions of the test are explained in Table 1. The modules were exposed to outdoor conditions on a rooftop on a rack facing North at an angle of 20° in Belo Horizonte, Brazil (19.9° S, 43.9° W). The modules were attached to resistive loads sized so that at STC (standard conditions) they would operate near the maximum power point. Current-voltage (I-V) curves of all modules were taken every hour and the environmental conditions (irradiance, humidity, ambient and system temperatures) were taken within each measurement and recorded. The data was then processed by an in-house software, which allows the monitoring of the performance and degradation of the modules over time.

**Table 1 - Outdoor test conditions**

| | |
|---|---|
| Light source | Sunlight |
| Temperature | Ambient |
| Relative humidity | Ambient |
| Environment | Outdoor |
| Characterization light source | Sunlight |
| Load | Maximum power point (MPP) |

## 3. RESULTS

The IV curves measured were stored in a computer and fed to the in-house outdoor data software. By reading all the curves, it identifies the electrical parameters and stores the information along with the environmental measurements. In the next sections, the results of the analysis of each material are presented. For the lifetime analysis, the terms T80 and Ts80, commonly used in the OPV field, are presented: T80 describes the time to reach 80% of the initial efficiency, whereas Ts80 refers to the time to reach 80% of the efficiency after the burn-in, in other words, the efficiency after the the fast degradation experienced in the first days of test.

### 3.1 Polymer A

Figure 2 shows how efficiency (Eff), fill factor (FF), open-circuit voltage (Voc), short-circuit current (Isc), series and shunt resistances (Rs and Rsh, respectively), measured at the condition of 1 sun, with a 5% range, evolve under operating conditions (mpp). The graph is normalized by the maximum point. It shows a significant drop of shunt resistance in the first days, causing an initial drop of 10% in efficiency, FF and Isc. Rs experienced a linear increase. The samples had reached T80 after 1.5 year; however, Ts80 had not yet been reached.

