
**PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIAS BIOLÓGICAS
(MICROBIOLOGIA APLICADA)**

**Disintegration evaluation of bioplastic elaborated with polysaccharides from
plant biomass**

MATEUS MANABU ABE

**Rio Claro -SP
2022**

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from plant biomass**

MATEUS MANABU ABE

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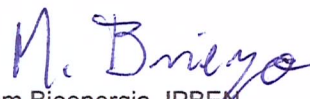
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ORIENTADOR: MICHEL BRIENZO

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Prof. Dr. MICHEL BRIENZO (Participação Virtual)

Laboratório de Caracterização de Biomassa / Instituto de Pesquisa em Bioenergia IPBEN



Prof. Dr MARIO GUIMARÃES JUNIOR (Participação Virtual)
CEFET



Profa. Dra. MARCIA REGINA DE MOURA AOUADA (Participação Virtual)

Departamento de Física e Química / Faculdade de Engenharia de Ilha Solteira - UNESP



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Abstract

Since 1950, the growing demand for plastic resins has increased the production of this material. This increase is due to the different applications of these materials, with advantages due to low cost, mechanical properties, water vapor barrier, chemical inertness and reduced or lack of biodegradation. Even with all the clear advantages of using synthetic plastics, the accumulation of this material represents a wide variety of problems such as outbreaks of disease proliferation, animal strangulation, damage to the fishing economy, causes of liver protein anomalies, the modifier of the physical-chemical biological soil profile, in addition to many other social and environmental impacts. Therefore, the development of biomaterials such as bioplastics from renewable and/or biodegradable sources is important to mitigate the environmental problems of plastics, at least in a few areas of the use of synthetic plastics. In this context, this study aimed to evaluate the addition of xylan in starch bioplastic's to verify biodegradation and possible ecotoxic effects. The bioplastics were prepared with 10, 15, and 25% (w/w) of xylan, in 5% (w/v) total polysaccharides including starch, dried at 30 °C. The bioplastic resulted in a continuous and homogeneous plastic matrix without cracks. The bioplastic was buried to evaluate the biodegradation showing disintegration after 13 days. The time period for composting and disintegration in the soil was short compared to plastics from petroleum. In general, the bioplastic did not negatively influence the germination and tissue development of seeds of *Cucumis sativus*, with 100% of seed germination. A positive influence was observed on the root and hypocotyl growth but with a temporary inhibition of *C. sativus* tissue exposed to 10-days biodegradation soil washing. The optical and photoprotective properties and the solubility in food simulants (waxy and acidic foods) of bioplastics were also analyzed. Also, employing Thermogravimetric Analysis, Dynamic-Mechanical Analysis, Differential Scanning Calorimetry Analysis, Scanning Electron Microscopy, the thermal resistance, mechanical resistance, crystallinity, and morphology of bioplastics were performed, respectively. The highest tensile strength was with the composition 15/25% (w/w) of xylan/starch (2.99 MPa). All bioplastic compositions resulted in homogeneous and bubble-free materials, and there was no difference in transparency at 600 nm (except for the bioplastic with alpha-cellulose and hemicellulose), however, between 200-400 nm of the wavelength of light, the bioplastics with higher concentrations of xylan reduced transmittance, probably due to the presence of lignin. The bioplastic with 25% xylan showed a small photoprotective capacity against the yeast *Saccharomyces cerevisiae* when exposed to UVC light. Solubility increases in acid simulants with plastics with higher xylan concentration (25% w/w), however, in fatty food simulants, the solubility of bioplastic with 25% (w/w) xylan was negligible. In general, the addition of xylan, alpha-cellulose, and holocellulose reduced the thermal resistance in relation to the pure starch-

based bioplastic, as well as reduced crystallinity with higher concentrations of xylan, except for the addition of alpha-cellulose and holocellulose.

Keywords: Bioplastics, polymers, biomass, biodegradation, ecotoxicity.

Resumo

Desde 1950, a crescente demanda por resinas plásticas aumentou a produção desse material. Este aumento deve-se às diferentes aplicações destes materiais, com vantagens devido ao baixo custo, propriedades mecânicas, barreira ao vapor de água, inércia química e reduzida ou não biodegradação. Mesmo com todas as claras vantagens do uso de plásticos sintéticos, o acúmulo desse material representa uma grande variedade de problemas como surtos de proliferação de doenças, estrangulamento de animais, prejuízos à economia pesqueira, causas de anomalias de proteínas hepáticas, modificação do perfil físicoquímico e biológico do solo, além de muitos outros impactos sociais e ambientais. Portanto, o desenvolvimento de biomateriais como os bioplásticos de fontes renováveis e/ou biodegradáveis é importante para mitigar os problemas ambientais dos plásticos, pelo menos em algumas áreas de uso de plásticos sintéticos. Nesse contexto, este trabalho teve como objetivo avaliar a adição de xilana em bioplásticos de amido para verificar a biodegradação e possíveis efeitos ecotóxicos. Os bioplásticos foram preparados com 10, 15 e 25% (m/m) de xilana, em 5% (m/v) de polissacarídeos totais incluindo amido, secos a 30 °C. O bioplástico resultou em uma matriz plástica contínua e homogênea sem rachaduras. O bioplástico foi enterrado e a desintegração ocorreu após 13 dias. O período para compostagem e desintegração no solo foi curto em comparação com plásticos de petróleo. Em geral, o bioplástico não influenciou negativamente na germinação e desenvolvimento tecidual das sementes de *Cucumis sativus*, com 100% de germinação das sementes. Uma influência positiva foi observada no crescimento da raiz e do hipocótilo, mas com uma inibição temporária do desenvolvimento do hipocótilo e da radícula de *C. sativus* exposto a lavagem do solo de 10 dias de desintegração. As propriedades ópticas e fotoprotetoras e a solubilidade em simuladores alimentares (alimentos cerosos e ácidos) de bioplásticos também foram analisadas. Além disso, empregando Análise Termogravimétrica, Análise Dinâmico-Mecânica, Análise Calorimétrica Diferencial de Varredura, Microscopia Eletrônica de Varredura, foram realizadas a resistência térmica, resistência mecânica, cristalinidade e morfologia dos bioplásticos, respectivamente. A maior resistência à tração foi com a composição 15/25% (w/w) de xilana/amido (2,99 MPa). Todas as composições de bioplásticos resultaram em materiais homogêneos e sem bolhas, e não houve diferença na transparência em 600 nm (exceto para o bioplástico com alfa-celulose e hemicelulose), porém, entre 200-400 nm do comprimento de onda da luz, os bioplásticos com maiores concentrações de xilana reduziu a transmitância, provavelmente devido à presença de lignina. O bioplástico com 25% de xilana apresentou reduzida capacidade fotoprotetora da levedura *Saccharomyces cerevisiae* quando exposta à luz UVC. A solubilidade aumenta em simuladores ácidos com plásticos com maior concentração de xilana (25% m/m), porém, em simuladores de alimentos gordurosos, a solubilidade do bioplástico com 25% (m/m) de xilana foi insignificante. Em geral, a adição de xilana, alfa-celulose e holocelulose reduziu a resistência

térmica em relação ao bioplástico à base de amido puro, assim como reduziu a cristalinidade com maiores concentrações de xilana, exceto pela adição de alfa-celulose e holocelulose.

Palavras-chaves: Bioplásticos, polímeros, biomassa, biodegradação, ecotoxicidade.

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CHAPTER I: INTRODUCTION AND OBJECTIVES

1. Introduction

From 1950 to 2015, around 8.3 billion tons of plastics were produced, of which 6.3 billion tons became waste. During this period, 79% of plastic waste ended up in landfills and different natural environments (GEYER et al., 2017). This growing demand for plastic production is a source of environmental concern due to the resistance to degradation and slow biodegradation of plastics. Therefore, the accumulation of plastic waste is a concern due to the ingestion of formed debris by fauna, landscape pollution, impacts on human health, in addition to the economic impacts (GREGORY, 2009; GOLDSTEIN and GOODWIN, 2013; UNEP, 2014; GEYER et al., 2017; ALABI et al., 2019). There are different approaches to mitigate the problems caused by the disposal of the large volume of plastic, which is directly related to the 4 R's (Reduce, Reuse, Recycle, and Recover) (PRATA et al., 2019). Some of the alternatives are recycling, incineration, and bioplastics development.

Recycling is a preferred alternative for the management of plastic waste which can generate new plastics of high quality (primary recycling) or inferior quality (secondary recycling) (PRATA et al., 2019). Even with the benefit of recycling in relation to the circular economy and environmental impacts, this represents a complex process, due to the need for several steps such as the separation of waste by the population, selection of different plastic polymers, elimination of contaminants, and the sale of plastics recycled. Therefore, recycling ends up being limited and expensive (GRADUS et al., 2017).

Incineration represents another alternative for the plastic waste management, which has advantages over recycling due to the use of polymeric mixtures, without the need for separation, decontamination, pre-treatment and result in energy production (PRATA et al., 2019). However, incineration can result in the release of CO₂ (worsening of the greenhouse effect), linear economy, production of ash with metallic and other contaminants, and toxic gases (BRUNNER et al., 2015; LIU et al., 2018; PRATA et al., 2019).

Considering the disadvantages of the recycling and incineration process, another approach that has been growing is the design of new types of materials, with a focus

mainly on biomaterials. Biomaterials such as bioplastics, when biodegradable, make it possible to reduce the accumulation of plastic in addition to enabling the development of materials from renewable sources. That is, represents a partial alternative for the plastic issue and also influences in management of bio-based waste (PRATA et al., 2019).

Due to the large demand for plastics in the last decades, mainly in the food packaging sector, in addition to the increased awareness of ecofriendly products, the production and studies related to bioplastics have increased (PRATA et al., 2019). Studies showed that in an optimistic scenario, the bioplastic production in 2030 may double in relation to the production of 2018 (DÖHLER et al., 2020). However, like other waste management and product development measures, the disadvantages and limitations of bioplastics are (1) price competitiveness with synthetic virgin plastics; (2) compliance with the properties required by the different applications (BALLESTEROS et al., 2018); (3) increase in the complexity of solid waste management (collection and specific installations) and (4) increase in biopolymer waste with the biodegradable seal, which may have a slow biodegradation rate (PRATA et al., 2019).

The use of polysaccharides from plant biomass, as lignocellulosic fibers, can be an alternative for the development of bioplastics with optimized properties. As well as reducing some disadvantages of common plastics, they are biodegradable, biocompatible, result in less CO₂ emissions (BALLESTEROS et al., 2018), can optimize the physicochemical properties. A contribution to lowering production costs due to the great availability of this waste, especially in countries with wide agricultural activity such as Brazil.

In this scenario, the use of polysaccharides and plant macromolecules represents an alternative for the production of biodegradable and renewable bioplastics. One of these molecules is starch, which represents the main carbon reserve polymer of vegetables (high availability). Starch is widely studied for the production of bioplastics as this polymer is biodegradable, renewable, biocompatible, a barrier to CO₂, in addition, represents a widely traded commodity when it comes to waste. However, pure starch bioplastics have disadvantages concerning their hydrophilic character and low mechanical strength. The addition of lignocellulosic fibers/macromolecules can alter the properties of starch-based bioplastics such as improving or reducing mechanical and water vapor barrier properties. In this way, a lignocellulosic component such as hemicellulose contains physical and chemical structures similar to starch, and from it,

these polymers can expand the possibilities of applying starch-based bioplastics. Xylan, one of the main hemicelluloses types, has been widely studied as an additive in cellulose and protein solutions. However, the mixture of xylan and starch for the production of bioplastics can result in advantages.

Another important aspect to be considered in the manufacture of bioplastics is the biodegradation process and ecotoxic effects. Recent studies show that the production of bioplastics can result in greater environmental impacts than synthetic plastics. Moreover, this occurs considering the need for the cultivation of plant biomass for application in bioplastics. However, the use of plant waste is an alternative to circumvent the environmental impacts of cultivation, in addition to being a strategy for managing plant organic waste.

Even with the use of organic residues from plant sources, the bioplastic elaborated with this material, still represents a carbon source of easy microbial assimilation, in addition to possibly altering the physicochemical profile of the soil and water. Thus, in addition to studies of the mechanical and vapor barrier properties of bioplastics, the possible environmental impacts of this technology must also be analyzed.

1.1. Objectives

The focus of this research was to verify the influence on the properties of starch-based bioplastics from the addition of xylan. The formation of continuous and homogeneous bioplastics was a criterion, evaluating mechanical and thermal resistance, with access to bioplastic disintegration, disintegration in the soil and composting system, and possible ecotoxic effects.

1.2. Specific objectives

- To evaluate the effect of xylan concentration on the starch-based bioplastics development;
- To assess the effect of xylan on the solubility, mechanical properties, thermal resistance in starch-based bioplastic;
- To evaluate the bioplastic time of composting and disintegration in the soil;

- To evaluate the impact on soil and water characteristics when exposed to bioplastic and assess a possible ecotoxic effects.

1.3. Study presentation and dissertation organization

This dissertation was carried out systematically according to the proposed aims. Therefore, to fulfill the proposed objective, this study was developed in chapters as presented in this document. In addition to this Chapter I - Introduction, this dissertation is composed of:

- Chapter II – Review article published in *Polymers*;
- Chapter III – Review article published in *Recycling*;
- Chapter IV – Article published in *Chemosphere*;
- Chapter V- Article in elaboration;
- Chapter VI- Conclusion.

Reference

- ALABI, O. A., OLOGBONJAYE, K. I., AWOSOLU, O., & ALALADE, O. E. (2019). Public and Environmental Health Effects of Plastic Wastes Disposal: A Review. *J Toxicol Risk Assess*, 5:021. doi.org/10.23937/2572- 4061.1510021
- BALLESTEROS, L. F., MICHELIN, M., VICENTE, A. A., TEIXEIRA, J. A., & CERQUEIRA, M. Â. (2018). Lignocellulosic Materials and Their Use in Bio-based Packaging. *Springer*.
- BRUNNER, P. H., & RECHBERGER, H. (2015). Waste to energy—Key element for sustainable waste management. *Waste Manag*, 37, 3–12.
- DÖHLER, N., WELLENREUTHER, C., & WOL, A. (2020). Market dynamics of biodegradable bio-based plastics: projections and linkages to European policies. Available in:> https://bioplasticseurope.eu/media/pages/downloads/scientific-publications/27c6775164-1604264924/hwwi_researchpaper_193.pdf<. Accessed in: 03 may 2021.
- GEYER, R., JAMBECK, J. R., & LAW, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances*, 3(7), e1700782.

- <https://doi.org/10.1126/sciadv.1700782>
- GOLDSTEIN, M., & GOODWIN, D. (2013). Gooseneck barnacles (*Lepas* spp.) ingest microplastic debris in the North Pacific Subtropical Gyre. *PeerJ*, 1, 184. <https://doi.org/https://doi.org/10.7717/peerj.184>
- GRADUS, R. H. J. M., NILLESEN, P. H. L., DIJKGRAAF, E., & VAN KOPPEN, R. J. (2017). A Cost-effectiveness Analysis for Incineration or Recycling of Dutch Household Plastic Waste. *Ecological Economics*, 135, 22–28. doi:10.1016/j.ecolecon.2016.12.021
- GREGORY, M. R. (2009). Environmental implications of plastic debris in marine settings- entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philos. Trans. R. Soc. B Biol. Sci*, 364, 2013–2025. <https://doi.org/10.1098/rstb.2008.0265>
- LIU, Z., ADAMS, M., & WALKER, T. R. (2018). Are exports of recyclables from developed to developing countries waste pollution transfer or part of the global circular economy? *Resour. Conserv. Recycl*, 136, 22–23.
- PRATA, J. C., SILVA, A. L. P., DA COSTA, J. P., MOUNEYRAC, C., WALKER, T. R., DUARTE, A. C., & ROCHA-SANTOS, T. (2019). Solutions and Integrated Strategies for the Control and Mitigation of Plastic and Microplastic Pollution. *International Journal of Environmental Research and Public Health*, 16, 13, 2411. doi:10.3390/ijerph16132411
- UNEP (United Nations Environment Programme). 2014. "Valuing Plastics: The Business Case for Measuring, Managing and Disclosing Plastic Use in the Consumer Goods Industry. Available in:><https://wedocs.unep.org/bitstream/handle/20.500.11822/9238/-Valuing%20plastic%3a%20the%20business%20case%20for%20measuring%2c%20managing%20and%20disclosing%20plastic%20use%20in%20the%20consumer%20goods%20industry-2014Valuing%20plasticsF.pdf?sequence=8&isAllowed=y><. Accessed in: 03 may 2021.

CHAPTER II: Advantages and disadvantages of bioplastics production from starch and lignocellulosic components

Abstract

The accumulation of plastic wastes in different environments has become a topic of major concern over the past decades; therefore, technologies and strategies aimed at mitigating the environmental impacts of petroleum products have gained worldwide relevance. In this scenario, the production of bioplastics mainly from polysaccharides such as starch is a growing strategy and a field of intense research. The use of plasticizers, the preparation of blends, and the reinforcement of bioplastics with lignocellulosic components have shown promising and environmentally safe alternatives for overcoming the limitations of bioplastics, mainly due to the availability, biodegradability and biocompatibility of such resources. This review addresses the production of bioplastics composed of polysaccharides from plant biomass and its advantages and disadvantages.

Keywords: Bioplastics, starch-based bioplastics, lignocellulosic fibers and Extraction process.

1. Introduction

Over the past two centuries, the significant growth of the world population and its consumption habits have led to several negative impacts on the environment. The development of a society with more sustainable production/consumption mechanisms should consider scenarios such as deforestation, water pollution, soil silting and solid waste accumulation. Regarding plastic wastes, they represent approximately 12% of the composition of the world's solid waste (KAZA et al., 2018), and their annual production has been increasing since 1950 and exceeded 6 billion tons of waste generated between 1950-2015 (GEYER et al., 2017).

Despite technologies and bioproducts (e.g., bioplastics) being an alternative for the mitigation of such environmental problems, a total replacement of synthetic plastics from petrochemical origin can hardly be considered in the short or even long term. On the other hand, certain applications of bioplastics may represent areas of large-scale potential replacement (THARANATHAN, 2003), for example, biodegradable materials for packaging and other short-lived use sectors are viable, since they constitute a large part of the total plastics production (HOPEWELL et al., 2009; LACKNER, 2015; LI et al., 2016; PAULA et al., 2018).

Bioplastics can be classified into materials derived directly from natural polymers (agro-polymers), with or without modifications (e.g., starch-based bioplastics and/or cellulose), polymers produced by microbial fermentation (e.g., polyhydroxyalcanoates-PHAs) and biomaterials chemically synthesized from renewable raw materials (e.g., polylactic acid - PLA, bio-polyethylene-BPE, bio-nylons and bio-polyurethanes). BPE is derived from the polymerization of ethylene from bio-ethanol; bio-nylons are produced via diacids from biomasses and bio-polyurethanes are fabricated from the incorporation of polyols of plant origin (QUEIROZ and COLLARES-QUEIROZ, 2009). However, even oils can represent a feedstock for the development of bioplastics.

Bioplastics from agro-polymers are derived from natural polymers such as polysaccharides (starch, cellulose, pectins, hemicellulose) and proteins (casein, zein, gluten, gelatin) that generally involve intra and intermolecular interactions and cross-links (crosslinking) between polymeric constituents, forming a semi-rigid three-dimensional polymeric network which retains the solvent (GUILBERT et al., 1995; THARANATHAN, 2003).

However, a large-scale production of bioplastics for different applications is limited by high costs, in comparison to synthetic plastics derived from fossil oil and concerns over functionality (PEELMAN et al., 2013). Different biopolymers used have disadvantages such as high water vapor permeability, oxygen permeability, fragility, low thermal resistance, low mechanical properties, vulnerability to degradation and low processability (GÁSPÁR et al., 2005; LIU, 2006; CABEDO et al., 2006; JOSHI, 2008; CYRAS et al., 2009; SHEN et al., 2009; YU et al., 2009; JAMSHIDIAN et al., 2010; MÜLLER et al., 2011).

The production and use of bioplastics instead of synthetic plastics (non-biodegradable and oil-based ones) reduce emissions of polluting gases and provide materials from renewable and/or biodegradable sources, availability of raw materials and a promising alternative for the destination of solid biomass residues. Regarding environmental problems such as greenhouse effect (the emission of greenhouse gases is a growing global concern, according to the Intergovernmental Panel on Climate Change (IPCC)), a 50% reduction in GHG emissions by 2050 is required for avoiding a 2 °C increase in the global temperature. Biomaterials such as bioplastics and biofuels are considered one of the mitigating measures in relation to global warming (NAIK et al., 2010; IPCC, 2014; LACKNER, 2015; NEULING, 2017; PAULA et al., 2018).

This review focuses on the different possibilities of bioplastics production from starch and lignocellulosic fibers, their advantages and disadvantages, and the procedures for obtaining natural polymers from plant biomass. Therefore, considering the development of several studies on the production of bioplastics from lignocellulosic fibers (from fractionation of the components or in natura and modified), in addition to the different applications that these bioplastics present, a review study on the characteristics (properties) of bioplastics and the processes for obtaining these polymers is justified.

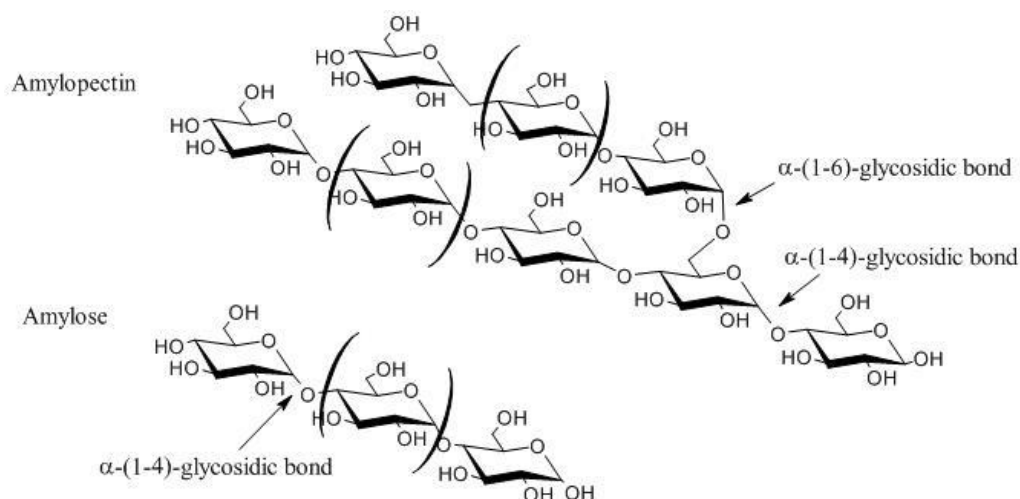
2. Starch-based bioplastics

2.1 Characteristics and structure of starch grain

Starch has a great industrial appeal, different industrial sectors use starch for different applications, such as beverages, textiles, paper and pharmaceuticals (SHARMA and SATYANARAYANA, 2013). Starch is insoluble in water and alcohol, composed of

molecules of amylopectin and amylose, which are composed of monomers of D-glucose (Figure 1) and represent the main storage polysaccharide in the vegetal cells.

Figure 1: Representation of the starch structure



Source: Elaborated by the author.

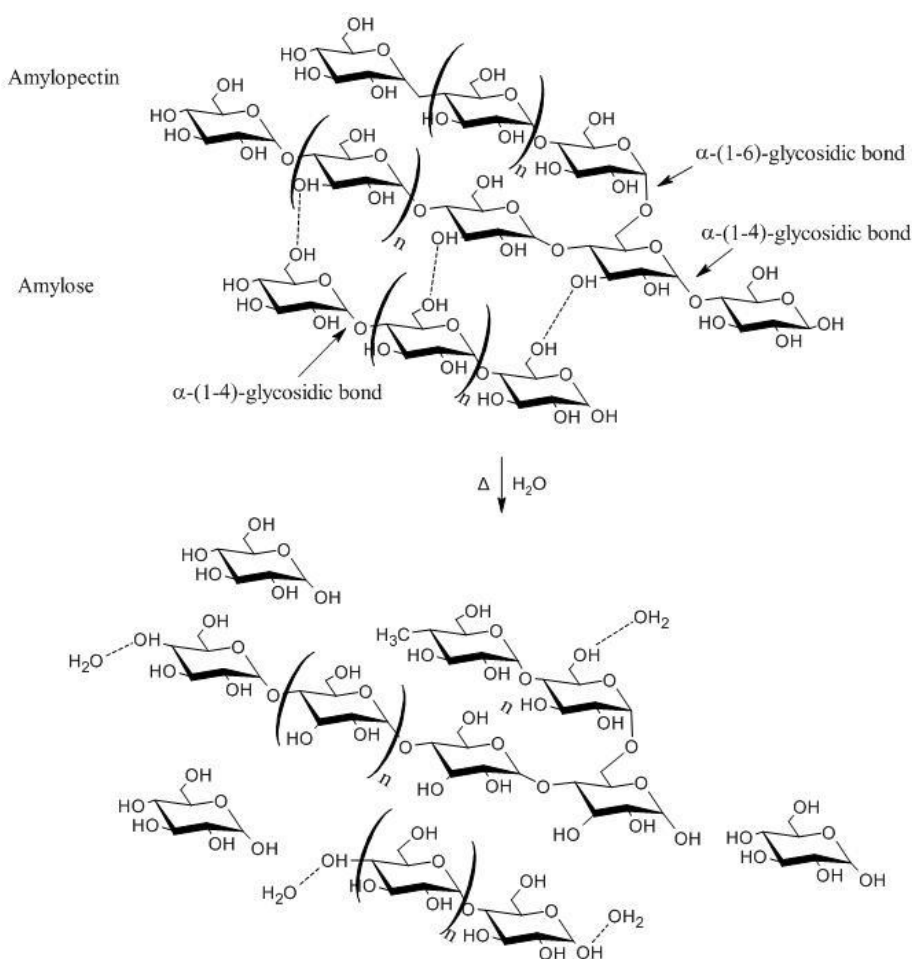
Similarly, to amylose and amylopectin, starch is a semi-crystalline polymer with linear regions; however, the α (1-6) branches of amylopectin reduce the degree of organization of the polymer (MATHLOUTHI, 1996; COMA, 2013). Amylopectin consists in a short chain of 10-60 units of linear and branched glucose, interconnected by α (1-4) and α (1-6) glycosidic bonds, whereas amylose is comprised of an unbranched linear chain of glucose monomers interconnected by α (1-4) glycosidic bonds. On average, percentage of amylopectin and amylose contained in starch ranges between 72-75% and 25-28%, respectively (SOUZA AND MAGALHÃES, 2010; SHARMA AND SATYANARAYANA, 2013).

2.2 Formation of filmogenic starch solution

Native starch molecules are linked through intermolecular interactions of the hydroxyl group and the oxygen of amylopectin and amylose. The polymers are joined by hydrogen bonds, which make it insoluble in cold water. However, its molecules can undergo significant changes when exposed to gelatinization temperatures, provoking the breakage of hydrogen bonds between starch components from the supply of thermal energy in an aqueous solution (Figure 2). In addition to the breakdown of hydrogen

bonds, the viscosity of the starch solution increases between amylose and amylopectin, from amylose leaching, structural loss in double helix of starch, birefringence and interactions between water and starch through free hydroxyls (PENG et al., 2007; HALLEY et al., 2007; COPELAND et al., 2009). Therefore, gelatinization begins in the amorphous regions of the polymer.

Figure 2: Gelatinization of starch



Source: Elaborated by the author.

Another process that can occur mainly with amylose molecules is retrogradation, or starch retrogradation, according to which a gelatinized solution shows interactions between amylose molecules and an increase in the ordering degree of hydrogen bonds. Therefore, the amylose chains crystallize with the formation of a double helix (JAILLAIS et al. 2006; ELIASSON, 2016) whereas starch retrogradation takes place more markedly when the solution is cooled. From the help of the plasticizer effect of

water and plasticizers, starch gelatinization provides thermoplastic starch for bioplastics formation, i.e., starch that has lost its original conformation and forms a melted gel similar to synthetic thermoplastics through swelling with water and other substances (AVEROUS, 2004; MA and YU, 2004; LIU, 2005).

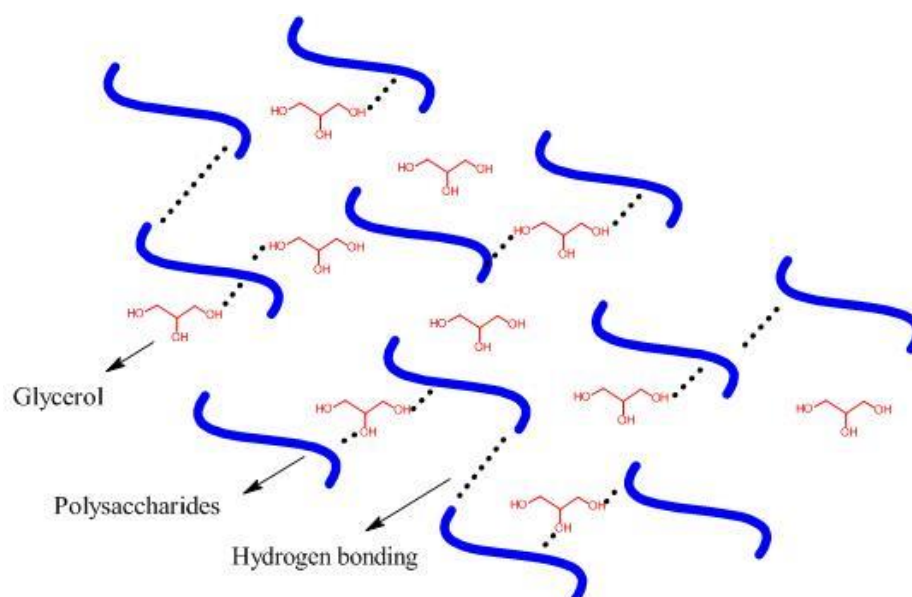
Bioplastics production from thermoplastic starch or another natural polymer (polysaccharide, lipid or protein) is completed with the deposition of the gelatinized filmogenic solution on a non-adherent surface. The solution is then dehydrated (in an oven for example), thus facilitating retrogradation due to the increase in intramolecular interactions between polymers from the reduction of the volume in the polymeric matrix. This procedure is known as Casting (MULLER et al., 2009).

Apart from casting, other conventional methods of large-scale industrial production (e.g., extrusion and injection-molding) are applied for bioplastics manufacture (LIU, 2006; MANOEL et al., 2017). Single-screw and twin-screw extruders are the two main types used for polymer processing. The key advantages of the former are relatively low cost and a favourable performance/cost ratio, whereas the latter promotes a more complex velocity profile on the molten material, guaranteeing better distributive and dispersive mixing, heat transfer, and heat control. Besides, they both have flexible modular designs and the screw configuration can be changed from soft melt mixing to vigorous mixing with high shear forces (OKSMAN et al., 2016).

Regarding biocomposites, extrusion can be even more efficient, since both melting and mixing occur in a one-step process, which decreases polymer and reinforcement degradation, improves efficiency and suitability for industrial applications that require continuous processing (HIETALA et al., 2014, TAHERI et al., 2020). However, the extrusion of biocomposites, particularly when nano-sized particles are used, can be challenging due to the dried nanomaterial's tendency to aggregate, thus hampering the feeding of the material into the extruder. A possible approach for solving the problem is to feed the nanoparticles in liquid form (known as liquid-assisted extrusion) with the use of atmospheric and vacuum ventings along the extruder for the removal of vaporized solvents (HERRERA et al., 2017). One of the most used technologies for processing polymers is injection moulding (Teixeira et al., 2012); it provides a good quality/cost ratio when a large production is intended and can potentially process bioplastics and biocomposites (PEREZ-PUYANA et al., 2016; SLEIMAN et al., 2018).

Polysaccharide-based bioplastics are brittle, non-continuous, rigid and fragile when formulated with no additive (GRÖNDAHL et al., 2004; GOKSU et al., 2007; SAXENA et al., 2009; PENG et al., 2011) and plasticizers' molecules used in the formulation of continuous bioplastics (GONTARD et al., 1993). Examples of plasticizers are glycerol and sorbitol, which are compatible with polysaccharides. The plasticizer effect results in higher flexibility of the bioplastics due to an increase in the interstitial volume of the polymeric matrix (WANG et al., 2014). Therefore, it reduces not only the glass transition temperature (T_g) (GOKSU et al., 2007; DAUDT et al., 2016), but also the number of polymer-polymer interactions (Figure 3), and increases the molecular mobility and hydrophilic degree of the bioplastics (WANG et al., 2014; DAUDT et al., 2016).

Figure 3: Polysaccharides and plasticizer interactions in the bioplastic matrix.



Source: Elaborated by the author.

The formulation of starch-based solutions with plasticizers increases water vapor permeability (WVP), elongation, and reduces tensile strength. Daudt et al. (2016) reported the elasticity modulus and tensile strength in bioplastics of rice flour decreased with increasing glycerol concentrations, besides of increased permeability to water vapor. The hydrophilic character of glycerol facilitates both adsorption and desorption of water molecules, thus increasing WVP (MALI, 2004).

