EVALUATION OF THE PHOTODEGRADATION IN ORGANIC SOLARCELLS

Lucas Phillip Z. G. de Moraes [a]
Antonia Sônia A. C. Diniz [a]
Lawrence L. Kazmerski [a,b]

[a] Green Solar – IPUC, Pontifica Universidade Catolica de Minas Gerais
[b] *Renewable and Sustainable Energy Institute (RASEI), University of Colorado Boulder, Boulder, Colorado USA*

e-mails: lpzgmoraes@sga.pucminas.br; asacd2012@gmail.com; solarpvkaz@gmail.com

Abstract. A "100%-renewables future" is now being envisioned. A major part is solar photovoltaics (PV), which has undergone rather incredible growth over the past decade and expected to reach >800 GW cumulatively installed worldwide in 2021. Emerging PV technologies to meet future needs include organic PV (OPV). Despite reaching efficiencies in the 16%-range, there remains a concern over reliability and associated degradation under operating conditions for these solar devices. In this scenario, this study aims to evaluate the effects of the photodegradation in OPV materials and devices. Specifically, the changes in the chemical, physical, electrical, and optical properties as a function of light exposure. In this paper is presented an initial study about the impact of meteorological variables, found in the Brazilian tropical climate zone, in the process of degradation of organic cells (OPV), through of the results obtained from spectral analysis.

Keywords: Solar Energy, Organic Photovoltaics (OPV), Photodegradation, Reliability

1. INTRODUCTION

The confluence of population growth, global climate change, environmental concerns, and issues with food and water is driving the world need for new clean electricity sources. Among the alternative energy is solar energy especially photovoltaics (PV), which has experienced both rapid price decreases for the consumer and improved performance (conversion efficiencies, reliability). Recent work (Mints, 2021), the 2020-PV shipments into the world markets were ~130 GW (a 5% increase over the previous year) despite the general economic slowdowns due to the pandemic. In many countries, solar PV has dropped below the generation costs of fossil fuels plants. Renewable energies, in general, have been growing rapidly, with a 100% renewable energy future being proposed as a viable energy pathway, possibly by mid-century (IEA, 2020). Among the renewable energy options, PV has advanced as the main focus for cost-effectiveand secure electricity production. One of the technologies that has been improved and is seen as promising is organic solar cell (OPV). The advantages of OPV are the demonstrated by the ability to manufacture by roll-to-roll processes that promote high volume and rapid production times, and extremely low cost of the materials and manufacturing process itself. Also, OPV offers special architectural potential for window coverings since the bandgaps of the absorbers can be tuned to match the spectrum and provide various colors—and be processed to range from transparent to semi-transparent to engineer the light to be transmitted through the glass window. The OPV also offers some applications for the mobility sector since these cells can be integrated into the existing vehicle structures without disrupting their form—and can provide electricity to power fans, lights, and other vehicle small electricity needs.

The Fig. 1 shows the efficiency of different solar cell technologies. It can be seen that the efficiency of OPV cells has been significantly improved in recent years, reaching values around 18% obtained in the laboratory. The increase in the efficiency of this technology, associated with its applicability, has driven the development of research related to performance this device in external conditions, as stability problems. Sengupta et al. (2011) inform there are various shades of stability, but the accelerated degradation due to the solar radiation that they receive remains a critical research area.
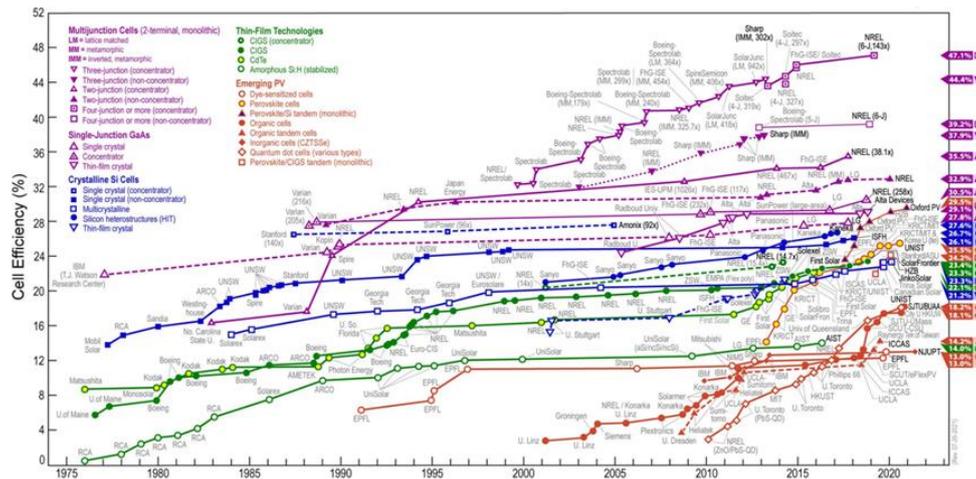
**Figure 1.** Evolution of cell efficiencies from 1975.
Source: NREL (2021).