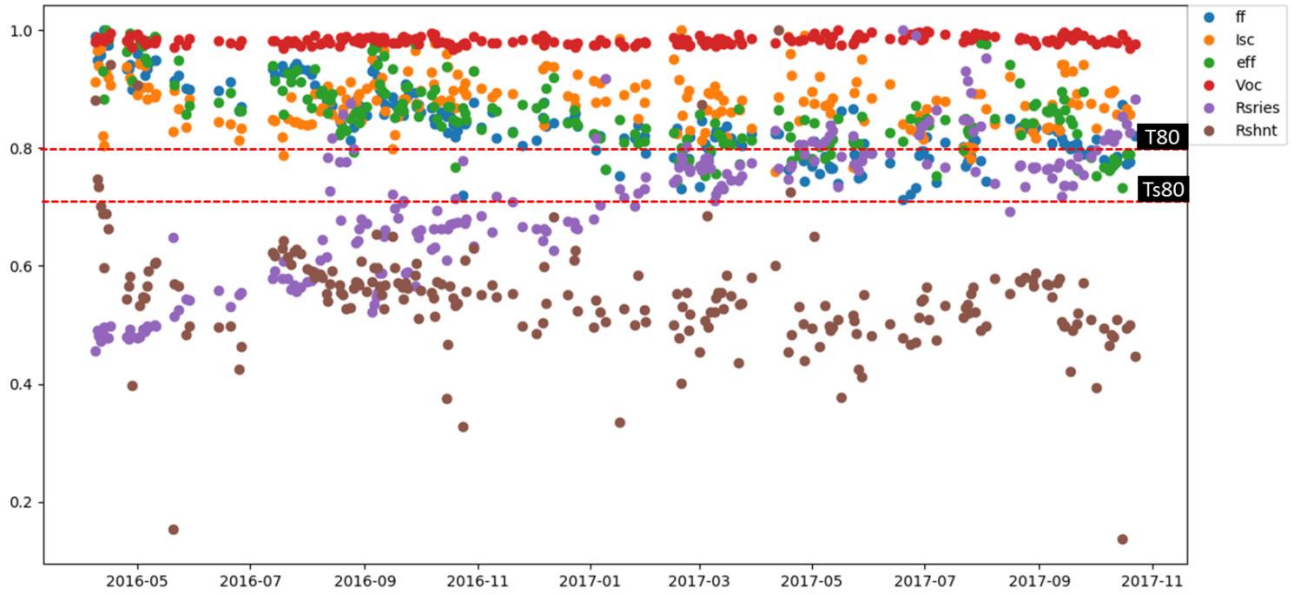


**Figure 2 - Evolution of the electrical parameter of Polymer A. The dashed lines represent T80 and Ts80.**

By analysing the performance at different irradiances, Figure 3 was obtained. It shows the absolute efficiency measured at different irradiances throughout the day, withing a 5% range: 1 sun, which is the standard irradiance value used for performance measurements, more frequent in hours close to midday; 0.5 sun; and 0.1 sun. It can be seen from the plot that the efficiency of the OPV devices is higher at low light levels, mostly common in the first and last hours of daylight, when the diffuse light is more significative than the direct one. However, the variation is also high at this low irradiance. This could be attributed both to the sensitivity of pyronometer at this low level and, most likely, to changes of irradiance levels during the measurements. Each IV measurement takes about 20 seconds to be completed and, with the current setup, the irradiance measurement is taken only once during this period. Thus, sudden changes in irradiance, due to the movement of clouds in the sky, are not accounted for and could lead to mismeasurements.

Besides the efficiency, also the lifetime seems to be dependend on the irradiance level. By a linear fit, the software estimated the lifetime or T80, a term commonly used in the OPV field to describe the time to reach 80% of the initial efficiency, as 1.7 year at 1 sun level; 2.8 years at 0.5sun; and as having an increasing trend at 0.1 sun.

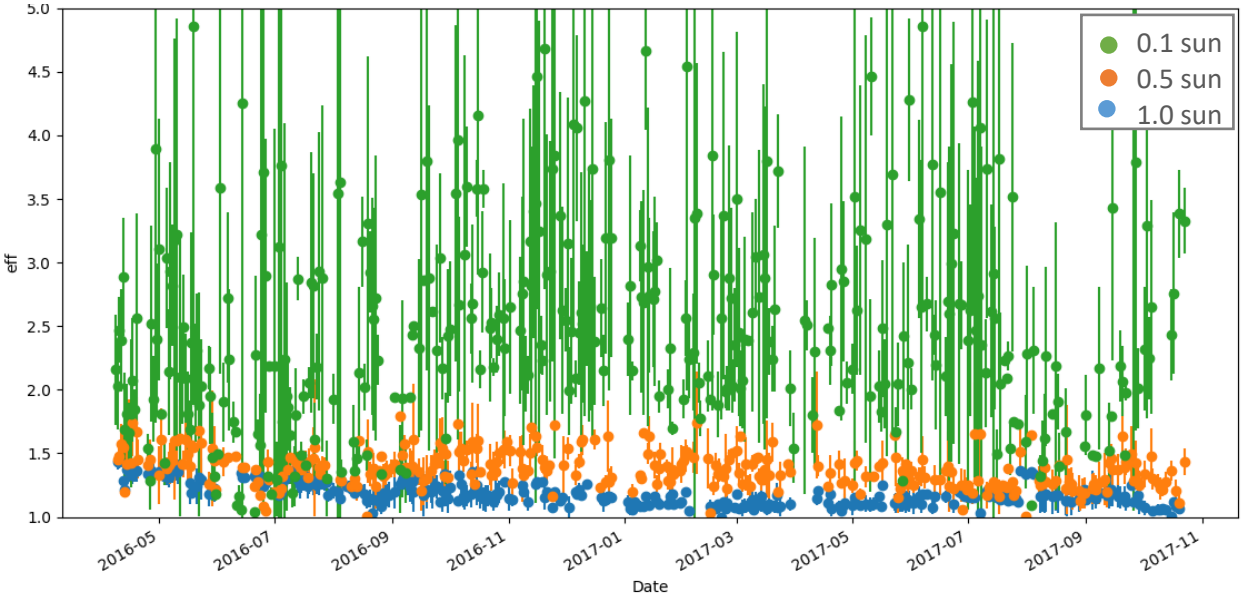


Figure 3 - Efficiency of Polymer A at multiple suns.

Using the data recorded in the experiment, the energy that would be generated by the modules during the test period was calculated by the software. With the modules being measured every hour, the daily generated energy was obtained by calculating the integral of the Gaussian function. For the fitting, two basic conditions had to be reached: at least 10 measurements during the day and at least one between 10am and 3pm (hours with higher irradiance levels). If the conditions were not satisfied for a specific day, the software estimated the energy based on the previous and following

days. Figure 4 presents the graph of the energy generated by a 288cm² active area Polymer A module and the environmental conditions recorded within the measurements. It shows how the energy generation varies according to the season: the experiment started in fall and the energy produced declines during winter (from June), when there are less sunny hours and the incident angle of the sunlight moves away from the normal. It raises again with the start of spring and is more irregular during summer (months around December), when it is the rainy season in Brazil. The cycle was then repeated, totalling 1.5 year of test and summing up to a total energy generated of 0.857 kWh, or 29.7 kWh/m².