Dias et al. (2010) observed a reduction in the tensile strength of starch-based

bioplastics from 10.9 MPa for 20% (w/w based on starch) of glycerol to 1.6 MPa for 30% (w/w based on starch). The same trend was observed with the replacement of glycerol for sorbitol as a plasticizer. The bioplastics with 20% and 30% of sorbitol showed, respectively, 22.3 and 11.2 MPa of tensile strength. Consequently, the reduction in the mechanical resistance increased elongation and the use of 20% and 30% of glycerol resulted in 2.8% and 59.8% elongations, respectively. Bioplastics plasticized with glycerol showed lower resistance capacity and higher elongation than those plasticized with sorbitol at the same plasticizer concentration. The explanation for such differences lies in the smaller size of the glycerol chain, which promotes a higher plasticizer capacity in relation to sorbitol, i.e., glycerol shows a greater ability to interact with the matrix polymers and a larger amount of water is retained (CUQ et al., 1997; RYU et al., 2002).

2.3 Properties and characteristics of starch-based bioplastics

Many of the properties and characteristics of starch are required for the use as coating or packaging material (e.g., biodegradability, biocompatibility, edible material (nutritional value), availability, relatively simple extraction process and low cost) (ZAHEDI et al., 2010; GHANBARZADEH et al., 2011; FALGUERA et al., 2011; SOUZA et al., 2012; KOWALCZYK AND BARANIAK, 2014; DANG AND YOKSAN, 2015; REIS et al., 2015). In addition to aforementioned characteristics, other properties such as odorless, tasteless, and generally nontoxic, characterize starch as a molecule with the potential to be applied for packaging applications (SHAH et al., 2016).

Other important features of starch-based bioplastics or any other polymer are color and transparency, related to marketing and consumer's acceptance for a given product, depending on the bioplastics application. Table 1 shows some studies on starch-based bioplastics elaboration and properties.

Starch-based bioplastics have the disadvantages of hydrophilicity, poor mechanical properties, low water vapor barrier property, and low freeze stability during bioplastics formation (LIU et al., 2009; XIE et al., 2013; DANG and YOKSAN, 2015; SABETZADEH et al., 2015; SHAH et al., 2016). However, depending on the amylose content in the polymeric starch matrix, certain bioplastics properties can change. Several procedures (e.g., physical, genetic, chemical, enzymatic and others) are

employed for altering the molecular structure of starch and, consequently, improving the properties of starch-based bioplastics (SHAH et al., 2016; KHAN et al., 2017).

The starch-based bioplastic properties are directly related to the raw material that originates this polymer (COMA, 2013), mainly due to the amylose and amylopectin proportion. This variation in starch molecule composition may be related to starch biosynthesis enzymes, soil type, and climatic conditions during plant growth (Singh et al., 2003). Due to the difference in the amylose/amylopectin ratio of the different starch botanical sources, the gel and bioplastics produced can present different gelatinization temperatures, mechanical and rheological properties (SINGH et al., 2003; MALI et al., 2006; HEJNA et al., 2019).

Thus, it is important to consider the type of starch used to elaborate bioplastics. In the study by Mali et al. (2006), the starch-based bioplastic from yam presented tensile strength superior to those from corn and potato starch, due to the yam containing higher amylose content (29% w/w). In the study by HEJNA et al. (2019), it was verified different gelatinization temperatures (95.4, 92.5 e 88.5 °C) for different starch sources (potato, maize e waxy maize, respectively). Daudt et al. (2016) and Dias et al. (2010) used different starch sources and the same plasticizer concentration, i.e., 20% w/w of glycerol in relation to the starch mass (Table 1). The authors reported the same elongation values, however, a remarkable difference in the tensile strength values.

Table 1. Production and properties of starch-based bioplastics.

Starch source (% w/v)	Tensile strength (MPa)	Elongation at break (%)	Water solubility (%)	Mixture * (% m/m)	Plasticizer *(% m/m)	Bioplastic processing method	Reference
Sweetpotato (2.5%)	7.96	77.92	...	None	Sorbitol (40%)	Casting	EHIVET et al. (2011)
Manioc (3%)	64.29	3.87	20.81	Gelatin/starc h (1:4)	Glycerol (10%)	Casting	FAKHOUR Y et al. (2012)
Manioc (3%)	108.28	6.57	28.88	Gelatin/starc	Glycerol	Casting	FAKHOUR

				h (4:1)	(10%)		Y et al. (2012)
Corn (5%)	26	3.6	...	Cellulose nanocrystals (aprox. 13%)	Glycerol (aprox. 26%)	Casting	AGUSTIN et al. (2014)
Corn (5%)	10	33.1	...	None	Glycerol (30%)	Casting	AGUSTIN et al. (2014)
Reag (2%)	5.21	22.25	77.54	Papaya (80%)	Glycerol (30%)	Casting	TULAMAN DI et al. (2016)
Rice (5%)	10.9	2.8	...	None	Glycerol (20%)	Casting	DIAS et al. (2010)
Sugar palm starch (8%)	7.74	46.66	>31	None	Glycerol/ Sorbitol 1:1 (30%)	Casting	SANYANG et al. (2016)
Cassava (5.26%)	1.14	0.22	13.48	None	Glycerol (20%)	Casting	OLUWASIN A et al. (2019)
Pinhão (5%)	18.56	2.8	...	None	Glycerol (20%)	Casting	DAUDT et al. (2016)
Arrowroot (2%)	3.9	45.3	...	None	Glycerol (30%)	Casting	MAKISHI et al. (2017)
Arrowroot (2%)	11.5	44.4	...	Gelatin (50%)	Glycerol (30%)	Casting	MAKISHI et al. (2017)

... =not reported, *= based on total dry mass

Makiski et al. (2017) ascribed low tensile strength and high elongation in Arrowroot-based bioplastics with starch only, and observed an improvement in the tensile strength of starch-based bioplastics blending with gelatin (Table 1). Fakhoury et al. (2012) obtained bioplastics from the same source and with differences in the starch/gelatin ratio, in which bioplastic with higher gelatin concentration showed superior mechanical resistance (Table 1). Gelatin protein is derived from the partial hydrolysis of collagen, and its properties are suitable for the formation of polymeric bioplastics. Gelatin increases intermolecular interactions due to an increase in the number of superficial protein chains (SOBRAL et al., 2001; FAKHOURY et al., 2012; VANIN et al., 2014).

In addition to botanical sources of starch and additives, the concentration and type of plasticizer can influence the bioplastics properties. Plasticizers increase the interstitial volume in the polymer matrix, which results in a reduction in the number of polymer-polymer bonds and thus affect mechanical (SANYANG et al., 2015; GONÇALVES et al., 2020), thermal (LÓPEZ et al., 2011), and barrier properties to water vapor (KIM et al., 2017; GONÇALVES et al., 2020).

Differences in mechanical and barrier properties of bioplastics, with different plasticizers at the same concentration are due to the plasticizing power of each molecule. For example, due to the smaller size of the glycerol chain, it has a greater plasticizer character than sorbitol. Another feature of plasticizers is their hydrophilicity, which allows starch bioplastics to biodegrade faster than with sorbitol. Therefore, depending on the application and compatibility of the plasticizer with the polymer matrix, different plasticizers can be applied (TYAGI AND BHATTACHARYA, 2019; ARIFA et al., 2021).

In the study by Sanyang et al. (2015), bioplastics developed from *Renga pinnata* starch and elaborated with different plasticizers (glycerol (G), sorbitol (S), and glycerol/sorbitol (GS) mixture) and concentrations (15%-45% (w/w, starch basis)), presented different properties. The tensile strength for bioplastics with G, S, and GS (15-45%) ranged between 9.59 to 1.67 MPa; 28.35 to 5.84 MPa, and 15.82 to 3.99 MPa, respectively. Mali et al. (2006) showed that yam starch-based bioplastic with different glycerol proportions (0-40% (w/w, starch basis) had reduced tensile strength with increasing plasticizer content (49 to 10 MPa), in addition to increased flexibility (3 to 25%), and water vapor permeability (WVP) (6.75 to $7.59 \times 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$). Other studies can be verified regarding the reduction of mechanical strength (Bourtoom, 2007;

López et al., 2011) and increase WTP with the addition of different hydrophilic plasticizers (BOURTOOM, 2007; BERTUZZI et al., 2007).

2.3.1. Properties and characteristics of starch-based bioplastics chemical modified

The chemical modification or the starch molecule derivatization may represent an approach aiming to improve the physicochemical and barrier properties of the native starch grain (ASHOK et al., 2016). Some of the most common chemical derivatization reactions are esterification (acetylation), etherification (hydroxypropylation), and oxidation (Figure 4).

In the study by Abel et al. (2021), the increase in the degree of acetylation and substitution of the starch hydroxyl groups (OH) led to a reduction in water absorption and water solubility. These results are consistent with the proposal of acetylation, in which the OH groups are replaced by acetic acid, thus reducing the hydrophilic character of the bioplastic.

Based on the results of Schmidt et al. (2019), different degrees of acetylation and plasticizers alter the mechanical properties, solubility, and water vapor barrier of starch-based bioplastics. The results showed the degree of substitution (DS) of 0.6 as the most promising compared to the DS of 1.1. The DS of 0.6 resulted in a bioplastic with a tensile strength of 8.42 MPa, solubility of 20.31 (g.100⁻¹), and a WVP of 2.34×10^{-7} g.m².h.Pa. While the tensile strength on the DS of 1.1 was 6.57 MPa, and the solubility and WVP did not change either. However, acetylation resulted in bioplastics with improved properties compared to native starch (SCHMIDT et al., 2019).

The improvement of bioplastics based on acetylated starch is due to the replacement of hydrophilic groups by acetyl, which results in a less flexible and hydroscopic bioplastic. For more information about the effect of different acetylation on starch-based bioplastic properties read (NEVORALOVÁ et al., 2019; SONDARI et al., 2019).

In the case of oxidized starch-based bioplastics, hypochlorite, hydrogen peroxide, permanganate, dichromate, persulfate and chlorate are common oxidizing agents in the starch oxidation reaction. The OH groups of sugars are replaced by carbonyl and carboxyl groups, usually on the carbon of number 2, 3 and/or 6 (ASHOK et al., 2016).

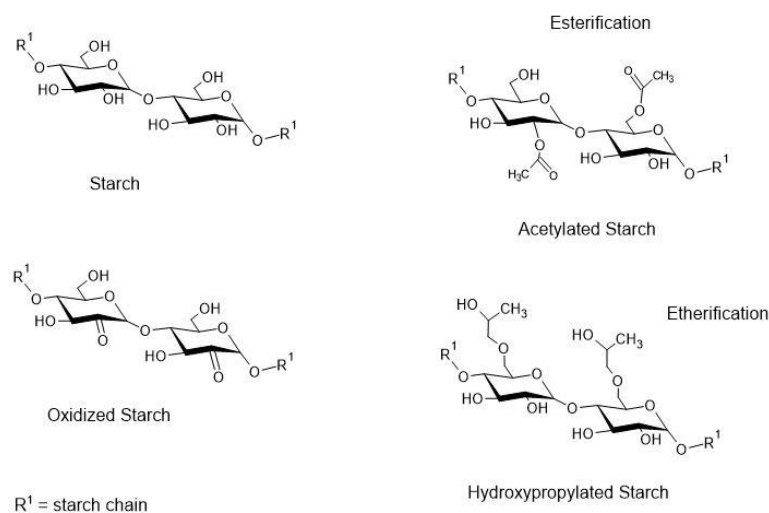
In the study by Oluwasina et al. (2021), bioplastics elaborated with oxidized starch (dialdehyde), had reduced water solubility (7.90-4.23%) and increased mechanical

strength (1.63–3.06 MPa), from the increase in the degree of starch oxidation. From different proportions of oxidized cassava starch (0, 20, 40 and 60%), the tensile strength (increased), flexibility (reduced) and water solubility (reduced) of the bioplastics was affected with the increase in content of starch oxidation. However, above 20% of oxidized starch there was no change in tensile strength (OLUWASINA et al., 2019).

By comparison, starch acetylation may result in a more hydrophobic and resistant bioplastic than oxidized starch-based bioplastics. This is due to the chemical nature of the hydroxyl substitution groups, that is, acetyl is more hydrophobic than carbonyl and carboxyl groups. Therefore, acetylated starch bioplastics hold less water and consequently result in a more compact matrix with optimized bonds between polymers. In the study by Sondari et al. (2019), acetylated starch bioplastics showed a contact angle of 60.41° and tensile strength of 16.35 MPa, while the same properties for the oxidized starch bioplastic were 45.47° and 13.38 MPa.

Hydroxypropylation in which the OH groups are replaced by hydroxypropyl ether, results in the weakening of the interactions between the starch chains. Thus, as in the case of oxidation modification, starch modified with an ether group retains more water (ASHOK et al., 2016) when compared to acetylated starch. Bioplastics developed with a high percentage of amylose (75%) and 20% glycerol resulted in materials with increased flexibility and reduced tensile strength, from the increase in the propylene oxide content (6-12% (w/w starch)). The tensile strength was 18.90 MPa (native starch), 15.66 MPa (6% propylene oxide) and 8.85 MPa (12% propylene oxide) (KIM et al., 2017). Effects on mechanical properties (reduction) were also observed in starch-based bioplastic with propylene oxide (WOGGUM et al., 2015).

Figure 4. Representation of modified starch



Source: Elaborated by the author.

2.3.2. Impact of chemical starch derivatization on biodegradation

Even though starch chemical modification in the manufacture of bioplastics can improve physicochemical and gas barrier properties, attention should be paid to the detriment of biodegradation properties (ABE et al., 2021). The reduction in the time and rate of biodegradation is related to the reduction in the degree of hydrophilicity of modified starch. From the chemical derivatization of starch, its solubility in water may be reduced, and in cases of optimization of the links between polymer chains, consequently the interactions of the starch chain with water molecules are reduced. Organisms, especially microorganisms, need moisture to proliferate and metabolize the bioplastic.

Based on Rivard et al. (1995), modified starch-based bioplastics show a delay in anaerobic biodegradation, however, it is noteworthy that the degree of substitution of acetylated starch is > 1.5 , in which there is an impact on the biodegradation rate. In the study by Šárka et al. (2011), PCL/acetylated starch blends after 2 months of composting degraded 25.3% and 29.8% (80/20 and 60/40 PCL/acetylated starch, respectively). While at the same proportion of PCL and native starch, disintegration was complete. Nevoralová et al. (2019) demonstrated that the biodegradation of starch acetate-based bioplastics can be monitored by starch DS. In a composting system, starch-based bioplastics with high DS resulted in a lower mineralization rate than starches with low or moderate DS. Based on the Oluwasina et al. (2021) results, starch bioplastics had the rate of biodegradation affected by chemical modification.

An alternative to improve the physicochemical and gas barrier properties of bioplastics, beyond ensuring biodegradation is the joining of different chemical derivatizations, and thus, taking advantage of the different potentials of each chemical modification. This approach is known as dual-modification (ASHOK et al., 2016) and can influence starch grain properties (GRANZA et al., 2015). This approach is interesting mainly due to the different degrees of hydrophilicity of acetylation, oxidation, and etherification.

3. Lignocellulose and biomass

Natural polymers from lignocellulose have been used for improving the mechanical properties (limited application) of bioplastics (OCHI, 2006; STEVENS et al., 2010; YANG et al., 2019), due to their biodegradation characteristics and reinforcement provided (Yang et al., 2019). Moreover, lignocellulose is an alternative to non-biodegradable synthetic fibers (YONG et al., 2015ab; YANG et al., 2019), and its benefits for the production of biomaterials include wide availability, renewable nature, low cost, and competitive specific mechanical properties (PANTHAPULAKKAL et al., 2006; CHING et al., 2016).

Due to their potential application, components of lignocellulosic fibers from sugarcane bagasse, rice straw, flax, Kenaf, hemp, forest wood and other sources have been widely used for reinforcement (OCHI, 2006; PANTHAPULAKKAL et al., 2006; SINGH and MOHANTY, 2007; WU, 2011; THAKUR et al., 2014; WU et al., 2017; BILO et al., 2018). Components from biomass, such as cellulose (nano-scaled, lignin and hemicellulose, are a strategic alternative to improve the bioplastics' properties (barrier, mechanical resistance, thermal resistance, solubility). Moreover, renewable and biodegradable resources have been used for minimizing the problem of accumulation and disposal of solid urban and agro-industrial wastes. Therefore, the generation of organic solid wastes enables their use for biotechnological purposes (VAVOURAKI et al., 2013; PHAM et al., 2015; HAFID et al., 2017).

Examples of high availability of biological vegetal sources include generation of sugarcane bagasse (global and annual production of approximately 1.69 million tons – Brazil is responsible for 43%) (HOFSETZ and SILVA, 2012), banana pseudo-stem (Brazilian production of 4 tons for each ton of fruit harvested approximately) (SOUZA et al., 2010, SHIMIZU et al., 2018), cassava starch (28.6 million tons worldwide production) (FAO, 2011), wheat bran (Brazilian production of approximately 2.6

thousand tons) (ABITRIGO, 2016), and food waste (1.6 billion tons) (FAO, 2013). Non-synthetic organic residues, mainly from organic compounds, represent an environmental problem if not correctly disposed, due to their chemical compositions (MOON et al., 2009; YAN et al., 2011; JIN et al., 2016).

Lignocellulosic fibers (lignin, hemicellulose and cellulose and extractives) can potentially be applied for the production of biomaterials and biomolecules such as bioplastics, thus reducing dependence on oil (FARHAT et al., 2017). Their use in biotechnological procedures can lead to an expansion of biorefineries (FARHAT et al., 2017) and generation of jobs in rural areas (NAIK et al., 2010; LACKNER, 2015; PAULA et al., 2018).

Mixture that uses natural biopolymers represents a source with potential for different applications. Among the different natural polymers, lignocellulosic residues from plant biomass are a resource for the production and improvement of the bioplastic's properties, such as mechanical properties, in addition to the great availability of these fibers represent a possibility of cheaper bioplastics (in terms of raw material availability) and an alternative for the lignocellulosic waste management. Bioplastics produced from mixtures of more than one type of polymer can show improved properties in comparison to individual polymers (KHAN et al., 2017).

3.1 Characteristics of cellulose

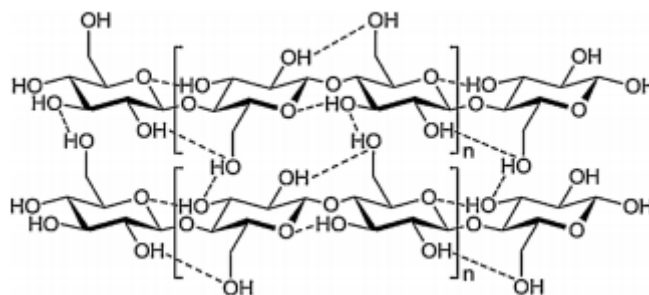
Cellulose is the most abundant natural organic compound on the planet, with an annual production of approximately 180 billion tons (PEREZ and MAZEAU, 2005; FESTUCCI-BUSELLI et al., 2007; PEELMAN et al., 2013). It represents the main polysaccharide in the constitution of the plant cell wall, divided into primary and secondary walls. The latter is subdivided into three layers, namely S1, S2 and S3, of which S2 guarantees the resistance characteristic of vegetable cells due to the greater thickening (approximately 90% of the cellulose in micro and microfibril forms) (FENGEL and WEGENER, 1984).

The characteristics of cellulose are insolubility in water, high molar mass and arrangement in nanofibers. Cellulose displays regions of poor organization and others highly crystalline, characterizing a semi-crystalline fiber. Due to such characteristics and the high resistance to enzymatic hydrolysis (recalcitrance) (MELATI et al., 2019),

lignocellulosic fibers provide plants with a structure that resists environmental and biological weathering (SCHMATZ et al., 2020).

Cellulose is biosynthesized not only by vegetable raw materials, but also by microorganisms such as algae, fungi, and bacteria (ZHANG and LYND, 2004; KLEMM et al., 2005; MESQUITA, 2012). Regardless of the organism or cellulose synthesis pathway, this polymer is classified as a homopolysaccharide of high molar mass and beta glycosidic bonds (1-4) (KLEMM et al., 2005; MESQUITA, 2012; LIAO et al., 2020). Its degree of polymerization (DP) is higher than 10,000 units of anhydroglucose; however, it varies according to the botanical source (LIAO et al., 2020). The properties of cellulose such as mechanical resistance and reduced interaction with water molecules are due to its arrangement. Polysaccharide chains that interact through hydrogen and hydrophobic bonds, via glucose monomers, result in a conformation of planar sheets (LIAO et al., 2020). Figure 5 displays the structure and interaction of cellulose chains. The glycosidic bond between two glucose monomers in the same cellulose polymer results in cellobiose (MESQUITA, 2012; LIAO et al., 2020).

Figure 5: Partial structure of cellulose



Source: Liao et al. (2020)

Therefore, cellulose can potentially be used for the manufacture of biomaterials such as bioplastics, and in several areas and industries (e.g., cosmetic, food and pharmaceutical industries (FAN et al., 2017; SUN et al., 2018)) due to its biodegradability, availability, non-toxicity, and biocompatibility (KUANG et al., 2018).

3.2 Bioplastics with cellulose

Cellulose is biodegradable and renewable (MATHEW et al. 2006), which is advantageous for sustainable applications. Improvements in the properties of different bioplastics, such as those based on starch and hemicellulose, with the addition of cellulose are one of its main advantages.

The addition of cellulose and carboxymethylcellulose to starch-based bioplastics reduced the water vapor permeability (WVP) (MÜLLER et al., 2009; GHANBARZADEH et al., 2011), respectively). However, the mechanical resistance increased from 3.9 to 9.8 MPa, and elongation at break was reduced from 42.2 to 25.8% (YU et al., 2009).

In comparison with pure thermoplastic starch, WVP is lower in cellulose, hemicellulose, zein and polycaprolactone bioplastics; however, starch-based bioplastics with cellulose show lower tensile strength values than pure starch-based bioplastics (GÁSPÁR et al., 2005). The mechanical properties of starch-based bioplastics with cellulose can be reduced with the addition of macro-size cellulose, due to the formation of energy concentration points in the bioplastic matrix when subjected to an axial force. Furthermore, the use of cellulose fibers on a macro scale may not represent an adequate reinforcement, since fibers agglomerate in the polymer matrix due to the different microfibers sizes. This result was reported by Chen et al. (2009ab), who used fresh pea husk fibers and fibers processed by acid hydrolysis, and by Xie et al. (2015). Therefore, the processing of cellulose alters the bioplastics' shape and structure, hence, their properties (XIE et al., 2015).

The reduction and standardization of cellulose fiber dimensions favor its application as reinforcement for bio-nanocomposites. Nanofibers smaller than the macro scale are classified as nanoparticles (three dimensions on the nano scale), nanotubes (two dimensions on the nanometric scale and a larger one (the third), forming an elongated structure, referred to as nanowhiskers), and nanolayers (only one dimension on the nanometric scale, in a sheet form) (KUMAR et al., 2009).

The literature reports improvements in the mechanical properties of biomaterials with the addition of cellulose nanowhiskers (LU et al., 2006; CHEN et al., 2009ab; WOHL et al., 2010; KAUSHIK et al., 2010; AGUSTIN et al., 2014;). Gordobil et al. (2014) and Hansen et al. (2012) also observed an increase in mechanical strength with the use of hemicellulose-based bioplastics with nanocellulose.

Such improvements are achieved through an adequate dispersion of the nanofibers in the polymeric matrix and optimization of the hydrogen bonds in the

bioplastic matrix. The interaction between polysaccharides and cellulose as reinforcement is favored by chemical similarity and intermolecular hydrogen bonds between hydroxyl groups of macromolecules (LU et al. 2006; CAO et al. 2008; CHEN et al. 2009b). In addition to mechanical reinforcement, biocomposites formulated with nanofibers have increased resistance to moisture due to the greater number of hydrophobic compounds (XIE et al., 2014). Moreover, the strong intermolecular interactions between cellulose and matrix, which increase the tortuous path, increase crystallinity, glass transition temperature (ANGLES and DUFRESNE, 2000), and gas diffusion through the material (ANGLES and DUFRESNE, 2000; MATHEW and DUFRESNE 2002; SREEKALA et al. 2008; SVAGAN et al. 2009; WAN et al. 2009).

The amount of cellulose must also be considered in the production of cellulose-based bioplastics, since its excess can cause agglomerations of cellulose granules in the polymeric matrix (CHEN et al., 2009a; XIE et al., 2014), thus reducing mechanical strength and barrier properties due to a lower optimization of hydrogen bonds (GUIMARÃES et al., 2016; DO LAGO et al., 2020).

3.2.1. Properties and characteristics of cellulose-based bioplastics chemical modified

The main cellulose derivative produced from the etherification process (cellulose ether) is carboxymethylcellulose “CMC” (ARAVAMUDHAN et al., 2014; SURIYATEM et al., 2020). The replacement of the hydroxyls of the cellulose monomeric unit by carboxymethyl groups occurs at carbon in the position 2, 3, or 6 (Figure 6) (MCDONALD et al., 2012). The use of CMC in the production of biomaterials is interesting due to its degradability, nontoxicity and availability of raw material.

Regarding microcrystalline cellulose “MC”, certain characteristics of CMC for the bioplastics development are solubility in water at different temperatures (use of water as a solvent), and reduction in the formation of particle agglomerates with other polymers (MA et al., 2008; ERGUN et al., 2016). The hygroscopic character of CMC is dependent on DS, degree of polymerization and distribution of ether group substitutions (ERGUN et al., 2016).

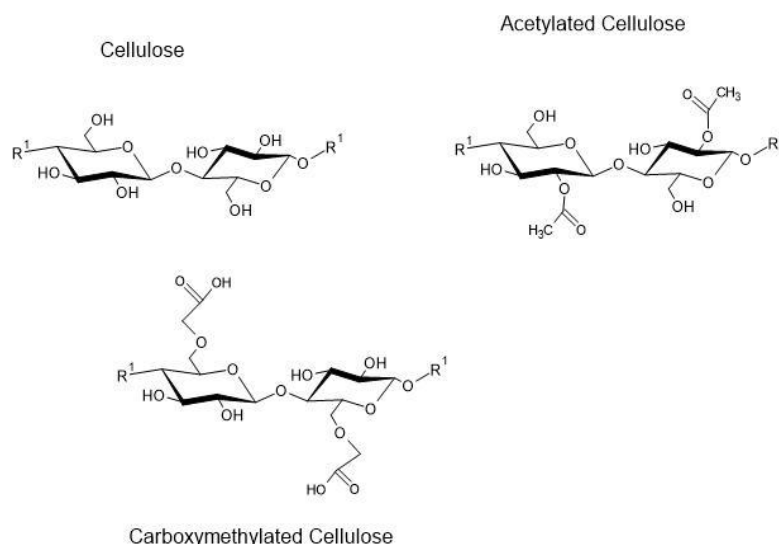
Starch-based bioplastics with added MC and CMC resulted in bioplastics with improved tensile strength (up to 9 wt%) compared to pure starch bioplastic (MA et al., 2008). However, bioplastic with MC resulted in a lower WVP and possibly less

interaction with the starch matrix (due to a greater degree of apparent agglomeration (12 wt% of MC)). This higher WVP of the starch/CMC bioplastic may be due to the hydrophilicity of the carboxymethyl group in the CMC. The greatest interaction with water and smoother surface morphology of bioplastics with CMC was reported by Tamara et al. (2020). The improvement of mechanical properties and increase WVP in bioplastics developed with CMC can be verified in other studies (TONGDEESOONTORN et al., 2011; MARGARETHA and RATNAWULAN, 2020; SURIYATEM et al., 2020). Conflicting results (TONGDEESOONTORN et al., 2011; TAMARA et al., 2020) of the effect of CMC on solubility in starch-based bioplastics may be the result of different factors such as botanical source, crystallinity, purity, processing, DS, and so on.

Cellulose acetate (Figure 6) or acetylated cellulose (CA) represents the native cellulose that has gone through the acetylation process. CA can be categorized into mono, di, or triacetate, with CA being insoluble in water. Cellulose DS is related to the reduction of WVP and the interaction of the bioplastic with water (MUGWAGWA and CHIMPHANGO, 2020). The reduction of WVP by the acetylation of cellulose is due to the replacement of hydroxyl groups (hydrophilic) by acetyl groups (hydrophobic) (AKKUS et al., 2018). That is, inhibiting the accumulation of water in the bioplastic (AYOUB et al., 2013).

In the study by Mugwagwa and Chimphango (2020), xylan-based bioplastics showed reduced solubility in water and food simulants (30.88% to 16.30%) after increasing the DS of nanocellulose (0 to 2.34). In the same study, hydrophobicity increased from 24.59° to 62.68° with DS from 0 to 2.34, respectively. In the study by Fei et al. (2015), the reduction in tensile strength (3.62 MPa to 2.06 MPa) of acetylated starch and cellulose-based bioplastic, occurred by the reduction of CA in relation to acetylated starch (SA) (1:9 and 7:3 SA:CA respectively).

Figure 6: Representation of modified cellulose



Source: Elaborated by the author

3.2.2. Impact of chemical cellulose derivatization on biodegradation

From the reduction in the interaction of acetylated starch with water, that is, the greater degree of hydrophobicity can result in a delay in the rate of biodegradation. The modification of cellulose may result in the need for different enzymes for hydrolysis, such as esterases which are common enzymes for native xylan hydrolysis (native xylan contains acetyl groups) (POLMAN et al., 2021). Therefore, the need for microorganisms that perform the deacetylation and de-esterification pathway is the need (JANG et al., 2007).

Increasing the concentration of acetylated starch, with a consequent reduction in CA, occurred a higher rate of biodegradation. The pure CA bioplastic degraded 30% approximately in 120 days. However, with the lowest CA concentration in the starch-based bioplastic, 52.43% biodegradation occurred after 120 days (FEI et al., 2015). Acetylated cellulose-based bioplastics showed a delay in anaerobic biodegradation, however, it is noteworthy that the degree of substitution of CA was >1.5, in which there is an impact on the biodegradation rate (RIVARD et al., 1995).

Ishigaki et al. (2000) isolated 35 bacteria from landfill, which showed a growth halo in CA emulsifying medium, however, few isolates degraded CA bioplastic with DS 1.7. The strain S2055 (*Bacillus* sp) was the only isolate capable of degrading more than 10% of the CA bioplastic. It is known that CA with a high degree of substitution is more resistant to biodegradation (BUCHANAN et al., 1993; NELSO et al., 1993). For more information, is indicated the consult of the specialized literature on the

biodegradation of CA by thermophilic aerobic and anaerobic microorganisms (GU et al., 1993; MOSTAFA et al., 2018).

Considering the hydrophilic and hygroscopic character of polymers as an important factor in biodegradation, the hydrophilic character of the carboxymethyl groups on the surface of CMC (YARADODDI et al., 2020) represents an important aggravating factor in maintaining the bioplastic integrity. In other words, the greater affinity of CMC with water in relation to CA can affect the biodegradation of carboxymethyl cellulose-based bioplastics. This effect of stimulating biodegradation due to the swelling of CMC with water may be related to the role of pH. A possible explanation for an acceleration of polymer degradation (abiotic and/or enzymatic) is the process of deprotonation of carboxylic acids and formation of carboxylate groups which have a high affinity for water (HUBBE et al., 2021). Finally, above pH 4.6, CMC is in its deprotonated form (FENG et al., 2008; EKICI, 2011).

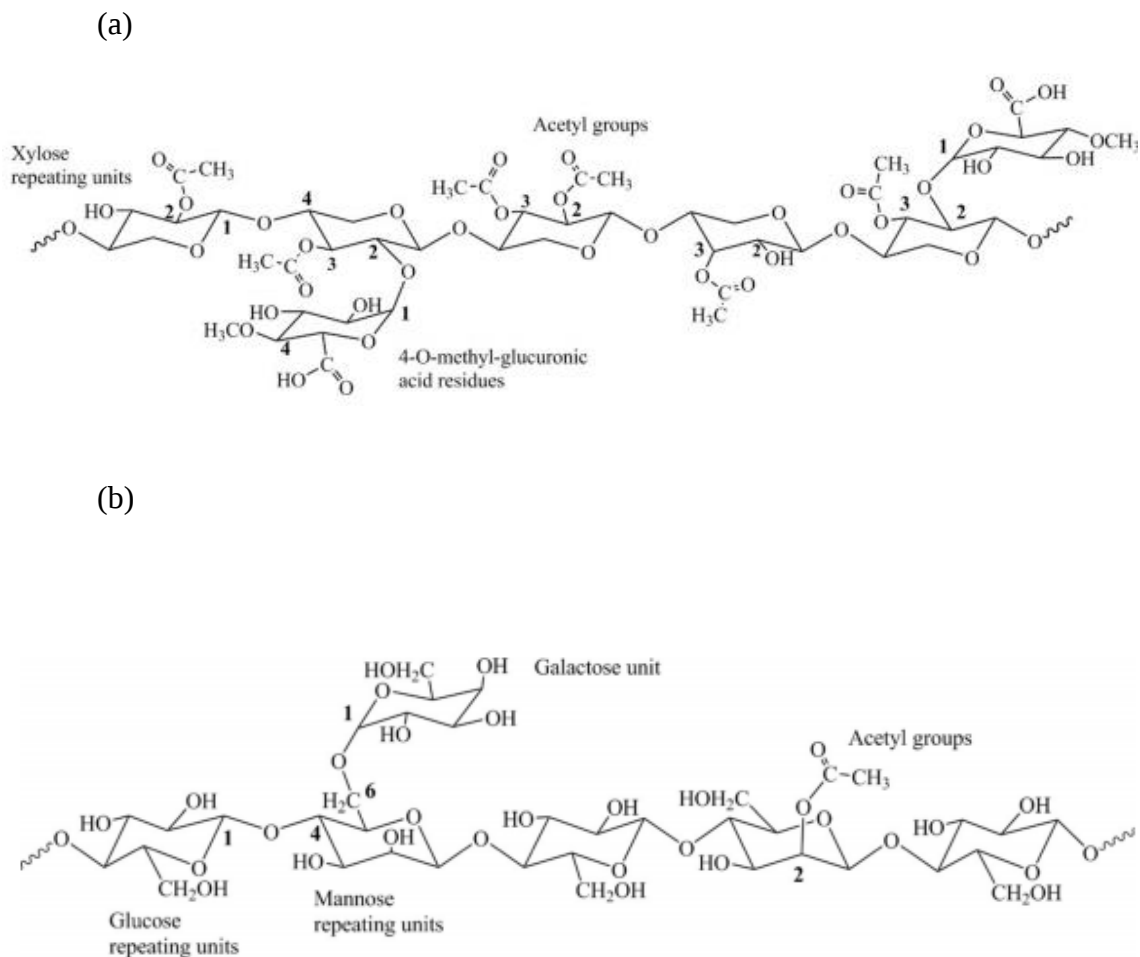
A proof that CMC is highly biodegradable, susceptible to microbial enzymes, and soluble in water, is its use in methods to verify the cellulolytic potential of different microorganisms. In these methods, microorganisms are cultivated in media with CMC as the only carbon source and the growth halo is indicative of the production and secretion of cellulolytic enzymes (SAINI et al., 2012).

