U.Porto Journal of Engineering, 6:1 (2020) 1-10
ISSN 2183-6493
DOI: 10.24840/2183-6493_006.001_0001

Received: 11 April, 2019
Revised: 4 May, 2019
Published: 29 April, 2020

Influence of Oat Hulls on Biodegradation of Biopolymer from Polylactic Acid

Desiree Lameo Silva[1], Larissa Oliveira Paulista[2], Pedro Henrique Presumido[3], Janksyn Bertozzi[4], Fabio Yamashita[5], Ana Paula Bilck[6], Tatiane Cristina Dal Bosco[7]

[1]Department of Environmental Engineering, Federal University of Technology - Paraná, Estr. dos Pioneiros, 3131 - Jardim Morumbi, Londrina - PR, Brazil (desiree_lameo@hotmail.com) ORCID 0000-0002-6151-9063; [2]Faculty of Engineering, University of Porto, Porto, Portugal (larissa-paulista@hotmail.com) ORCID 0000-0002-2360-9885; [3]Faculty of Engineering, University of Porto, Porto, Portugal (pedrohpresumido@gmail.com) ORCID 0000-0001-8134-9594; [4]Departament of Chemical Engineering, Federal University of Technology - Paraná, Estr. dos Pioneiros, 3131 - Jardim Morumbi, Londrina - PR, Brazil (janksyn@gmail.com) ORCID 0000-0002-5680-613X; [5]Department of Food Science and Technology, Londrina State University, Rodovia Celso Garcia Cid - Pr 445 Km 380 - University Campus, Londrina - PR, Brazil (fabioy@uel.br) ORCID 0000-0002-9280-0683; [6]Department of Food Science and Technology, Londrina State University, Rodovia Celso Garcia Cid - Pr 445 Km 380 - University Campus, Londrina - PR, Brazil (ap.bilck@gmail.com) ORCID 0000-0002-0432-3945; [7]Department of Environmental Engineering, Federal University of Technology - Paraná, Estr. dos Pioneiros, 3131 - Jardim Morumbi, Londrina - PR, Brazil (tatianebosco@utfpr.edu.br) ORCID 0000-0002-2470-9853

Abstract

The production of biopolymers has been shown to be one of the most viable alternatives for the reduction of the use of conventional plastics. The oat hulls are a by-product with great ability to be incorporated into the production of biopolymers since it is a lignocellulosic compound. The lignin present in its composition can improve the strength of the material, however, it can also hamper its degradation. The aim of this study was to evaluate the degradation levels of composites produced from starch and polylactic acid with absence (T1) and presence of oat hulls (T2) through the Sturm test. In T2 it was a more uniform and smooth biopolymer. In addition, the use of oat hulls favored CO_2 production, 8% more than T1. Although the loss of dry mass in T1 was 3% higher, it was possible to observe degradation in T2.

Author Keywords. Inoculum, Sturm Test, Degradation, Solid Waste, Oat, Lignin.

Type: Research Article
Open Access Peer Reviewed CC BY

1. Introduction

The disposal of solid waste is one of the challenges faced by modern society, as increasingly new living habits, consumption and new technologies result in the generation of a larger amount of waste and a greater diversity of materials, especially plastics. In addition, it is known that most of the waste generated is classified as organic and have great potential for decomposition when properly treated.

However, it is known that the packaging of solid waste is usually made in plastic, distributed for free or paid of charge in commerce, increasing its quantity in landfills and its permanence in the environment. Plastic bags in the environment result in a high environmental cost. The production

of bags consumes oil, water and energy, emits gases and generates liquid effluents with toxic characteristics (Demetrious and Crossin 2019). One of the solutions to this environmental problem is the recycling or reuse of this waste. Thus, the material can return the productive chain of the products in the form of a resource and not as a discard (Cooper and Gutowski 2017).