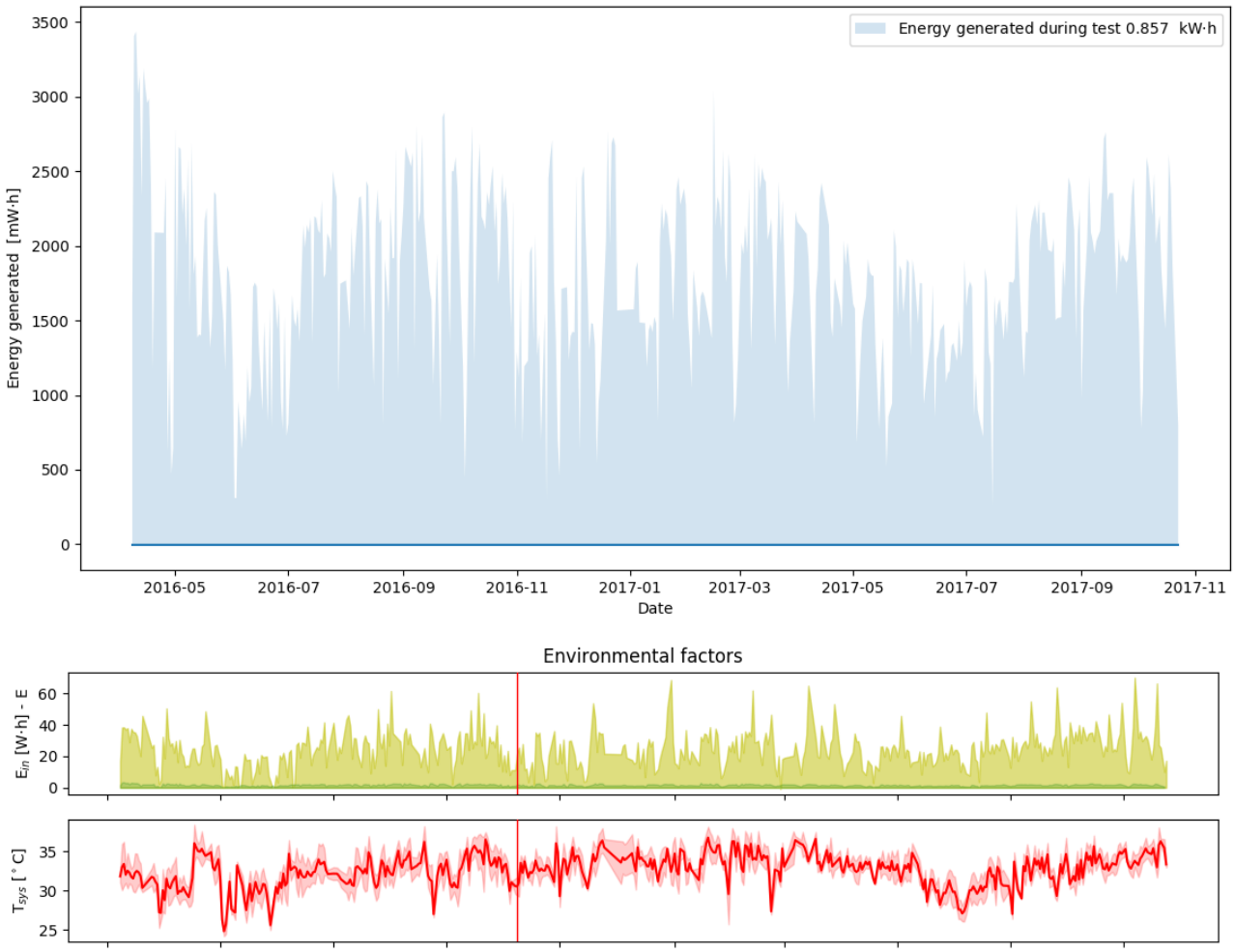


**Figure 4 - Energy generated by Polymer A during the test and the respective environmental conditions: incident irradiance and system temperature.**

### 3.2 Polymer B

Figure 5 shows the electrical parameters measured over time for Polymer B, normalized by the maximum value. The test started in September 2016 and for the first 15 days the efficiency has undergone an increase of 40%, which was mainly led by an increase in shunt resistance and current. This behavior could be associated to an annealing effect due to the irradiance and temperature increase, which might have positively altered and/or reset the morphology of the material. After this period of increase, a linear degradation can be observed, mostly due to the Rs, which has affected the most the FF. Voc, as in the previous cases, is not altered and Isc is fairly stable during the test, oscillating apparently due to the seasons and irradiance levels. If the performance at the beginning of the measurements is considered, the lifetime of these modules (T80) was not yet reached. However, it is common, in lifetime evaluations, to consider the efficiency after the burn-in period as the initial one. In this case, Ts80 was reached after 1.2 year.