3.3 Hemicellulose

Hemicellulose is a constituent of plant biomass, together with lignin and cellulose, they become the major constituents of plant cell wall forming a lignocellulosic complex. In this complex, it represents the second most abundant polymer in lignocelluloses (ANWAR et al., 2014; SHAHZADI et al., 2014; BRIENZO et al., 2016). However, unlike cellulose, it consists of different monomeric units, namely mannose, arabinose, xylose, glucose and galacturonic acid (FARHAT et al., 2017; FREITAS et al., 2019) whose content can vary according to the botanical origin (FARHAT et al., 2017). Figure 7 illustrates such constitutional differences. In hardwoods, the major component of hemicellulose is O-acetyl-4-O-methylglucuronoxylan (with substitution on carbon 2 of xylopyranose backbone units by 4-Omethyl glucuronic acid and 70% substitution on carbon 2 and 3 of the xylopyranose units by acetyl group). In softwood, however, the main hemicellulose component is O-acetyl-galactoglucomannan, whose structure is formed mainly by units

of glucose and mannose through beta (1-4) interactions with alpha (1- 6) linked galactose units attached to the glucose and mannose units (FARHAT et al., 2017). The acetylation degree in carbon 2 and 3 corresponds to approximately 20% (KUSEMA et al., 2013; AYOUB et al., 2013).

Figure 7: Representation of hemicellulose constituents



(a) O-acetyl-4-O-methylglucuronoxylan, (b) O-acetylgalactoglucomannan.

Source: Farhat et al. (2017)

Xylan is one of the constituents of hemicellulose present in different agribusiness residues (sugarcane bagasse, wheat straw, sorghum, corn stalks and cobs), besides forest residues and hardwood pulping (KAYSERILIOGLU et al., 2003; MIKKONEN and TENKANEN, 2012). In other words, xylan is the monomeric carbohydrate predominates in most plants, in addition to representing one-third of the

renewable biomass on planet earth (KAYSERILIOGLU et al., 2003). All these characteristics make it a potential source of biotechnological applications such as the manufacture of biomaterials.

3.3.1. Bioplastics with xylan

Since hemicellulose is highly available, it is a promising source for obtaining of chemicals and materials (CHERUBINI, 2010; BRIENZO et al., 2016; FREITAS et al., 2019; ALVES et al., 2020); however, its applications are limited due to its high heterogeneity, low mechanical properties, hydrophilic character and difficult formation of continuous bioplastics (GOKSU et al. 2007; ESCALANTE et al., 2012; CHEN et al., 2016).

Hemicellulose can be used in bioplastics manufacture, medical applications, hydrogels and cosmetics (GABRIELLI et al., 2000; OLIVEIRA et al., 2010) because of its biodegradability, biocompatibility, and easy chemical changes (FANG et al., 2000; SALAM et al., 2011). However, it requires alterations for providing better properties and, consequently, achieving higher valorization. Chemical changes in hemicellulose and cross-links between hemicellulose molecules and blends with other polymers are alternatives for overcoming the difficulties in its use.

Wang et al. (2014) used citric acid as a crosslinking agent in xylan-based bioplastics blend with polyvinyl alcohol and observed a strong link between the filmogenic matrices due to the formation of ester bonds between the molecules and hydrogen bonds. The bioplastic elongation increased from 15.1% to 249.5%; however, the tensile strength was reduced when citric acid acted as a plasticizer.

Gordobil et al. (2014) developed filmogenic solutions with modified xylan and nanocellulose to improve the bioplastics' physical properties. The acetylation and bleaching of the polymeric components increased both tensile strength and Young's modulus and reduced elongation. Gordobil et al. (2014) and Stevanic et al. (2012) demonstrated the addition of adequate amounts of nanocellulose to xylan-based bioplastics increased the bioplastics' mechanical properties and hydrophobicity. The authors obtained higher values than those achieved by Goksu et al. (2007), who used only xylan in the formulation of the bioplastic matrix and reported lignin is necessary for the obtaining of continuous xylan-based bioplastics.

The blending of hemicellulose with other polymers can improve the properties of biomaterials formed by hemicellulose. Several studies have reported the addition of biopolymers to hemicellulose-based bioplastics as a strategy to improve their mechanical properties. Table 2 shows the mechanical properties of blends of hemicellulose-based bioplastics with biopolymers. After an extensive review of the literature, the authors of this review did not find studies that reported the development of blends of bioplastics with starch and xylan, therefore, the present work addresses a new research strategy on bioplastics.

Table 2: Properties of blends of hemicellulose-based bioplastics.

Hemicellulose (%w/w)*	Blendwith (% w/w)*	Tensilestre ngth (MPa)	Elongation at break (%)	E (MPa)	Reference
Xylan (64-75%)	Nanocellulose (10%)	20.2	2.6	1,578	Peng et al. (2011)
Xylan (50%)	Nanocellulose (50%)	57	1.7	5,700	Hansen et al. (2012)
Arabinoxylan (85%)	Microcellulose (15%)	95	<15	2,500	Mikkonenet al (2012)
Galactoglucoma nnans (85%)	Microcellulose (15%)	>15 <20	>3 <4	>800 <1,000	Mikkonen et al (2011)
Xylan (20%)	Gluten (80%)	>7 <8	>1 <50	>130 <150	Kayserilioglu et al. (2003)
Xylan (10%)	Microcellulose (90.9%)	>160 <175	...	>160 <175	Long et al. (2019)
Xylan (95%)	Nanocellulose (5%)	51	2.9	3,200	Gordobil et al. (2014)

Arabinoxylan (95%)	Bacterial Cellulose (5%)	68	8.1	2,700	Stevanic et al. (2011)
Arabinoxylan (75%)	Nanocellulose (25%)	108	6	4,800	Stevanic et al. (2012)

---=not reported. *=based on total dry polysaccharides

As shown, different proportions of nanocellulose and plant raw materials of hemicellulose result in different tensile strength values, elongation and elasticity or young modulus. According to the tensile strength data in Table 2, the resistance values of hemicellulose-based bioplastics reinforced with biopolymers (as micro and nanocellulose) are close or even higher than those of commercial non-biobased polymers (e.g., CellophaneTM and low density polyethylene (LDPE)) (ALLEN, 1986; BRISTON, 1988; PHAN THE et al. 2009; HANSEN et al. 2012). However, elasticity is one of the properties that require improvements (HANSEN et al., 2012).

The reasons for using cellulose as reinforcement (Table 2) are due to its chemical similarity and compatibility with hemicellulose (HANSEN et al., 2012), as well as the strong interactions between cellulose and hemicelluloses of xyloglucan type and between cellulose and glucomannan (HANSEN et al., 2012; BRUMER et al., 2004; JEAN et al., 2009; AKERHOLM and SALMEN 2001). Moreover, cellulose nanofibers improve bioplastics, reducing their rate and permeability to water vapor. Hansen et al. (2012) and Saxena and Ragauskas. (2009) showed that nanocellulose addition improves the properties of xylan-based bioplastic. Due to its high crystallinity (higher than 60%) and dense network of polymeric bonds formed by hydrogen bonds, whisker-type nanocellulose produces a tortuous path in bioplastics, since it works as a barrier structure, thus hampering the transport of water molecules through the material (SAXENA and RAGAUSKAS, 2009).

As in the case of starch and cellulose chain chemical changes, there are implications for the biodegradation of bioplastics based on modified hemicellulose, however, the information in the literature is limited. Therefore, it is recommended to read our recent review article (ABE et al., 2021), in which the influence of polysaccharide modifications on biodegradation is reported.

4. Extraction of starch and lignocellulosic components

Regarding the development of bioplastic materials with the addition of natural polymers such as lignocellulosic fibers, the steps that precede the formulation and modification stages of such materials must be considered, since the extraction and purification processes of the lignocellulosic fibers from the biomass are responsible for the economic viability of the fibers application, hence, the final material's price. The processes will also define the quality and characteristics of the final materials, because they influence the properties of the bioplastic films formed and their suitability for a particular application.

The choice of biomass must be considered for manufacturing processes and further transformations of starch, due to its different characteristics and compositions. Tubers, for example, contain a very small amount of proteins and fats, which facilitates the isolation of starch (MOORTHY, 2004). The most common sources of commercial starch are cereals such as corn, rice and wheat, with more than 60% starch, as well as the roots or tuberos of cassava and potato, with approximately 16–24% of starch in weight (LACERDA et al., 2014; ZHU, 2017; KHLESTKIN et al., 2018).

The unit operations for the extraction of starch start with disintegration - the plant cell walls are opened, thus exposing their starch granules (SAENGCHAN et al., 2015). The next steps are extraction, in which starch is separated from the fibers, and purification, especially from proteins. Starch is then concentrated, and finally dried (BRANCO et al., 2019).

The industrial process of starch isolation separates starch from protein, usually using an alkaline solution (DÍAZ et al., 2016; CHOI et al., 2017). Different alkaline agents, such as detergents and sodium hydroxide or sodium hypochlorite, can be employed as extraction solvents (LEE et al., 2007); however, concerns over the disposal of effluents arise due to their use (DÍAZ et al., 2016). Such methods have been proven effective for the production of starch films (VERSINO AND GARCÍA, 2014), and important considerations include avoidance of amylolytic or mechanical damage to the starch granules, effective deproteinization of starch, and minimization of the loss of small granules (LINDEBOOM et al., 2004).

Hydrothermal processing with microwave-assisted extraction can optimize the process, since it is considered a green and safe technology for starch extraction, due to its ease of use, possibility of using only water as extraction solvent, short extraction times, higher performance, and lower solvent consumption (GALANAKIS, 2012;

LARA-FLORES et al., 2018). Therefore, it has been applied on industrial scale for the obtaining of bioactive compounds (ARAÚJO et al., 2020).

In a cost-effective and efficient isolation of cellulose from biomass, the cellulose source should ideally come from economically viable and easily accessible agro-wastes, as the amount of cellulose in various natural sources can vary, depending on the species and the lifetime of the plants. From a technological point of view, the evaluation of lignin content is crucial for the optimization of the pretreatment necessary for the extraction of pure cellulose pulp (TRACHE et al., 2017). Indeed, lignin is considered the hardest chemical component to be removed from lignocellulosic materials (TRACHE et al., 2016).

Initially, the material is subjected to a water-washing process for the removal of dirt/impurities and water-soluble extractives. The biomass compounds closely linked to cellulose, such as hemicellulose and lignin, are then removed. The complexity of the composition of lignocellulosic materials hampers the penetration of chemical agents, thus requiring a pretreatment for the breakage of the structure and facilitation of chemical processes, hence, economy.

Kraft pulping uses a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) in a digester to dissolve lignin and hemicellulose (TRACHE et al., 2017). The strong base disrupts OH bonding in the fiber network structure by ionizing the hydroxyl groups of various materials in fibers (MAJEED et al., 2013). Such a process is addressed in research on cellulose extraction for film formation, and widely used on an industrial scale, with 96% market dominance (TRACHE et al., 2017; ZULHAM et al., 2018; WEI et al., 2020).

The addition of sodium sulphide facilitates ether cleavage and controls undesirable condensation reactions, resulting in high yield of strong fibers. However, it generates sulphite derivatives, which may link to cellulose and cause environmental problems within disposal (ROBLES et al., 2018; FERREIRA et al., 2018). Many treatments free from chlorine and/or sulfide have been developed towards reducing the environmental impacts of the pulping process (TRACHE et al., 2017; MOKHENAAND JOHN, 2019). Due to strict environmental regulations, organosolv has emerged as an alternative owing to its unique features (FERREIRA et al., 2018; ROBLES et al., 2018).

After pulping, the resulting material can undergo a bleaching step, or delignification, which uses different bleaching agents such as chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), ozone (O_3), or peracetic acid (TRACHE et al., 2017). The

use of chlorine dioxide has excelled that of elemental chlorine in controlling parameters such as chemical and biochemical demand for oxygen and total solids, as it more effectively minimizes the polluting load of bleaching effluents. Significant pollution reductions have been achieved, however, its use still causes environmental concerns (KAUR et al., 2018).

Similar procedures can be adopted for hemicellulose extraction, especially regarding bioplastics formation (MUGWAGWA and CHIMPHANGO, 2020). Since hemicelluloses exhibit an amorphous structure, they are more vulnerable to degradation than cellulose, and some extreme methods can be responsible for their hydrolysis into monomers. Although the alkali treatment under moderate conditions cannot break glycosidic bonds between hemicellulose monomers, it is suitable for the obtaining of hemicellulose of high polymerization degree (SARTORI et al., 2003).

The most applied hemicellulose isolation method involves an alkaline reaction usually with NaOH or KOH (MUGWAGWA and CHIMPHANGO, 2020), which dissolves hemicelluloses and lignin, cleaving the phenyl glycoside bonds, esters and benzyl ethers linkages between such structures, hydrolyzing uronic and acetic esters, and swelling cellulose, decreasing its crystallinity (JACKSON, 1977; SPENCER and AKIN, 1980).

Low-boiling-point organic solvents such as ethanol, methanol, butanol, and acetone can be used in alkaline reactions for biomass fractionation for avoiding extremely high temperatures and reducing environmental impacts and energy consumption (MESA et al., 2011; GURAGAIN et al., 2016). Although the method also recovers solvent by distillation, high costs are associated with wastewater used for washing the resulting material, which limits its economic viability on a large scale (LAURE et al., 2014).

From an environmental point of view, enzymatic extraction is more acceptable than chemical procedures (ESCARNOT et al., 2012). It uses specific hemicellulose-degrading enzymes to obtain hemicellulose from biomass, and, although slower than other methods, the degree of polymerization obtained can be controlled by both reaction time and enzyme activity applied.

The complete use of the biomass compounds is required so that the process becomes a more profitable investment. Therefore, the isolation of lignin with few changes in its structure may be advantageous, since it can be used for specific

applications, such as production of resins, adhesives, carbon fiber, activated carbon, among others (SOUZA et al., 2020).

During biomass fragmentation by alkali treatment, lignin is degraded into soluble fragments and then separated either with the removal of the reaction solvent, or by lignin precipitation (Jiang and Hu, 2016; Rashid et al., 2016). However, overly severe extraction conditions may induce substantial changes in the original lignin structure (RASHID et al., 2016; WANG and CHEN, 2016). Among such processes, organosolv pretreatment with ethanol or acetic acid has been widely used (FERRER et al., 2013) and organic acids such as acetic acid and formic acid yield a high-quality product (GUNASEKARAN et al., 2019).

5. Environmental impact of polysaccharide-based bioplastics from plant biomass

The following information provides an overview of the bioplastics developing implications, in order to complete the pros and cons using plant biomass, that is, in an attempt to allow a broader study of the impacts of plant biomass-based bioplastics, without any intention to overshadow the clear importance and benefits of the biomaterials development and use.

To see the theory and methods of calculating the carbon, ecological, and water footprint, check the material by Korol et al. (2020). But briefly, the carbon footprint refers to the measurement (CO_2 equivalent) of emissions of CO_2 and other gases in the GHG (greenhouse gases) category. The human need for natural resources of the biosphere for different services and products can be measured by the ecological footprint, and the water footprint refers to direct and indirect consumption demand for freshwater in the development of a product or technology.

In the study by Korol et al. (2020) the carbon, ecological and water footprints of cotton fibers (CF), jute (FJ), and kenaf (FK) added to synthetic plastic polypropylene (PP) were analyzed. The results showed, in relation to the carbon footprint, the CF, FJ, and FK fibers had a lower impact (3, 18, and 18% respectively) compared to PP. This measurement is related to the use of energy and petroleum processing in the manufacture of propylene and polymerization. Regarding the ecological footprint, the FJ and FK fibers showed less impact (8.2 and 9.4% reduction, respectively), however, due to the cultivation and harvest of CF fibers occurring in greater quantity and not being manual (use of machinery and energy expenditure), these had a high ecological

footprint (an increase of 52%). However, the water footprint in the study by Korol et al. (2020), proved to be alarmingly more worrisome from the point of view of natural plant-based resource use. The use of fibers added to the PP pellet is responsible for 286% (FK), 758% (FJ), and 891% (CF) of the increase in the water footprint.

This increase in the water footprint of plant biomass in applications of blends with synthetic polymers is mostly related to water resources applied in irrigation. The increase in the water footprint, resulting from the use of plant biomass, was also observed in another study by Korol et al. (2019).

Based on Broeren et al. (2017), even though the application of native starch in bioplastics results in reduced GHG emission (up to 80%) and nonrenewable energy use NREU (up to 60%), these natural polysaccharides can result in an increase in the potential for eutrophication (up to 400%) and land use (0.3 –1.3 m² yr/kg), compared to petrochemical plastics.

However, these negative impacts about the use of bioplastics or additives based on plant biomass are debatable, as the implications of the arable land use and water resources due to the cultivation and harvesting of these biomasses can be mitigated through the approach of reusing agro-industrial and urban wastes. In addition to reducing the environmental impacts mentioned above, the use of waste from the wood industry, crops, urban, and popping is a management alternative to agro-industrial and urban organic solid waste.

In the study by Broeren et al. (2017), through the life cycle assessment approach (LCA), blends with starch residues (waste from fries potato processing), depicted a reduction in the eutrophication potential (up to 40%), land use (up to 60%), GHG and NREU (reduction <10% for both), compared to virgin starch. The reduction of the water footprint can also be reduced through the use of residues from vegetal biomass, to take advantage of residues from different crops.

Conclusions

This review has addressed the state-of-the-art of the production of bioplastics from polysaccharides from plant biomass, as well as the advantages and disadvantages of using starch and lignocellulosic components (as additive and main component) for their development. Academic and industrial efforts have been devoted towards new and improved polymers, production methods and sources for the obtaining of

polysaccharides, that can strategically reduce petroleum consumption in the production of plastic and replace partially the conventional synthetic and non-biodegradable plastic materials. Moreover, the production of bioplastics from plant biomass represents a model for the recycling and management of such waste with positive economic effects. However, the disadvantages (mechanical strength, gas barrier properties, processability of natural polymers and economic viability) related to the production of bioplastics from polysaccharides must be studied towards the expansion of the fields of application of such materials. This study showed that the application of lignocellulosic fibers has a high potential for application in bioplastics, since they result in the improvement of the properties of bioplastics, in addition to being an alternative to reuse a biomass with great availability.

References

- ABE, M. M., BRANCIFORTI, M. C., BRIENZO, M. (2021). Biodegradation of Hemicellulose-Cellulose-Starch-Based Bioplastics and Microbial Polyesters. *Recycling*, 6, 22. <https://doi.org/10.3390/recycling6010022>
- ABEL, O. M., IFEANYI, E. G., CHINELO, A. S., AGBAJOR, G. K., & IMANAH, J. E. (2021). Surface Hydrophobicity of Starch Acetate for Enhanced Bioplastic Properties. *J. Mater. Environ. Sci.* 12, 4, 497-510.
- ABITRIGO (Associação Brasileira da Indústria do Trigo). (2016). Evolução moagem e consumo de farinha–2005-2015. Available in: <http://abitrito.com.br/>. Accessed in: 21 set 2020.
- AGUSTIN, M. B., AHMMAD, B., ALONZO, S. M. M., & PATRIANA, F. M. (2014). Bioplastic based on Starch and Cellulose Nanocrystals from Rice Straw. *Journal of Reinforced Plastics and Composites*, Paper No. 0731684414558325.
- AKERHOLM, M., & SALMEN L. (2001). Interactions between wood polymers studied by dynamic FT-IR spectroscopy. *Polymer*, 42, 963–969.
- AKKUS, M., OZKAN, N., & BAKIR, U. (2018). Efficient acetylation of xylans by exploiting the potassium acetate formed during the alkaline extraction. *Journal of Polymers and the Environment*. 26, 8, 3397–3403. <https://doi.org/10.1007/s10924-018-1221-8>.
- ALLEN, W. R. (1986). Structural applications for flexible packaging: innovations in pouch forms and uses. *Polym Plast Technol Eng*, 25, 295–320.

- ALVES, R. C., MELATI, R. B., CASAGRANDE, G. M. S., CONTIERO, J., PAGNOCCA, F. C., & BRIENZO, M. (2020). Sieving process selects sugarcane bagasse with lower recalcitrance to xylan solubilization. *Journal of Chemical Technology & Biotechnology*. doi:10.1002/jctb.6541
- ANGLES, M. N., & DUFRESNE, A. (2000). Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. *Macromolecules*, 33, 22, 8344–8353.
- ANWAR, Z., GULFRAZ, M., & IRSHAD, M. (2014). Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: A brief review. *J. Rad. Res. App. Sci*, 7, 163-173.
- ARAÚJO, R. G., RODRÍGUEZ-JASSO, R. M., RUIZ, H. A., GOVEA-SALAS, M., ROSAS-FLORES, W., AGUILAR-GONZÁLEZ, M. A., PINTADO, M. E., LOPEZ-BADILLO, C., LUEVANOS, C., & AGUILAR, C. N. (2020). Hydrothermal–Microwave Processing for Starch Extraction from Mexican Avocado Seeds: Operational Conditions and Characterization. *Processes*, 8, 7, 759. <https://doi.org/10.3390/pr8070759>.
- ARAVAMUDHAN, A., RAMOS, D. M., NADA, A. A., KUMBAR, S. G. (2014). Natural Polymers. *Natural and Synthetic Biomedical Polymers*. 67–89. doi:10.1016/b978-0-12-396983-5.00004-1
- ASHOK, A., MATHEW, M., & REJEESH C. R. (2016). Innovative value chain development of modified starch for a sustainable environment: a review. *Int J Polym Sci Eng*. 2, 1, 20–32.
- AVEROUS, L. (2004). Biodegradable multiphase systems based on plasticized starch – Part C: Polymers reviews. *Journal of Macromolecular Science*, 44, 231-274.
- AYOUB, A., VENDITTI, R. A., PAWLAK, J. J., SADEGHIFAR, H., & SALAM, A. (2013). Development of an acetylation reaction of switch grass hemicellulose in ionic liquid without catalyst. *Industrial Crops and Products*, 44, 306– 314. doi:10.1016/j.indcrop.2012.10.036
- BILO, F., PANDINI, S., SARTORE, L., DEPERO, L.E., GARGIULO, G., BONASSI, A., FEDERICI, S., & BONTEMPI, E. (2018). A sustainable bioplastic obtained from rice straw. *J. Clen. Prod*, 200, 357–368. doi: 10.1016/j.jclepro.2018.07.252.
- BRANCO, F. P., NAKA, M. H., & CEREDA, M. P. (2019). Granulometry and Energy Consumption as Indicators of Disintegration Efficiency in a Hammer Mill Adapted to Extracting Arrowroot Starch (*Maranta Arundinacea*) in Comparison to Starch Extraction from Cassava. *Engenharia Agrícola*, 39, 3, 341–349.

- <https://doi.org/10.1590/1809-4430-eng.agric.v39n3p341-349/2019>.
- BRIENZO, M., CARVALHO, A. F. A., FIGUEIREDO, F. C., & NETO, P. O. (2016). Sugarcane bagasse hemicellulose properties, extraction technologies and xylooligosaccharides production. In G. L. Riley (Ed.). *Food waste*. 155–188.
- BRISTON, J. H. (1988). *Plasticfilms*. 3rd edn. Wiley, New York
- BROEREN, M. L. M., KULING, L., WORRELL, E., & SHEN, L. (2017). Environmental impact assessment of six starch plastics focusing on wastewater-derived starch and additives. *Resources, Conservation and Recycling*. 127, 246–255. doi:10.1016/j.resconrec.2017.09.001
- BRUMER, H., ZHOU, Q., BAUMANN, M. J., CARLSSON, K., & TEERI, T. T. (2004). Activation of crystalline cellulose surfaces through the chemoenzymatic modification of xyloglucan. *J AmChem Soc*, 126, 5715– 5721.
- BUCHANAN, C. M., GARDNER, R. M., & KOMAREK, R. J. (1993). Aerobic biodegradation of cellulose acetate. *J. Appl. Polym. Sci.* 47, 1709-1719.
- Cabedo, L., Feijoo, J. L., Villanueva, M. P., LAGARÓN, J. M., & GIMÉNEZ, E. (2006). Optimization of biodegradable nanocomposites based on a PLA/PCL blends for food packaging applications. *Macromol. Symp*, 233, 191–197. <https://doi.org/10.1002/masy.200690017>
- CAO, X., CHEN, Y., CHANG, P. R., MUIR, A. D., & FALK, G. (2008). Starch-based nanocomposites reinforced with flax cellulose nanocrystals. *Express Polym Lett*, 2, 7, 502–510.
- CHEN, Y., LIU, C., ANDERSON, D. P., HUNEAULT, M. A., & CHANG, P. R. (2009a). Pea starch based composite films with pea hull fibres and pea hull fibre-derived nanowhiskers. *Polymer Engineering and Science*, in press. doi:10.1002/pen.21290
- Chen, Y., Liu, C., Chang, P. R.; Cao, X., & ANDERSON, D. P. (2009b). Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: effect of hydrolysis time. *Carbohydrate Polymers*, 76, 607 - 615.
- CHEN, G. G., Q.I, X. M., GUAN, Y., PENG, F., YAO, C. L., & SUN, R. C. (2016). High Strength Hemicellulose-Based Nanocomposite Film for Food Packaging Applications. *ACS Sustainable Chemistry & Engineering*, 4,4, 1985– 1993. doi:10.1021/acssuschemeng.5b01252
- CHERUBINI, F. (2010). The biorefinery concept: Using biomass instead of oil for

- producing energy and chemicals. *Energy Conversion and Management*, 51, 7, 1412–1421. <https://doi.org/10.1016/j.enconman.2010.01.015>.
- CHING, Y. C., ERSHAD, A., LUQMAN, C. A., CHOO, K. W., YONG, C. K., SABARIAH, J. J., CHUAH, C. H., & LIOU, N. S. (2016). Rheological properties of cellulose nanocrystal-embedded polymer composites: A review. *Cellulose*, 23, 1011–1030.
- CHOI, J. M., PARK, C. S., BAIK, M. Y., KIM, H. S., CHOI, Y. S., CHOI, H. W., SEO, D. H. (2017). Enzymatic extraction of starch from broken rice using freeze-thaw infusion with food-grade protease. *Starch – Stärke*, 70, 1–2, 1700007. <https://doi.org/10.1002/star.201700007>.
- COMA, V. (2013). Polysaccharide-based Biomaterials with Antimicrobial and Antioxidant Properties. *Polímeros*, 23, 3, 287–297.
- COPELAND, L., BLAZEK, J., SALMAN, J., & TANG, M.C. (2009). Form and functionality of starch. *Food Hydrocolloids*, 23, 1527–1534.
- CUQ, B., GONTARD, N., CUQ, J. L., & GUILBERT, S. (1997). Selected functional properties of fish myofibrillar protein-based films as affected by hydrophilic plasticizers. *Journal of Agricultural and Food Chemistry*. 45, 622–626.
- CYRAS, V. P., SOLEDAD, C. M., & ANALÍA, V. (2009). Biocomposites based on renewable resource: Acetylated and non acetylated cellulose cardboard coated with polyhydroxybutyrate. *Polymer*. 50, 6274–6280. <https://doi.org/10.1016/j.polymer.2009.10.065>
- DANG, M. K., & YOKSAN, R. (2015). Development of thermoplastic starch blown film by incorporating plasticized chitosan. *Carbohydr Polym*. 115, 575–81.
- DAUDT, R. M., AVENA-BUSTILLOS, R. J., WILLIAMS, T., WOOD, D. F., KÜLKAMP-GUERREIRO, I. C., MARCZAK, L. D. F., & MCHUGH, T. H. (2016). Comparative study on properties of edible films based on pinhão (*Araucaria angustifolia*) starch and flour. *Food Hydrocolloids*. 60, 279–287.
- DIAS, A. B., MÜLLER, C. M., LAROTONDA, F. D., & LAURINDO, J. B. (2010). Biodegradable films based on rice starch and rice flour. *J. Cereal Sci*, 51, 213–219.
- DÍAZ, A., DINI, C., VIÑA, S. Z., & GARCÍA, M. A. (2016). Starch extraction process coupled to protein recovery from leguminous tuberous roots (*Pachyrhizus ahipa*). *Carbohydrate Polymers*, 152, 231–240. <https://doi.org/10.1016/j.carbpol.2016.07.004>.
- DO LAGO, R. C., DE OLIVEIRA, A. L. M., CORDASSO DIAS, M., DE

- CARVALHO, E. E. N., DENZIN TONOLI, G. H., & DE BARROS VILAS BOAS, E. V. (2020). Obtaining cellulosic nanofibrils from oat straw for biocomposite reinforcement: Mechanical and barrier properties. *Industrial Crops and Products*, 148, 112264, 2020. doi:10.1016/j.indcrop.2020.112264
- EHIVET, F. E., MIN, B., PARK, M. K., & OH, J. H. (2011). Characterization and antimicrobial activity of sweet potato starch-based edible film containing origanum (*Thymus capitatus*) oil. *Journal Food Science*, 76, 178–184.
- ELIASSON, A.C. (2016). Starch: physicochemical and functional aspects. *Carbohydrates in Food*, 10, 479- 578.
- ERGUN, R., GUO, J., HUEBNER-KEESE, B. (2016). Cellulose. *Encyclopedia of Food and Health*. 694–702. doi:10.1016/b978-0-12-384947-2.00127-6
- EKICI, S. (2011). Intelligent poly(N-isopropylacrylamide)-carboxymethyl cellulose full interpenetrating polymeric networks for protein adsorption studies. *Journal of Materials Science*. 46, 9, 2843–2850. doi:10.1007/s10853-010-5158-0
- ESCALANTE, A., GONÇALVES, A., BODIN, A., STEPAN, A., SANDSTRÖM, C., TORIZ, G., & GATENHOLM, P. (2012). Flexible oxygen barrier films from spruce xylan. *Carbohyd. Polym*, 2012, 87, 2381-2387.
- ESCARNOT, E., AGUEDO, M., & PAQUOT, M. (2012). Enzymatic hydrolysis of arabinoxylans from spelt bran and hull. *Journal of Cereal Science*, 55, 243–253. <https://doi.org/10.1016/j.jcs.2011.12.009>.
- FAKHOURY, F. M., MARIA MARTELLI, S., CANHADAS BERTAN, L., YAMASHITA, Y., INNOCENTINI MEI, L. H., & COLLARES QUEIROZ, F. P. (2012). Edible films made from blends of manioc starch and gelatin—influence of different types of plasticizer and different levels of macromolecules on their properties. *LWT Food Sci. Technol*, 49, 149-154.
- FALGUERA, V., QUINTERO, P. J., JOSE, J. A., MUNOZ, A., & IBARZ, A. (2011). Edible films and coatings: structures, active function and trends in their use. *Trends Food Sci Technol*, 22, 6, 292–303.
- FAN, G. Z., WANG, Y. X., SONG, G. S., YAN, J. T., & LI, J. F. (2017). Preparation of microcrystalline cellulose from rice straw under microwave irradiation. *Journal of Applied Polymer Science*, 134. <https://doi.org/10.1002/app.44901>.
- FANG, J. M., SUN, R. C., TOMKINSON, J., & FOWLER, P. (2000). Acetylation of wheat straw hemicellulose B in a new non-aqueous swelling system. *Carbohyd. Polym*, 41, 379- 387.