On the other hand, biodegradable polymeric materials have been increasingly studied, including for the manufacture of plastic bags and food trays. Biodegradable polymers can be degraded from microorganisms such as bacteria, fungi and algae and depend on environmental conditions (Ray and Bousmina 2005). All polymeric materials originating from renewable raw material are classified as biopolymers, such as corn, sugarcane, potatoes, beet, sugar (Groot and Borén 2010; Armentano et al. 2013; Ruiz, Pastor, and Acevedo 2013). These materials have a much shorter life cycle than conventional polymers from non-renewable sources and are biodegradable.

In order to know the viability of the polymer in relation to its biodegradation, it is necessary to perform tests proving its degradability. Studies of the biodegradability and compostability of products and packaging based on biopolymers available in the market are important, since their results can be based on policies that determine the disposal with the organic residues, once their compostability has been proved.

Analysis of the degradability of a compound can be done by the Sturm Test. In this test, the carbon dioxide (CO_2) content, produced by the microorganisms, can be converted into degradation efficiency of the material (Sturm 1973). The Sturm Test is adopted as one of the methods of analysis established by Standards Australia (2005), International Standard Regulating methods of final aerobic biodegradability of plastics based on organic compounds under controlled conditions.

Lignocellulosic residues increase the flexibility of biopolymers and the resistance to moisture, making this material with chemical and physical properties closer to conventional packages (Salgado et al. 2008). The oat hulls are a residue of the agroindustry and have a lignin content around 22% of their composition (Hauly et al. 2004). In addition, this waste is generated in large quantities, it has no economic value and there is need of destination to the correct location. Thus, the oat hulls out shell incorporated into biopolymers made from starch may be a good alternative to improve the quality of the biopolymer and to destine the residue of oat production.

In this sense, the aim of this study was to evaluate the biodegradability of biopolymers of renewable source with the addition of the by-product of oat hulls by the Sturm Test methodology.

2. Materials and Methods

2.1. Experimental apparatus

The Sturm Test (Sturm 1973) was used for the experiments done in triplicate (Figure 1). In this methodology, it was used the quantification of CO_2 as an evaluation factor for active microbiological media.

For this experimental apparatus, the atmospheric air passes through 250 mL of 6 $mol.L^{-1}$ NaOH solution to remove oxygen. Then, this oxygen air feeds the reactor containing the ratio of 6:1 by volume of inoculum and biopolymer (totaling 200 mL). Finally, the generated CO_2 was captured by 100 mL of 0.5M NaOH and quantified by Sequential Injection Analysis (SIA).

Subsequently, in the samples contained in the reactor (biopolymer + inoculum) were taken to the oven at 110 ºC for 24 h to find the dry mass, and to compare it with the initial dry mass, in order to determine the loss of actual mass that occurred during the process.

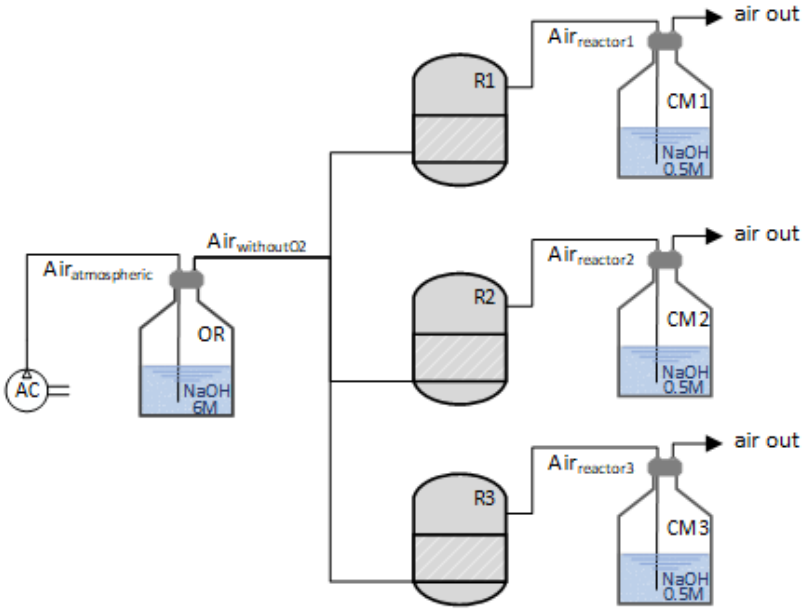

Figure 1: Experimental apparatus used in the Sturm Test

Note: AC – air compressor, OR – oxygen remover, R – reactor, CM – capture and measurement

2.2. Inoculum

In this study, the inoculum was used to stabilize and matured organic material, coming from the sludge composting process of the dairy effluent treatment plant and tree pruning. This inoculum was firstly sieved with a 0.5 cm mesh, which falls within the range of 0.5 cm to 1 cm by Standards Australia (2005).