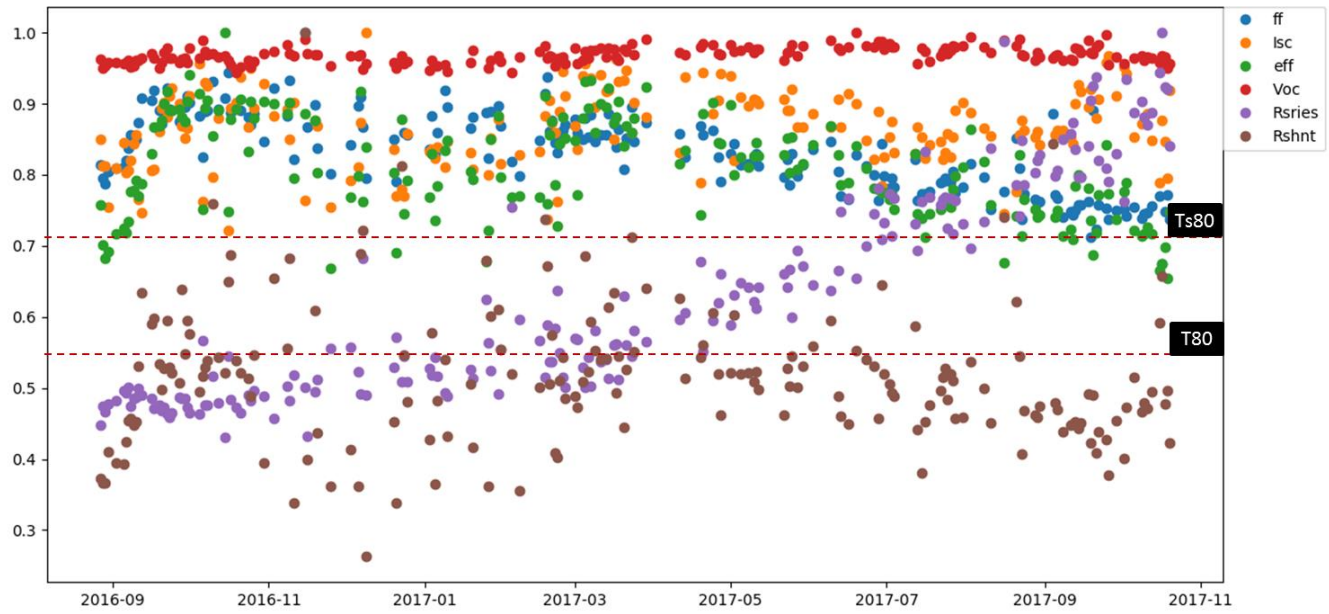


**Figure 5 - Evolution of the electrical parameter of Polymer B. The 2 dashed lines represent T80 and Ts80.**

The analysis under different irradiance levels is showed in Figure 6, with absolute efficiency levels. As in the previous case, the efficiency increases at low light levels, as well as the lifetime. By a double linear fit performed by the software, the lifetime of the modules were estimated as 1.5 year for both 1 and 0.5 sun, while for 0.1 sun the estimation was of 2.5 years.