- FARHAT, W., VENDITTI, R., HUBBE, M., TAHA, F., BECQUART, A., & AYOUB, A. (2017). Review of Water Resistant Hemicellulose-Based Materials: Processing and Applications. *ChemSusChem*, 10, 305– 323.
- FEI, Z., HUANG, S., YIN, J., ET AL. (2015). Preparation and Characterization of Bio-based Degradable Plastic Films Composed of Cellulose Acetate and Starch Acetate. *J Polym Environ*. 23, 383–391. <https://doi.org/10.1007/s10924-015-0711-1>
- FENG, X., LEDUC, M., & PELTON, R. (2008). Polyelectrolyte complex characterization with isothermal titration calorimetry and colloid titration. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 317, 1-3, 535–542. doi:10.1016/j.colsurfa.2007.11.053
- FENGEL, D., & WEGENER, G. (1984). Wood: chemistry, ultrastructure, reactions. Berlin; New York: W. de Gruyter.
- FERREIRA, F. V., MARIANO, M., RABELO, S. C., GOUVEIA, R. F., & LONA, L. M. F. (2018). Isolation and surface modification of cellulose nanocrystals from sugarcane bagasse waste: From a micro- to a nano-scale view. *Applied Surface Science*, 436, 1113–1122. <https://doi.org/10.1016/j.apsusc.2017.12.137>.
- FERRER, A., VEGA, A., RODRÍGUEZ, A., JIMÉNEZ, L. (2013). Acetosolv pulping for the fractionation of empty fruit bunches from palm oil industry. *Bioresource Technology*, 132, 115–120. <https://doi.org/10.1016/j.biortech.2012.12.189>.
- FESTUCCI-BUSELLI, R. A., OTONI, W. C., & JOSHI, C. P. (2007). Structure, organization, and functions of cellulose synthase complexes in higher plants. *Brazilian Journal of Plant Physiology*, 19, 1, 1–13. doi:10.1590/s1677-04202007000100001
- FOOD AND AGRICULTURE ORGANIZATION (FAO), (2011). Prognóstico agropecuário: análise da conjuntura agropecuária safra 2010/11: mandioca. 2011. Available in: <http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor>. Accessed in: 23 fev 2020.
- FOOD AND AGRICULTURE ORGANIZATION FOOD (FAO). (2013). Wastage footprint: Impacts on natural resources. Available in: <http://www.fao.org/3/i3347e/i3347e.pdf>. Accessed in: 11 out 2020. Freinkel, S. Plastic: a toxic love story. HMH.
- FREITAS, C., CARMONA, E., & BRIENZO, M. (2019). Xylooligosaccharides production process from lignocellulosic biomass and bioactive effects. *Bioactive*

- GALANAKIS, C. M. (2012). Recovery of high added-value components from food wastes: Conventional, emerging technologies and commercialized applications. *Trends in Food Science & Technology*, 26, 2, 68–87. <https://doi.org/10.1016/j.tifs.2012.03.003>.
- GÁSPÁR, M., BENKO, Z., DOGOSSY, G., RÉCZEY, K., & CZIGÁNY, T. (2005). Reducing water absorption in compostable starch-based plastics. *Polym. Degrad. Stab*, 90, 563–569. <https://doi.org/10.1016/j.polymdegradstab.2005.03.012>
- GEYER, R., JAMBECK, J. R., & LAW, K. L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv*, 3, 25–29. <https://doi.org/10.1126/sciadv.1700782>
- GHANBARZADEH, B., ALMASI, H., & ENTEZAMI A. A. (2011). Improving the barrier and mechanical properties of corn starch-based edible films: effect of citric acid and carboxymethyl cellulose. *Ind Crops Prod*, 33, 229–35.
- GOKSU, E. I., KARAMANLIOGLU, M., BAKIR, U., YILMAZ, L., & YILMAZER, U. (2007). Production and characterization of films from cotton stalk xylan. *Journal of Agricultural and Food Chemistry*, 55, 26, 10685–10691.
- GONTARD, N., GUILBERT, S., & CUQ, J. L. (1993). Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film. *Journal of Food Science*, 58, 1, 206–211.
- GORDOBIL, O., EGÜÉS, I., URRUZOLA, I., & LABIDI, J. (2014). Xylan–cellulose films: Improvement of hydrophobicity, thermal and mechanical properties. *Carbohydrate Polymers*, 112, 56–62. doi:10.1016/j.carbpol.2014.05.060
- GRANZA, A. G., TRAVALINI, A. P., FARIAS, F. O., COLMAN, T. A. D., SCHNITZLER, E., & DEMIATE, I. M. (2015). Effects of acetylation and acetylation–hydroxypropylation (dual-modification) on the properties of starch from Carioca bean (*Phaseolus vulgaris* L.). *Journal of Thermal Analysis and Calorimetry*. 119, 1, 769–777. doi:10.1007/s10973-014-4092-9
- GRÖNDAHL, M., ERIKSSON, L., & GATENHOLM, P. (2004). Material properties of plasticized hardwood xylans for potential application as oxygen barrier films. *Biomacromolecules*, 5, 4, 1528–1535.
- Gu, J. D., Eberiel, D. T., McCarthy, S. P., GROSS, R. A. (1993). Cellulose acetate biodegradability upon exposure to simulated aerobic composting and anaerobic bioreactor environments. *Journal of Environmental Polymer Degradation*. 1, 2, 143–153. doi:10.1007/bf01418207

- GUILBERT, S., GONTARD, N., & CUQ, B., (1995). Technology and applications of edible protective films. *Packag. Technol. Sci*, 8, 339–346. <https://doi.org/10.1002/pts.2770080607>
- GUIMARÃES, I. C., DOS REIS, K. C., MENEZES, E. G. T., RODRIGUES, A. C., DA SILVA, T. F., DE OLIVEIRA, I. R. N., & VILAS BOAS, E. V. B. (2016). Cellulose microfibrillated suspension of carrots obtained by mechanical defibrillation and their application in edible starch films. *Industrial Crops and Products*, 89, 285–294. doi:10.1016/j.indcrop.2016.05.024
- GUNASEKARAN, V., RAMESH, S., SATHIASIVAN, K., SHANKAR, M., RAJESH, M., & TAMILARASAN, K. (2019). Simultaneous organosolv pretreatment and detoxification of agro-biomass for efficient lignin extraction and characterization. *Chemical Papers*, 74, 1, 273–283. <https://doi.org/10.1007/s11696-019-00876-w>.
- GURAGAIN, Y. N., BASTOLA, K. P., MADL, R. L., & VADLANI, P. V. (2016). Novel Biomass Pretreatment Using Alkaline Organic Solvents: A Green Approach for Biomass Fractionation and 2,3-Butanediol Production. *Bioenerg Res*, 9, 643–655. <https://doi.org/10.1007/s12155-015-9706-y>.
- HAFID, H. S., RAHMAN, N. A. A., SHAH, U. K. M., BAHARUDDIN, A. S., & ARIFF, A. B. (2017). Feasibility of using kitchen waste as future substrate for bioethanol production. *Renew. Sustain. Energy Rev*, 74, 671- 686.
- HALLEY, P. J., TRUSS, R. W., MARKOTSIS, M. G., CHALEAT, C., RUSSO, M., SARGENT, A. L., TAN, I., & SOPADE, P. A. (2007). A review of biodegradable thermoplastic starch polymers. *Polymer Durability and Radiation Effects*, Edited by M. C. Celina and R. A. Assink. United States: American Chemical Society. 287-300. <https://doi.org/10.1021/bk-2007-0978.ch024>
- HANSEN, N. M. L., BLOMFELDT, T. O. J., HEDENQVIST, M. S., & PLACKETT, D. (2012). Properties of plasticized composite films prepared from nanofibrillated cellulose and birch wood xylan. *Cellulose*, 19, 2015–2031.
- HERRERA, N., SINGH, A. A., SALABERRIA, A. M., LABIDI, J., MATHEW, A. P., & OKSMAN, K. (2017). Triethyl citrate (TEC) as a dispersing aid in polylactic acid/chitin nanocomposites prepared via liquid-assisted extrusion. *Polymers*, 9. <https://doi.org/10.3390/polym9090406>
- HIETALA, M., ROLLO, P., KEKÄLÄINEN, K., OKSMAN, K. (2014). Extrusion processing of green biocomposites: Compounding, fibrillation efficiency, and fiber dispersion. *J. Appl. Polym. Sci*, 131, 1–9. <https://doi.org/10.1002/app.39981>

- HOFSETZ, K., & SILVA, M. A. (2012). Brazilian sugarcane bagasse: Energy and non-energy consumption. *Biomass & Bioenergy*, 46, 564-573.
- HOPEWELL, J., DVORAK, R., & KOSIOR, E. (2009). Plastics recycling: Challenges and opportunities. *Philos. Trans. R. Soc. B Biol. Sci*, 364, 2115–2126. <https://doi.org/10.1098/rstb.2008.0311>
- HUBBE, M. A., LAVOINE, N., LUCIA, L. A., DOU, C. (2021). Formulating bioplastic composites for biodegradability, recycling, and performance: A Review. *BioResources*. 16, 1, 2021-2083.
- IPCC. Climate Change (2014). Synthesis Report. In: Pachauri RK, Meyer LA, editors. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team]. Geneva, Switzerland: IPCC, 151.
- ISHIGAKI, T., KAWAGOSHI, Y., IKE, M., & FUJITA, M. (2000). Abundance of polymer degrading microorganisms in seabased solid waste landfill site. *J. Basic Microbiol*, 90, 400– 405.
- JACKSON, M. G. (1977). Review article: The alkali treatment of straws. *Animal Feed Science and Technology*, 2, 105–130. [https://doi.org/10.1016/0377-8401\(77\)90013-x](https://doi.org/10.1016/0377-8401(77)90013-x).
- JACOB, R. F. (2006). Estudo das Propriedades das Blendas de Amido Termoplástico e Látex Natural. 2006. Tese (Doutor em Ciências – Físico-Química), Instituto de Química de São Carlos. Universidade de São Paulo, São Paulo.
- JAILLAIS, B., OTTENHOF, M. A., FARHAT, I. A., & RUTLEDGE, D. N. (2006). Outer-product analysis (OPA) using PLS regression to study the retrogradation of starch. *Vibrational Spectroscopy*, 40, 10-19.
- JAMSHIDIAN, M., TEHRANY, E. A., IMRAN, M., JACQUOT, M., & DESOBRY, S. (2010). Poly-Lactic Acid: Production, applications, nanocomposites, and release studies. *Compr. Rev. Food Sci. Food Saf*, 9, 552–571. <https://doi.org/10.1111/j.1541-4337.2010.00126.x>
- JANG, J., LEE, H. S., & LYOO, W. S. (2007). Effect of UV irradiation on cellulase degradation of cellulose acetate containing TiO₂. *Fibers and Polymers*. 8, 1, 19–24. doi:10.1007/bf02908155
- JEAN, B., HEUX, L., DUBREUIL, F., CHAMBAT, G., & COUSIN, F. (2009). Nonelectrostatic building of biomimetic cellulose-xyloglucan multilayers. *Langmuir*, 25, 3920–3923.

- JIANG, Z., & HU, C. (2016). Selective extraction and conversion of lignin in actual biomass to monophenols: A review. *Journal of Energy Chemistry*, 25, 6, 947–956. <https://doi.org/10.1016/j.jechem.2016.10.008>.
- JIN, Y., LI, Y., & LI, J. (2016). Influence of thermal pretreatment on physical and chemical properties of kitchen waste and the efficiency of anaerobic digestion. *J. Environ. Manage*, 180, 291-300.
- JOSHI, S. (2008). Can nanotechnology improve the sustainability of biobased products? The case of layered silicate biopolymer nanocomposites. *J. Ind. Ecol*, 12, 474–489. <https://doi.org/10.1111/j.1530-9290.2008.00039.x>
- KAUR, D., BHARDWAJ, N. K., & LOHCHAB, R. K. (2018). Environmental Aspect of Using Chlorine Dioxide to Improve Effluent and Pulp Quality During Wheat Straw Bleaching. *Waste and Biomass Valorization*, 10, 1231-1239. doi:10.1007/s12649-017-0193-6
- KAUSHIK, A., SINGH, M., & VERMA, G. (2010). Green nanocomposites based on thermoplastic starch and steam exploded cellulose nanofibrils from wheat straw. *Carbohydr Polym*, 82, 337-345.
- KAYSERILIOGLU, B. S., BAKIR, U., YILAMZ, L., & AKKAS, N. (2003). Use of xylan, an agricultural by-product, in wheat gluten based biodegradable films: mechanical, solubility and water vapor transfer rate properties. *Bioresource Technology*, 87, 3, 239–246. doi:10.1016/s0960-8524(02)00258-4
- KAZA, S., YAO, L. C., BHADA-TATA, P., & VAN WOERDEN, F. (2018). What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050., Urban Development Series. World Bank:, Urban Development Series. World Bank: Washington, DC.
- KHAN, B., BILAL KHAN NIAZI., M., SAMIN, G., & JAHAN, Z. (2017). Thermoplastic starch: A possible biodegradable food packaging material—a review. *Journal of Food Process Engineering*, 40, 12447.
- KHLESTKIN, V. K., PELTEK, S. E., & KOLCHANOV, N. A. (2018). Review of direct chemical and biochemical transformations of starch. *Carbohydrate Polymers*, 181, 460–476. <https://doi.org/10.1016/j.carbpol.2017.10.035>.
- KIM, H. Y., JANE, J., LAMSAL, B. (2017). Hydroxypropylation improves film properties of high amylose corn starch. *Industrial Crops and Products*. 95, 175–183. doi:10.1016/j.indcrop.2016.10.025
- KLEMM, D., HEUBLEIN, B., FINK, H. P. & BOHN, A. (2005). Cellulose: fascinating

- biopolymer and sustainable raw material. *Angew. Chemie Int*, 44, 3358–3393.
- KOROL, J., HEJNA, A., BURCHART-KOROL, D., CHMIELNICKI, B., & WYPIÓR, K. (2019). Water Footprint Assessment of Selected Polymers, Polymer Blends, Composites, and Biocomposites for Industrial Application. *Polymers*. 11, 11, 1791. doi:10.3390/polym11111791
- KOROL, J., HEJNA, A., BURCHART-KOROL, D., & WACHOWICZ, J. (2020). Comparative Analysis of Carbon, Ecological, and Water Footprints of Polypropylene-Based Composites Filled with Cotton, Jute and Kenaf Fibers. *Materials*. 13, 16, 3541. doi:10.3390/ma13163541
- KOWALCZYK, D., & BARANIAK, B. (2014). Effect of candelilla wax on functional properties of biopolymer emulsion films. A comparative study. *Food Hydrocoll*, 41, 195–209.
- KUANG, Y., CHEN, C., PASTEL, G., LI, Y., SONG, J., MI, R., KONG, W., LIU, B., JIANG, Y., & YANG, K. (2018). Conductive Cellulose Nanofiber Enabled Thick Electrode for Compact and Flexible Energy Storage Devices. *Advanced Energy Materials*, 8, 1802398. <https://doi.org/10.1002/aenm.201802398>.
- KUMAR, A. P., DEPAN, D., SINGH TOMER, N., & SINGH, R. P. (2009). Nanoscale particles for polymer degradation and stabilization – trends and future perspectives. *Prog Polym Sci*, 34, 6, 479–515.
- KUSEMA, B. T., TÖNNÖV, T., MÄKI-ARVELA, P., SALMI, T., WILLFÖR, S., HOLMBOM, B., & MURZIN, D. Y. (2013). Acid hydrolysis of O-acetyl-galactoglucomannan. *Cataly. Sci. Technol*, 3, 116–122.
- LACERDA, L. G., COLMAN, T. A. D., BAUAB, T., DA SILVA CARVALHO FILHO, M. A., DEMIATE, I. M., DE VASCONCELOS, E. C., & SCHNITZLER, E. (2014). Thermal, structural and rheological properties of starch from avocado seeds (*Persea americana*, Miller) modified with standard sodium hypochlorite solutions. *Journal of Thermal Analysis and Calorimetry*, 115, 2, 1893–1899. <https://doi.org/10.1007/s10973-013-3349-z>
- LACKNER, M. (2015). Bioplastics-biobased plastics as renewable and/or biodegradable alternatives to petroplastics. *Kirk-Othmer Encycl. Chem. Technol*, 6, 1–41. [https://doi.org/DOI: 10.1002/0471238961.koe00006](https://doi.org/DOI:10.1002/0471238961.koe00006)
- LARA-FLORES, A. A., ARAÚJO, R. G., RODRÍGUEZ-JASSO, R. M., AGUEDO, M., AGUILAR, C. N., TRAJANO, H. L., & RUIZ, H. A. (2017). Bioeconomy and Biorefinery: Valorization of Hemicellulose from Lignocellulosic Biomass and

- Potential Use of Avocado Residues as a Promising Resource of Bioproducts. *In Energy, Environment, and Sustainability*, 141–170. Springer Singapore. https://doi.org/10.1007/978-981-10-7431-8_8.
- LAURE, S., LESCHINSKY, M., FRÖHLING, M., SCHULTMANN, F., & UNKELBACH, G. (2014). Assessment of an organosolv lignocellulose biorefinery concept based on a material flow analysis of a pilot plant. *Cell Chem. Technol*, 48, 793–798.
- LEE, H., HTOON, A., & PATERSON, J. (2007). Alkaline extraction of starch from Australian lentil cultivars Matilda and Digger optimised for starch yield and starch and protein quality. *Food Chemistry*, 102, 3, 551–559. <https://doi.org/10.1016/j.foodchem.2006.03.042>.
- LI, W. C., TSE, H. F., & FOK, L. (2016). Plastic waste in the marine environment: A review of sources, occurrence and effects. *Sci. Total Environ.* 566–567, 333–349. <https://doi.org/10.1016/j.scitotenv.2016.05.084>
- LIAO, Y., DE BEECK, B. O., THIELEMANS, K., ENNAERT, T., SNELDERS, J., DUSSELIER, M., COURTIN, C. M., SELS, B. F. (2020). The role of pretreatment in the catalytic valorization of cellulose. *Molecular Catalysis*, 487, 110883.
- LINDEBOOM, N., CHANG, P. R., TYLER, R. T. (2004). Analytical, Biochemical and Physicochemical Aspects of Starch Granule Size, with Emphasis on Small Granule Starches: A Review. *Starch - Stärke*, 56, 34, 89–99. <https://doi.org/10.1002/star.200300218>.
- LIU, Z. (2005). Edible films and coatings from starches. In: HAN, J. H. (Ed). *Innovations in food packaging*, Elsevier: Amsterdam, The Netherlands. 318-336.
- LIU, L. (2006). Bioplastics in food packaging: Innovative Technologies for Biodegradable Packaging. 2006. <http://www.iopp.org/files/public/SanJoseLiuCompetitionFeb06.pdf>. Accessed 10.10.2012
- LIU, H., XIE, F., YU, L., CHEN, L., & LIN, L. (2009). Thermal processing of starch-based polymers. *Prog Polym Sci*, 34, 1348–68.
- LONG, L., SHEN, F., WANG, F., TIAN, D., & HU, J. (2019). Synthesis, characterization and enzymatic surface roughing of cellulose/xylan composite films. *Carbohydrate Polymers*. doi:10.1016/j.carbpol.2019.02.086
- LU, Y., WENG, L., & CAO, X. (2006). Morphological, thermal and mechanical properties of ramie crystallites – reinforced plasticized starch biocomposites.

- Carbohydr Polym*, 63, 2, 198–204.
- MA, X., & YU, J. (2004). The effects on plasticizers containing amide groups on the properties of thermoplastic starch. *Starch/Starke*, 56, 545-551.
- MA, X., CHANG, P. R., & YU, J. (2008). Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. *Carbohydrate Polymers*, 72, 3, 369–375. doi:10.1016/j.carbpol.2007.09.002
- MAJEED, K., JAWAID, M., HASSAN, A., ABU BAKAR, A., ABDUL KHALIL, H. P. S., SALEMA, A. A., & INUWA, I. (2013). Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. *Materials & Design*, 46, 391–410. doi:10.1016/j.matdes.2012.10.044.
- MAKISHI, G., AMORIM, E., GATTI, M., DITCHFIELD, C., BRANCO, I., & MORAES, I. (2017). Physical Properties and Water Vapour Permeability of Blends Produced with Gelatin and Modified Maranta Arundinacea Starch. *Chemical Engineering Transactions*, 57, 1855-1860.
- MALI, S., GROSSMANN, M. V. E., GARCÍA, M. A., MARTINO, M. N., & ZARITZKY, N. E. (2004). Barrier, mechanical and optical properties of plasticized yam starch films. *Carbohydrate Polymers*, 56, 2, 129-135.
- MANOEL, A. F., CLARO, P. I. C., MATTOSO, L. H. C., MARCONCINI, J. M., & MANTOVANI, G. L. (2017). Thermoplastic Waxy Starch Films Processed by Extrusion and Pressing: Effect of Glycerol and Water Concentration. *Materials Research*, 20, 353–357. doi:10.1590/1980
- MARGARETHA, L., & Ratnawulan. (2020). The effect of addition sorbitol and carboxymethyl cellulose (CMC) on the quality of biodegradable plastics from avocado seed starch. *Pillar of Physics*, 13, 103-112.
- MATHEW, A. P., & DUFRESNE, A. (2002). Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. *Biomacromolecules*, 3, 3, 609–617.
- MATHEW, A. P., OKSMAN, K., & SAIN, M. (2006). The effect of morphology and chemical characteristics of cellulose reinforcements on the crystallinity of polylactic acid. *Journal of Applied Polymer Science*, 101, 300–310.
- MATHLOUTHI, M. (1996). Emballage et conservation des produits alimentaire. *Polytechnica*, Paris.
- MAYNARD, F. (1999). “Edible film and method”, European Patent 0935921.

- MCDONALD, J. E., ROOKS, D. J., MCCARTHY, A. J. (2012). Methods for the Isolation of Cellulose-Degrading Microorganisms. *Methods in Enzymology*. 349–374. doi:10.1016/b978-0-12-415931-0.00019-7
- MELATI, R. B., SHIMIZU, F. L., OLIVEIRA, G., PAGNOCCA, F. C., SOUZA, W., SANT'ANNA, C., & BRIENZO, M. (2019). Key Factors Affecting the Recalcitrance and Conversion Process of Biomass. *Bioenerg. Res*, 12, 1–20. <https://doi.org/10.1007/s12155-018-9941-0>
- MESA, L., GONZÁLEZ, E., CARA, C., GONZÁLEZ, M., CASTRO, E., & MUSSATTO, S. I. (2011). The effect of organosolv pretreatment variables on enzymatic hydrolysis of sugarcane bagasse. *Chemical Engineering Journal*, 168, 1157–1162. <https://doi.org/10.1016/j.cej.2011.02.003>.
- MESQUITA, J. P. (2012). Nanocristais de celulose para preparação de bionanocompósitos com quitosana e carbonos nanoestruturados para aplicações tecnológicas e ambientais. 2012. 165. Tese (Doutorado em Ciências) - Universidade Federal de Minas Gerais, Belo Horizonte.
- MIKKONEN, K. S., STEVANIC, J. S., JOLY, C., DOLE, P., PIRKKALAINEN, K., SERIMAA, R., & TENKANEN, M. (2011). Composite films from spruce galactoglucomannans with microfibrillated spruce wood cellulose. *Cellulose*, 18, 3, 713–726. doi:10.1007/s10570-011-9524-0
- MIKKONEN, K. S., PITKÄNEN, L., LILJESTRÖM, V., MABASA BERGSTRÖM, E., SERIMAA, R., SALMÉN, L., & TENKANEN, M. (2012). Arabinoxylan structure affects the reinforcement of films by microfibrillated cellulose. *Cellulose*, 19, 2, 467–480. doi:10.1007/s10570-012-9655-y
- MIKKONEN, K.S., & TENKANEN, M. (2012). Sustainable food-packaging materials based on future biorefinery products: Xylans and mannans. *Trends in Food Science & Technology*. 28, 2, 90–102. doi:10.1016/j.tifs.2012.06.012
- MOKHENA, T. C., & John, M. J. (2019). Cellulose nanomaterials: new generation materials for solving global issues. *Cellulose*, 27, 3, 1149–1194. <https://doi.org/10.1007/s10570-019-02889-w>.
- MOON, H. C., SONG, S., KIM, J. C., SHIRAI, Y., LEE, D. H., KIM, J. K., CHUNG, S. O., KIM, D. H., OH, K. K., & CHO, Y. S. (2009). Enzymatic hydrolysis of food waste and ethanol fermentation. *Int. J. Energ. Res*, 33, 164–172.
- MOORTHY, S. N. (2004). Tropical sources of starch. *Starch in Food*, 321–359. Elsevier. <https://doi.org/10.1533/9781855739093.2.321>.

- MOSTAFA, N. A., FARAG, A. A., ABO-DIEF HALA M., TAYEB, A. M. (2018). Production of biodegradable plastic from agricultural wastes. *Arabian Journal of Chemistry*, 11, 4, 546–553. doi:10.1016/j.arabjc.2015.04.008
- MUGWAGWA LINDLEEN, R., & CHIMPHANGO, A. F. A. (2020). Enhancing the functional properties of acetylated hemicellulose films for active food packaging using acetylated nanocellulose reinforcement and polycaprolactone coating. *Food Packaging and Shelf Life*, 24, 100481. <https://doi.org/10.1016/j.fpsl.2020.100481>.
- MÜLLER, C. M. O., LAURINDO, J. B., & YAMASHITA, F. (2009). Effect of cellulose fibers addition on the mechanical properties and water vapor barrier of starch-based films. *Food Hydrocoll*, 23, 1328 -1333.
- MÜLLER, C. M. O., LAURINDO, J. B., & YAMASHITA, F. (2011). Effect of nanoclay incorporation method on mechanical and water vapor barrier properties of starch-based films. *Ind. Crops Prod*, 33, 605–610. <https://doi.org/10.1016/j.indcrop.2010.12.021>
- NAIK, S. N., GOUD, V. V., ROUT, P. K., & DALAI, A. K. (2010). Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 14, 578-597. DOI: 10.1016/j.rser.2009.10.003
- NELSON, M., MCCARTHY, S. P., & GROSS, R. A. (1993). Isolation of a *Pseudomonas paucimobilis* capable of using insoluble cellulose acetate as a sole carbon source. *Proc. ACS Div., Polym. Mat. Sci. Eng.* 67, 139-140.
- NEULING, U., & KALTSCHMITT, M. (2017). Review of biofuel production - Feedstocks, processes and market. *Journal of Oil Palm Research*, 29, 137-167. DOI: 10.21894/jopr.2017.2902.01
- NEVORALOVÁ, M., KOUTNÝ, M., UJČÍČ, A., HORÁK, P., KRED TUSOVÁ, J., ŠERÁ, J., RŮŽEK, L., RŮŽKOVÁ, M., KREJČÍKOVÁ, S., ŠLOUF, M., KRULIŠ, Z. (2019). Controlled biodegradability of functionalized thermoplastic starch based materials. *Polym. Degrad. Stab.* 170. 10.1016/j.polymdegradstab. 2019.108995
- OCHI, S. (2006). Development of high strength biodegradable composites using Manila hemp fiber and starch-based biodegradable resin. *Composites Part A: Applied Science and Manufacturing*, 37, 11, 1879–1883.
- OKSMAN, K., AITOMÄKI, Y., MATHEW, A. P., SIQUEIRA, G., ZHOU, Q., BUTYLINA, S., TANPICHAI, S., ZHOU, X., & HOOSHMAND, S. (2016). Review of the recent developments in cellulose nanocomposite processing.

- Compos. Part A Appl. Sci. Manuf*, 83, 2–18.
<https://doi.org/10.1016/j.compositesa.2015.10.041>
- OLABARRIETA, I. (2005). Strategies to improve the aging, barrier and mechanical properties of chitosan, whey and wheat gluten protein films. 2005. These (Doctored), Department of Fiber and Polymer Technology, Royal Institute of Technology, Stockholm, Sweden.
- OLIVEIRA, E. E., SILVA, A. E., JUNIOR, T. N., GOMES, M. C. S., AGUIAR, L. M., MARCELINO, H. R., ARAUJO, I. B., BAYER, M. P., RICARDO, N. M. P. S., OLIVEIRA, A. G., & EGITO, E. S. T. (2010). Xylan from corn cobs, a promising polymer for drug delivery: production and characterization. *Bioresour Technol*, 101:5402–6.
- OLUWASINA, O. O., OLALEYE, F. K., OLUSEGUN, S. J., OLUWASINA, O. O., & MOHALLEM, N. D. S. (2019). Influence of oxidized starch on physico mechanical, thermal properties, and atomic force micrographs of cassava starch bioplastic film. *International Journal of Biological Macromolecules*, 135, 282-293. PMID:31128189. <http://dx.doi.org/10.1016/j.ijbiomac.2019.05.150>
- OLUWASINA, O. O., AKINYELE, B. P., OLUSEGUN, S.J., OLUWASINA, O., MOHALLEM, N. D. S. (2021). Evaluation of the effects of additives on the properties of starch-based bioplastic film. *SN Appl. Sci.* 3, 421. <https://doi.org/10.1007/s42452-021-04433-7>
- PANTHAPULAKKAL, S., ZERESHKIAN, A., & SAIN, M. (2006). Preparation and characterization of wheat straw fibers for reinforcing application in injection molded thermoplastic composites. *Bioresour. Technol*, 97, 265–272.
- PASSADOR, F. R., PESSAN, L. A., & RODOLFO A. R. (2006). Estado de mistura e dispersão da fase borrachosa em blendas PVC/NBR. *Polímeros*, 16, 174-181.
- PAUL, D. R., & NEWMAN, S. (1978). “Polymers blends”, vol.1, *Academic Press*, New York.
- PAULA, F. C., PAULA, C. B. C., & CONTIERO, J. (2018). Prospective Biodegradable Plastics from Biomass Conversion Processes. *Biofuels - State Dev*, <https://doi.org/10.5772/intechopen.75111>
- PEELMAN, N., RAGAERT, P., DE MEULENAER, B., ADONS, D., PEETERS, R., CARDON, L., VAN IMPE, F., DEVLIEGHERE, F. (2013). Review: Application of bioplastics for food packaging. *Trends Food Sci. Technol*, 32, 128–141. <https://doi.org/10.1016/j.tifs.2013.06.003>

- PELISSARI, F. M., ANDRADE-MAHECHA, M. M., SOBRAL, P. J. D. A., & MENEGALLI, F. C. (2013). Comparative study on the properties of flour and starch films of plantain bananas (*Musa paradisiaca*). *Food Hydrocolloids*, 30, 2, 681-690.
- PENG, L., ZHONGDONG, L., & KENNEDY, J. F. (2007). The study of starch nano-unit chain in the gelatinization process. *Carbohydrate Polymers*, 68, 360-366.
- PENG, X. W., REN, J. L., ZHONG, L. X., & SUN, R. C. (2011). Nanocomposite films based on xylanrich hemicelluloses and cellulose nanofibers with enhanced mechanical properties. *Biomacromolecules*, 12, 9, 3321–3329.
- PÉREZ, S., & MAZEAU, K. (2005). Conformations, Structures, and Morphologies of Celluloses. In: Dimitriu, S., Ed., *Polysaccharides: Structural Diversity and Functional Versatility*, Marcel Dekker, Inc., New York. 41-68.
- PEREZ-PUYANA, V., FELIX, M., ROMERO, A., & GUERRERO, A. (2016). Effect of the injection moulding processing conditions on the development of pea protein-based bioplastics. *J. Appl. Polym. Sci*, 133, 1–9. <https://doi.org/10.1002/app.43306>
- PHAM, T. P. T., KAUSHIK, R., PARSHETTI, G. K., MAHMOOD, R., & BALASUBRAMANIAM, R. (2015). Food waste-to-energy conversion technologies: current status and future directions. *Waste Manag*, 38, 399-408.
- PHAN THE, D., DEBEAUFORT, F., VOILLEY, A., & LUU, D. (2009). Biopolymer interactions affect the functional properties of edible films based on agar, cassava starch and arabinoxylan blends. *J Food Eng*, 90, 548–558.
- POLMAN, E. M. N., GRUTER, G. J. M., PARSONS, J. R., & TIETEMA, A. (2021). Comparison of the aerobic biodegradation of biopolymers and the corresponding bioplastics: A review. *Sci. Total Environ*. 753, 141953.
- RASHID, T., KAIT, C.F., REGUPATHI, I., & MURUGESAN, T. (2016). Dissolution of kraft lignin using Protic Ionic Liquids and characterization. *Industrial Crops and Products*. 84, 284–293. <https://doi.org/10.1016/j.indcrop.2016.02.017>.
- RIVARD, C., MOENS, L., ROBERTS, K., BRIGHAM, J., KELLEY, S. (1995). Starch esters as biodegradable plastics: Effects of ester group chain length and degree of substitution on anaerobic biodegradation. *Enzyme and Microbial Technology*. 17, 9, 848–852. doi:10.1016/0141-0229(94)00120-g
- ROBLES, E., FERNÁNDEZ-RODRÍGUEZ, J., BARBOSA, A.M., GORDOBIL, O., & CARREÑO, N. L. V., LABIDI, J. (2018). Production of cellulose nanoparticles from blue agave waste treated with environmentally friendly processes.

<https://doi.org/10.1016/j.carbpol.2018.01.015>.