Disler *et al.* (2012), Jorgensen *et al.* (2012), Karakawa *et al.* (2020), Mateker and Mcgehee, (2017), Schroeder *et al.* (2014), Wong *et al.* (2014) report that the lifetime of a fullerene-based organic solar cell as an electron acceptor has been researched for over 10 years. According to Peters *et al.* (2012), the degradation is a change between the electrode and the organic material, thus causing a faster deterioration in its early stage followed by more gradual deterioration over time. On the other hand, Reese *et al.* (2010) show that deterioration through the addition of fullerene is one of the main factors that contribute to the decrease in the photocurrent produced in the long term. Karakawa *et al.* (2020) reported the performance of highly durable inverted thin-film organic solar cells (P3HT: PCBM), manufactured under continuous light irradiation in the air.

The photodegradation of organic solar cells (OPV) can be caused by the deterioration of organic molecules (Chambon *et al.*, 2011; Manceau *et al.*, 2009; Pacios *et al.*, 2006; Rivaton *et al.*, 2010), oxidation in the electrodes(Lloyd *et al.*, 2009), delamination, and the reaction of the organic layer with the electrode(Davis and Pemberton (2009) and Lloyd *et al.*, 2011), photobleaching(Wang *et al.*, 2014), among others.

According to Callister and Rethwisch (2010), polymers are made up of repetitions of small structural units known as monomers. These monomeric units can be obtained through polymerization reactions, which through covalent interatomic bonds are joined to the units, which in turn form the polymer chain.

As discussed by Vacha and Habuchi (2010), these polymeric materials are known as organic semiconductors, which have optoelectronic proprieties similar to inorganic semiconductors, however with mechanical characteristics and properties identical to those of plastics). Organic semiconductors are considered to be organic polymeric materials and have their basic atomic structure of carbon (C) and hydrogen (H) in their composition. These materials can be divided into two groups, small organic semiconductors molecules, and polymeric organic semiconductors, both of which have similar chemical structures. The electronic characteristics of these materials occur in alternating double (π and σ) and single (σ) bonds between the atoms in the main chain (carbon atoms). In this way, the binding of a polymer is due to alternation in its main chain. The electrons in a conjugated system that participate in the π bond are displaced, thus making this type of bond responsible for the optoelectronic properties of the materials.

The Fig. 2 shows some examples of conjugated polymers and bound organic molecules the are widely used in the active layer of organic photovoltaic cells, with polymers as electron donors [MEH-PPV (Poly(2-methoxy-5-(2)-ethylhexyloxy)-1,4-phenylene vinylene), MDMO-PPV (Poly(2-methoxy-5-[(3,7-dimethyloctoxy)phenylenevinylene]], P3HT [Poly(3-hexylthiophene)] and PTB7 [Poly(4,7-bis[(2-Ethylhexyl)oxy]benzo[1,2-b:4,5b´] dithiophine-2-6-dii][3,4-b]-thieno[3,4-b]-thiophenediyl]) and fullerene derivatives, organic molecules as electron acceptors, PC61BM [[6-6]-phenyl-C61-methylbutrate] and (PC71BM [[6-6]-phenyl-C71-methylbutrate]. Where it is possible to visualize in each compound a variation of double (π) and single (σ) bonds.
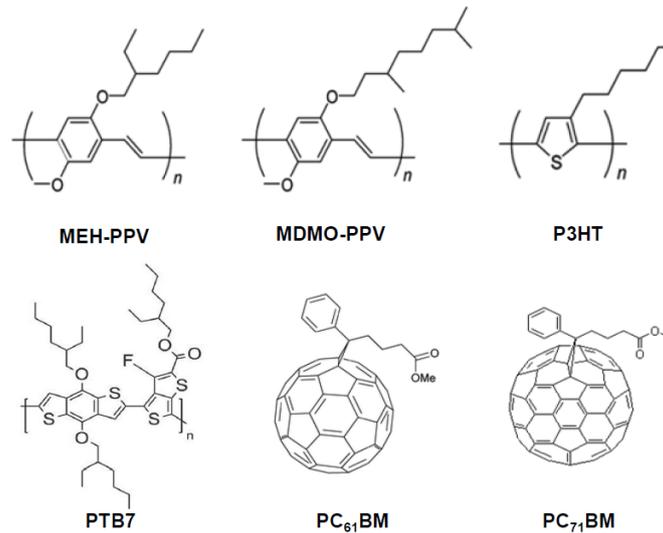
Figure 2. Polymers and conjugated organic molecules.
Source: Araujo (2018).