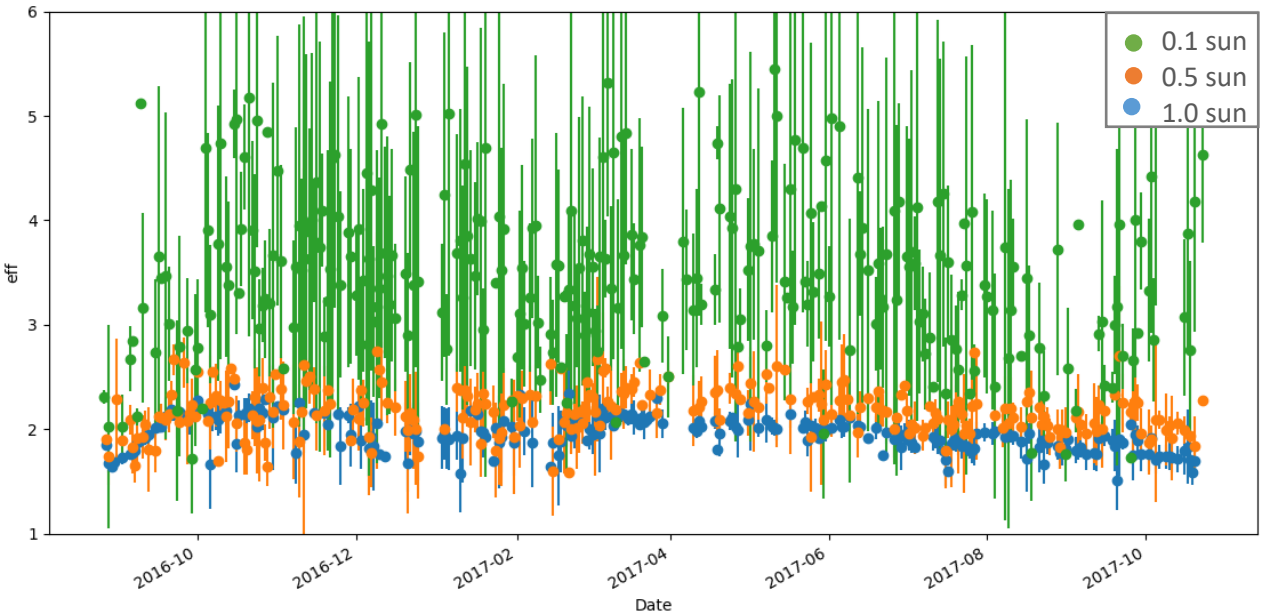


**Figure 6 - Efficiency of Polymer B at multiple suns.**

The graph of the energy generated throghout the test is shown in Figure 7. It has a similar form as in the previous case. The test started in spring and the seasons can be recognized easily: the summer rain in the months around December caused some irregularity in the energy generation, with alternating low and high peaks, while in winter (July), the energy production was lower. The total energy generated in 14 months was 0.079 kWh for a module of 21.6cm², or 36.6 kWh/m².

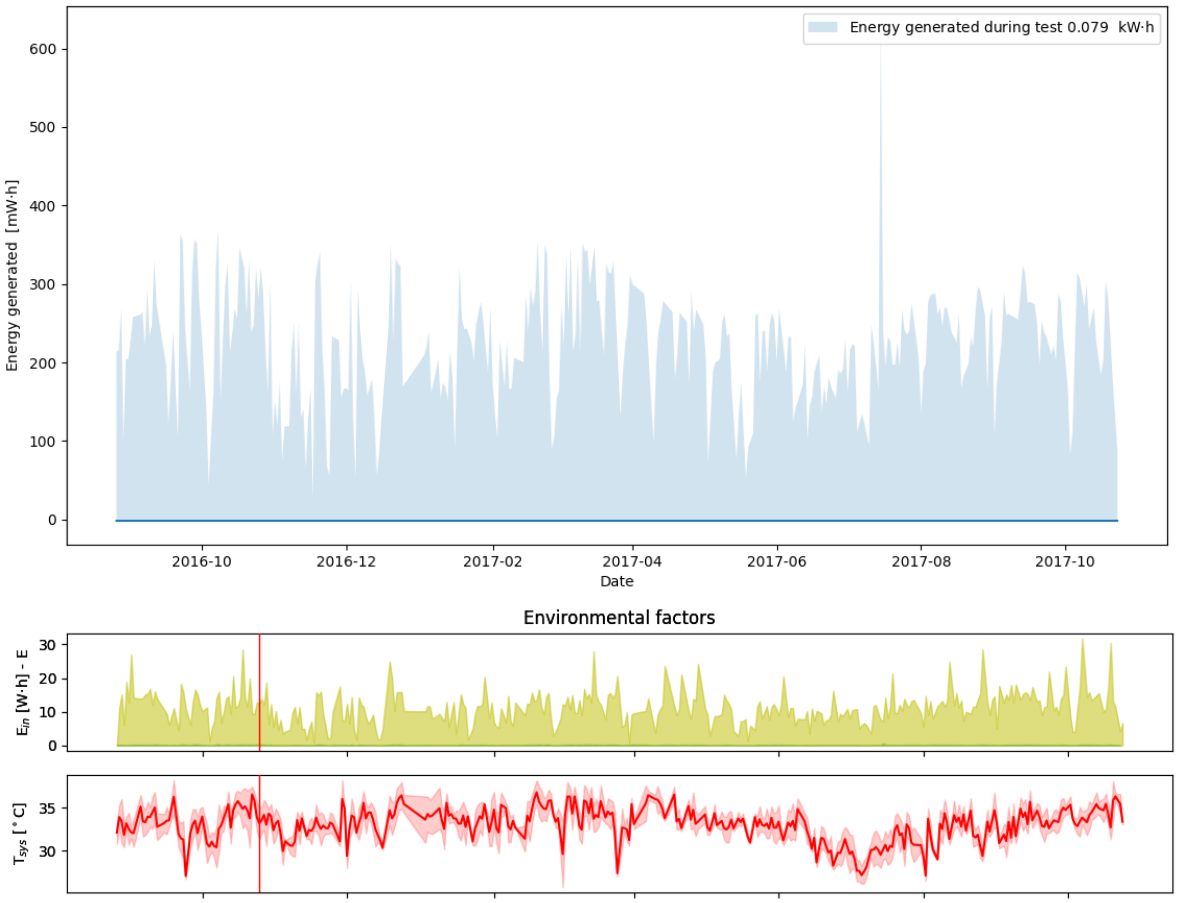


**Figure 7 - Energy generated by Polymer B during the test and the respective environmental conditions: incident irradiance and system temperature.**