The inoculum was characterized initially and at the end of the experimental period, following the analyzes: pH, humidity, electric conductivity, C:N ratio and fixed solids, volatile solids by American Public Health Association (1998) and organic carbon by Walkley–Black procedures (Walkley and Black 1934; Walkley 1947). The initial parameters of the inoculum are described in Table 1.

Parameters	Inoculum
pH	7.8
Electric conductivity (uS cm^{-1})	6.3±0.3
Fixed solids (%)	13.5±0.2
Volatile solids (%)	86.4±0.2
Humidity (%)	22.9±2.5
Organic carbon (%)	34.7±0.1
Nitrogen (%)	3.1±0.3
C/N	11.2±0.9:1

Table 1: Composition of the inoculum

2.3. Biopolymer

The biopolymers were produced in science and Food Technology department, State University of Londrina (UEL), Brazil. The trays of biopolymers were produced with native cassava starch (Indemil, Brazil), glycerol (Dinamica, Brazil), and polylactic acid (PLA) (Ingeo 4043D, NatureWorks LLC, Cargill, USA) and a presence/absence of micronized oat hulls. Once the micronized oat hulls had, every 100 g, in its composition: 4.64 g of ashes, 3.95 g of protein, 2.12 g of lipids, 23.13 g of cellulose, 25.25 g of hemicellulose and 3.8 g of lignin, the components were manually mixed and extruded in a pilot single screw extruder (BGM, EL-25 model, Brazil) to produce pellets. The five heating zones and a matrix six 2 mm holes, and the barrel temperature profile was set at 90/180/180/140 °C with a screw speed of 30 rpm. For the current study two formulations were tested without and with oat hulls (T1 and T2, respectively). The composition of the biopolymers tested can be seen in Table 2.

Treatment	Stemming cassava starch (g. 100g^{-1})	Polylactic acid (g. 100g^{-1})	Glycerol (g. 100g^{-1})	Micronized oat hulls (g. 100g^{-1})
T1	45	15	40	-
T2	35	15	40	10

Table 2: Composition of the biopolymers tested

A polymer is certified as biodegradable if the material emits about 90% of the total theoretical CO_2 in a maximum time of 180 days according to Standards Australia (2005). Thus, the degradation of the polymer was evaluated by the consumption of CO_2, by the loss of mass and by the external surface and fractures by scanning electron microscopy (SEM) (FEI Quanta 200, Oregon, USA), FEI Quanta 200 electronic microscope, at the Food Technology Laboratory of the Federal Technological University of Paraná, Londrina campus.

The SEM (FEI Quanta 200, Oregon, USA) was used to obtain micrographs of the surfaces and fractures of the trays. The samples were dried in a desiccator with anhydrous calcium chloride for 15 days, then submerged in liquid nitrogen and broken (cryogenic fracture). The surfaces and fractures were coated with a thin layer of gold (40-50 nm) and they were analyzed using an accelerator voltage of 30 kV. The magnitude of the observation was defined at the time of analysis.

3. Results and Discussion

3.1. Inoculum

The inoculum at the end of both treatments obtained very similar results. The pH value did not change (7.8 to 7.9 and 7.7 in treatments T1 and T2, respectively). These values are in accordance with Standards Australia (2005), which requires a pH of 7 to 14.

Conductivity is related to the way the salts are dissolved in a compound. In fact, the initial inoculum was 6.3 µS cm^{-1} and increased to 46.9 µS cm^{-1} and 48.3 µS cm^{-1} for T1 and T2, respectively. This situation can be explained by the degradation and dissolution of salts of the biopolymers in the inoculum.