- RYU, S. Y., RHIM, J. W., ROH, H.J., & KIM, S. S. (2002). Preparation and physical properties of zein coated high amylose corn starch film. *Lebensmittel-Wissenschaft und Technologie*, 35, 680–686.
- QUEIROZ, A. U. B., & COLLARES-QUEIROZ, F. P. (2009). Innovation and industrial trends in bioplastics. *Polym. Rev*, 49, 65–78. <https://doi.org/10.1080/15583720902834759>
- REIS, L. C. B., BATISTA, R., CAROLINA, O. S., ALVES DA SILVA, J. B., MARTINS, A. C., NUNES, I. L., & DRUZIAN, J. I. (2015). Active biocomposites of cassava starch: the effect of yerba mate extract and mango pulp as antioxidant additives on the properties and the stability of a packaged product. *Food Bioproduct Process*, 94, 382–91.
- SABETZADEH, M., BAGHERI, R., & MASOOMI, M. (2015). Study on ternary low density polyethylene/linear low density polyethylene/thermoplastic starch blend films. *Carbohydr Polym*, 119,126–33.
- SAENGCHAN, K., NOPHARATANA, M., LERDLATTAPORN, R., & SONGKASIRI, W. (2015). Enhancement of starch-pulp separation in centrifugal-filtration process: Effects of particle size and variety of cassava root on free starch granule separation. *Food and Bioproducts Processing*, 95, 208–217. <https://doi.org/10.1016/j.fbp.2015.05.008>.
- SAINI, JITENDRA & ARTI, & TEWARI, LAKSHMI. (2012). Simultaneous Isolation and Screening of Cellulolytic Bacteria: Selection of Efficient Medium. *Journal of Pure and Applied Microbiology*. 6. 1339-1344.
- SALAM, A., PAWLAK, J. J., VENDITTI, R. A., & EL-TAHLAWY, K. (2011). Incorporation of carboxyl groups into xylan for improved absorbency. *Cellulose*, 18, 1033-1041.
- SALAS-VALERO, L. M., TAPIA-BLÁCIDO, D. R., & MENEGALLI, F. C. (2015). Biofilms based on Canihua flour (*Chenopodium Pallidicaule*): design and characterization. *Química Nova*, 38, 14-21.
- SANYANG, M. L., SAPUAN, S. M., JAWAID, M., ISHAK, M. R., & SAHARI, J. (2016). Development and characterization of sugar palm starch and poly (lactic acid) bilayer films. *Carbohydrate Polymers*, <http://dx.doi.org/10.1016/j.carbpol.2016.03.051>

- ŠÁRKA, E., KRULIŠ, Z., KOTEK, J., RŮŽEK, L., KORBÁŘOVÁ, A., BUBNÍK, Z., RŮŽKOVÁ, M. (2011). Application of wheat B-starch in biodegradable plastic materials. *Czech J. Food Sci.* 29, 232–242.
- SARTORI, J., POTTHAST, A., ECKER, A., SIXTA, H., ROSENAU, T., & KOSMA, P. (2003). Alkaline degradation kinetics and CE-separation of cello- and xylooligomers. *Part I. Carbohydrate Research*, 338, 1209–1216. [https://doi.org/10.1016/s0008-6215\(03\)00115-0](https://doi.org/10.1016/s0008-6215(03)00115-0).
- SAXENA, A., ELDER, T. J., PAN, S., & RAGAUSKAS, A. J. (2009). Novel nanocellulosic xylan composite film. *Composites Part B: Engineering*, 40, 8, 727–730.
- SAXENA, A., & RAGAUSKAS, A. J. (2009). Water transmission barrier properties of biodegradable films based on cellulosic whiskers and xylan. *Carbohydrate Polymers*, 78, 2, 357–360. doi:10.1016/j.carbpol.2009.03.039
- SCHMATZ, A. A., TYHODA, L., & BRIENZO, M. (2019). Sugarcane biomass conversion influenced by lignin. *Biofuels, Bioproducts and Biorefining*. doi:10.1002/bbb.2070
- SCHMIDT, V. C. R., BLANCO-PASCUAL, N., TRIBUZI, G., & LAURINDO, J. B. (2019). Effect of the degree of acetylation, plasticizer concentration and relative humidity on cassava starch films properties. *Food Science and Technology*. 39, 2, 491-499. <https://dx.doi.org/10.1590/fst.34217>
- SHAH, U., NAQASH, F., GANI, A., & MASOODI, F. A. (2016). Art and Science behind Modified Starch Edible Films and Coatings: A Review. *Comprehensive Reviews in Food Science and Food Safety*. 15.
- SHARMA, A., & SATYANARAYANA, T. (2013). Microbial acid-stable α -amylases: Characteristics, genetic engineering and applications. *Process Biochemistry*, 48, 201-211.
- SHAHZADI, T., MEHMOOD, S., IRSHAD, M., ANWAR, Z., AFROZ, A., ZEESHAN, N., RASHID, U., & SUGHRA, K. (2014). Advances in lignocellulosic biotechnology: A brief review on lignocellulosic biomass and cellulases. *Advances in Bioscience and Biotechnology*, 5, 246-251. doi: 10.4236/abb.2014.53031.
- SHEN, L., HAUFE, J., & PATEL, M. K. (2009). Product overview and market projection of emerging bio-based plastics PRO-BIP 2009 Utrecht The Netherlands. *Eur. Polysacch. Netw. Excell. Eur. Bioplastics*, 243.
- SHIMIZU, F. L., MONTEIRO, P. Q., GHIRALDI, P. H. C., MELATI, R. B.,

- PAGNOCCA, F. C., DE SOUZA, W., & BRIENZO, M. (2018). Acid, alkali and peroxide pretreatments increase the cellulose accessibility and glucose yield of banana pseudostem. *Ind Crop Prod*, 115, 62–68.
- SINGH, S., & MOHANTY, A. (2007). Wood fiber reinforced bacterial bioplastic composites: Fabrication and performance evaluation. *Compos. Sci. Technol*, 67, 1753–1763. doi: 10.1016/j.compscitech.2006.11.009
- SLEIMAN, G. E. H., COLOMINES, G., DETERRE, R., PETIT, I., LEROY, E., & BELHABIB, S. (2018). PHBV crystallization under injection molding conditions: Influence of packing pressure and mold temperature. *J. Renew. Mater*, 6, 270–276. <https://doi.org/10.7569/JRM.2017.634179>
- SOBRAL, P. J. A., MENEGALLI, F. C., HUBINGER, M. D., & ROQUES, M. A. (2001). Mechanical, water vapour barrier and thermal properties of gelatin based edible films. *Food Hydrocolloids*, 15, 423-432. DOI: 10.1016/S0268-005X(01)00061-3
- SONDARI, D., FALAH, F., SURYANINGRUM, R., SARI, F. P., SEPTEFANI, A. A., RESTU, W. K., & SAMPORA, Y. (2019). Biofilm Based on Modified Sago Starch: Preparation and Characterization. *Reaktor*. 19, 3, 125- 130, <http://dx.doi.org/10.14710/reaktor.19.3.125-130>
- SOUZA, P. M., & MAGALHÃES, P. O. (2010). Application of microbial α -amilase in industry – A review. *Brasilian Journal of Microbiology*, 41, 850–861.
- SOUZA, O., FEDERIZZI, M., COELHO, B., WAGNER, T. M., & WISBECK, E. (2010). Biodegradação de resíduos lignocelulósicos gerados na bananicultura e sua valorização para a produção de biogás. *Revista Brasileira de Engenharia Agrícola e Ambiental*, 14, 4, 438- 443.
- SOUZA, A. C., BENZE, R., FERRAO, E. S., DITCHFIELD, C., COELHO, A. C. V., & TADIN, C. C. (2012). Cassava starch biodegradable films: influence of glycerol and clay nanoparticle content on tensile and barrier properties and glass transition temperature. *LWT: Food Sci Technol*, 46, 1, 110–7.
- SOUZA, R. E., GOMES, F. J. B., BRITO, E. O., & COSTA LELIS, R. C. (2020). A review on lignin sources and uses. *J Appl Biotechnol Bioeng*, 7, 3, 100-105. DOI: [10.15406/jabb.2020.07.00222](https://doi.org/10.15406/jabb.2020.07.00222).
- SREEKALA, M. S., GODA, K., & DEVI, P. V. (2008). Sorption characteristics of water, oil and diesel in cellulose nanofiber reinforced corn starch resin/ramie fabric composites. *Compos Interfaces*, 15, 281–299.

- SPENCER, R. R., & AKIN, D. E. (1980). Rumen Microbial Degradation of Potassium Hydroxide-treated Coastal Bermudagrass Leaf Blades Examined by Electron Microscopy. *Journal of Animal Science*, 51, 1189–1196. <https://doi.org/10.2527/jas1980.5151189x>.
- STEVANIC, J. S., JOLY, C., MIKKONEN, K. S., PIRKKALAINEN, K., SERIMAA, R., RÉMOND, C., TORIZ, G., GATENHOLM, P., TENKANEN, M., & SALMÉN, L. (2011). Bacterial nanocellulose-reinforced arabinoxylan films. *Journal of Applied Polymer Science*, 122, 2, 1030–1039. <https://doi.org/10.1002/app.34217>
- STEVANIC, J. S., BERGSTRÖM, E. M., GATENHOLM, P., BERGLUND, L., & SALMÉN, L. (2012). Arabinoxylan/nanofibrillated cellulose composite films. *Journal of Materials Science*, 47, 18, 6724–6732. doi:10.1007/s10853-012-6615-8
- STEVENS, E. S., KLAMCZYNSKI, A., & GLENN, G. M. (2010). Starch-lignin foams. *Express Polym. Lett*, 4, 311– 320. doi: 10.3144/expresspolymlett.2010.39
- SUN, B., ZHANG, M., & NI, Y. (2018). Use of sulfated cellulose nanocrystals towards stability enhancement of gelatin-encapsulated tea polyphenols. *Cellulose*, 25, 5157–5173. <https://doi.org/10.1007/s10570-018-1918-9>
- SURIYATEM, R., NOIKANG, N., KANKAM, T., JANTANASAKULWONG, K., LEKSAWASDI, N., PHIMOLSIRIPOL, Y., INSOMPHUN, C., SEESURIYACHAN, P., CHAIYASO, T., JANTRAWUT, P. (202). Physical Properties of Carboxymethyl Cellulose from Palm Bunch and Bagasse Agricultural Wastes: Effect of Delignification with Hydrogen Peroxide. *Polymers*. 12, 1505.
- SVAGAN, A. J., HEDENQVIST, M., & BERGLUND, L. (2009). Reduced water vapour sorption in cellulose nanocomposites with starch matrix. *Compos Sci Technol*, 69, 3–4, 500–506.
- TAHERI, H., HIETALA, M., & OKSMAN, K. (2020). One-step twin-screw extrusion process of cellulose fibers and hydroxyethyl cellulose to produce fibrillated cellulose biocomposite. *Cellulose*, 27, 8105–8119. <https://doi.org/10.1007/s10570-020-03287-3>
- TAMARA, T., SUMARI, NAZRIATI, & ARNI, S. (2020). Properties of cassava starch-based bioplastics and CMC with sorbitol as A plasticizer. *IOP Conference Series: Earth and Environmental Science*. 456, 012077. doi:10.1088/1755-1315/456/1/012077
- TEIXEIRA, P., PONTES, A., & HENRIQUES, E. (2012). Effect of the injection

- moulding processing conditions on biopolymers final properties. *Mater. Sci. Forum*, 730–732, 20–25. <https://doi.org/10.4028/www.scientific.net/MSF.730-732.20>
- THAKUR, V. K., THAKUR, M. K., RAGHAVAN, P., & KESSLER, M. R. (2014). Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review. *ACS Sustain. Chem. Eng*, 2, 1072– 1092. doi: 10.1021/sc500087z
- THARANATHAN, R. N. (2003). Biodegradable films and composite coatings: Past, present and future. *Trends Food Sci. Technol*, 14, 71–78. [https://doi.org/10.1016/S0924-2244\(02\)00280-7](https://doi.org/10.1016/S0924-2244(02)00280-7)
- TONGDEESOONTORN, W., MAUER, L., WONGRUONG, S., SRIBURI, P., & RACHTANAPUN, P. (2011). Effect of carboxymethyl cellulose concentration on physical properties of biodegradable cassava starch-based films. *Chem. Cent. J.* 5, 1–8.
- TRACHE, D., HUSSIN, M. H., HAAFIZ, M. K. M., & THAKUR, V. K. (2017). Recent progress in cellulose nanocrystals: sources and production. *Nanoscale*, 9, 5, 1763–1786. <https://doi.org/10.1039/c6nr09494e>.
- TRACHE, D., HUSSIN, M. H., HUI CHUIN, C. T., SABAR, S., FAZITA, M. R. N., TAIWO, O. F. A., HASSAN, T. M., & HAAFIZ, M. K. M. (2016). Microcrystalline cellulose: Isolation, characterization and bio-composites application—A review. *International Journal of Biological Macromolecules*, 93, 789–804. <https://doi.org/10.1016/j.ijbiomac.2016.09.056>.
- TULAMANDI, S., RANGARAJAN, V., RIZVI, S. S. H. SINGHAL, R. S., CHATTOPADHYAY, S. K., & SAHA, N. C. (2016). A biodegradable and edible packaging film based on papaya puree, gelatin, and defatted soy protein. *Food Packaging & Shelf Life*, 10, 60-71.
- VANIN, F. M., HIRANO, M. H., CARVALHO, R. A., MORAES, I. C. F., BITTANTE, A. M. Q. B., & SOBRAL, P. J. A. (2014). Development of active gelatin-based nanocomposite films produced in an automatic spreader. *Food Research International*, 63, 16-24. DOI: 10.1016/j.foodres.2014.03.028
- VAVOURAKI, A. L., ANGELIS, E. M., & KOMAROS, M. (2013). Optimization of thermo-chemical hydrolysis of kitchen waste. *Waste Management*, 33, 3, 740-745. <https://doi.org/10.1016/j.wasman.2012.07.012>
- VERSINO, F., & GARCÍA, M. A. (2014). Cassava (*Manihot esculenta*) starch films

- reinforced with natural fibrous filler. *Industrial Crops and Products*, 58, 305–314. <https://doi.org/10.1016/j.indcrop.2014.04.040>.
- XIE, F., POLLET, E., HALLEY, J. P., & AVEROUS, L. (2013). Starch-based nano-biocomposites. *Prog Polym Sci*, 38, 1590–628.
- XIE, F., POLLET, E., HALLEY, P.J., & AVÉROUS, L. (2014). Advanced Nano-biocomposites Based on Starch. *Polysaccharides*, 1–75. doi:10.1007/978-3-319-03751-6_50-1
- XIE, F., AVÉROUS, L., HALLEY, P. J., & LIU, P. (2015). Mechanical performance of starch-based biocomposites. *Biocomposites*, 53–92.
- WAN, Y. Z., LUO, H., HE, F., LIANG, H., HUANG, Y., & LI, X. L. (2009). Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites. *Compos Sci Technol*, 69, 7–8, 1212–1217.
- WANG, S., REN, J., LI, W., SUN, R., & LIU, S. (2014). Properties of polyvinyl alcohol/xylan composite films with citric acid. *Carbohydrate Polymers*, 103, 94–99.
- WANG, G., CHEN, H. (2016). Enhanced lignin extraction process from steam exploded corn stalk. *Separation and Purification Technology*, 157, 93–101. <https://doi.org/10.1016/j.seppur.2015.11.036>
- WEI, X., ZHANG, L., WANG, J., LI, J., & ZHOU, W. (2020). Preparation of cellulose film in ionic liquid by high shearing and application in pineapple preservation. *Materials Research Express*, 7, 2, 025313. <https://doi.org/10.1088/2053-1591/ab73fd>.
- WOEHL, M. A., CANESTRARO, C. D., MIKOWSKI, A., SIERAKOWSKI, M. R., RAMOS, L. P., & WYPYCH, F. (2010). Bionanocomposites of thermoplastic starch reinforced with bacterial cellulose nanofibres: effect of enzymatic treatment on mechanical properties. *Carbohydr. Polym*, 80, 3, 866–873.
- WOGGUM, T., SIRIVONGPAISAL, P., WITTAYA, T. (2015). Characteristics and properties of hydroxypropylated rice starch based biodegradable films. *Food Hydrocoll*. 50, 54–64
- WU, Q., RABU, J., GOULIN, K., SAINLAUD, C., CHEN, F., JOHANSSON, E., OLSSON, R. T., & HEDENQVIST, M. S. (2017). Flexible strength-improved and crack-resistant biocomposites based on plasticised wheat gluten reinforced with a flax-fibre-weave. *Compos. Part A Appl. Sci. Manuf*, 94, 61–69. doi:

- 10.1016/j.compositesa.2016.12.016.
- YAN, S., LI, J., CHEN, X., WU, J., WANG, P., YE, J., & YAO, J. (2011). Enzymatic hydrolysis of food waste and ethanol production from the hydrolysate. *Renew Energy*, 36, 1259-65.
- YANG, J., CHING, Y. C., & CHUAH, C. H. (2019). Applications of Lignocellulosic Fibers and Lignin in Bioplastics: A Review. *Polymers*, 11, 5, 751. <https://doi.org/10.3390/polym1105075>
- YARADODDI, J. S., BANAPURMATH, N. R., GANACHARI, S. V. et al., (2020). Biodegradable carboxymethyl cellulose based material for sustainable packaging application. *Sci Rep*. 10, 21960. <https://doi.org/10.1038/s41598-020-78912-z>
- YONG, C. K., CHING, Y. C., LUQMAN, C. A., & LIOU, N. S. (2015a). Effect of fiber orientation on mechanical properties of kenaf-reinforced polymer composite. *BioResources*, 10, 2597–2608. doi: 10.15376/biores.10.2.2597-2608
- YONG, C. K., CHING, Y. C., AFZAN, M., LIM, Z. K., & CHONG, K. E. (2015b). Mechanical and thermal properties of chemical treated oil palm empty fruit bunches fiber reinforced polyvinyl alcohol composite. *J. Biobased Mater. Bioenergy*, 9, 231–235.
- YU, J., YANG, J., LIU, B., & MA, X. (2009). Preparation and characterization of glycerol plasticized-pea starch/ZnO-carboxymethylcellulose sodium nanocomposites. *Bioresour. Technol*, 100, 2832–2841. <https://doi.org/10.1016/j.biortech.2008.12.045>
- ZAHEDI, Y., GHANBARZADEH, B., & SEDAGHAT, N. (2010). Physical properties of edible emulsified films based on pistachio globulin protein and fatty acids. *J Food Eng*, 100, 1,102–8.
- ZHANG, Y. H. P., & LYND, L. R. (2004). Toward an aggregated understanding of enzymatic hydrolysis of cellulose: Noncomplexed cellulase systems. *Biotechnology and Bioengineering*, 88, 7, 797-824.
- ZHU, F. (2017). Structures, properties, modifications, and uses of oat starch. *Food Chemistry*. 229, 329–340. <https://doi.org/10.1016/j.foodchem.2017.02.064>.
- ZULHAM EFENDI SINAGA, M., GEA, S., PANINDIA, N., & ALFINSYAH SIHOMBING, Y. (2018). The Preparation of All-Cellulose Nanocomposite Film from Isolated Cellulose of Corncobs as Food Packaging. *Oriental Journal of Chemistry*, 34, 1, 562–567. <https://doi.org/10.13005/ojc/340166>.

CHAPTER III: Biodegradation of hemicellulose-cellulose-starch-based bioplastics and microbial polyesters

Abstract

The volume of discarded solid wastes, especially plastic, which accumulates in large quantities in different environments, has substantially increased. Population growth and the consumption pattern of societies associated with unsustainable production routes have caused the pollution level to increase. Therefore, the development of materials that help mitigate the impacts of plastics is fundamental. However, bioplastics can result in a misunderstanding about their properties and environmental impacts, as well as incorrect management of their final disposition, from misidentifications and classifications. This chapter addresses the aspects and factors surrounding the biodegradation of bioplastics from natural (plant biomass (starch, lignin, cellulose, hemicellulose, and starch)) and bacterial polyester polymers. Therefore, the biodegradation of bioplastics is a factor that must be studied, because due to the increase in the production of different bioplastics, they may present differences in the decomposition rates.

Keywords: biodegradation, bioplastics, lignocellulosic fibers, microbial polyesters.

1. Introduction

Consumption demands for industrialized materials such as plastics in their various applications have increased over the past years. This consumption is generating residues, which require alternatives for their proper disposal and recycling. Disposal, recycling, and plastic substitution are potential research areas towards urgent and necessary solutions. Most commercial plastics come from the petrochemical industry, which uses natural gas and fossil hydrocarbons as feedstock. Such synthetic plastics are biodegradable and degradable only for a long period. Therefore, they are considered neither biodegradable nor renewable (SINGH et al., 2017). Synthetic polymers, such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), nylon, polyester (PS) and epoxy are examples of plastic components of high resistivity, chemical and biological inertness, resistance, flexibility and other interesting properties (NAGALAKSHMAIAH et al., 2016; MARIANO et al., 2017; NAGALAKSHMAIAH et al., 2017; NAGALAKSHMAIAH et al., 2019).

At the beginning of the large-scale production of synthetic plastic materials, their properties seemed adequate for good quality development. However, such materials are non-biodegradable, thus generating large accumulations of residues in different landscapes. Thus, they have been a cause of growing concerns due to environmental problems. New materials based on biological sources have been developed towards solving or reducing the above-mentioned problems. However, in addition to be renewable and biodegradable, bioplastics must have vapors barrier properties and mechanical properties that meet the different applications of this material, and the attention has now evolved towards the possible ecotoxic effects of bioplastics and active properties for a cover of food.

The names of biodegradable and/or bioplastic products given by companies and reported in the literature, when drawn up wrongly, can lead to misunderstandings by the general public due to incorrect classifications of the polymeric materials (LACKNER, 2015; Nazareth et al., 2018; HARDING et al., 2017; IWATA, 2015). A bioplastic can be biodegradable or not. However, a biodegradable material does not necessarily come from a biological source. Towards the avoidance of errors, the following definitions, reported in this article, must be clarified:

- *Plastics* are polymeric matrices comprised of organic polymers of high molecular weight and other substances, such as fillers, colors, and

additives (LACKNER, 2015). In general, the synthetic route is predominant in the synthesis of the material.

- *Bioplastic* refers to materials that are biodegradable, bio-based or both. Although the term bioplastic is generally used to distinguish polymers derived from fossil resources, it is worth mentioning that bioplastics may come from petroleum (LACKNER, 2015). The prefix "bio" of bioplastic does not necessarily mean this material is environmentally friendly (LACKNER, 2015).
- *Biomass* is a source of natural organic carbon that may originate from animals or vegetables raised/cultivated by humans or that spontaneously emerge in terrestrial and marine environments (BONECHI et al., 2017).

Different biotic and abiotic factors contribute to the different degradation processes (KABIR et al., 2020). Thermal, mechanical and chemical degradation, as well as photodegradation, are examples of abiotic degradation. A degradation process is related to the fragmentation of material into small elements or molecules, or just physical and chemical changes in a polymer. Due to high temperatures, polymers can be thermally degraded. The chemical bonds in their chains are broken by a thermo-degradation effect (CRAWFORD and QUINN, 2017).

Mechanical degradation is an abiotic degradation mechanism that occurs through shear forces (due to aging, turbulence in water and air, snow pressure, and other factors), tension and/or compression. Under environmental conditions, it acts synergistically with different abiotic factors (LUCAS et al., 2008).

Abiotic chemical degradation occurs by the degradative effect of chemicals substances, and represent one of the most important mechanisms of abiotic degradation, since the polymer matrix is affected by atmospheric or agrochemical pollutants, such as oxygen (i.e., O₂ or O₃), which produce free radicals through oxidation, attacking covalent bonds (Lucas et al., 2008). Abiotic chemical degradation differs from biotic chemical degradation, mainly regarding the origin of the chemical with a degrading effect.

Photodegradation is the process of degradation of polymers by the action of light, resulting in the oxidation of the material. UV rays interact with chromophores groups of polymers (carbonyl, hydroxyls, and aldehydes), which are degraded by chain

fission, photoionization, crosslinking, and oxidation reaction (FAIRBROTHER et al., 2019; KABIR et al., 2020; NIAOUNAKIS, 2015; LUCAS et al., 2008).

Microbial Biodegradation is a degradation process of polymers and other materials through the action of microorganisms (KABIR et al., 2020) resulting in CO₂ and/or methane, water, cell biomass, and energy. However, in the natural environment and even in the process of controlled biodegradation, abiotic effects help or even occur synergistically with biodegradation. This consideration of synergism is important for the elaboration of biodegradation procedures.

With environmental concern, this review evaluated the biodegradation process (considering the synergistic action of biotic and abiotic agents) of bioplastics elaborated with polysaccharides from plant biomass and microbial polyesters. Also, addressing the definitions, biodegradation mechanism and factors that affect the biodegradative process of bioplastics. The scope of this review does not address the biodegradation of bioplastics produced from polymers of animal origin (natural polymer) and bioplastics derived from petroleum (PBAT, PBS, PVA, PCL, and PGA (BÁTORI et al., 2018). However, the definitions presented in this review do not exclude these types of bioplastics.

2. Problems related to plastics

The current geological era, the so-called Anthropocene, is exposed to the influence of human actions in different environments. Indicators from such anthropic actions are biodiversity reduction, deforestation, climate, and other environmental changes (CRUTZEN, 2006). However, materials produced by human society, like plastics, are also indicators of the Anthropocene. Plastics directly (i.e., environmental impacts from the plastic production chain) affect different environments (e.g., terrestrial and marine).

An environment in which plastic waste currently generates several problems, is the oceans, due to the large accumulation of these materials. The plastic that reaches the oceans mostly is generated in coastal population regions, where the disposal and management of this waste is destined for uncontrolled landfills (JAMBECK et al., 2015). Due to urban runoff and inland waterways, such plastics reach oceans and are transported via tide and winds. It is estimated that between 4.8 and 12.7 million metric

tons of plastics produced in the continent (distribution varies according to the analyzed location) reached the marine environment in 2010 (JAMBECK et al., 2015).

In recent years, environmental concerns (e.g., harmful effects of plastics on the environment, since they are not biodegradable (GEYER et al., 2017), or slowly degraded) have been intensified. Large accumulations of floating plastics in the oceans have been reported- approximately 1.8 trillion pieces of plastic have been quantified in the Great Pacific Garbage Patch (GPGP) (LEBRETON et al., 2018). The ingestion of plastic fragments by the marine fauna is a major concern due to their small size (JAMBECK, et al., 2015; WRIGHT et al., 2013, GOLDSTEIN and GOODWIN, 2013), the so-called microplastics, which are smaller than 5 mm (WRIGHT et al., 2013). Besides, since plastic fragments are present on the surface and floor of oceans, as well as in several maritime regions (coastal areas) and the Arctic sea ice, strategies, as a reduction in inputs (JAMBECK, et al., 2015) and the elaboration/utilization of biodegradable materials, would be adequate measures to reduce the impacts of plastics.

Even with the area of studies on the impacts of plastics on fauna and for the various organisms still under development, some studies point to the occurrence of toxicological effects of this synthetic waste (DE SÁ et al., 2015; CANESI et al., 2015). A plastic intake and entanglement can lead to the lower life quality of organisms, loss of mobility, external and internal injuries, blockage of digestion, and other harms (GREGORY, 2009). GOLDSTEIN and GOODWIN (2013) identified the presence of microplastics (mainly PE, PS, and PP) in the digestive tract of 33.5% of *Gooseneck crustaceans* (*Lepas spp.*).

The development of innovative technologies represents a means for both sustainable development (BOONS et al., 2013; DE CARVALHO AND BARBIERI, 2012) and the growth of emerging countries, such as Brazil, whose sustainable energy has been highlighted by innovation technologies. Thus, even with bioplastic not representing a material for total replacement of non-biodegradable plastic, researches and production of bioplastics are a technological alternative for the development of a more sustainable and balanced society. Therefore, aligning with the current trend (socio-political and environmental), in which concerns with the environment is growing.

3. Biodegradation process

The biodegradation of materials occurs by the action of microorganisms, such as fungi and bacteria (PATHAK and NAVNEET 2017), and is classified as physical, chemical, and enzymatic according to modifications in the materials. Biodegradation is a natural process of vital importance for nutrients and energy recycling (PALMISANO and PETTIGREW, 1992). Microorganisms use organic material as a source of nutrition for their metabolism; except for the substances used in metabolic incorporation, the rest is oxidized by cellular respiration, thus leading to the formation of simple and small submetabolites, released in the environment (DE PAOLI, 2008; CRISPIM and GAYLARDE, 2005).

Biodegradation due to physical degradation occurs from the adhesion of microorganism species to the surface of organic materials through the secretion of a gum (CAPITELLI et al., 2006) produced by microorganisms. This gum represents a complex matrix made of natural polymers (e.g., polysaccharides and proteins). Such a thick complex, together with microorganisms, infiltrates the material and changes its volume, size, pores distribution, moisture content, and thermal transfers. A few microorganisms (e.g., filamentous fungi) lead to cracks in the materials due to mycelial growth, i.e., both their durability and resistance properties are reduced (BONHOMME et al., 2003; LUCAS et al., 2008). Microorganism biofilms are a matrix that protects microorganisms from different environmental conditions and results in a major change in materials (LUCAS et al., 2008; FLEMMING, 1998).

Biodegradation by chemical degradation refers to the production of chemical substances by living organisms, which facilitate and increase the speed of the process. Emulsifying substances produced by microorganisms help the exchange between hydrophobic and hydrophilic phases, which are important interactions for the penetration of microorganisms in the polymeric material (WARSCHEID and BRAAMS, 2000). Such a lime formation (polymers secreted by microorganisms mixed with different microbial species) improves the material deterioration. It represents a point of accumulation of polluting and chemical substances (abiotic chemical degradation), thus benefitting microbial proliferation (ZANARDINI et al., 2000).

Examples of chemical substances released into the environment by microorganisms, which play an important role in chemical biodegradation, are nitrous acid, nitric acid, and sulfuric acid. All of these compounds are produced by chemolithotrophic bacteria, such as *Nitrosomonasspp*, *Nitrobacterspp*, and *Thiobacillusspp*, respectively (WARSCHEID and BRAAMS, 2000; CRISPIM and

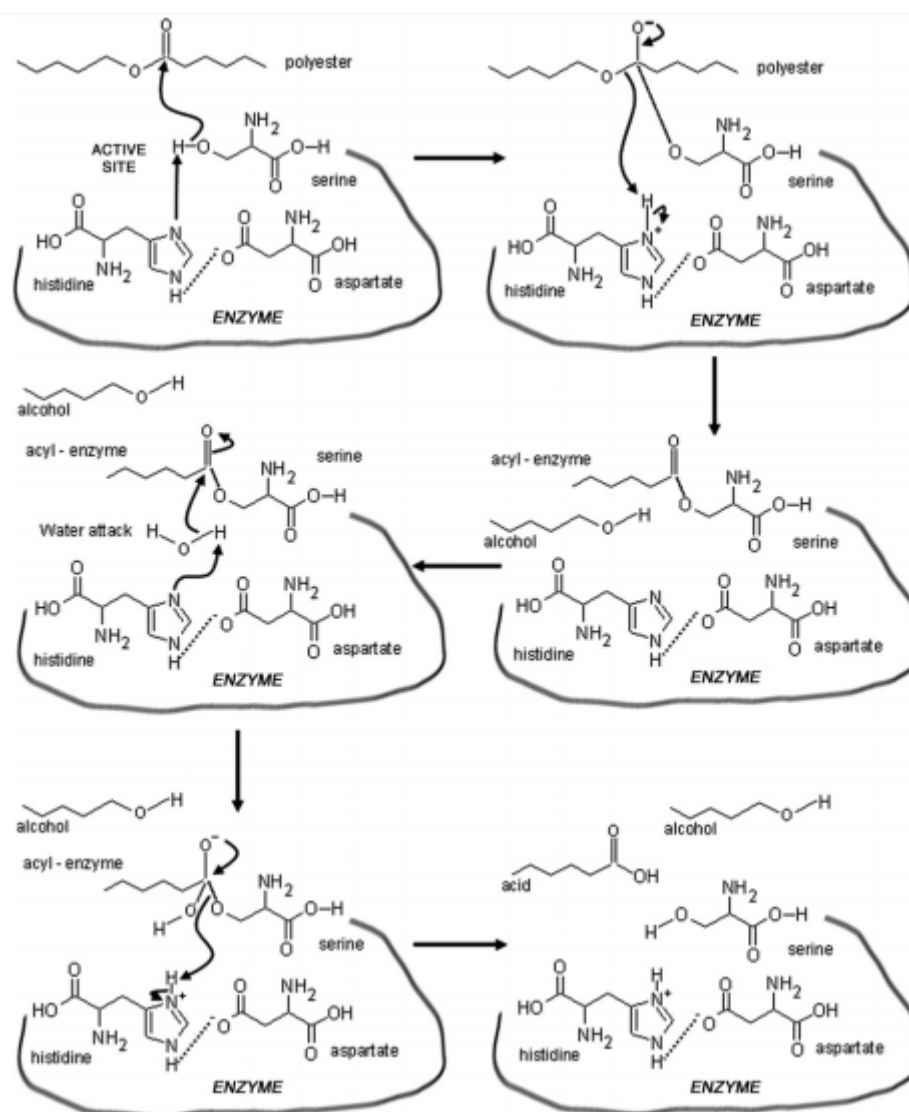
GAYLARDE, 2005; RUBIO et al., 2006). Apart from the action of chemical substances generated by those organisms, chemoorganotrophic microorganisms generate organic acids with potential for chemical degradation (e.g., oxalic, citric, gluconic, glutaric, glyoxalic, oxaloacetic, and fumaric acids).