### 3.3 Polymer C

Polymer C exhibited a different behavior from the materials discussed above, as presented in Figure 8, with normalized values. It had a much faster degradation, which was led by a decrease in both Isc and FF, the last one influenced mostly by Rs. Three different periods of degradation can also be distinguished: the burn-in, which is characterized by a sudden drop in efficiency in the first days after exposure to light; a slower degradation period in the first six months of test; and a faster one afterwards, which coincides with the beginning of the summer season. T80 was already reached in the burn-in period and Ts80, which takes into account the efficiency after burn-in as the initial one, was reached in 0.6 year.

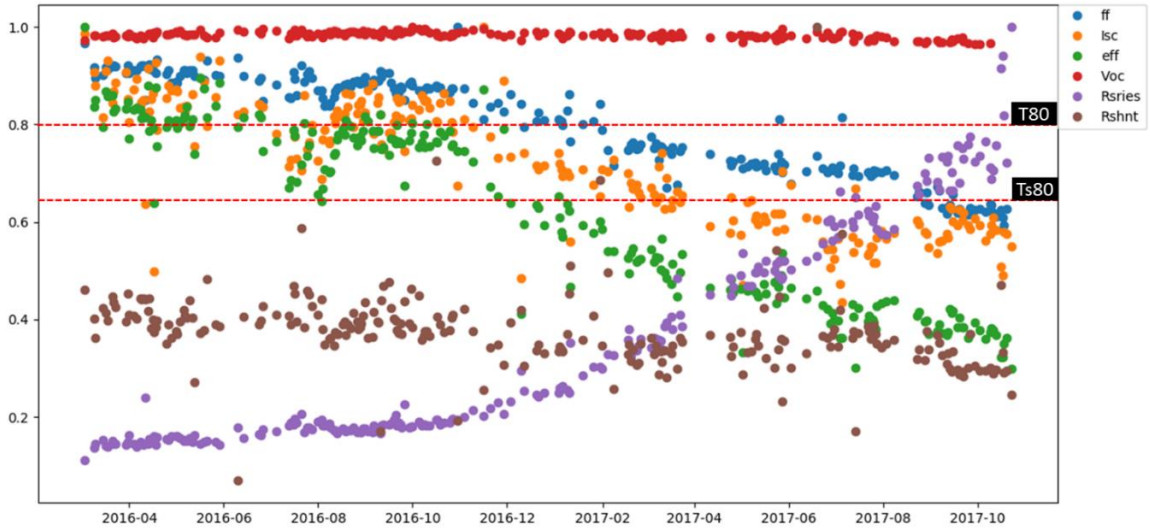


**Figure 8 - Evolution of the electrical parameter of Polymer C. The 2 dashed lines represent T80 and Ts80. For clarity reasons, an offset was applied to Rsh.**

Figure 9 shows the lifetime analysis for Polymer C under multiple irradiance levels, with absolute efficiencies. No significant difference can be seen in terms of lifetime between 1 and 0.5 sun: in both cases, Ts80 is reached in 0.6 year. For 0.1 sun, it is expected to last 1.76 year.