The organic solar cells are an active layer in which there is a mixture of two semiconductors (acceptor and donor)–a biphasic film. This active layer can have one or more conductivelayers, a mixture of materials, or even a combination of materials. In the work of Araujo (2018), the materials that makeup this active layer are generally made of a conductive polymer and an electronegative organic molecule. Figure 3 shows the cross-sectional representation of an inorganic solar cell and an organic solar cell (OPV). The photovoltaic effectoccurs when the sunlight strikes the organic cell through a transparent electrode.
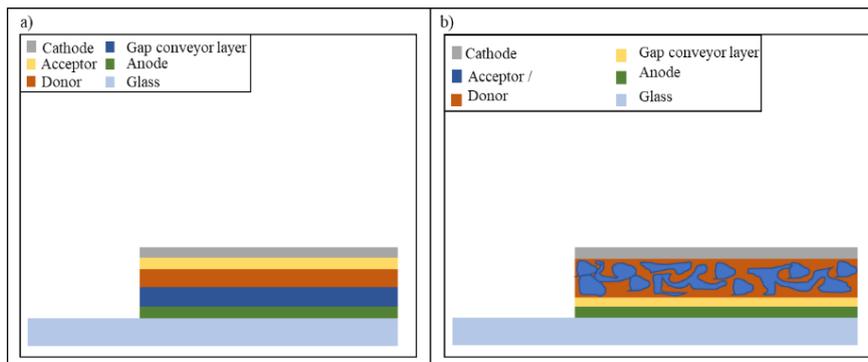
Figure 3. Cross-sectional representation of (a) inorganic solar cell. In the active layer, the electron donor and acceptor materials are separated by an electrical interface of junction; and, (b) organic solar cell, with an active layer in which the electron donor and acceptor materials are mixed.
**Source:** Author developed.

When the sunlight reaches the OPV device, it is absorbed by the electron-donating material, a polymer (Bloom *et al.,* 2007; Mihailetchi *et al.*, 2004; and Guo *et al,* 2010). After the photon is absorbed by the polymer (electron donor), the electron is moved from the state of HOMO (Highest Occupied Molecular Orbit) to the LUMO state (Lowest Unoccupied Molecular Orbit). According to Araujo (2018), Tamai *et al.* (2015), Braun (1984), Deibel and Dyakonov (2010), the free charges (constituting a photocurrent) are finally collected by the respective electrodes, and the process of converting sunlight into electricity is completed.

The organic solar cell is in commercial use—and Brazil has one of the world's few OPV manufacturing facilities (called SUNEW localized in Southeast region, in Belo Horizonte). The OPV can be seen as an attractive technology in the solar photovoltaic area, due to application variability, such as indoor lighting, vehicle electricity augmentation, energy windows, solar lighting, and small structure power, for example, in bus stops (Tempesta *et al.*, 2010). Although the OPV cells efficiency is increasing (4% below the efficiency of CdTe cell (NREL, 2021)), to eventually compete in the major PV applications 15-30 year timeframes, issues relating to stability and service life must be solved.

In this scenario, the purpose of this research is to investigate the degradation in OPV material and device, considering the Brazil's climatic conditions. The major focus is on photodegradation issues—that is the loss of output power as a

function of incoming sunlight spectrum, intensity, and duration. The focus is on correlating the electrical and optical properties (bandgap, electrical and thermal parameters, optical transmission/absorption) with changes in the material chemical and structural properties. The initial phase focuses on organic absorber materials most used in the manufacture: fullerene and P3HT. In the second phase, commercial materials and devices were used to assess their stability under the Brazil operating conditions. The objective of this study is to establish the chemical, physical, electrical, and optical changes caused by photodegradation in organic solar cells (OPV).