The action mechanisms of such acids (organic or inorganic) are diverse and include an increase in surface erosion when adhering to the material surface (LUGAUSKAS et al., 2003). The use of those acids as nutrients benefits the growth of filamentous fungi and bacteria (LUCAS et al., 2008). Another action mechanism of biotic chemical degradation is the oxidation of organic material. Certain fungi and bacteria have specific proteins in their membrane that capture iron-chelating compounds (siderophores) (PELMONT, 2005). With this mechanism microorganisms capture cations from a matrix.

Biodegradation by enzymatic degradation occurs due to the depolymerization of polymeric chains of a matrix through the action of hydrolase enzymes that catalyze the reactions of chemical bonds breakage adding a water molecule. These bonds are ether, peptide-like, and ester, present in biodegradable bioplastics. The main enzymes are amylases and cellulases, which cleave starch and cellulose polymers, respectively. However, other enzymes (breakage of ester bonds), such as esterases and lipases, can degrade co-polyesters.

A mechanism that explains the action of hydrolases (e.g., depolymerase) in polyesters hydrolysis (synthetic and natural) through biodegradation is related to three amino acids, namely serine, histidine, and aspartate. A hydrogen bond is formed when a component reacts with the histidine ring, thus guiding interaction between histidine and serine, and forming an alcohol group of high nucleophilic character (-O). Histidine plays a deprotonating role for serine, i.e., as a base. The alkoxide group includes an ester bond and generates an acyl-enzyme and an alcohol group. Finally, a free enzyme and a terminal carboxyl group are generated by the action of the water molecule under an acyl-enzyme. This entire enzymatic degradation process is termed catalytic triad (ABOU ZEID, 2001; BELAL, 2003), and the products generated are metabolized or not by microorganisms that have depolymerizing enzymes. Therefore, a consortium of microorganisms is important for complete biodegradation (LUCAS et al., 2008). Figure 1 depicts the mechanism of action of depolymerizes and the catalytic triad.

Figure 1: Enzymatic hydrolysis of polymers and catalytic site of depolymerase enzymes

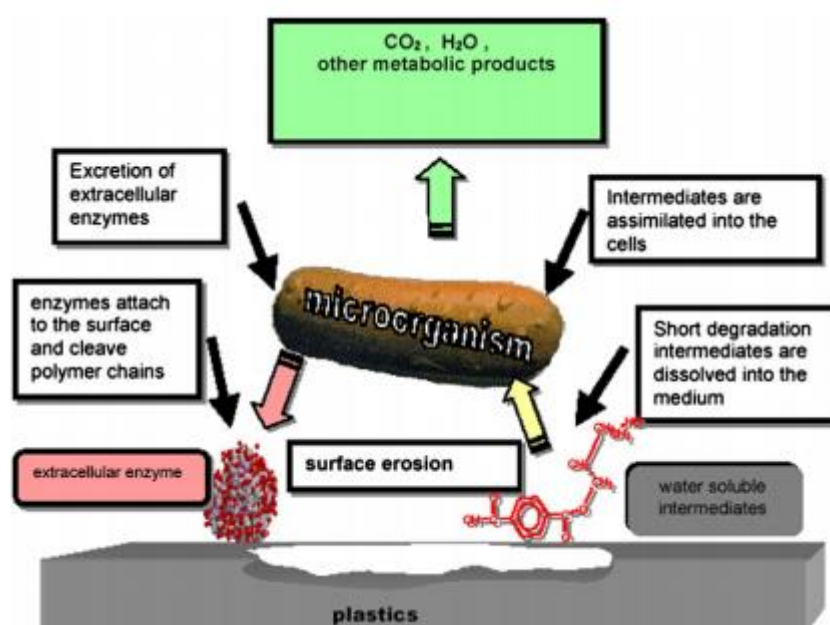


Source: Lucas et al. (2008)

Apart from the biodegradation of cellulose, starch, and polyesters, hemicellulose is another polymer that can be degraded by microbial enzymes. A catalytic action of hemicellulases (enzymatic pool) on different types of hemicellulose polysaccharides produces monomeric sugars, acetic acids (FREITAS et al. 2019). For example, enzymes that degrade xylan (hemicellulose from grasses) are endo-1,4- β -xylanase (cleavage results in oligosaccharides), xylan 1,4- β -xylosidase (cleavage of oligosaccharides generate by xylan, which forms xylose monomers), and accessory enzymes, such as xylan-esterases, ferulic and p-coumaric-esterases, α -L-arabinofuranosidases, and α -4-O-methyl glucuronidase (TERRONE et al., 2020). Both enzymes act synergistically so that xylans and hemicellulose mannans of some types of plant cell walls are

depolymerized (PÉREZ et al., 2002). Nevertheless, some polymers are not biodegraded by common enzymatic hydrolysis, i.e., polymers can be oxidized by enzymes such as laccase, dioxygenase, peroxidases, monooxygenase, and oxidases (COSTA et al., 2015). Thus, such enzymes are not hydrolases and influence the cleavage process of polymers differently from hydrolases (oxygen insertion, hydroxylation, oxidation, and free radical formation lead to polymer cleavage) (COSTA et al., 2015). Figure 2 depicts the enzymatic biodegradation process.

Figure 2: Enzymatic biodegradation process

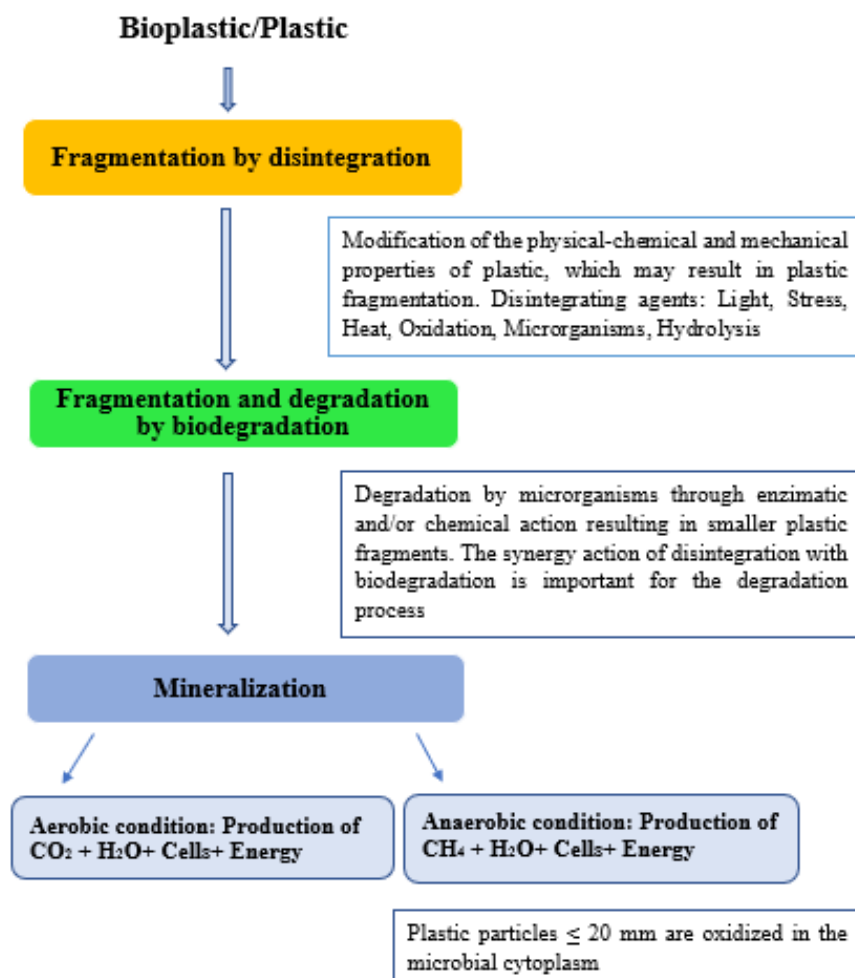


Source: MUELLER (2006).

The result of biodegradation, for example of bioplastic from natural polymers (e.g., polysaccharides) is the generation of small molecules from a polymer. Microorganisms cannot employ large substances insoluble in water for obtaining organic or inorganic nutrients for their metabolism. They produce enzymes and chemicals used in extracellular environments and, therefore, depolymerize the materials. After hydrolysis and/or oxidative action of microorganism enzymes on different polymers, which results in monomers, metabolism oxidation occurs. In this system, organic compounds lead to a loss of electrons and the consequent production of ATP molecule (adenosine triphosphate). This is the last biodegradation stage, in which organic matter is mineralized. The microorganisms use smaller and simple organic

molecules, such as oligomers and monomers, for their metabolic activities. However, byproducts are generated from microbial metabolism (e.g., carbon dioxide - aerobic degradation), water, biomass, methane, and hydrogen sulfide (anaerobic degradation) (PREMRAJ and Doble, 2005; KUMAR and MAITI, 2016). Figure 3 displays the biotic and abiotic degradation of plastic.

Figure 3: Disintegration, biodegradation and mineralization process of plastic polymeric materials.



Source: Based on Krzan et al. (2006)

3.1 Factors that influence biodegradation

The microbial population available is a key factor for biodegradation in an environment (soil, air, and water), and several properties (e.g., the chemical constitution of materials) affects the efficiency of the biodegradation process (PLATT, 2006). Chemical composition influences the biodegradation of plastics through different

patterns of crystallinity, hydrophilic and hydrophobic character, conformational flexibility, polymer accessibility, surface area, molecular weight, melting temperature, hydrolyzable and oxidizable bonds in polymer chains, morphology, and stereoconfiguration (RANI-BORGES et al. 2016; PRIYANKA and ASCHANA, 2011; PALMISANO and PETTIGREW, 1992).

Crystallinity influences biodegradability because it affects the accessibility of the enzyme to the material polymer. More organized regions of polymers (crystalline) tend to hinder enzymatic hydrolysis since catalytic proteins diffuse with greater difficulty. On the other hand, water molecules diffuse more easily between amorphous (less organized) regions, and enzymes can easily access the material polymers in such regions (DE PAOLI, 2008).

The polarity of bioplastics directly influences biodegradation, since materials developed with hydrophobic polymers are less susceptible to enzymatic attack. Degrading microorganisms depend on a hydrophilic surface to adhere to and catalyze the depolymerization reaction by means of hydrolytic enzymes. However, this enzymatic accessibility to the material is reduced on hydrophobic polymeric surfaces. This impediment occurs not only because the microorganisms and enzymes are more hydrophilic, but also due to the aqueous medium (usual water), in which the enzyme is contained, to have their contact with the material (bioplastic) reduced. For example, glycolic polyacids (PGA) are more easily biodegraded than poly (lactic acids) (PLA), since PLA is more hydrophobic) (GUNATILAKE and ADHIKARI, 2003).

Blends in a polymeric bioplastic matrix are common when it is desired to obtain materials with certain characteristics (PLATT, 2006), and also interfere with biodegradation (increase or reduce biodegradation), since the different components of biocomposites can influence the accessibility of the enzyme to the polymeric material in different ways.

The molecular weight of polymers affects the biodegradability of plastics, since the heavier the molecular weight, the greater the difficulty for microorganisms to break it down and assimilate. Therefore, the lower the molecular weight of the polymer, the easier the biodegradation, since the need for extracorporeal digestion is reduced. Aliphatic polyester is one of the few biodegradable polymers of high molecular weight (LUCAS et al., 2008). However, it is worth mentioning that in addition to the molecular weight, the types of bonds in the polymeric chain (considering that bioplastic, like

plastic, is formed by a polymeric matrix), and different chemical groups in polymers influence the biodegradation process.

Although the term "bio" degradation is directly correlated with the fragmentation of a polymer by the action of microorganisms, these microorganisms do not act in isolation on the polymeric material, since abiotic agents influence the fragmentation efficiency. The abiotic degradation of organic matter such as thermal, mechanical, chemical, and by the action of light are examples of degradative processes. These processes work synergistically with biodegradation, reducing the material to dimensions that allow microbial assimilation (PROIKAKIS et al., 2006; LUCAS et al., 2008).

3.2 Assessment and biodegradation quantification

Biodegradation can be measured through metabolic products, physical and chemical properties of plastics/bioplastic, acidification of the medium, and other ways. CO₂ is a product of biodegradation, more specifically, of the oxidation of organic matter, and can be used for direct or indirect measurement of material biodegradation over a period of time. Its content released in a degradation process is quantified by the respirometry technique, which can use a closed CO₂ production and a capture system. International methods, such as ASTM D5338-15 and ISO 14855-2: 2018 are applied for the quantification of the CO₂ produced in a microbial degradation process.

The measurement of consumed oxygen (ISO 17556: 2003) is another method of quantifying biodegradation by respirometry. Respirometry involves techniques that measure parameters indicative of cellular respiration. The higher the consumption of oxygen and the release of CO₂ by microorganisms, the better the biodegradation indicator. For details and examples of other standard methods of respirometry analysis (ASTM, EN, and ISO), see specialized literature (PAVEL et al., 2019).

Methane molecules can also be used for measurements of materials biodegradation. However, unlike the above-mentioned respirometry techniques, CH₄, CO₂, and other gases quantification is generally conducted under anaerobic conditions. Analysis methods such as ASTM D5511-02, ISO 14853:2016, and ISO 15985:2014 are used for this purpose.

Apart from microbial proliferation in plastic/bioplastics materials, analyses of color change, surface roughness, cracks, and holes are also alternatives for checking the deterioration of materials (LUCAS et al., 2008, LUGAUSKAS et al., 2003). Analysis

parameters can be used especially for materials of difficult biodegradation and low CO₂ release. However, the results of such analyses (e.g., microbial growth in the polymeric matrix) are not recommended for the conclusion of biodegradation or abiotic degradation directly (LUCAS et al., 2008). Additional techniques, such as electron microscopy, photon microscopy, microscopy of polarization, and atomic force microscopy reinforce the results (LUCAS et al., 2008; ZHAO et al., 2005; TSUJI et al., 2006).

The physical properties of plastics/bioplastics (e.g., tensile strength, elongation at break, modulus of elasticity, crystallinity, cold crystallization temperature, and glass transition temperature) can be measured as biodegradation indicators. The weight loss of a sample determined by the burial method can be used in plastic/bioplastic biodegradation analyses, although it may result from the solubility and volatility of certain substances (LUCAS et al., 2008). The analysis of weight loss of bioplastics by burying in soil, or composting systems, may result in conclusion errors, since in addition to the mass of the soil or compost account for the variation in the bioplastic mass, in bioplastics washing processes (a step which precedes weighing procedures), can cause fragmentation and loss of material derived from bioplastic. Thus, even though the method of analyzing mass loss is frequently reported in the literature, as is usual in determining the biodegradation of bioplastics, this technique ends up being difficult to perform (MEDINA JARAMILLO et al., 2016). Recent articles evaluating the biodegradation of bioplastics by burying in soil and compost has used image evaluation as a tool for analysis, that is, the reduction of the area of bioplastics, detected by image registration (from the insertion of the bioplastic in a mold/grid with known dimensions) (BALAGUER et al., 2015; PIÑEROS-HERNANDEZ et al., 2017).

The indication of biodegradation through products generated by microorganisms is another way of measuring the process. For example, the biodegradation of polymeric cellulose materials can be measured according to the release of glucose (ABURTO et al., 1999), or the quantification of 1,4-butanediol as an indicator of the biodegradation of PBA and PBS polymers (LINDSTRÖM et al., 2004).

The increase in microbial biomass (weight or number of cells) is indicative of a biodegradation process since a single source of carbon (plastic or bioplastic material) in a closed environment can point out the occurrence of biodegradation and/or surface changes and molecular rearrangements. However, conclusive statements about the amount of mineralized material cannot be directly made.

The evaluation and quantification of bioplastic and/or plastic biodegradation by the above-mentioned methods can be conducted in an aqueous medium and soil. However, each condition of analysis imposes different requirements, which leads to different responses from different methods.

3.3 Biodegradation of bio-based polymers bioplastics

In this topic, biodegradation of bioplastics developed with polysaccharides from plant biomass/lignocellulose and microbial polyesters was followed as the scope of this review. It was exemplified the biodegradation of a category of bioplastics, those developed with natural polymers (vegetable and microbial). Therefore, this review does not intend to address issues related to the development of bioplastics of vegetable and microbial origin, advantages and disadvantages in addition to the viability of this material (related to the economic aspects and properties of bioplastics). To obtain this information, it is recommended reading of the specialized literature (YANG ET AL., 2019; LACKNER, 2015; FARHAT ET AL., 2017; OCHI, 2016).

3.3.1 Biodegradation of plant-based polymers bioplastics

In the study by Bilo, the mass loss of bioplastics from rice straw showed complete degradation after 105 days (BILO et al., 2018). Rice straw bioplastics were composed mainly of cellulose and trifluoroacetic acid. On the first day of contact with the soil, the bioplastic showed an increase in mass, due to the phenomenon of water absorption by the material. According to the authors, its mechanical properties are similar to those of polystyrene (bioplastic in the dry state).

The mass loss of bioplastics consisting of acetylated starch and acetylated sugarcane fibers (lignin, hemicellulose, and cellulose) resulted in 24.2 to 39.3% degradation after 5 weeks (FITCH-VARGAS et al., 2019). The acetyl group may have created stable biodegradable sites; however, an increasing effect on the crystallinity of the bioplastic with the addition of cellulose may have contributed to the low biodegradation rate due to the restriction effect of the microbial enzyme's activity. In addition to the crystallinity and chemical structure of cellulose, microbial diversity, carbon availability and the period of biodegradation considered can influence its depolymerization.

Bioplastics (glycerol, acetylated starch, and acetylated nanocellulose composition) subjected to biodegradation in a petri dish with *Trametes versicolor* were completely degraded in 60 days, and after 40 days with starch and non-acetylated reinforcement. The starch bioplastics were completely biodegraded after 30 days, and the addition of cellulose to the formulation of bio-based plastics resulted in a longer biodegradation time (BABAEE et al., 2015). Water and moisture absorption is important in the biodegradation process of bioplastics (OLUWASINA et al., 2019). The starch-based bioplastics investigated in this study were composed of different concentrations of oxidation starch (20, 40, and 60%). Oxidation decreases biodegradation due to reduced swelling and water absorption from the soil by bioplastic.

Hemicellulose is another natural plant-derived polymer of potential application for the development of bioplastics. However, in addition to the elaboration that biomaterial, the study of the biodegradation of these carbohydrates in bioplastics has not received attention, as the area of use of hemicellulose for bioplastic focus on physicochemical properties and modifications of this macromolecule. The bioplastic based on xylan (of the hemicellulose type of grasses) and blended with gelatine was completely biodegraded after 15 days of conditioning (determined by the burial procedure) (LUCENA et al., 2017). This bioplastic was considered 100% biodegradable since the sample could not be recovered for weighing. A bioplastic made with 50% xylan (from beechwood) and PVA (polyvinyl alcohol) was 56% biodegraded after 30 days by burial in soil (WANG et al., 2014). PVA reduced the biodegradation of the bioplastic produced by the PVA/xylan mixture. The sample with 25% xylan was 42.2% biodegraded after 30 days of burial in soil.

Xylan was grafted with poly-(ϵ -caprolactone) (PCL), and biodegradation was evaluated by BOD (biological oxygen demand). The biodegradation (aerobic and activated sludge) kinetics of bioplastics with high concentrations of PCL was delayed in comparison to materials made with pure hemicellulose or with lower graft concentrations (FARHAT et al., 2018). Despite changes in the kinetics, the biodegradation property of the bioplastic was not altered and ranged between 95.3 and 99.7%.

Recalcitrant substances also influence the biodegradation of natural polymers. Lignin is a constituent of lignocellulosic fibers, shows the highest degree of recalcitrance in the plant cell wall (SCHMATZ et al., 2020; MELATI et al., 2019). This polymeric complex of phenylpropane units hinders the biodegradation of the material or

products that contain it, such as bioplastics, and reduces the contact surface of lignocellulosic fibers with degrading enzymes (MELATI et al., 2019). Lignin requires different enzymes to degrade due to the different units that comprise its polymeric complex (FIGUEIREDO et al., 2018). In anaerobic environments lignin may persist biodegradation for a longer time, with this process is primarily more efficient in aerobic environments (VAN SOEST, 1994), due to the catalytic action involved in oxygen.

Starch and lignin (lignosulfonate) bioplastics were completely biodegraded after 4-month burial (CAMPAGNER et al., 2014). Biodegradation was measured through the analysis of CO₂ and morphological characteristics. The samples with lignin analyzed after 5 weeks of biodegradation tests were fragmented, however, small residues of the bioplastic were identified. After the 2-month burial, the samples with lignin showed a significant biodegradation effect, with small fragments of the material still observed. After 4 months of testing, residues of bioplastic fragments were no longer detected. A bioplastic made from the addition of lignin (1.2% w/t) to the bio-PTT matrix (Bio-poly (trimethylene terephthalate)) increased its weight loss through biodegradation in soil (GUPTA et al., 2015). In 140-day burial, bio-PTT/lignin bioplastic showed more than 50% mass weight loss.

A higher CO₂ emission was reported from films with lignin in comparison to the bioplastic composed only of starch, due to the greater amount of carbon atoms in its formulation (CAMAGNER et al., 2014). However, such CO₂ may have originated from the metabolism of soil organic compounds, i.e., the bioplastic may have stimulated the microbial degradation of stable organic compounds in the soil through the priming effect. A strategy for the biodegradation of bioplastics composed of lignin, due to the recalcitrance of this phenolic complex, is the application of UV radiation prior to chemical, microbiological and/or enzymatic treatments. Lignin is susceptible to photodegradation due to the UV effect (THAKUR et al., 2014). After photodegradation, other treatment combinations can be applied for the degradation or biodegradation of lignocellulosic fibers, such as enzymatic or oxidative treatments. One of the advantages of using lignin in the development of thermoplastic formulations is its processing at high temperatures (AGRAWAL et al., 2014). However, studies using lignin in the bioplastic formulation, have not received much attention.

3.3.1.1 Biodegradation/enzymatic degradation of plant-based polymers bioplastics in relation to derivatization

The assessment of biodegradation, disintegration, and enzymatic degradation of bioplastics made with natural polymers (such as proteins, starch, cellulose, and hemicellulose) is not recurrent in the literature. Biodegradation has received lower attention when compared to the objective of most studies, which is to evaluate the physicochemical and mechanical properties of the materials. However, this limitation in the studies is even greater when compared to the biodegradation of bioplastics made with modified polymers.

The comparison between bioplastics developed from unmodified and modified hemicellulose presents few studies intending to analyze the enzymatic degradation (ARNLING BÅÅTH et al., 2018) and biodegradation. This low number of studies with hemicellulose could be related to the difficulties in obtaining a plastic polymer matrix from this heterogeneous vegetable polysaccharide. However, in addition to the analysis of the physicochemical properties of modified bioplastics, the effects of chemical, physical, and biological (and enzymatic) modifications of polymers on biodegradation must be considered. The enzymes involved in the enzymatic degradation of unmodified and modified polysaccharides may be different. Moreover, a more complex enzymatic pool will be required for modified polysaccharides.

As pending groups are attached to the polysaccharides chain, new enzymes will be required for further hydrolysis. According to a recent review article, physical modifications of polysaccharides hardly result in a change in the biodegradation process (POLMAN et al., 2021). However, chemical changes result in different degradation mechanisms. Considering a chemical similarity, the enzymatic degradation of cellulose acetate can be catalyzed by acetyl esterases, an enzyme common for xylan deacetylation. The modification or functionalization of polysaccharides may result in a reduction in biodegradation since modified bioplastics (acetylated cellulose, acetylated xylan, acetylated starch, starch propionate, starch butyrate, starch valerate, and starch hexanoate) showed a reduction in anaerobic biodegradation (RIVARD et al. 1995). For example, the degree substitution (DS) > 1.5, 1.5, 1.2 for starch, cellulose and modified xylan (acetylated), respectively, represented the minimum modification necessary to delay the biodegradation of bioplastics.

The chemical modifications of the polysaccharides that make up bioplastics, such as acetylation, increase the degree of hydrophobicity of the polymers and the plastic matrix. This has the advantage of to reduce the solubilization of the polymers in

polar solutions (GRÖNDAHL et al., 2003). However, resulted in a decrease the enzymatic degradation. It was observed a reduction in two mannases of *Cellvibrio japonicus* (CjMan5A and CjMan26A), with reduced catalytic activities on galactoglucomannan substrates (hemicellulose) due to the decrease of the solubility of the polymers (ARNLING BÅÅTH et al., 2018). Other studies in the literature showed the influence of chemical modification of hemicellulose in relation to solubility, thermal resistance, crystallinity (TSERKI et al., 2005) and biodegradation rate (TSERKI et al., 2006). Therefore, the diffusion of water by the composite and biodegradation is a parameter affected by chemical derivatization.

Modified xylans with an increase in the DS reduced enzymatic degradation by xylanolytic enzyme (GLASSER et al., 1995). However, a rapid biodegradation rate (80%) on the first day of the evaluation was achieved for (hydroxypropyl) xylan. Substitutions above 1.5 reduced enzymatic degradability by 10%. However, the modification of cellulose with hydroxypropyl led to a reduction in biodegradation (20% in 18 days). Regarding the DS and the enzymatic activity, the article justifies the limitation of the recognition of the xylanolytic enzyme to the substrate due to chemical modification. In addition to the sterile impediment, when it changes the polysaccharide polarity through modification, it may be another explanation for the degradability reduction (MITCHELL et al., 1990).

Modifications of polysaccharides may result in a less hydrophobic bioplastic, favoring the process of biological and abiotic degradation. Xylan carboxymethylation for bioplastic production showed an increase in water absorption at high relative humidity, demonstrating, therefore, the hydrophilic character of the carboxymethyl groups (ALEKHINA et al., 2014). Carboxymethylation is a procedure for the production of hemicellulose-based bioplastics with increases in hydrophilic characteristics (GENG et al., 2020). This procedure results in the development of environmentally favorable materials considering biodegradation.

A modification of hemicellulose by subtraction of chemical constituents may result in a different biodegradation process. An enzymatic modification of arabinoxylan resulted in an increase in the bioplastic crystallinity as the arabinose content was reduced (HEIKKINEN et al., 2013; HÖIJE et al., 2008). In both of these studies, the effects of enzymatic modification of hemicellulose in relation to biodegradation were not evaluated. However, the increase in crystallinity may be a retarding factor in the bioplastic biodegradation due to the degree of organization of the molecules limiting

enzymatic action, probably reducing the water absorption effect and reducing microbial growth.

The different modifications in natural bio-based polymers (for example, polysaccharides) may result in a difficulty in biodegradation or enzymatic degradation. The rate of degradation of these materials can reduce in a given period. However, the material can still be metabolized or degraded using enzymes. For example, acetylated xylan is the form found in natural lignocellulosic materials, therefore, although acetyl groups result in a delay in biodegradation, these polysaccharides are biodegradable by microbial enzymes, such as xylanases and esterases, whereas the acetylated xylan form is predominant in the environment.

3.3.2 Biodegradation of microbe-based polymers bioplastics

Under the nutritional abundance of carbon and nitrogen, some bacteria can synthesize energy reserve polymer (inclusions). Polymers like polyhydroxyalkanoate (PHA) (intracellular granules), can be produced via microbial fermentation of biomass (animal or vegetable). Regarding applications, these natural polymers are an important alternative for the manufacture of bioplastic materials since they are biodegradable and biocompatible, and used in the medical field (KJELDSEN et al., 2018). With the 41% increase in world production of PHAs between 2010-2017, this polyester has become a polymer of significant interest in the development of bioplastics. The properties of this microbial polyester can contribute to a reduction of environmental impacts due to the closed carbon cycle generated by biodegradation (MEEREBOER et al., 2020).

There is a growing interest in the development of materials formulated with PHAs, the study of the biodegradability of these materials. However, factors that influence the degradation of composites and bioplastics are necessary. Some of the marine microorganisms that are known to degrade PHAs (SUZUKI et al., 2021) are *Aestuariibacter halophilus* S23; *Alcanivorax* sp. 24; *Alcanivorax dieselolei* B-5; *Pseudoalteromonas haloplanktis*; *Alteromonas* sp. MH53; *Bacillus* sp.; *Bacillus* sp. strain NRRL B-14911; *Bacillus* sp. MH10; *Comamonas testosteroni* YM1004; *Enterobacter* sp.; *Aliiglaciecola lipolytica*; *Gracilibacillus* sp; *Marinobacter* sp. NK-1; *Nocardiopsis aegyptia*; *Pseudoalteromonas* sp. NRRL B-30083; *Pseudoalteromonas gelatinilytica* NH153; *Pseudoalteromonas shioyasakiensis* S35; *Pseudomonas stutzeri* YM1006; *Psychrobacillus* sp. PL87; *Rheinheimera* sp. PL100; *Shewanella* sp. JKCM-

AJ-6,1 α ; *Streptomyces* sp. SNG9. Terrestrial microbial representatives degraders PHAs (VOLOVAA et al., 2015) are *Alcaligenes faecalis*; *Pseudomonas lemoignei*; *Acinetobacter* sp.; *Acinetobacter schindleri*; *Bacillus* sp.; *Pseudomonas* sp.; *Stenotrophomonas maltophilia*; *Variovorax paradoxus*; *Stenotrophomonas rhizophilia*; *Penicillium* sp.; *Purpureocillium lilacinum*; *Verticillium lateritium*; *Burkholderia* sp.; *Nocardiopsis* sp.; *Streptomyces* sp.; *Bacillus cereus*; *Burkholderia* sp.; *Cupriavidus* sp.; *Gongronella butleri*; *Penicillium oxalicum*.

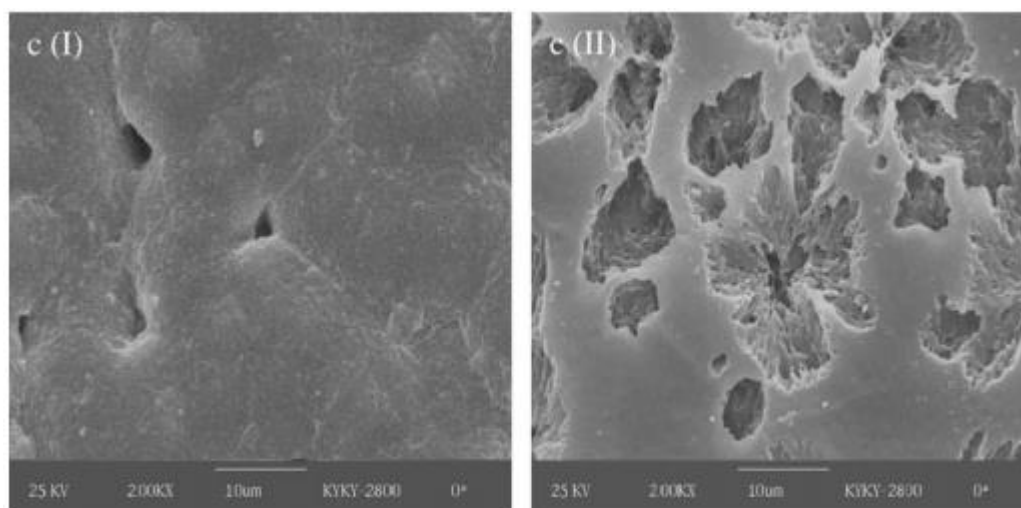
As in polysaccharide-based bioplastics, crystallinity in polyester bioplastics from microbial synthesis plays an important role in the biodegradation process. In bioplastics with higher proportions of amorphous regions, depolymerization occurs more quickly through abiotic or biotic action. For example, higher biodegradation was obtained with hydroxybutyrate (PHB), hydroxybutyrate-co-hydroxyvalerate (PHBV-40), PHBV-20, and P (3HB, 4HB) (10 % mol of 4HB) and PHBV-3 (WENG et al., 2011). According to the quantification of CO₂ in a composting vessel, PHBV-40 and P (3HB, 4HB) (10% mol 4HB) showed the highest degrees of biodegradation, due to a reduction in crystallinity with the addition of higher percentages of HV (valerate hydroxide - indicated by the numbering in front of the acronym) and 4HB. Biodegradation was 90.5%, 89.3%, 80.2%, 90.3% and 79.7% in 110 days of analysis for bioplastics formulated by PHBV-40, PHBV-20, PHBV-3, P (3HB, 4HB) and PHB, respectively.

The advantage of using PHBV in comparison to PHB is the ease of processing and good toughness. Certain PHBV disadvantages such as low thermal stability and a high degree of crystallinity must be overcome (WENG et al., 2011). Improvements, mediated by chemical changes, must be performed together with the preservation of the material's biodegradation property, which, depending on the HV percentage, maybe rigidity or flexibility, similarly to commercial synthetic plastics (polyethylene, polypropylene, and polyvinylchloride), and assurance of biodegradation of the formulated bioplastic (WENG et al., 2011).