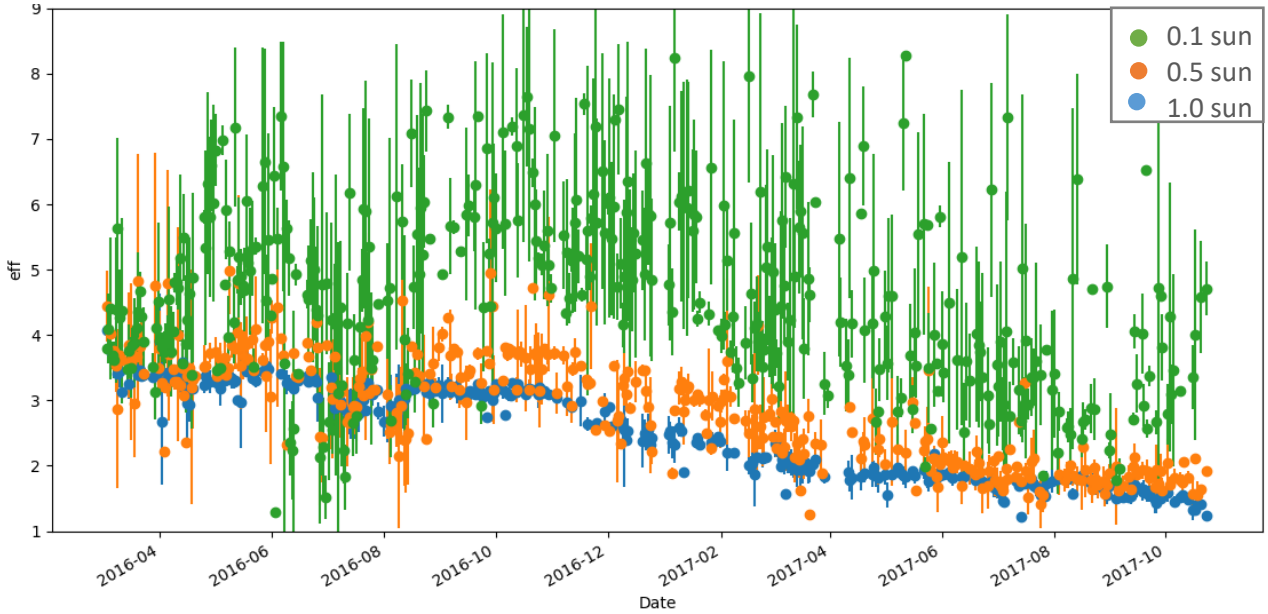


**Figure 9. Lifetime analysis under multiple suns for Polymer C.**

Finally, the energy generated is presented in Figure 10. The same seasonal behavior can be observed, but what should be highlighted here is the decrease of energy generation over time due to the degradation of the electrical parameters previously showed, which can be seen by the decrease of the peaks in each cycle. Over the period of the test, 1.5 year, a module of 21.6cm² of active area generated 0.146 kWh, or 69.5 kWh/m².