In the Fig. 4 are shown some applications of organic solar cells.
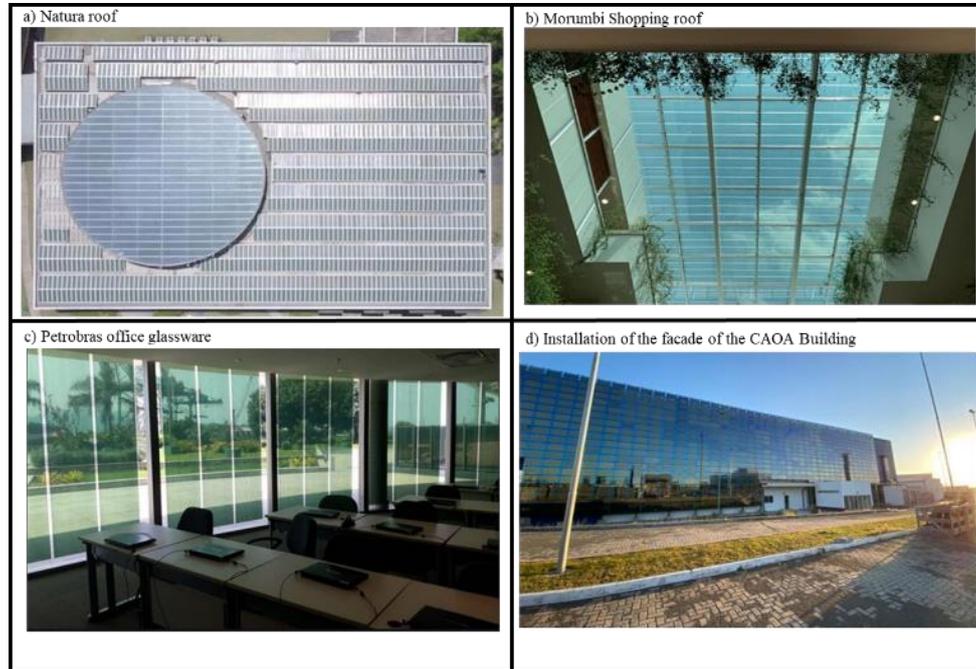
Figure 4. Examples of applications of organic solar cells in buildings in Brazil.
Source: SUNEW.

2. EXPERIMENTAL PROCEDURE

To analyze the performance of an organic cell, electrical tests were carried out on this device installed outdoors at GREEN (the Energy Studies Group or Energy Studies Group Laboratories) at Pontifical Catholic University of Minas Gerais (PUC Minas), localized in Belo Horizonte, Brazil (latitude -19.92°, longitude -43.99°). The electrical parameters as short-circuit current (I_{sc}), open circuit voltage (V_{oc}) and maximum power (P_{max}), were measured from organic cell and the meteorological variables of the site were monitored. This solar irradiance was measured using both a Si reference solar cell and a calibrated pyranometer used in the GREEN (ISO 17025 accredited laboratory). All devices had their temperatures recorded using a thermocouple—and the temperature mapping (thermography) of the devices was carried out with an infrared camera.

Physical properties were analyzed with a scanning electron microscope and an atomic force microscope to observe surface properties and any changes that occur. Changes in optical properties were monitored through analysis of the transmission behavior measured using a scanning spectrophotometer over the wavelength range 350 to 1300 µm. Chemical and compositional changes were determined using the Fourier Transform Infrared Spectroscopy (FTIR).

3. ELECTRICAL PARAMETERS

The most important electrical parameters that must be considered in a photovoltaic cell are current, voltage, and maximum power. It is possible to demonstrate a cell through its output parameters (voltage and current), in relation to its input parameters, for example, incident solar irradiance and operating cell temperature.

When the module reaches the maximum power (P_{max}), the maximum power current (Imp) and the maximum power voltage (V_{mp}) is generated. Other factors must also be considered for the electrical characterization of a photovoltaic cell, namely, the short-circuit current (I_{sc}), which is obtained from the terminals when they are at the same reference level, in other words, it means short-circuited, and the open-circuit voltage (V_{oc}), identified when the cell is not connected to any load, that is, when there is no current circulation.