The initial humidity had 54.71%, but after 40 days of experiment the material was visually dry and correction had to be made following the rules (AS ISO 14885). Even with this correction at the end of the treatment, the humidity dropped to 32% in T1 and T2 (Figure 2-a). The loss of

moisture may be related to the retention of water in the biopolymers through their pores and by microbial activity (Cooper and Gutowski 2017).

In addition, the C:N ratio was from 11.2:1 to 13.5:1 and 12.6:1 for T1 and T1, respectively. The organic carbon remained constant (Figure 2-b), but the nitrogen values decreased from 3.11±0.26% to 2.72±0.10% and 2.79±0.05%. This means that the microorganisms used the available nitrogen in the inoculum to degrade the biopolymers. Besides that, there was a small increase in volatile solids from 86.47±0.22% to 89.02±0.75% and 87.34±0.93% to T1 and T2, respectively. This increase may be related to the growth of decomposing microorganisms (Figure 2-c).

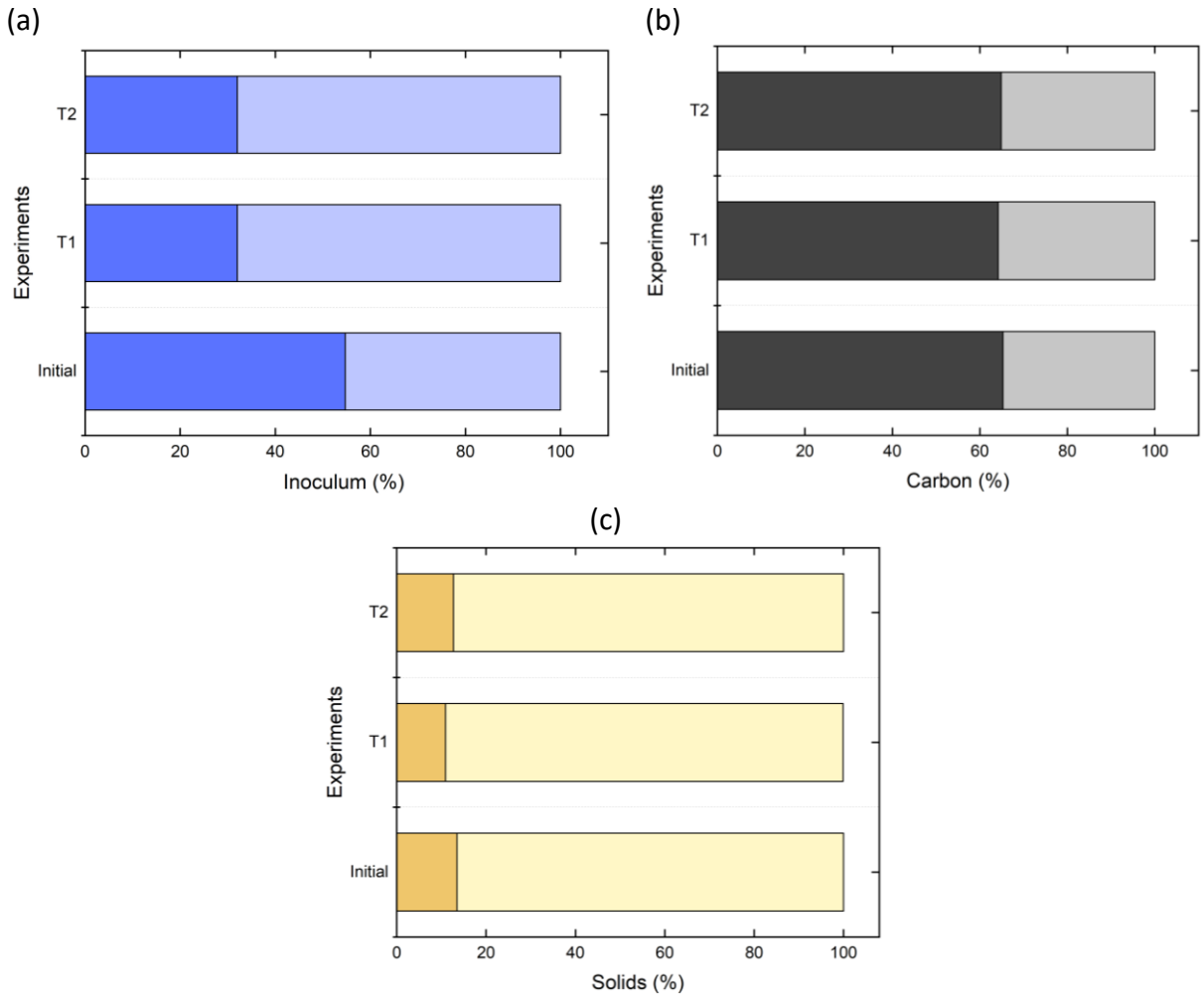

Figure 2: Inoculum parameters after the Sturm Test:
(a) humidity and dry mass; (b) organic carbon and inorganic carbon;
(c) volatile solids and fixed solids

Note: T1 – treatment without oat hulls, T2 – treatment with oat hulls

3.2. Biopolymer

The addition of oat hulls favored the metabolic pathways for CO_2 production. The accumulated average CO_2 production for T2 was 42.79±0.89 g (Figure 3-b) and T1 was of 39.36±0.65 g (Figure 3-a). According to Banik (2004), the composition of the oat hulls is: 29.6-32.7% of organic carbon, 28.59-61.05% α-cellulose, 3.40%-9.28% fat and wax, 15.07%-22.08% lignin, 13.08%-26.01%

pentosan and 1.26%-4.49% ash. The CO_2 production may have been generated by aerobic microorganisms, by the decomposition of carbonaceous matter and/or nitrogenous organic matter.

Daily CO_2 production for both treatments is very high in the first 10 days and then decreases. Then, over time there is an increase and decrease in CO_2 production. In other words, within 10 days an organic matter of easy degradation was broken, followed by the generation of some by-product that has inhibited the microorganisms that generate CO_2 (Figure 3).