A commercial Ecoflex bioplastic (commercial product of BASF) was compared to PHB and poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) in activated sludge for 18 days. Bioplastics composed of PHBHHx showed a higher degree of biodegradability than Ecoflex and PHB, with weight losses of 40, 20, and 5%, respectively (WANG et al., 2004). The low crystallinity and morphology of the surface of the bioplastic proved a determining factor in the biodegradation process, observed mainly in bioplastics with 12% HHx (hydroxyhexanoate), which displayed a rough and

porous surface before and after undergoing activated exposure to sludge and lipases (Figure 4).

Figure 4: Surface morphology of bioplastic made with PHB (12% HHx) before and after degradation



Source: Wang et al. (2004)

Besides surface morphology and crystallinity of the bioplastics, other factors, such as mixing components, depth of burial (due to environmental and/or microbial differences), and time of exposure to the soil also determine the biodegradability degree. In the study performed by WENG et al. (2013), evaluating through appearance and fragmentation, the following results were achieved for the biodegradation of polymeric blends (poly (3-hydroxybutyrate-co-4-hydroxybutyrate and poly (lactic acid) - (P (3HB, 4HB)/PLA)): In the first month of testing, blends composed of 100% P (3HB, 4HB) and those with 25% PLA showed loss of integrity (appearance), whereas in the second month, both bioplastics had been almost completely biodegraded. This behavior was similar for the different depths of burial used (20 and 40 cm); however, at 20 cm and 2 months of testing, a greater difficulty was observed in the collection of fragments of blends with 75% of P (3HB, 4HB). For both depths of burial, the higher the concentration of PLA in the blends, the longer the biodegradation time. However, the biodegradation behavior was the opposite for higher concentrations of P (3HB, 4HB). Polymer blends with 100% and 75% P (3HB, 4HB) were degraded more easily at 20 cm

depth, although the presence of PLA in the bioplastics represented a delay in biodegradability at both depths tested. At 40 cm, PLA suffered greater disintegration, due to the anaerobic conditions, providing better conditions for degradation of the PLA, as reported by the authors (WENG et al., 2013).

In addition to temperature, bioplastic composition, crystallinity, degree of hydrophilicity and environmental conditions in relation to oxygen concentration, another factor that must be taken into account is the abundance of microbial biomass and the efficiency of fungi and bacteria biodegradation in different environments. The biodegradation of microbial polyesters by fungi was reported as dominant in soil (VOLOVAA et al., 2015). However, the biodegradation of polymers in aquatic (marine) medium was faster with the use of bacteria (MOROHOSHI et al., 2018; SHRUTI and KUTRALAM-MUNIASAMY, 2019).

PHA bioplastics as well as other bioplastics have limitations in their applications and achievements due to the high cost, low mechanical resistance, and impairment of biodegradation in functionalization processes and mixtures with other polymers (MEEREBOER et al., 2020). In addition to the low ductility property, one of the main disadvantages of using PHAs in the production of bioplastics is the formation of brittle bioplastics, properties that can be improved by mixing biodegradable polymers from oil. However, the sustainability of bioplastic manufacturing is affected since the use of oil in the extraction and refinement stage generates the carbon dioxide production (GIRONI and PIEMONTE, 2011). Another impact that should be considered in the production of PHA bioplastics with synthetic polymers such as the use of PCL is the reduction in the rate of biodegradation (NARANCIC et al., 2018). However, the development of polyester bioplastics with bio-based fibers origin (blends development), such as lignocellulosic fibers, can assist in overcoming the low ductility property of bioplastics (MEEREBOER et al., 2020). This blend reduces costs, ensuring a biodegradable and renewable product.

The application of polyhydroxyalkanoate as a bioplastic has major limitations (e.g., its production costs for replacing conventional plastics (KOURMENTZA et al., 2017)). A potential alternative for the optimization of PHA production technologies is the use of organic residues, such as lignocellulosics (JIANG et al., 2016). As an example, hemicellulose (BERTRAND et al., 1990; LOPES et al., 2009; LEE, 1998), cellulose (NDUKO et al., 2012) and a mixture of hemicellulose and cellulose hydrolyzate (CESARIO et al., 2014) have been used for the production of microbial

polyesters, such as PHA and P3HB (PHB). However, the use of lignocellulosic fibers poses limitations mainly related to the production yield and generation of inhibitory substances for PHA-producing microorganisms (JIANG et al., 2016). Table 1 shows some properties and biodegradation times of different biodegradable bioplastics produced from biopolymers.

Poly(lactic acid) (PLA) is another polyester that may be partially derived from the microbial fermentation of biopolymers. The lactic acid produced by the bacteria is polymerized by a chemical route, thus forming PLA, which offers several advantages, such as rigidity and miscibility with other biodegradable plastics. However, in several application areas (e.g., manufacture of 3D printers), its fibers have been used by Brazilian companies due to the PLA lower heat loss in comparison to oil-derived plastics (JONES, 2020). Nevertheless, bioplastics from bacterial polyesters should be considered, since PHAs like PBH present several advantages in comparison to PLA (CHEN, 2009). Table 1 shows some properties and biodegradation times of different biodegradable bioplastics produced from biopolymers.

Table 1: Properties and biodegradation time of different biodegradable bioplastics produced from biopolymers

Bioplastic type	Polymer type	CONB	BPR	PAB	TS (MPa)	E (%)	Reference
PHB nanofiber	Polyester	Soil, 30 °C and 80% humidity	100% in 21days	Weight loss	...	...	ALTAEE et al. (2016)
PHB/Starch	Polyester	Sludge, 35 °C, anaerobic	93.8% in 190 days	Biogas quantification	...	...	GUTIERREZ-WING et al. (2010)
PHB	Polyester	Compost, 55 °C and 70% humidity	Approx . 80% in 28 days	CO ₂ quantification	1015	...	TABASI and AJJI (2015)
PHA	Polyester	Seawater	100% in 1.5 to 3.5	Literature review	...	...	DILKES-HOFFMAN et al. (2019)

years

PHA	Polyester	Soil, 12–15 cm depth and 35% humidity	30% in 60 days	Weight loss	16.2	600.3	(WU, 2014)
PHA/Rice husk	Polyester/Fibers	Soil, of 12–15 cm depth and 35% humidity	>90% in 60 days	Weight loss	7.5	< 400	WU (2014)
PHA	Polyester	Soil, 20 °C and 60% humidity	48.5% in 280 days	CO ₂ quantification	...	...	GÓMEZ and MICHEL (2013)
PHBV/Starch	Polyester/ Polysaccharide	Liquid medium	100% in 31 days	CO ₂ quantification	21.01	10.85	COELHO et al. (2008)
PHBV/NPK	Polyester/ Fertilizer	Soil, 25-30 °C and 65% humidity	68.66% in 112 days	Weight loss	...	...	HARMAEN et al. (2016)
PHBV/Starch	Polyester/ Polysaccharide	Soil, 25 °C and 20% humidity	>60% in 150 days	Weight loss	~7	~3.2	MAGALHÃES and ANDRADE (2013)
Starch	Polysaccharide	Soil, 3.5 cm depth and 65% humidity	30% in 5 days	Weight loss	1.88	0.45	OLUWASINA et al. (2019)
Starch	Polysaccharide	Marine water with sediment	Approx . 69% in 236 days	BOD	4.7*	211	TOSIN et al. (2012)
Starch	Polysaccharide	Microorganisms in a plate, 25 °C and 75% humidity	100% in 30 days	Weight loss	8.6	52	BABAEI et al. (2015)

Starch/Cellulose	Polysaccharide/ Modified	Microorganisms in plate, 25 °C and 75% humidity	100% in 60 days	Weight loss	14.7	50	BABAE et al. (2015)
Cellulose	Polysaccharide	Soil	100% in 105 days	Weight loss	45	6.1	BILO et al. (2018)
Cellulose/Starch	Polysaccharide	Soil/ humus, 25 °C and 75% humidity	24.2 to 39.3% in 35 days	Weight loss	5.6 to 35.0	13.1 to 21.7	FITCH-VARGAS et al. (2019)
Hemicellulose/ Gelatin	Polysaccharide/ Partially hydrolyzed protein	Soil/manure	100% in less than 15 days	Weight loss	...	...	LUCENA et al. (2017)
PLA/Starch	Poly(lactic acid) /Polysaccharide	Compost and 58 °C	79.7% in 90 days	Weight loss	...	...	SARASA et al. (2009)

CONB= Biodegradation conditions; BPR= Biodegradation period and rate; PAB= Biodegradation analysis procedure; TS= Tensile strength; E= elongation; ...= not reported; *=Newton (N)

Bioplastics are renewable and/or biodegradable and display good mechanical properties such as tensile strength similar to certain synthetic plastics in common use (Table 1). Polypropylene and polystyrene, fossil-based synthetic plastics, show TS between 25-40 MPa and 30-55MPa, respectively (FITCH-VARGAS et al., 2019), whereas it ranges between 55–124 and 9–17 for CellophaneTM and low-density polyethylene (LDPE), respectively (ALLEN, 1986; BRISTON, 1988). This similarity of mechanical properties of bioplastics and plastics was also reported by HANSEN et al. (2012). Therefore, even if at present and in the future, the total replacement of non-biodegradable plastic from petroleum, is something unlikely, for some applications, such as bioplastics for use in agriculture (mulch) and packaging (short lifetime), this technology can represent one of the alternatives (along with other actions and technologies) to mitigate the environmental impacts related to plastics.

3.3.2.1 Effect of the bio-based polymer addition on the biodegradation rate of PHAs bioplastics

The addition of bio-based polymers in polyester microbial biocomposites is vast in the literature (SÁNCHEZ-SAFONT et al., 2018; ALBUQUERQUE et al., 2020; MEEREBOER et al., 2020). The bio-based polymers application, mainly lignocellulosic fibers, is due to the improvement in the biodegradation rate of the formulated bioplastic (MEEREBOER et al., 2020). This improvement in the biodegradation of PHAs biocomposite is related to the increase in hydrophilicity and water absorption by bioplastics. A mixture of 30% Sisal fibers (wt) and PHBV resulted in increased water absorption of 14% compared to pure PHBV (0.8%) (DANGTUNGEE et al., 2014). The use of Kenaf fibers (main cellulose) in the blend with poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HHx)], resulted in a greater loss of mass in biodegradation in soil due to greater water absorption and microbial binding sites in the microbial polyester from binding with Kenaf fiber (JOYYI et al., 2017). This study suggested that the accelerated deterioration of the blend (reduction of mechanical properties), after 6 burial weeks (soil) was due to the weakening of the adhesion between the fiber/[P(3HB-co-3HHx)], with the access of water to the internal hydrophobic regions of the polymer.

The use of hemicellulose with PHAs is also an alternative to increase the blends biodegradation rate in relation to pure microbial polyesters (MEEREBOER et al., 2020). Bioplastics from PHBV/Peach Palm Particles (lignocellulosic fiber with considerable hemicellulose content) were biodegraded faster than pure PHBV in soil (BATISTA et al., 2010). The authors reported cracks, corrosion, and discoloration after 2 months of biodegradation. The poor adhesion between the fiber/PHBV interface, which resulted in greater water absorption and accessibility of soil microorganisms, was suggested as contributed to the deterioration.

Starch, another polysaccharide from vegetable biomass, can also be used in the production of bioplastics with reduced biodegradation time. The mixture of starch and PHBV (50/50% wt) was fully biodegraded in the soil after 33 days, i.e., there was a 50% reduction in biodegradation time compared to pure PHBV (ROSA et al., 2013). The addition of starch reduced the crystallinity of the blend, facilitating the absorption of water by the matrix and increased the enzymatic activity on the surface and in the inner region of the blend. There was an increase in the biodegradation of PHA/starch

blends as the starch content increased in the formulation, with biodegradation of PHA/30% starch (wt) corresponding to 44% in 6 months of burial in soil (KRATSCH et al., 2015).

Chemical modifications of polysaccharides, such as cellulose acetylation (cellulose acetate) can result in partial or total inhibition of blends biodegradation, due to reduced solubilization and hydrophobicity of the fibers. The acetyl and butyryl group in cellulose reduced the rate of biodegradation of the PHB blend/modified cellulose due to the impediment of the substituents and reduced the blends/water interactions (WANG et al., 2003). However, in the same study, the mechanical properties were improved by increasing the concentration of cellulose acetate butyrate. Related to cellulose, the degree of substitution above 2.5 results in the inhibition of biodegradation (MEEREBOER et al., 2020). However, some chemical modifications can positively influence the biodegradation of microbial and bio-based polymer blends. This improvement in biodegradation is due to the increase in the contact area surface of the fibers, resulting from the surface treatments of the fibers, such as, an increase in the fiber rugosities with the application of NaOH, which removes the hemicellulose and lignin fibers (MEEREBOER et al., 2020).

Lignin is the most recalcitrant constituent of lignocellulosic fibers due to the complexity of the composition of this phenolic macromolecule (DATTA et al., 2017; POLMAN et al., 2021). The lignin enzymatic catalytic degradation needs different enzymes (FIGUEIREDO et al., 2018; POLMAN et al., 2021), or even the synergy of an enzyme complex. The inclusion of lignin in the blends of PHAs and PLA results in steric impediment of the enzyme and reduction of the degree of hydrophilicity, which is shown in the literature as a factor in reducing the biodegradation of polyester blends (KRATSCH et al., 2015; MEEREBOER et al., 2020). For example, the biodegradation in soil of the PHA/lignin blend was 4% after 24 weeks, which was lower than the rate of biodegradation of the PHA/10% starch, PHA/cellulose (11.1 and 100% respectively) (KRATSCH et al., 2015). An alternative for obtaining bioplastics from microbial polyesters, with guaranteed polymer biodegradability, is the use of enzymes and microorganisms capable of catalyzing the breakdown of lignin. The main enzymes involved in lignin oxidoreduction are laccases (Lac), lignin peroxidase (LiP), and manganese peroxidase (MnP) (POLMAN et al., 2021), and the recently discovered enzymes dye-decolorizing peroxidases and unspecific peroxygenase (DATTA et al., 2017; SANTACRUZ-JUAREZ et al., 2021).

The application of specific microorganisms that degrade lignin and/or PHAs can be an alternative to improve the biodegradation of the blends of these polymers. In nature, these enzymes act synergistically, and some microorganisms can produce the three enzymes, while others only produce a few of the necessary enzymes (POLMAN et al., 2021). LiP has a key role in the degradation of lignin, due to the distinct characteristics of the active site of the enzyme. However, the catalytic action of LiP is mediated by H_2O_2 , which is generated by Lac (Santacruz-Juarez et al., 2021). The effectiveness of the microorganisms is essential for the biodegradation of PHA/lignin blends, as some microorganisms such as *Phanerochaete chrysosporium* are considered excellent for the degradation of lignin (DATTA et al., 2017; CHIO et al., 219). However, Brown-rot fungi due to the degradation mechanisms of lignin not being oxidative, presents a reduced degradation process of lignin (POLMAN et al., 2021). Another example is the case of the bacteria *Streptomyces viridosporus*, which can result in a reduced degradation process of lignin since this bacterium acts in the non-phenolic regions of lignin (DATTA et al., 2017; POLMAN et al., 2021).

Conclusions

Advances in the development of materials and technologies with fewer environmental impacts are highly expected, mainly due to the progress in the area of biopolymers over the past two decades. However, biopolymers application and use in the various sectors of society is limited, i.e., the annual production of bioplastics compared to plastics is still low. In this way, the use of plant biomass and microbial polyesters can help the development of bioplastic feasible, due to the availability of resources, biocompatibility, biodegradability and generally does not result in ecotoxicity. However, the physicochemical and biodegradation properties must be considered for the study of the optimization of bioplastic from natural polymers. Several actions must be taken so that bioplastic can become a reality on a large scale. The state of São Paulo (Brazil) has established a law that prohibits the supply of disposable plastic products to commercial establishments, which may increase the production scale of some bioplastics, thus reducing costs. The approval of a law by the Chinese government that prohibits the import of international plastic wastes for recycling can also encourage the production of bioplastics. An increase in the production and distribution of bioplastics is not sufficient for the development of a more conscious and

sustainable society, i.e., care must be taken for the identification of a bioplastic and/or biodegradable material towards no final consumers' mistakes and no unsuitable actions or disposal habits.

References

- ABOU ZEID, D. M. (2001). Anaerobic biodegradation of natural and synthetic polyesters. *Technischen Universität Carolo-Wilhelmina zu Braunschweig*.
- ABURTO, J., ALRIC, I., THIEBAUD, S., BORREDON, E., BIKIARIS, D., PRINOS, J., & PANAYIOTOU, C. (1999). Synthesis, characterization, and biodegradability of fatty-acid esters of amylose and starch. *J. Appl. Polym. Sci*, 74, 1440–1451.
- AGRAWAL, A., KAUSHIK, N., & BISWAS, S. (2014). Derivatives and Applications of Lignin—An Insight. *SciTech J*, 1, 30–36.
- ALBUQUERQUE, R. M, MEIRA, H. M., SILVA, I. D. L., GALDINO, C. J. S., ALMEIDA, F .C. G., AMORIM, J. D. P., VINHAS, G. M., COSTA, A. F. S., & SARUBBO, L. A. (2020). Production of a bacterial cellulose/poly(3-hydroxybutyrate) blend activated with clove essential oil for food packaging. *Polymers and Polymer Composites*, 096739112091209. doi:10.1177/0967391120912098
- ALEKHINA, M., MIKKONEN, K. S., ALÉN, R., TENKANEN, M., & SIXTA, H. (2014). Carboxymethylation of alkali extracted xylan for preparation of bio-based packaging films. *Carbohydr. Polym*, 100, 89–96. <https://doi.org/10.1016/j.carbpol.2013.03.048>
- ALLEN, W. R. (1986). Structural applications for flexible packaging: Innovations in pouch forms and uses. *Polym. Plast. Technol. Eng*, 25, 295–320. <https://doi.org/10.1080/03602558608070087>
- ALTAEI, N., EL-HITI, G. A., FAHDIL, A., SUDESH, K., & YOUSIF, E. (2016). Biodegradation of different formulations of polyhydroxybutyrate films in soil. *Springerplus*, 5, 762. <https://doi.org/10.1186/s40064-016-2480-2>
- ANDERSON, A. J., & DAWES, E. A. (1990). Occurrence, metabolism, metabolic role, and industrial uses of bacterial polyhydroxyalkanoates. *Microbiol. Rev*, 54, 450–472.
- ARNLING BÅÅTH, J., MARTÍNEZ-ABAD, A., BERGLUND, J., LARSBRINK, J.,

- VILAPLANA, F., & OLSSON, L. (2018). Mannanase hydrolysis of spruce galactoglucomannan focusing on the influence of acetylation on enzymatic mannan degradation. *Biotechnology for Biofuels*, 11, 1. doi:10.1186/s13068-018-1115-y
- ASTM D5338-15, 2015. Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures. ASTM Int. West Conshohocken, PA.
- ASTM D5511-02, 2002. Standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic-digestion conditions. ASTM Int. West Conshohocken, PA.
- AVELLA, M., ROTA, G.L., MARTUSCELLI, E., RAIMO, M., SADOCCO, P., ELEGIR, G., & RIVA, R. (2000). Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and wheat straw fibre composites: thermal, mechanical properties and biodegradation behaviour. *Journal of Materials Science*, 35, 829–836. <https://doi.org/10.1023/A:1004773603516>
- BABAEI, M., JONOOBI, M., HAMZEI, Y., & ASHORI, A. (2015). Biodegradability and mechanical properties of reinforced starch nanocomposites using cellulose nanofibers. *Carbohydr. Polym*, 132, 1–8. <https://doi.org/10.1016/j.carbpol.2015.06.043>
- BALAGUER, M. P., VILLANOVA, J., CESAR, G., GAVARA, R., & HERNANDEZ-MUNOZ, P. (2015). Compostable properties of antimicrobial bioplastics based on cinnamaldehyde cross-linked gliadins. *Chemical Engineering Journal*, 262, 447.
- BATISTA, K. C., SILVA, D. A. K., COELHO, L. A. F., PEZZIN, S. H., & PEZZIN, A. P. T. (2010). Soil Biodegradation of PHBV/Peach Palm Particles Biocomposites. *Journal of Polymers and the Environment*, 18, 3, 346–354. doi:10.1007/s10924-010-0238-4
- BÁTORI, V., ÅKESSON, D., ZAMANI, A., TAHERZADEH, M. J., & SÁRVÁRI HORVÁTH, I. (2018). Anaerobic degradation of bioplastics: A review. *Waste Management*, 80, 406–413.
- BELAL, E. S. (2003). Investigations on biodegradation of polyesters by isolated mesophilic microbes. Technische Universität Carolo-Wilhelmina zu Braunschweig.
- BERTRAND, J. I., RAMSAY, B. A., RAMSAY, J. A., & CHAVARIE, C. (1990). Biosynthesis of poly- β hydroxyalkanoates from pentoses by *Pseudomonas pseudoflava*. *Appl. Environ. Microbiol*, 56, 3133–3138.

- BHATTACHARYA, P., LIN, S., TURNER, J. P., & KE, P. C. (2010). Physical adsorption of charged plastic nanoparticles affects algal photosynthesis. *J. Phys. Chem. C*, 114, 16556–16561.
- BIELY, P., MACKENZIE, C. R., PULS, J., & SCHNEIDER, H. (1986). Cooperativity of Esterases and Xylanases in the Enzymatic Degradation of Acetyl Xylan. *Nat Biotechnol*, 4, 731–733.
- BILO, F., PANDINI, S., SARTORE, L., DEPERO, L. E., GARGIULO, G., BONASSI, A., FEDERICI, S., & BONTEMPI, E. (2018). A sustainable bioplastic obtained from rice straw. *J. Clean. Prod*, 200, 357–368. <https://doi.org/doi:10.1016/j.jclepro.2018.07.252>
- BONECHI, C., CONSUMI, M., DONATI, A., LEONE, G., MAGNANI, A., TAMASI, G., & ROSSI, C. (2017). Biomass: An overview. *Bioenergy Systems for the Future*, <https://doi.org/10.1016/B978-0-08-101031-0.00001-6>
- BONHOMME, S., CUER, A., DELORT, A. M., LEMAIRE, J., SANCELME, M., & SCOTT, G. O. (2003). Environmental biodegradation of polyethylene. *Polym. Degrad. Stab*, 81, 441–452. [https://doi.org/10.1016/S0141-3910\(03\)00129-0](https://doi.org/10.1016/S0141-3910(03)00129-0)
- BRIASSOULIS, D. (2005). The effects of tensile stress and the agrochemical Vapam on the ageing of low density polyethylene (LDPE) agricultural films. Part I. Mechanical behaviour. *Polym. Degrad. Stab*, 88, 489–503. <https://doi.org/10.1016/j.polymdegradstab.2004.11.021>
- BRISTON, J. H. (1988). Plastic films, 3rd ed. Wiley, New York.
- CAMPAGNER, M. R., DA SILVA MORIS, V. A., PITOMBO, L. M., DO CARMO, J. B., & DE PAIVA, J. M. F. (2014). Polymeric films based on starch and lignosulfonates: Preparation, properties and evaluation of biodegradation. *Polimeros*, 24, 740–751. <https://doi.org/10.1590/0104-1428.1700>
- CANESI, L., CIACCI, C., BERGAMI, E., MONOPOLI, M. P., DAWSON, K. A., PAPA, S., CANONICO, B., & CORSI, I. (2015). Evidence for immunomodulation and apoptotic processes induced by cationic polystyrene nanoparticles in the hemocytes of the marine bivalve *Mytilus*. *Mar. Environ. Res*, 111, 34–40.
- CAPITELLI, F., PRINCIPI, P., & SORLINI, C. (2006). Biodeterioration of modern materials in contemporary collections: can biotechnology help? *Trends Biotechnol*, 24, 8, 350–354.
- CESÁRIO, M. T., RAPOSO, R. S., DE ALMEIDA, M. C. M. D., VAN KEULEN, F., FERREIRA, B. S., & DA FONSECA, M. M. R. (2014). Enhanced bioproduction

- of poly-3-hydroxybutyrate from wheat straw lignocellulosic hydrolysates. *N. Biotechnol*, 31, 104–113. <https://doi.org/10.1016/j.nbt.2013.10.004>
- CARVALHEIRO, F., SILVA-FERNANDES, T., DUARTE, L. C., & GÍRIO, F. M. (2008). Wheat Straw Autohydrolysis: Process Optimization and Products Characterization. *Applied Biochemistry and Biotechnology*, 153, 1-3, 84–93. doi:10.1007/s12010-008-8448-0
- CHANDRA, R., & RUSTGI, R. (1998). Biodegradable polymers. *Prog. Polym. Sci*, 23, 1273–1335.
- CHEN, G. (2009). A microbial polyhydroxyalkanoates (PHA) based bio- and materials industry. *Chem. Soc. Rev*, 38, 2434–46. <https://doi.org/doi:10.1039/b812677c>
- CHIO, C., SAIN, M., & QIN, W. (2019). Lignin utilization: a review of lignin depolymerization from various aspects. *Renew. Sust. Energ. Rev*, 107, 232–249. <https://doi.org/10.1016/j.rser.2019.03.008>
- COELHO, N. S., ALMEIDA, Y. M. B., & VINHAS, G. M. (2008). A biodegradabilidade da blenda de poli(β -Hidroxibutirato-co-Valerato)/amido anfótero na presença de microrganismos. *Polímeros*, 18, 270–276. <https://doi.org/10.1590/s0104-14282008000300014>
- COSTA, C. Z., ALBUQUERQUE, M. C. C., BRUM, M., & CASTRO, A. (2015). Microbial and enzymatic degradation of polymers: a review. *Quim. Nova*, 38, 259–267. <https://doi.org/http://dx.doi.org/10.5935/0100-4042.20140293>
- CRAWFORD, C. B., & QUINN, B. (2017). Physiochemical properties and degradation. *Microplastic Pollutants*, <https://doi.org/10.1016/b978-0-12-809406-8.00004-9>
- CRISPIM, C. A., & GAYLARDE, C. C. (2005). Cyanobacteria and biodeterioration of cultural heritage: A review. *Microb. Ecol*, 49, 1–9. <https://doi.org/10.1007/s00248-003-1052-5>
- CRUTZEN, P. J. (2006). The anthropocene. *Earth Syst. Sci. Anthr*, 13–18. https://doi.org/10.1007/3-540-26590-2_3
- DANGTUNGEE, R., TENG SUTHIWAT, J., BOONYASOPON, P., & SIENGCHIN, S. (2014). Sisal natural fiber/clay-reinforced poly(hydroxybutyrate-co-hydroxyvalerate) hybrid composites. *Journal of Thermoplastic Composite Materials*, 28, 6, 879-895. doi:10.1177/0892705714563128
- DATTA, R., KELKAR, A., BARANIYA, D., MOLAEI, A., MOULICK, A., MEENA, R. S., & FORMANEK, P. (2017). Enzymatic degradation of lignin in soil: a review. *Sustain*, 9, 1163. <https://doi.org/10.3390/su9071163>

- DE CARVALHO, A. P., & BARBIERI, J. C. (2012). Innovation and sustainability in the supply chain of a cosmetics company: A case study. *J. Technol. Manag. Innov*, 7, 144–156. <https://doi.org/10.4067/s0718-27242012000200012>
- DE PAOLI, M. A. (2008). Degradação e Estabilização de Polímeros. *Artliber*, 1, 286.
- DE SÁ, L. C., LUÍS, L. G., & GUILHERMINO, L. (2015). Effects of microplastics on juveniles of the common goby (*Pomatoschistus microps*): confusion with prey, reduction of the predatory performance and efficiency, and possible influence of developmental conditions. *Environ. Pollut*, 196, 359–362.
- DILKES-HOFFMAN, L. S., LANT, P. A., LAYCOCK, B., & PRATT, S. (2019). The rate of biodegradation of PHA bioplastics in the marine environment: A meta-study. *Mar. Pollut. Bull*, 142, 15–24. <https://doi.org/10.1016/j.marpolbul.2019.03.020>
- DOI, Y., & FUKUDA, K. (1994). Biodegradable plastics and polymers. Elsevier Science.
- FAIRBROTHER, A., HSUEH, H.-C., KIM, J. H., JACOBS, D., PERRY, L., GOODWIN, D., WHITE, C., WATSON, S., & SUNG, L.-P. (2019). Temperature and light intensity effects on photodegradation of high-density polyethylene. *Polymer Degradation and Stability*, doi:10.1016/j.polymdegradstab.2019.05.002
- FARHAT, W., VENDITTI, R., AYOUB, A., PROCHAZKA, F., FERNÁNDEZ-DE-ALBA, C., MIGNARD, N., TAHA, M., & BECQUART, F. (2018). Towards thermoplastic hemicellulose: Chemistry and characteristics of poly-(ϵ -caprolactone) grafting onto hemicellulose backbones. *Mater. Des*, 153, 298–307. <https://doi.org/10.1016/j.matdes.2018.05.013>
- FIGUEIREDO, P., LINTINEN, K., HIRVONEN, J. T., KOSTIAINEN, M. A., & SANTOS, H. A. (2018). Properties and chemical modifications of lignin: Towards lignin-based nanomaterials for biomedical applications. *Prog. Mater. Sci*, 93, 233–269. <https://doi.org/10.1016/j.pmatsci.2017.12.001>
- FREITAS, C, CARMONA, E, & BRIENZO, M. (2019). Xylooligosaccharides production process from lignocellulosic biomass and bioactive effects. *Bioactive Carbohydrates and Dietary Fibre*, 18:100-184. <https://doi.org/10.1016/j.bcdf.2019.100184>
- FITCH-VARGAS, P. R., CAMACHO-HERNÁNDEZ, I. L., MARTÍNEZ-BUSTOS, F., ISLAS-RUBIO, A. R., CARRILLO-CAÑEDO, K. I., CALDERÓN-CASTRO, A., JACOBO-VALENZUELA, N., CARRILLO-LÓPEZ, A., DELGADO-NIEBLAS,

- C. I., & AGUILAR-PALAZUELOS, E. (2019). Mechanical, physical and microstructural properties of acetylated starch-based biocomposites reinforced with acetylated sugarcane fiber. *Carbohydr. Polym*, 219, 378–386. <https://doi.org/10.1016/j.carbpol.2019.05.043>
- FLEMMING, H. C. (1998). Relevance of biofilms for the biodeterioration of surfaces of polymeric materials. *Polym. Degrad. Stab*, 59, 309–315. [https://doi.org/10.1016/s0141-3910\(97\)00189-4](https://doi.org/10.1016/s0141-3910(97)00189-4)
- GENG, W., VENDITTI, R. A., PAWLAK, J. J., PAL, L., & FORD, E. (2020). Carboxymethylation of hemicellulose isolated from poplar (*Populus grandidentata*) and its potential in water-soluble oxygen barrier films. *Cellulose*, 27, 3359–3377. <https://doi.org/10.1007/s10570-020-02993-2>
- GEYER, R., JAMBECK, J. R., & LAW, K. L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv*, 3, 19–24. <https://doi.org/10.1126/sciadv.1700782>
- GIRONI, F., & PIEMONTE, V. (2011). Bioplastics and petroleum-based plastics. *Strengths and Weaknesses Energy Sources Part A*, 33, 1949–1959.
- GLASSER, W. G., RAVINDRAN, G., JAIN, R. K., SAMARANAYAKE, G., & TODD, J. (1995). Comparative Enzyme Biodegradability of Xylan, Cellulose, and Starch Derivatives†. *Biotechnol. Prog*, 11, 552–557. <https://doi.org/10.1021/bp00035a009>
- GOLDSTEIN, M., & GOODWIN, D. (2013). Gooseneck barnacles (*Lepas* spp.) ingest microplastic debris in the North Pacific Subtropical Gyre. *PeerJ*, 1, 184. <https://doi.org/https://doi.org/10.7717/peerj.184>
- GÓMEZ, E. F., & MICHEL, F. C. (2013). Biodegradability of conventional and bio-based plastics and natural fiber composites during composting, anaerobic digestion and long-term soil incubation. *Polym. Degrad. Stab*, 98, 2583–2591. <https://doi.org/10.1016/j.polymdegradstab.2013.09.018>
- GREGORY, M. R. (2009). Environmental implications of plastic debris in marine settings- entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philos. Trans. R. Soc. B Biol. Sci*, 364, 2013–2025. <https://doi.org/10.1098/rstb.2008.0265>
- GU, J. D. (2003). Microbiological deterioration and degradation of synthetic polymeric materials: Recent research advances. *Int. Biodeterior. Biodegrad*, 52, 69–91. [https://doi.org/10.1016/S0964-8305\(02\)00177-4](https://doi.org/10.1016/S0964-8305(02)00177-4)
- GUNATILLAKE, P. A., & ADHIKARI, R. (2003). Biodegradable synthetic polymers