Another fundamental parameter for this characterization is the Fill Factor (FF) obtained through the ratio of the measured maximum power to the product of short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}).

$$I = I_{ph} - I_0 \left(e^{\left(\frac{V+IR_S}{a} \right)} - 1 \right) - \frac{V+IR_S}{R_{sh}} \tag{1}$$

Considering the relation with the resistances, the Eq. (1) can be described as:

$$I = I_{ph} - I_0 \left(e^{\left(\frac{V+IR_S}{a} \right)} - 1 \right) - \frac{V+IR_S}{R_{sh}} \tag{2}$$

Where I_{ph} means the current photo-generated by the device, I_0 refers to the reverse saturation current of the diode without the presence of light, V means voltage applied to the diode terminals, a is modified ideality factor, R_s and R_{sh} are the series resistance and the shunt resistance, respectively. The series resistances ohmic losses of the solar cell. It can be seen the ideal is for the shunt resistance presents high values, avoiding the emergence of an alternative path for the photogenerated current, which would reduce the output current of the photovoltaic module. In the case of series resistance, the lower the resistance, the grater performance of the module. The modified ideality factor (*a*) can be obtained used the Eq. (2).

$$a = \frac{n\,k\,T}{e} \tag{3}$$

Where *n* means ideality factor of the diode, *k* means the Boltzmann constant ($1,381 \times 10^{-23}\,{}^J\!/_K$), e is the charge of aa electron ($1,602 \times 10^{-19}$C) and *T* means the equivalent operating temperature (in Kelvin).

Fig. 5 presents the representative electrical circuit of a solar cell, considering a diode, being useful when studying the behavior of several solar cells connected in series and parallel.
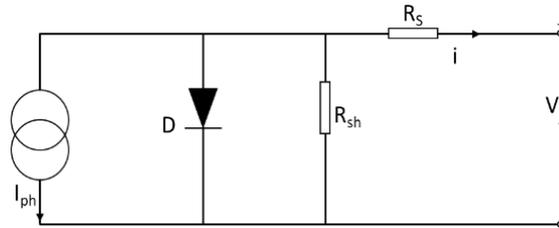
Figure 5. Scheme of an equivalent circuit of a solar cell.
Source: Author developed.

According to Lorenzo (2000), if the cell remains in an open circuit (I = 0), it will self-polarize with a certain voltage, where is greater than it can support in the generation region. This voltage is translated from the open-circuit voltage (V_{oc}) and its value is such that the
photogenerated current is fully compensated by the bias current, in other words, $I_{ph} = I_D(V_{oc})$. In this case, the Eq. (1) can be expressed as:

$$V_{oc} = \frac{nkT}{e} \ln \left[\frac{I_{ph}}{I_0} + 1 \right] \tag{4}$$

The Eq. (4) shows that V_{oc} increases with the logarithm of I_{ph}, therefore, it increases with solar irradiance. On the other hand, V_{oc} decreases with temperature since the term $\frac{nkT}{e}$ is compensated by the variation of the exponential of I_0 with temperature.

$$I = I_{sc} \left[1 - exp \left(-\frac{e(V_{oc}-V)}{nkT} \right) \right] \tag{5}$$

When a solar cell is connected to a resistive load, the power offered to the resistance is given by P=V×I, and for this power offered to be maximum, it will be necessary to have the point (I_M, V_M), where the coordinates of the maximum power point.
Eq. (5) deduces the general condition of maximum.

$$\left[\frac{dI}{dV}\right]_{MAX} = -\frac{I_M}{V_M} \tag{6}$$

Applying Eq. (1) to Eq. (6), Eq. (7) is obtained:

$$I_M = \frac{I_{ph}+I_0}{1+\frac{nkT}{eV_M}} \tag{7}$$

3. RESULTS AND DISCUSSION

The experimental analysis was developed at GREEN PUC Minas, localized in Belo Horizonte inserted in the tropical climate zone in Brazil, with time exposures of the cells and organic materials. The purposes of these experiments are two-fold: (1) to measure any changes in the electrical and/or optical properties of the solar cells and materials as a function of exposure time considering the in climate condition of the site; and (2) to provide comparisons between various organic PV materials as a function of this exposure. The optical (transmission) of the organic test materials are measured for any changes as well as the I-V characteristics of the OPV devices.