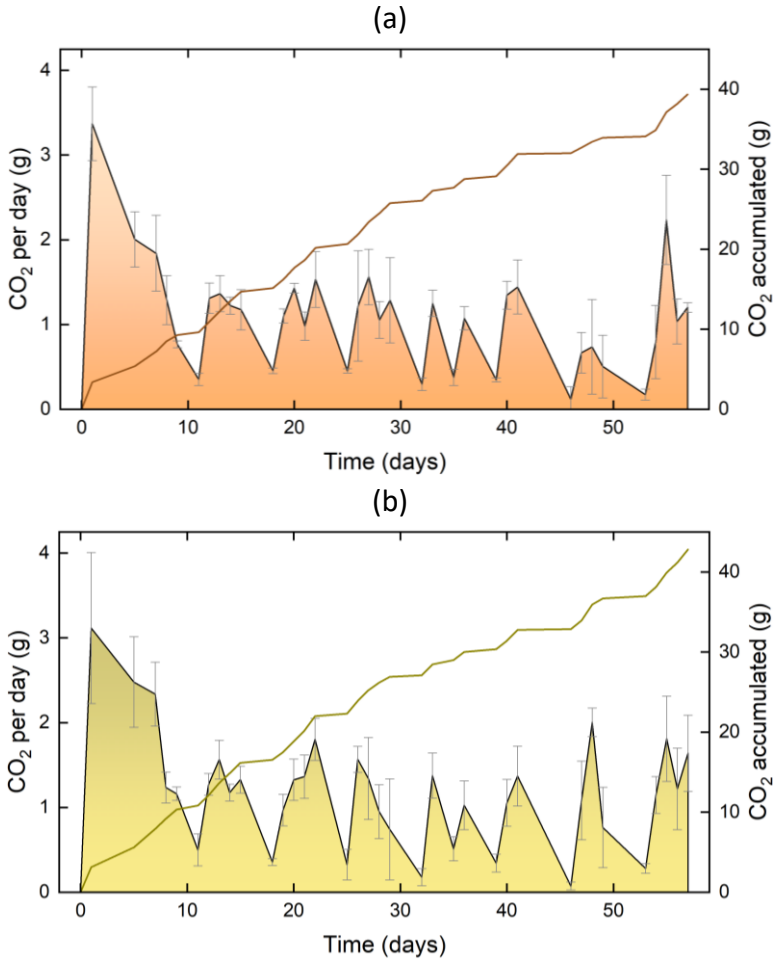

Figure 3: The average yield of triplicates of treatments T1 (a) and T2 (b), for CO_2: accumulated (line graph) and per day (area chart with triplicate standard deviations)

Note: T1 – treatment without oat hulls, T2 – treatment with oat hulls

The T1 treatment had a 3% increase in dry mass (Table 3) loss in relation to treatment with oat hulls (T2). However, the higher CO_2 production was in T2 treatment, reaching 8% difference in relation to T1. Considering that the system used was adiabatic, one can intuit that more different forms of the mass of carbon were formed. Those that were not monitored were lost during the tests, which explains the higher values of mass reduction in relation to carbon evolution (Table 3). Some possible forms of loss of mass by water (aerobic reaction), in addition, methane and oxides of nitrogen and sulfur (anaerobiosis).

Biopolymer	Initial dry mass (g)	Final dry mass (g)	Weight loss (g)	Carbon evolution (g)
T1	69.00	60.47	8.53	10.74
T2	67.00	59.05	7.95	11.68

Table 3: Difference of the initial and final dry mass for T1 and T2 treatment

Note: T1 – treatment without oat hulls, T2 – treatment with oat hulls

According to the microscopy images, it was possible to observe the color change in the biopolymer with the addition to the oat hulls (Figure 4-1 and 2). After treatment, T1 presented visually more microorganisms than T2 (Figure 4-1a and 2a).