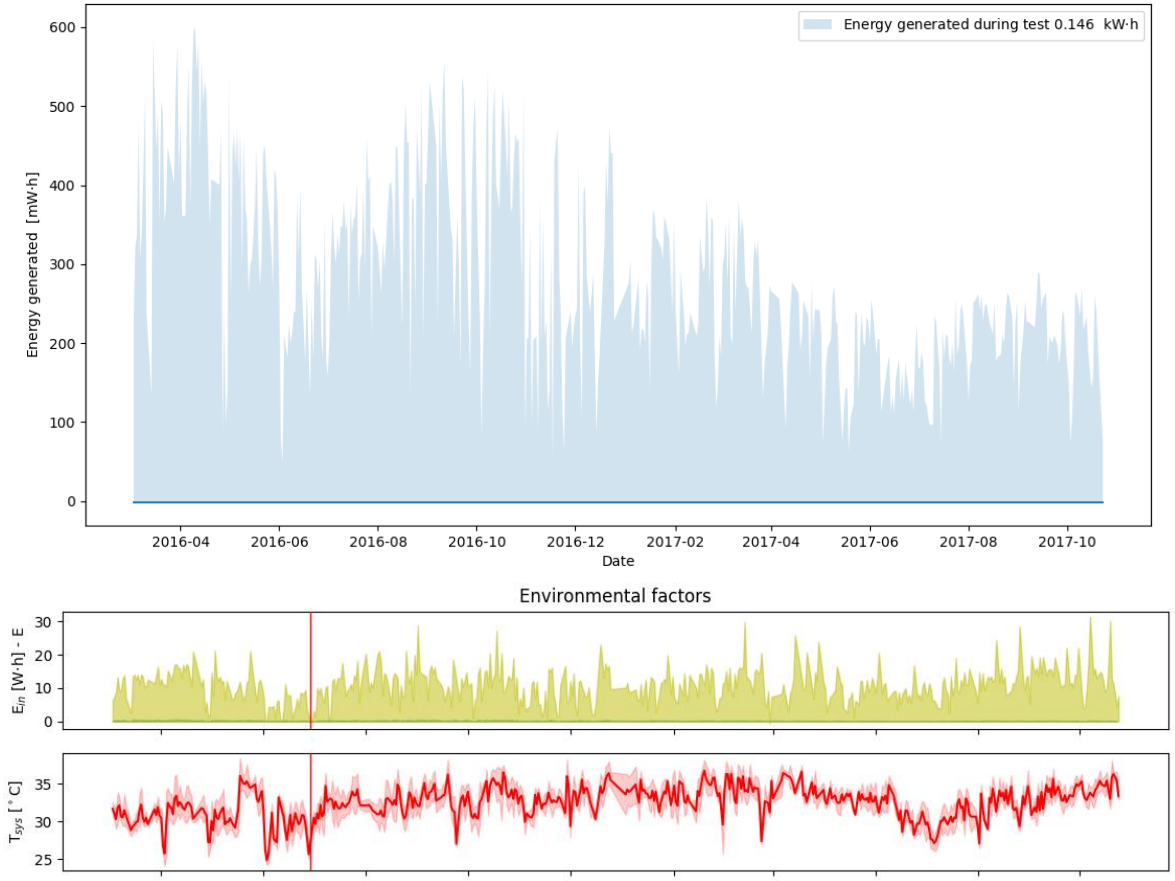


**Figure 10 - Energy generated by Polymer C during the test and the respective environmental conditions: incident irradiance and system temperature.**

## 4. DISCUSSION

Comparing the performance of the three materials during the outdoor test, it is clear that Polymers A and B are more stable than C. All samples were encapsulated with the same material and process, thus, it could be said that intrinsic factors (active layer, interlayers and electrodes), rather than extrinsic (encapsulation and contacts), were responsible for the differentiated degradation observed. The causes associated to this could be grouped in two different categories: chemical and physical modifications. Chemical modifications are associated to internal reactions, which cause alterations in the chemical structure of the molecules, while physical modifications are linked to changes between crystalline and amorphous structures, as well as with changes in the mixture donor/acceptor (Gevorgyan, et al., 2017). In this specific case, it is likely that the molecular weight ($M_z$) of the polymers played a big role in causing physical changes in the structure. Polymers A, B and C have $M_z$ values of 64k, 190k and 32k, respectively, and the lifetime results show that the ones with higher molecular weight are more stable, which is in accordance with what has been published for non-encapsulated devices (Ding, et al., 2016). Polymer C, which has a low molecular weight, is more mobile and the exposure to illumination and heat could have caused a change in morphology, leading to phase segregation, as well as an increase in the density of recombination centers, decreasing Isc. It has also experienced a significant loss in FF. Series resistance has increased by a factor of 5 during the test period, much higher than in the other polymers, which indicates a reduction in the interfacial charge transfer efficiency between the different layers, e.g. bulk material degradation (Grossiord, et al., 2012).

Polymers A and C had undergone a burn-in phase, which reduced the modules' efficiencies by 10 and 20% respectively. All Polymers used in this study are fullerene C60 based and their current and efficiency loss could be linked to photo-induced dimerization, which reduces the electron mobility (Heumueller, et al., 2016). In an opposite direction, Polymer B had an increase in efficiency in the first days, followed by an increase in fill factor and short-circuit current. This behavior could be associated to an annealing effect due to the irradiance and increase in temperature, which might have positively altered the morphology of the material.

It should be highlighted the importance of the environmental factors in the performance and degradation of the devices. As Polymer C seems to be more susceptible to photo degradation and temperature than the others, it is possible that the starting period of the test has also influenced its loss of performance. The modules were exposed to outdoor conditions at the end of summer and beginning of fall, when the irradiance levels are high, as well as the ambient temperature. As it was observed, summer was the season that affected the most the performance of this polymer, triggering a faster degradation rate. Furthermore, the energy generated has clearly varied with the seasons and at low lights the devices have showed relative higher efficiencies and longer lifetimes, although with different behaviors. This could be taken as an indication that the location of the OPV installation is a very important factor for its performance. If installed at higher latitudes, where the temperature is not so high and the direct irradiance is lower, it could be expected that the OPV modules would last longer; whereas in equatorial regions, more energy would be produced in the early days at the cost of a shorter lifetime. If true, it may be an indication that the lifetime of the OPV should be measured not in time, but in terms of potential energy generated, functioning as an energy tank: it can deliver a limited energy that could be slowly consumed under favorable climate conditions or quickly on extreme weathers.

## 5. CONCLUSION

Accelerated tests have been proposed under the ISOS-protocol to shorten the evaluation of the stability of OPV devices, but they fail to answer the question about their life time in real operational conditions. As outdoor tests remain the most reliable way to identify long-term failure mechanisms and the lifetime of devices, they were used in this study to compare the stability of three different photoactive materials under operational conditions (ISOS-O-2). Over the test period, two polymers had not yet reached their lifetime (Ts80), while one of them presented a large loss of its electrical parameters and reached Ts80 in 0.6 year. The results point at a lower resistance of this material to light exposure and temperature, that could be attributed to its lower molecular weight. Furthermore, it was observed for all polymers tested a higher efficiency and lifetime under lower light levels, which indicates that the OPV is very dependent on the irradiance level and, therefore to the location of the installation. To prove the dependency of these variables to the latitude and climate conditions, further work must be carried out by analysing outdoor data in different locations.

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