Fig. 6 shows its subdivisions and the solar cell inside the equipment for carrying out the UV-vis test. Figure 8 shows the spectrum found for 3 different areas of the studied organic solar cell. The spectrum for different wavelengths is presented, showing the begging of its degradation process.
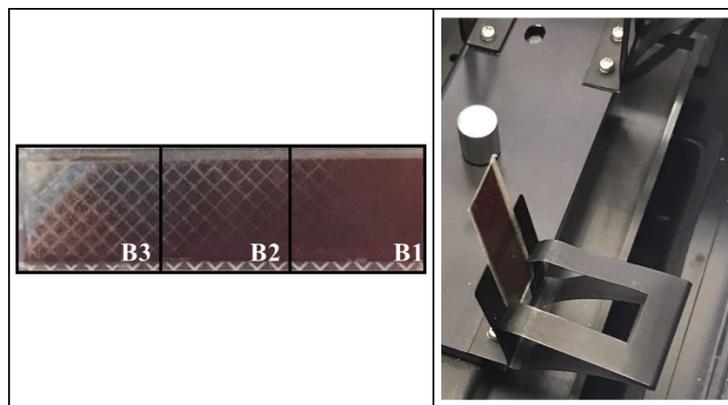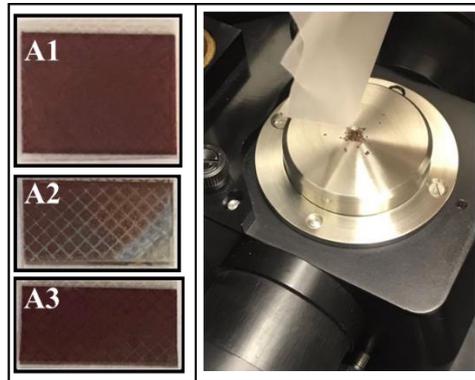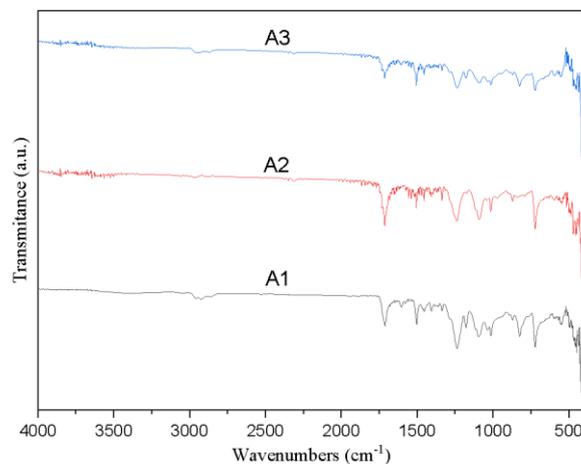

Figure 6. Solar cell subdivision scheme.
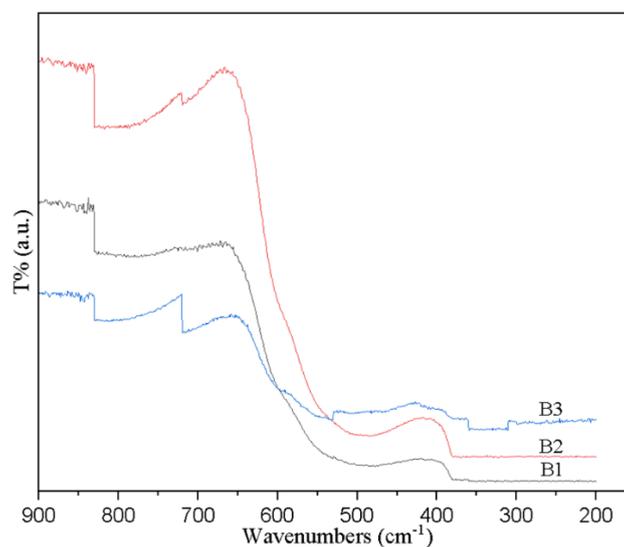
Figure 7. Solar cell spectrum at various wavelengths in the UV-vis test.

In the Fig. 7 is possible to notice that as the equipment moves towards the degraded part is spectrum changes. When the wavelength is between 300 cm-1 and 600 cm-1, it is noticed that the most degraded area has a lower absorbance, while in the others the pattern is similar.