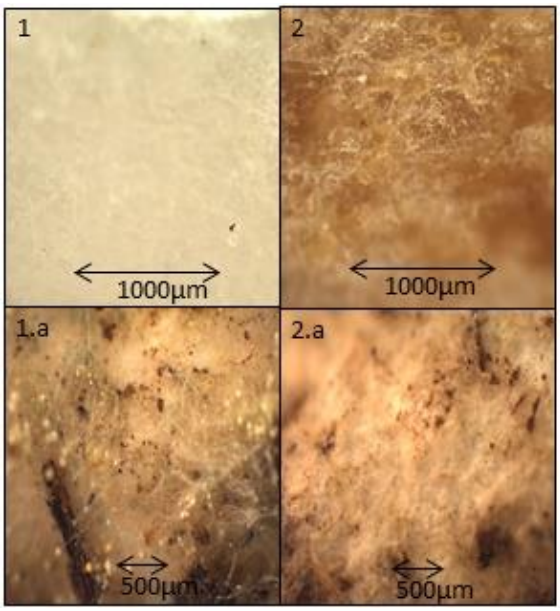

Figure 4: Microscope images of the biopolymer with (2) and without (1) oat hulls and at the after of the experiment (a)

According to the SEM images the surface of the biopolymer with oat hulls (T2) is smoother and more regular (Figure 5-1.i and 2.i). This regular surface may be related to the presence of lignin in oat hulls (Salgado et al. 2008). Visually perceive that the biopolymer with oat hulls presents larger particles and less porous relatively to the biopolymer without oat hulls (Figure 5-1.ii and 2.ii). These pores that are seen in these images are responsible for the retention of water in the biopolymers, causing the loss of moisture in the inoculum (Cooper and Gutowski 2017).

After the Sturm test, there was actually a degradation of both biopolymers (Figure 5-1.ia and 2.ia). It was possible to observe in T1 fracture (Figure 5-1.iia) a greater abundance of microorganisms compared to T2. In addition, there are non-degraded filaments in T2 (Figure 5-2.iia). One explanation is that oat hulls are a lignocellulosic material. In this case, lignin is a material more difficult to biodegrade and often requires specific microorganisms for its decomposition (Ahmad et al. 2010; Crawford and Crawford 1980).