Figure 8 shows its subdivisions and the solar cell macerated inside the equipment to perform the Fourier Transform Infrared Spectroscopy (FTIR) test. Figure 9 shows the spectra found for the 3 different areas of the studied organic solar cell.

Figure 8. Solar cell subdivision scheme.

Figure 9. Solar cell spectrum at various wavelengths in the FTIR test.

The Figure 9 shows that as the equipment moves towards the degraded part is spectrum changes. When the wavelength ranges from 1250 cm^{-1} to 750 cm^{-1}, it is possible to notice that curve A2 is very far from curve A1, that is, the one the served as the basis for defining its degradation.

Conclusion

The advancement of organic solar cell and their applications, it aimed to investigate an aspect of photodegradation in solar devices and what effects this degradation has on chemical, physical, electrical and optical properties.

Thus, it is realized that with direct exposure to radiation and high temperatures during working hours, producing electrical energy, it is concluded that these two factors contribute to an accelerated reduction in the useful life of organic solar cells (OPV). Some studies try to further delay the useful life of the organic layer, replacing the PC61BM or PC71BM molecule with another one that is not susceptible to degrade so quickly.

It is important to emphasize that the results presented in this work are initial obtained in research in which the objective is to investigate the performance of organic cells considering the influence of climate factors.

Acknowledgments

References

Anna Gabriella Tempesta, Luiz Carlos Mariano, Kaike R. M. Pacheco, Talitha R. C. dos Santos, Fabiana Brito, and Lucimara Stolz Roman, Organic photovoltaic panels for bus rapid transit stations in Curitiba – a viability study. In, Proc *IEA SHC International Conference on Solar Heating and Cooling for Buildings and Industry 2019, Santiago, Chile.*

C. Deibel and V. Dyakonov, "Polymer-fullerene bulk heterojunction solar cells," *Reports Prog. Phys.*, vol. 73, no. 9, 2010, DOI: 10.1088/0034-4885/73/9/096401.

C. L. Braun, "Electric field assisted dissociation of charge transfer states as a mechanism of photocarrier production," *J. Chem. Phys.*, vol. 80, no. 9, pp. 4157–4161, 1984, doi: 10.1063/1.447243.

Callister, William D. Jr.; Rethewisch, David G. *Materials science and engineering: an introduction*. [S.l: s.n.], 2010. v. 8.

Chambon, Sylvain *et al.* Photo- and thermo-oxidation of poly(p-phenylene-vinylene) and phenylene-vinylene oligomer. *Polymer Degradation and Stability*, v. 96, n. 6, p. 1149–1158, 2011. Disponível em: <http://dx.doi.org/10.1016/j.polymdegradstab.2011.02.002>.

Davis, Robert J.; Pemberton, Jeanne E. Surface Raman spectroscopy of the interface of tris-(8-hydroxyquinoline) aluminum with Mg. *Journal of the American Chemical Society*, v. 131, n. 29, p. 10009–10014, 2009.

Distler, Andreas *et al.* Effect of PCBM on the photodegradation kinetics of polymers for organic photovoltaics. *Chemistry of Materials*, v. 24, n. 22, p. 4397–4405, 2012.

E. Sengupta *et al.*, "Photoinduced degradation studies of organic solar cell materials using kelvin probe force and conductive scanning force microscopy," *J. Phys. Chem. C*, vol. 115, no. 40, pp. 19994–20001, 2011, DOI: 10.1021/jp2048713.

F. L. Araújo, "Estudo das propriedades de transporte e recombinação de cargas em células solares orgânicas: efeitos de aditivo e de degradação," p. 133, 2018.

International Energy Agency - World Energy Outlook 2020 (IEA). Available at: https://www.iea.org/reports/world-energy-outlook-2020. Accessed on: Feb. 20, 2021.

J. Guo, H. Ohkita, H. Benten, and S. Ito, "Charge generation and recombination dynamics in poly(3-hexylthiophene)/ fullerene blend films with different regioregularities and morphologies," *J. Am. Chem. Soc.*, vol. 132, no. 17, pp. 6154–6164, 2010, doi: 10.1021/ja100302p.

Jørgensen, Mikkel *et al.* Stability of polymer solar cells. *Advanced Materials*, v. 24, n. 5, p. 580–612, 2012.