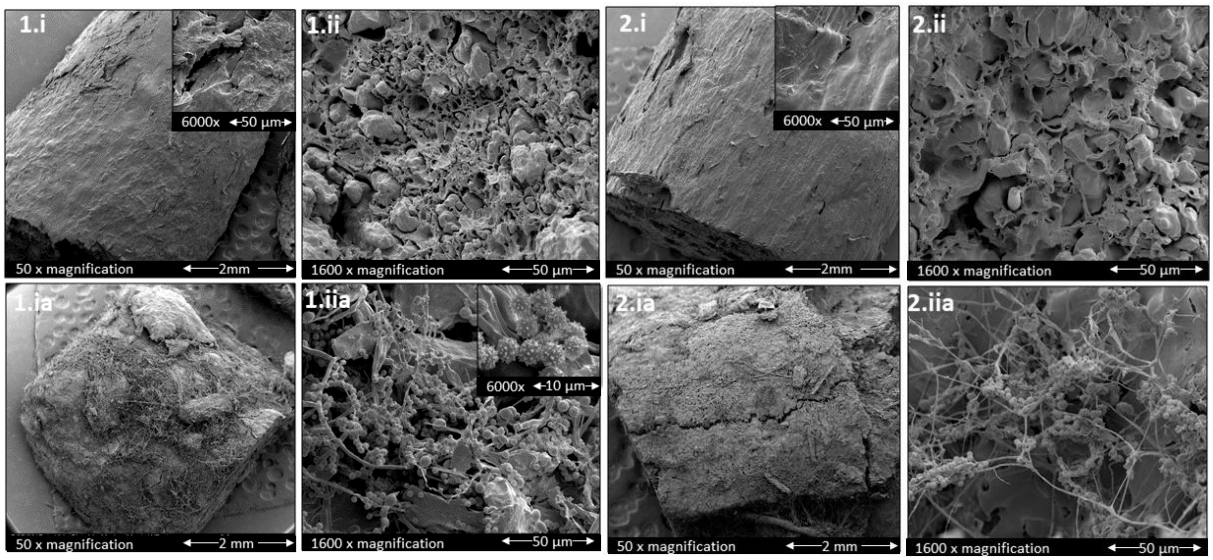

Figure 5: Scanning electron microscope (SEM) images of the biopolymer with (2.i) and without (1.i) oat hulls, images with tangential split (ii), and at the after (a) treatment

4. Conclusions

In relation to the inoculum analysis, it was possible to observe the increase of the conductivity and the volatile solids, in addition, the decrease of nitrogen and humidity. These parameters confirm that there was the production of biomass tied to the nitrogen consumption in inoculum and consequently the degradation of the biopolymers.

Moreover, the use of oat hulls favored the production of CO_2 by microorganisms (production of 8% more than T1). However, both the microscopy and scanning electron microscope (SEM) in the tangential split images that there was a greater abundance of microorganisms in the treatment T1 (without oat hulls). This fact was evidenced by the greater loss of dry mass in this treatment, with more 3% loss of dry mass in relation to T2. In addition, it was evidenced by SEM images a smoother and more regular surface with the use of oat hulls.

These aspects are directly related because the oat hulls are a lignocellulosic residue. Although, it was noticeable that lignin had a small impact on the degradation of the material. The high concentration of lignin in oat hulls generated a visually more regular biopolymer. Therefore, the use of oat hulls in biopolymers was viable, but it results in a bigger time to the degradation.

References

Ahmad, M., C. R. Taylor, D. Pink, K. Burton, D. Eastwood, G. D. Bending, and T. D. H. Bugg. 2010. "Development of novel assays for lignin degradation: Comparative analysis of bacterial and fungal lignin degraders". *Molecular BioSystems* 6, no. 5: 815-21. https://doi.org/10.1039/b908966g.

American Public Health Association. 1998. *Standard methods for the examination of water and wastewater*. Washington DC: American Public Health Association, American Water Works Association and Water Environmental Federation.