Karakawa, Makoto *et al.* Factors contributing to degradation of organic photovoltaic cells. *Organic Electronics*, v. 76, n. September 2019, p. 105448, 2020. Disponível em: <https://doi.org/10.1016/j.orgel.2019.105448>.

Lloy, Matthew T. *et al.* Impact of contact evolution on the shelf life of organic solar cells. *Journal of Materials Chemistry*, v. 19, n. 41, p. 7638–7642, 2009.

Lloy, Matthew T. *et al.* Influence of the hole-transport layer on the initial behavior and lifetime of inverted organic photovoltaics. *Solar Energy Materials and Solar Cells*, v. 95, n. 5, p. 1382–1388, 2011. Disponível em: <http://dx.doi.org/10.1016/j.solmat.2010.12.036>.

Manceu, Matthieu *et al.* The mechanism of photo- and thermooxidation of poly(3-hexylthiophene) (P3HT) reconsidered. *Polymer Degradation and Stability*, v. 94, n. 6, p. 898–907, 2009.

Mateker, William R.; MCgehee, Michael D. Progress in Understanding Degradation Mechanisms and Improving Stability in Organic Photovoltaics. *Advanced Materials*, v. 29, n. 10, 2017.

National Renewable Energy Laboratory (NREL) – Available at: https://www.nrel.gov/pv/cell-efficiency.html. Acessed on: Feb. 20, 2021.

Pacios, Roberto *et al.* Effects of photo-oxidation on the performance of poly [2-methoxy-5- (3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene]:[6,6]-phenyl C 61-butyric acid methyl ester solar cells. *Advanced Functional Materials*, v. 16, n. 16, p. 2117–2126, 2006.

Peters, Craig H. *Et al.* The mechanism of burn-in loss in a high efficiency polymer solar cell. *Advanced Materials*, v. 24, n. 5, p. 663–668, 2012.

Reese, Matthew O. *Et al.* Photoinduced degradation of polymer and polymer-fullerene active layers: Experiment and theory. *Advanced Functional Materials*, v. 20, n. 20, p. 3476–3483, 2010.

Rivaton, Agnès *et al.* Light-induced degradation of the active layer of polymer-based solar cells. *Polymer Degradation and Stability*, v. 95, n. 3, p. 278–284, 2010.

Schroeder, Bob C. *Et al.* Enhancing Fullerene-Based Solar Cell Lifetimes by Addition of a Fullerene Dumbbell. *Angewandte Chemie - International Edition*, v. 53, n. 47, p. 12870–12875, 2014.

Soto, W.; Klein, S. A.; Beckman, W. A. Improvement and validation of a model for a photovoltaic array performance. Solar Energy, v. 80, p. 78 – 88, 2006.

SUNEW: Greenest Energy Everywhere. *In*: Examples of applications of organic solar cells. [*S. L.*], 2021. Available at:https://sunew.com.br/. Accessed on: 20 Feb. 2021.

V. D. Mihailetchi, L. J. A. Koster, J. C. Hummelen, and P. W. M. Blom, "Photocurrent generation in polymer-fullerene bulk heterojunctions," *Phys. Rev. Lett.*, vol. 93, no. 21, pp. 19–22, 2004, DOI: 10.1103/physrevlett.93.216601.

Vacha, Martin; HABUCHI, Satoshi. Conformation and physics of polymer chains: A single-molecule perspective. *NPG Asia Materials*, v. 2, n. 4, p. 134–142, 2010.

Wang, Nana *et al.* Photodegradation of small-molecule organic photovoltaics. *Solar Energy Materials and Solar Cells*, v. 125, p. 170–175, 2014. Disponível em: <http://dx.doi.org/10.1016/j.solmat.2014.03.005>.

Wong, Him Cheng *et al.* Morphological stability and performance of polymer-fullerene solar cells under thermal stress: The impact of photoinduced PC60BM oligomerization. *ACS Nano*, v. 8, n. 2, p. 1297–1308, 2014.

Y. Tamai, H. Ohkita, H. Benten, and S. Ito, "Exciton Diffusion in Conjugated Polymers: From Fundamental Understanding to Improvement in Photovoltaic Conversion Efficiency," *J. Phys. Chem. Lett.*, vol. 6, no. 17, pp. 3417–3428, 2015, doi: 10.1021/acs.jpclett.5b01147.