Armentano, I., N. Bitinis, E. Fortunati, S. Mattioli, N. Rescignano, R. Verdejo, M. A. Lopez-Manchado, and J. M. Kenny. 2013. "Multifunctional nanostructured PLA materials for

packaging and tissue engineering". *Progress in Polymer Science* 38, no. 10-11 (october-november): 1720-47. https://doi.org/10.1016/j.progpolymsci.2013.05.010.

Banik, S. 2004. "Jute caddis - A new substrate for biogas production". *Journal of Scientific and Industrial Research* 63, no. 9: 747-51. http://nopr.niscair.res.in/handle/123456789/5496.

Cooper, D. R., and T. G. Gutowski. 2017. "The environmental impacts of reuse: A review". *Journal of Industrial Ecology* 21, no. 1 (february): 38-56. https://doi.org/10.1111/jiec.12388.

Crawford, D. L., and R. L. Crawford. 1980. "Microbial degradation of lignin". *Enzyme and Microbial Technology* 2, no. 1 (january): 11-22. https://doi.org/10.1016/0141-0229(80)90003-4.

Demetrious, A., and E. Crossin. 2019. "Life Cycle Assessment of paper and plastic packaging waste in landfill, incineration, and gasification-pyrolysis". *Journal of Material Cycles and Waste Management* 21, no. 4 (july): 850-60. https://doi.org/10.1007/s10163-019-00842-4.

Groot, W. J., and T. Borén. 2010. "Life Cycle Assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand". *International Journal of Life Cycle Assessment* 15, no. 9 (november): 970-84. https://doi.org/10.1007/s11367-010-0225-y.

Hauly, M. C. O., C. Tamanini, A. S. Oliveira, M. G. A. Felipe, E. V. Canettieri, and E. J. Cândido. 2004. "Avaliação da casca de aveia para produção biotecnológica de xilitol". *Acta Scientiarum. Technology* 26, no. 2: 117-23. https://doi.org/10.4025/actascitechnol.v26i2.1509.

Ray, S. S., and M. Bousmina. 2005. "Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world". *Progress in Materials Science* 50, no. 8 (november): 962-1079. https://doi.org/10.1016/j.pmatsci.2005.05.002.

Ruiz, M., K. Pastor, and A. Acevedo. 2013. "Biodegradability of disposable products in a vermicomposting system [Biodegradabilidad de artículos desechables en un sistema de composta con lombriz]". *Informacion Tecnologica* 24, no. 2: 47-56. https://doi.org/10.4067/S0718-07642013000200007.

Salgado, P. R., V. C. Schmidt, S. E. Molina Ortiz, A. N. Mauri, and J. B. Laurindo. 2008. "Biodegradable foams based on cassava starch, sunflower proteins and cellulose fibers obtained by a baking process". *Journal of Food Engineering* 85, no. 3 (april): 435-43. https://doi.org/10.1016/j.jfoodeng.2007.08.005.

Standards Australia. 2005. *Plastic materials - Determination of the ultimate aerobic biodegradability and disintegrati*. AS ISO 14855-2005.

Sturm, R. N. 1973. "Biodegradability of nonionic surfactants: Screening test for predicting rate and ultimate biodegradation". *Journal of the American Oil Chemists Society* 50, no. 5 (may): 159-67. https://doi.org/10.1007/BF02640470.

Walkley, A., and I. A. Black. 1934. "An examination of the degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method". *Soil Science* 37, no. 1 (january): 29-38. https://doi.org/10.1097/00010694-193401000-00003.

Walkley, A. 1947. "A critical examination of a rapid method for determining organic carbon in soils - effect of variations in digestion conditions and of inorganic soil constituents". *Soil Science* 63, no. 4 (april): 251-64. https://doi.org/10.1097/00010694-194704000-00001.

Acknowledgments

This research was supported by CNPq (Concelho Nacional de Desenvolvimento Científico e Tecnológico). The authors gratefully acknowledge UEL (Universidade Estadual de Londrina) due to the production of the biopolymers and the analysis of the biopolymers. They also acknowledge UTFPR (Universidade Tecnológica Federal do Paraná) for the infrastructure provided and for carrying out some analysis.