- for tissue engineering. *Eur. Cells Mater*, 5, 1–16.
<https://doi.org/10.22203/eCM.v005a01>
- GUPTA, A. K., MOHANTY, S., & NAYAK, S. K. (2015). Influence of addition of vapor grown carbon fibers on mechanical, thermal and biodegradation properties of lignin nanoparticle filled bio-poly(trimethylene terephthalate) hybrid nanocomposites. *RSC Adv*, 5, 56028–56036. <https://doi.org/10.1039/c5ra07828h>
- GUTIERREZ-WING, M. T., STEVENS, B. E., THEEGALA, C. S., NEGULESCU, I. I., & RUSCH, K. A. (2010). Anaerobic biodegradation of polyhydroxybutyrate in municipal sewage sludge. *J. Environ. Eng*, 136, 709–718.
[https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0000208](https://doi.org/10.1061/(ASCE)EE.1943-7870.0000208)
- HALL, J., MATOS, S., SILVESTRE, B., & MARTIN, M. (2011). Managing technological and social uncertainties of innovation: The evolution of Brazilian energy and agriculture. *Technol. Forecast. Soc. Change*, 78, 1147–1157.
<https://doi.org/10.1016/j.techfore.2011.02.005>
- Hansen, N. M. L., Blomfeldt, T. O. J., Hedenqvist, M. S., & PlacKETT, D. V. (2012). Properties of plasticized composite films prepared from nanofibrillated cellulose and birch wood xylan. *Cellulose*, 19, 2015–2031. <https://doi.org/10.1007/s10570-012-9764-7>
- HARDING, K. G., GOUNDEN, T., & PRETORIUS, S. (2017). “Biodegradable” Plastics: A Myth of Marketing? *Procedia Manuf*, 7, 106–110.
<https://doi.org/10.1016/j.promfg.2016.12.027>
- HARMAEN, A. S., KHALINA, A., ALI, H. M., & AZOWA, I. N. (2016). Thermal, Morphological, and Biodegradability Properties of Bioplastic Fertilizer Composites Made of Oil Palm Biomass, Fertilizer, and Poly(hydroxybutyrate-co-valerate). *Int. J. Polym. Sci*, 1–8. <https://doi.org/10.1155/2016/3230109>
- HEIKKINEN, S. L., MIKKONEN, K. S., PIRKKALAINEN, K., SERIMAA, R., JOLY, C., & TENKANEN, M. (2013). Specific enzymatic tailoring of wheat arabinoxylan reveals the role of substitution on xylan film properties. *Carbohydr. Polym*, 92, 733–740. <https://doi.org/10.1016/j.carbpol.2012.09.085>
- HÖLJE, A., STEMEMALM, E., HEIKKINEN, S., TENKANEN, M., & GATENHOLM, P. (2008). Material properties of films from enzymatically tailored arabinoxylans. *Biomacromolecules*, 9, 2042–2047.
<https://doi.org/10.1021/bm800290m>
- HUANG, S. J., & EDELMAN, P. G. (1995). An overview of biodegradable polymers

- and biodegradation of polymers. *Degradable Polymers*, Springer Netherlands, Dordrecht, pp. 18–28. https://doi.org/10.1007/978-94-011-0571-2_2
- ISO 14855-2. (2018). Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions- Method by analysis of evolved carbon dioxide - Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test. ISO.
- ISO 17556:2003 (2003). Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved. ISO.
- IWATA, T. (2015). Biodegradable and bio-based polymers: Future prospects of eco-friendly plastics. *Angew. Chemie - Int.*, 54, 3210–3215. <https://doi.org/10.1002/anie.201410770>
- JAMBECK, J. R., JI, Q., ZHANG, Y. G., LIU, D., GROSSNICKLE, D. M., & LUO, Z. X. (2015). Plastic waste inputs from land into the ocean. *Science*, 347, 768–771. <https://doi.org/10.1126/science.1260879>
- JENINGS, D. H., & LYSEK, G. (1996). Fungal Biology: Understanding the Fungal Lifestyle. *BIOS Scientific Publisher*, Oxford, UK.
- JIANG, G., HILL, D. J., KOWALCZUK, M., JOHNSTON, B., ADAMUS, G., IRORERE, V., & RADECKA, I. (2016). Carbon sources for polyhydroxyalkanoates and an integrated biorefinery. *Int. J. Mol. Sci*, 17, 1157. <https://doi.org/10.3390/ijms17071157>
- JONES, F. (2020). A promessa dos bioplásticos. FAPESP. <https://revistapesquisa.fapesp.br/a-promessa-dos-bioplasticos/>. (accessed 6.20.20).
- JOYYI, L., AHMAD THIRMIZIR, M. Z., SALIM, M. S., HAN, L., MURUGAN, P., KASUYA, K.I., MAURER, F. H. J., ZAINAL ARIFIN, M. I., & SUDESH, K. (2017). Composite properties and biodegradation of biologically recovered poly(3HB-co-3HHx) reinforced with short kenaf fibers. *Polymer Degradation and Stability*. doi: 10.1016/j.polymdegradstab.2017.01.004.
- KABIR, E., KAUR, R., LEE, J., KIM, K.H., & KWON, E. E. (2020). Prospects of biopolymer technology as an alternative option for non-degradable plastics and sustainable management of plastic wastes. *J. Clean. Prod*, 258, 120536. <https://doi.org/10.1016/j.jclepro.2020.120536>
- KJELDSSEN, A., PRICE, M., LILLEY, C., GUZNICZAK, E., & ARCHER, I. (2018). A Review of Standards for Biodegradable Plastics. *Ind. Biotechnol. Innov. Cent*,

- KLEEBERG, I., HETZ, C., KROPPESTEDT, R. M., MÜLLER, R. J., & DECKWER, W. D. (1998). Biodegradation of aliphatic-aromatic copolyesters by *Thermomonospora fusca* and other thermophilic compost isolates. *Appl. Environ. Microbiol*, 64, 1731–1735. <https://doi.org/10.1128/aem.64.5.1731-1735.1998>
- KOURMENTZA, C., PLÁCIDO, J., VENETSANEAS, N., BURNIOL-FIGOLS, A., VARRONE, C., GAVALA, H. N., & REIS, M. A. M. (2017). Recent advances and challenges towards sustainable polyhydroxyalkanoate (PHA) production. *Bioengineering*, 4, 55. <https://doi.org/10.3390/bioengineering4020055>
- KRATSCH, H. A., SCHRADER, J. A., MCCABE, K. G., SRINIVASAN, G., GREWELL, D., & GRAVES, W. R. (2015). Performance and biodegradation in soil of novel horticulture containers made from bioplastics and biocomposites. *HortTechnology*, 25, 119–131.
- Krzan, A., Hemjinda, S., Miertus, S., Corti, A., & CHIELLINI, E. (2006). Standardization and certification in the area of environmentally degradable plastics. *Polym. Degrad. Stab*, 91, 2819–2833. <https://doi.org/10.1016/j.polymdegradstab.2006.04.034>
- KUMAR, S., & MAITI, P. (2016). Controlled biodegradation of polymers using nanoparticles and its application. *RSC Adv*, 6, 67449–67480. <https://doi.org/10.1039/c6ra08641a>
- LACKNER, M. (2015). Bioplastics-biobased plastics as renewable and/or biodegradable alternatives to petroplastics. *Kirk-Othmer Encycl. Chem. Technol*, 6, 1–41. <https://doi.org/DOI: 10.1002/0471238961.koe00006>
- LADISCH, M. R., LIN, K. W., VOLOCH, M., & TSAO, G. T. (1983). Process considerations in the enzymatic hydrolysis of biomass. *Enzyme Microb. Technol*, 5, 82–102. [https://doi.org/10.1016/0141-0229\(83\)90042-X](https://doi.org/10.1016/0141-0229(83)90042-X)
- LEBRETON, L., SLAT, B., FERRARI, F., SAINTE-ROSE, B., AITKEN, J., MARTHOUSE, R., HAJBANE, S., CUNSOLO, S., SCHWARZ, A., LEVIVIER, A., NOBLE, K., DEBELJAK, P., MARAL, H., SCHOENEICH-ARGENT, R., BRAMBINI, R., & REISSER, J. (2018). Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic. *Sci. Rep.*, 8, 1–15. <https://doi.org/10.1038/s41598-018-22939-w>
- LEE, S. Y. (1998). Poly(3-hydroxybutyrate) production from xylose by recombinant *Escherichia coli*. *Bioprocess Eng*, 18, 397–399.

<https://doi.org/10.1007/s004490050462>

- LEE, H. S., CHO, D., & HAN, S. O. (2008). Effect of natural fiber surface treatments on the interfacial and mechanical properties of henequen/polypropylene biocomposites. *Macromol. Res*, 16, 411–417. <https://doi.org/10.1007/BF03218538>
- LINDSTRÖM, A., ALBERTSSON, A.C., & HAKKARAINEN, M. (2004). Quantitative determination of degradation products an effective means to study early stages of degradation in linear and branched poly(butylene adipate) and poly(butylene succinate). *Polym. Degrad. Stab*, 83, 487–493. <https://doi.org/10.1016/j.polymdegradstab.2003.07.001>
- LOPES, M. S. G., ROCHA, R. C. S., ZANOTTO, S. P., GOMEZ, J. G. C., & SILVA, L. F. (2009). Screening of bacteria to produce polyhydroxyalkanoates from xylose. *World J. Microbiol. Biotechnol*, 25, 1751–1756. <https://doi.org/10.1007/s11274-009-0072-9>
- LUCAS, N., BIENAIME, C., BELLOY, C., QUENEUEDEC, M., SILVESTRE, F., & NAVA-SAUCEDO, J. E., 2008. Polymer biodegradation: Mechanisms and estimation techniques - A review. *Chemosphere*, 73, 429–442. <https://doi.org/10.1016/j.chemosphere.2008.06.064>
- LUCENA, C. A. A., DA COSTA, S. C., ELEAMEN, G. R. D. A., MENDONÇA, E. A. D. M., & OLIVEIRA, E. E. (2017). Desenvolvimento de biofilmes à base de xilana e xilana/gelatina para produção de embalagens biodegradáveis. *Polimeros*, 27, 35–41. <https://doi.org/10.1590/0104-1428.2223>
- LUGAUSKAS, A., LEVINSKAITE, L., & PEČIULYTE, D. (2003). Micromycetes as deterioration agents of polymeric materials. *Int. Biodeterior. Biodegrad*, 52, 233–242. [https://doi.org/10.1016/S0964-8305\(03\)00110-0](https://doi.org/10.1016/S0964-8305(03)00110-0)
- MAGALHÃES, N. F., & ANDRADE, C. T. (2013). Properties of melt-processed poly(hydroxybutyrate-co-hydroxyvalerate)/ starch 1:1 blend nanocomposites. *Polimeros*, 23, 366–372. <https://doi.org/10.4322/polimeros.2013.034>
- MARIANO, M., PILATE, F., DE OLIVEIRA, F. B., KHELIFA, F., DUBOIS, P., RAQUEZ, J. M., & DUFRESNE, A. (2017). Preparation of Cellulose Nanocrystal-Reinforced Poly(lactic acid) Nanocomposites through Noncovalent Modification with PLLA-Based Surfactants. *ACS Omega*, 2, 2678–2688. <https://doi.org/10.1021/acsomega.7b00387>
- MARTEN, E., MÜLLER, R. J., & DECKWER, W. D. (2003). Studies on the enzymatic hydrolysis of polyesters - I. Low molecular mass model esters and aliphatic

- polyesters. *Polym. Degrad. Stab*, 80, 485–501. [https://doi.org/10.1016/S0141-3910\(03\)00032-6](https://doi.org/10.1016/S0141-3910(03)00032-6)
- MEDINA JARAMILLO, C., GUTIÉRREZ, T. J., GOYANES, S., BERNAL, C., & FAMÁ, L. (2016). Biodegradability and plasticizing effect of yerba mate extract on cassava starch edible films. *Carbohydrate Polymers*, 151, 150-159.
- MEEREBOER, K.W., MISRA, M., & MOHANTY, A. K. (2020). Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites. *Green Chem*, 2, 2-40. [10.1039/d0gc01647k](https://doi.org/10.1039/d0gc01647k)
- MELATI, R. B., SHIMIZU, F. L., OLIVEIRA, G., PAGNOCCA, F. C., DE SOUZA, W., SANT'ANNA, C., & BRIENZO, M. (2019). KEY FACTORS AFFECTING THE RECALCITRANCE AND CONVERSION Process of Biomass. *Bioenergy Res*, 12. <https://doi.org/10.1007/s12155-018-9941-0>
- Mitchell, D., Grohmann, K., Himmel, M., Dale, B., & SCHROEDER, H. (1990). Effect of the degree of acetylation on the enzymatic digestion of acetylated xylans. *J. Wood Chem. Technol*, 10, 111–121. <https://doi.org/10.1080/02773819008050230>
- MOROHOSHI, T., OGATA, K., OKURA, T., & SATO, S. (2018). Molecular characterization of the bacterial community in biofilms for degradation of poly (3-Hydroxybutyrate-co-3-Hydroxyhexanoate) films in seawater. *Microbes Environ. ME*, 17052.
- MUELLER, R. J. (2006). Biological degradation of synthetic polyesters-Enzymes as potential catalysts for polyester recycling. *Process Biochem*, 41, 2124–2128. <https://doi.org/10.1016/j.procbio.2006.05.018>
- NAGALAKSHMAIAH, M., AFRIN, S., MALLADI, R. P., ELKOUN, S., ROBERT, M., ANSARI, M. A., SVEDBERG, A., & KARIM, Z. (2019). Biocomposites: Present trends and challenges for the future. *Green Compos. Automot. Appl*, 197–215. <https://doi.org/10.1016/B978-0-08-102177-4.00009-4>
- NAGALAKSHMAIAH, M., EL KISSI, N., & DUFRESNE, A. (2016). Ionic Compatibilization of Cellulose Nanocrystals with Quaternary Ammonium Salt and Their Melt Extrusion with Polypropylene. *ACS Appl. Mater. Interfaces*, 8, 8755–8764. <https://doi.org/10.1021/acsami.6b01650>
- Nagalakshmaiah, M., Nechyporchuk, O., El Kissi, N., & DuFRESNE, A. (2017). Melt extrusion of polystyrene reinforced with cellulose nanocrystals modified using poly[(styrene)-co-(2-ethylhexyl acrylate)] latex particles. *Eur. Polym. J*, 91, 297–306. <https://doi.org/10.1016/j.eurpolymj.2017.04.020>

- NARANCIC, T., VERSTICHEL, S., REDDY CHAGANTI, S., MORALES-GAMEZ, L., KENNY, S. T., DE WILDE, B., BABU PADAMATI, R., & O'CONNOR, K. E. (2018). Biodegradable Plastic Blends Create New Possibilities for End-of-Life Management of Plastics but They Are Not a Panacea for Plastic Pollution. *Environ. Sci. Technol*, 52, 10441–10452. doi: 10.1021/acs.est.8b02963.
- NAZARETH, M., MARQUES, M. R. C., LEITE, M. C. A., & CASTRO, Í. B. (2018). Commercial plastics claiming biodegradable status: Is this also accurate for marine environments? *J. Hazard. Mater*, 366, 714–722. <https://doi.org/10.1016/j.jhazmat.2018.12.052>
- NDUKO, J. M., SUZUKI, W., MATSUMOTO, K., KOBAYASHI, H., OOI, T., FUKUOKA, A., & TAGUCHI, S. (2012). Polyhydroxyalkanoates production from cellulose hydrolysate in *Escherichia coli* LS5218 with superior resistance to 5-hydroxymethylfurfural. *J. Biosci. Bioeng*, 113, 70–72. <https://doi.org/10.1016/j.jbiosc.2011.08.021>
- NIAOUNAKIS, M. (2015). Properties. *Biopolym. Appl. Trends*, 91–138. https://doi.org/10.1007/1-4020-4733-9_2
- OCHI, S. (2006). Development of high strength biodegradable composites using Manila hemp fiber and starch-based biodegradable resin. *Compos. Part A Appl. Sci, Manuf*, 37, 1879–1883. <https://doi.org/10.1016/j.compositesa.2005.12.019>
- OLUWASINA, O. O., OLALEYE, F. K., OLUSEGUN, S. J., OLUWASINA, OLAYINKA O., & MOHALLEM, N. D. S. (2019). Influence of oxidized starch on physicommechanical, thermal properties, and atomic force micrographs of cassava starch bioplastic film. *Int. J. Biol. Macromol*, 135, 282–293. <https://doi.org/10.1016/j.ijbiomac.2019.05.150>
- PALmisano, A. C., Pettigrew, C. A. (1992). Biodegradability of Plastics. *Bioscience*, 42, 680–685. <https://doi.org/doi:10.2307/1312174>
- PATHAK, V. M., & NAVNEET. (2017). Review on the current status of polymer degradation: a microbial approach. *Bioresour. Bioprocess*, 4. <https://doi.org/10.1186/s40643-017-0145-9>
- PAVEL, S., KHATUN, A., & HAQUE, M. M. (2020). Nexus Among Bio-plastic, Circularity, Circular Value Chain & Circular Economy. *SSRN Electron. J.* <https://doi.org/10.2139/ssrn.3509954>
- PELMONT, J. (2005). Biodégradations et métabolismes. Les bactéries pour les technologies de l'environnement. EDP, Sciences.

- PÉREZ, J., MUÑOZ-DORADO, J., DE LA RUBIA, T., & MARTÍNEZ, J. (2002). Biodegradation and biological treatments of cellulose, hemicellulose and lignin: An overview. *Int. Microbiol*, 5, 53–63. <https://doi.org/10.1007/s10123-002-0062-3>
- PHAN THE, D., DEBEAUFORT, F., VOILLEY, A., & LUU, D. (2009). Biopolymer interactions affect the functional properties of edible films based on agar, cassava starch and arabinoxylan blends. *J. Food Eng*, 90, 548–558. <https://doi.org/10.1016/j.jfoodeng.2008.07.023>
- PIÑEROS-HERNANDEZ, D., MEDINA-JARAMILLO, C., LÓPEZ-CÓRDOBA, A., & GOYANES, S. (2017). Edible cassava starch films carrying rosemary antioxidant extracts for potential use as active food packaging. *Food Hydrocolloids*, 63, 488–495.
- PLATT, K. D. (2006). *Biodegradable Polymers*. Woodhead Publishing Ltd., Cambridge, UK.
- POLMAN, E. M. N., GRUTER, G. J. M., PARSONS, J. R., & TIETEMA, A. (2020). Comparison of the aerobic biodegradation of biopolymers and the corresponding bioplastics: A review. *Science of The Total Environment*, 753, 141953. [doi:10.1016/j.scitotenv.2020.141953](https://doi.org/10.1016/j.scitotenv.2020.141953)
- PREMRAJ, R., & DOBLE, M. (2005). Biodegradation of Polymers. *Indian J Biotechnol*, 4, 186–193.
- PRIYANKA, N., & ARCHANA, T. (2011). Biodegradability of Polythene and Plastic By The Help of Microorganism: A Way for Brighter Future. *J. Environ. Anal. Toxicol*, 1, 1–4. <https://doi.org/10.4172/2161-0525.1000111>
- PROIKAKIS, C. S., MAMOUELOS, N. J., TARANTILI, P. A., & ANDREOPOULOS, A. G. (2006). Swelling and hydrolytic degradation of poly(d,l-lactic acid) in aqueous solutions. *Polym. Degrad. Stab*, 91, 614–619. <https://doi.org/10.1016/j.polymdegradstab.2005.01.060>
- RANI-BORGES, B., FARIA, A. U., DE CAMPOS, A., GONÇALVES, S. P. C., & MARTINS-FRANCHETTI, S. M. (2016). Biodegradation of additive PHBV/PP-co-PE films buried in soil. *Polimeros*, 26, 161–167. <https://doi.org/10.1590/0104-1428.2127>
- RIVARD, C., MOENS, L., ROBERTS, K., BRIGHAM, J., & KELLEY, S. (1995). Starch esters as biodegradable plastics: Effects of ester group chain length and degree of substitution on anaerobic biodegradation. *Enzyme Microb. Technol*, 17, 848–852. [https://doi.org/10.1016/0141-0229\(94\)00120-G](https://doi.org/10.1016/0141-0229(94)00120-G)

- ROBERTS, D. J., NICA, D., ZUO, G., & DAVIS, J. L. (2002). Quantifying microbially induced deterioration of concrete: Initial studies. *Int. Biodeterior. Biodegrad*, 49, 227–234. [https://doi.org/10.1016/S0964-8305\(02\)00049-5](https://doi.org/10.1016/S0964-8305(02)00049-5)
- RONG, M. Z., ZHANG, M. Q., LIU, Y., YANG, G. C., & ZENG, H. M. (2001). The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. *Compos. Sci. Technol*, 61, 1437-1447.
- ROSA, D. S., RODRIGUES, T. C., GRAÇAS FASSINA GUEDES, C., & CALIL, M. R. (2003). Effect of thermal aging on the biodegradation of PCL, PHB-V, and their blends with starch in soil compost. *Journal of Applied Polymer Science*, 89, 13, 3539–3546. doi:10.1002/app.12537
- RUBIO, C., OTT, C., AMIEL, C., DUPONT-MORAL, I., TRAVERT, J., & MARIEY, L. (2006). Sulfato/thiosulfato reducing bacteria characterization by FT-IR spectroscopy: A new approach to biocorrosion control. *J. Microbiol. Methods*, 64, 287–296. <https://doi.org/10.1016/j.mimet.2005.05.013>
- SÁNCHEZ-SAFONT, E., ARRILLAGA, A., ANAKABE, J., CABEDO, L., & GAMEZ-PEREZ, J., (2018). Toughness Enhancement of PHBV/TPU/Cellulose Compounds with Reactive Additives for Compostable Injected Parts in Industrial Applications. *International Journal of Molecular Sciences*, 19, 7, 2102. doi:10.3390/ijms19072102
- SANTACRUZ-JUAREZ, E., BUENDIA-CORONA, R. E., RAMÍREZ, R. E., & SANCHEZ, S. (2021). Fungal enzymes for the degradation of polyethylene: Molecular docking simulation and biodegradation pathway proposal. *Journal of Hazardous Materials*, 411, 125118.
- SARASA, J., GRACIA, J. M., & JAVIERRE, C. (2009). Study of the biodisintegration of a bioplastic material waste. *Bioresour. Technol*, 100, 3764–3768. <https://doi.org/10.1016/j.biortech.2008.11.049>
- SHRUTI, V. C., & KUTRALAM-MUNIASAMY, G. (2019). Bioplastics missing link in the era of microplastics. *Science of The Total Environment*, 134139. doi:10.1016/j.scitotenv.2019.134139
- SINGH, A. A., AFRIN, S., & KARIM, Z. (2017). Green Composites: Versatile Material for Future. *Green Energy Technol*, 24–44. <https://doi.org/10.1007/978-3-319-49382-4>
- SCHMATZ, A. A., TYHODA, L., & BRIENZO, M. (2020). Sugarcane biomass influenced by lignin. *Biofuels Bioprod Bioref*, 14, 469–480.

- STANDARDIZATION, I.O.F. (2014). Plastics — Determination of the ultimate anaerobic biodegradation under high-solids anaerobic-digestion conditions — Method by analysis of released biogas.
- STANDARDIZATION, I.O.F. (2016). Plastics — Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system — Method by measurement of biogas production.
- SUZUKI, M., TACHIBANA, Y., & KASUYA, K. (2021). Biodegradability of poly(3-hydroxyalkanoate) and poly(ϵ -caprolactone) via biological carbon cycles in marine environments. *Polym J*, 53, 47–66. <https://doi.org/10.1038/s41428-020-00396-5>
- TABASI, R. Y., & AJJI, A. (2015). Selective degradation of biodegradable blends in simulated laboratory composting. *Polym. Degrad. Stab.* 120, 435–442. <https://doi.org/10.1016/j.polymdegradstab.2015.07.020>
- TERAMOTO, N., URATA, K., OZAWA, K., SHIBATA, M. (2004). Biodegradation of aliphatic polyester composites reinforced by abaca fiber. *Polymer Degradation and Stability*, 86, 3, 401–409. doi:10.1016/j.polymdegradstab.2004.04.026
- TERRONE, C. C., NASCIMENTO, J. M. F., TERRASAN, C. R. F., BRIENZO, M., & CARMONA, E. C. (2020). Salt-tolerant α -arabinofuranosidase from a new specie *Aspergillus hortai* CRM1919: Production in acid conditions, purification, characterization and application on xylan hydrolysis. *Biocatalysis and Agricultural Biotechnology*, 23, 101460. <https://doi.org/10.1016/j.bcab.2019.101460>
- TCHMUTIN, I., RYVKINA, N., SAHA, N., & SAHA, P. (2004). Study on biodegradability of protein filled polymer composites using dielectric measurements. *Polym. Degrad. Stab.* 86, 411–417. <https://doi.org/10.1016/j.polymdegradstab.2004.05.012>
- THAKUR, V. K., THAKUR, M. K., & GUPTA, R. K. (2014). Review: Raw Natural Fiber-Based Polymer Composites. *Int. J. Polym. Anal. Charact*, 19, 256–271. <https://doi.org/10.1080/1023666X.2014.880016>
- THELLEN, C., COYNE, M., FROIO, D., AUERBACH, M., WIRSEN, C., & RATTO, J. A. (2008). A processing, characterization and marine biodegradation study of melt-extruded polyhydroxyalkanoate (PHA) films. *J. Polym. Environ*, 16, 1–11. <https://doi.org/10.1007/s10924-008-0079-6>
- TOSIN, M., WEBER, M., SIOTTO, M., LOTT, C., & INNOCENTI, F. D. (2012). Laboratory test methods to determine the degradation of plastics in marine environmental conditions. *Front. Microbiol.* 3, 1–9.

<https://doi.org/10.3389/fmicb.2012.00225>

- TSERKI, V., MATZINOS, P., KOKKOU, S., & PANAYIOTOU, C. (2005). Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part I. Surface chemical modification and characterization of waste flour. *Compos. Part A Appl. Sci. Manuf*, 36, 965–974. <https://doi.org/10.1016/j.compositesa.2004.11.010>
- TSERKI, V., MATZINOS, P., & PANAYIOTOU, C. (2006). Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part II. Development of biodegradable composites using treated and compatibilized waste flour. *Compos. Part A Appl. Sci. Manuf*, 37, 1231–1238. <https://doi.org/10.1016/j.compositesa.2005.09.004>
- TSUJI, H., ECHIZEN, Y., & NISHIMURA, Y. (2006). Photodegradation of biodegradable polyesters: A comprehensive study on poly(l-lactide) and poly(ϵ -caprolactone). *Polym. Degrad. Stab*, 91, 1128–1137. <https://doi.org/10.1016/j.polymdegradstab.2005.07.007>
- VAN SOEST, P. J. (1994). Nutritional ecology of the ruminant. Cornell University Press.
- VERT, M., DOI, Y., HELLWICH, K. H., HESS, M., HODGE, P., KUBISA, P., & RINAUDO, M., SCHUÉ, F. (2012). Terminology for biorelated polymers and applications (IUPAC Recommendations 2012). *Pure Appl. Chem*, 84, 377–410. <https://doi.org/https://doi.org/10.1351/PAC-REC-10-12-04>
- VOLOVAA, T. G., BOYANDINA, A. N., & PRUDNIKOVAB, S. V. (2015). Biodegradation of polyhydroxyalkanoates in natural soils. *J. Sib. Fed. Univ. Biol.*, 2, 152-167.
- WALLACE, G., CHESSON, A., LOMAX, J. A., & JARVIS, M.C. (1991). Lignin-carbohydrate complexes in graminaceous cell walls in relation to digestibility. *Anim. Feed Sci. Technol*, 32, 193–199. [https://doi.org/10.1016/0377-8401\(91\)90022-K](https://doi.org/10.1016/0377-8401(91)90022-K)
- WANG, T., CHENG, G., MA, S., CAI, Z., & ZHANG, L. (2003). Crystallization behavior, mechanical properties, and environmental biodegradability of poly(?-hydroxybutyrate)/cellulose acetate butyrate blends. *Journal of Applied Polymer Science*, 89, 8, 2116–2122. doi:10.1002/app.12359
- WANG, S., REN, J., LI, W., SUN, R., & LIU, S. (2014). Properties of polyvinyl alcohol/xylan composite films with citric acid. *Carbohydr. Polym*, 103, 94–99.

- <https://doi.org/10.1016/j.carbpol.2013.12.030>
- WANG, Y. W., MO, W., YAO, H., WU, Q., CHEN, J., & CHEN, G. Q. (2004). Biodegradation studies of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). *Polym. Degrad. Stab*, 85, 815–821. <https://doi.org/10.1016/j.polymdegradstab.2004.02.010>
- WARSCHEID, T., & BRAAMS, J. (2000). Biodeterioration of stone: a review. *Int. Biodeter. Biodegr*, 46, 343–368.
- WENG, Y. X., WANG, L., ZHANG, M., WANG, X. L., & WANG, Y. Z. (2013). Biodegradation behavior of P(3HB,4HB)/PLA blends in real soil environments. *Polym. Test*, 32, 60–70. <https://doi.org/10.1016/j.polymertesting.2012.09.014>
- WENG, Y. X., WANG, X. L., & WANG, Y. Z. (2011). Biodegradation behavior of PHAs with different chemical structures under controlled composting conditions. *Polym. Test*, 30, 372–380. <https://doi.org/10.1016/j.polymertesting.2011.02.001>
- WITT, U., EINIG, T., YAMAMOTO, M., KLEEGERG, I., DECKWER, W. D., & MÜLLER, R. J. (2001). Biodegradation of aliphatic-aromatic copolyesters: Evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. *Chemosphere*, 44, 289–299. [https://doi.org/10.1016/S0045-6535\(00\)00162-4](https://doi.org/10.1016/S0045-6535(00)00162-4)
- WRIGHT, S. L., THOMPSON, R. C., & GALLOWAY, T. S. (2013). The physical impacts of microplastics on marine organisms: a review. *Environ. Pollut*, 178, 483–492. <https://doi.org/10.1016/j.envpol.2013.02.031>
- WU, C. S. (2014). Preparation and Characterization of Polyhydroxyalkanoate Bioplastic-Based Green Renewable Composites from Rice Husk. *J. Polym. Environ*, 22, 384–392. <https://doi.org/10.1007/s10924-014-0662-y>
- YANG, J., CHING, Y. C., & CHUAH, C. H. (2019). Applications of Lignocellulosic Fibers and Lignin in Bioplastics: A Review. *Polymers*, 11, 751.
- ZANARDINI, E., ABBRUSCATO, P., GHEDINI, N., REALINI, M., & SORLINI, C. (2000). Influence of atmospheric pollutants on the biodeterioration of stone. *Int. Biodeterior. Biodegrad*. 45, 35–42. [https://doi.org/10.1016/S0964-8305\(00\)00043-3](https://doi.org/10.1016/S0964-8305(00)00043-3)
- ZHAO, J. H., WANG, X. Q., ZENG, J., YANG, G., SHI, F. H., & YAN, Q. (2005). Biodegradation of poly(butylene succinate-co-butylene adipate) by *Aspergillus versicolor*. *Polym. Degrad. Stab*, 90, 173–179. <https://doi.org/10.1016/j.polymdegradstab.2005.03.006>

CHAPTER IV: Production and assessment of the biodegradation and ecotoxicity of xylan and starch-based bioplastics

Abstract

The development of novel renewable (and preferably biodegradable) materials has become recurrent due to the growing concerns with the environmental impacts of the high volume of plastic waste produced from oil-based sources over the past decades. This study aimed at the development of bioplastics from a mixture of starch and xylan in variable ratios, and the combined effect of α -cellulose and holocellulose extracted from sugarcane bagasse added to the process. The disintegration of the bioplastics was evaluated in both soil and composting. The ecotoxicity analyses with *Saccharomyces cerevisiae*, *Bacillus subtilis* and seeds of *Cucumis sativus* were conducted after biodegradation. All formulations based on 5% (w/v) of total polysaccharides were dried at 30 °C and resulted in homogeneous (non-brittle) bioplastics. The composting results showed that all bioplastic formulations disintegrated in 3 days, whereas the 25/75% (xylan/starch, w/w) formulation vanished in soil within 13 days. The ecotoxicity data showed no inhibition of microbial growth after biodegradation, yielding 100% of seeds germination. Despite the positive influence of the bioplastic disintegration on the root and hypocotyl growth, temporary inhibition of *C. sativus* tissues exposed to 10-day biodegradation soil washing was observed. The study demonstrated the xylan/starch bioplastics result in non-ecotoxic soil disintegrable materials.

Keywords: Renewable material, disintegrable bioplastics, soil disintegration, biomass

1. Introduction

Plastic material represents 12% of urban solid waste (KAZA et al., 2018). It is estimated that 4 to 12 million metric tons of plastic waste produced in coastal regions (worldwide distribution) reached the marine environment in 2010 (JAMBECK et al., 2015), resulting in the concerning accumulation of non-biodegradable plastics (GEYER et al., 2017). Some plastics degrade slowly (25-90 years for PET (Edge, 1991), <1000 years for HDPE (*High-density polyethylene*) (ROWE et al., 2009)), and are produced from non-renewable fossil hydrocarbons at rates higher than their degradation rates. Microplastics (≤ 5 mm size) are currently considered ubiquitous and persistent in the marine environment (WRIGHT et al., 2013) due to their low weight and high durability (MOORE, 2008; THOMPSON et al., 2009). A biodegradable material could contribute to decreasing the environmental impact.

Increasing concerns with the environmental impacts of plastic residues are logical and justifiable as plastic components remain long in the environment. Between 1950-2015, 79% of all plastic produced (>6 billion tons) became waste and the total recycled content was only 9% (GEYER et al., 2017). Among the alternatives, bioplastics have arisen as feasible ones and include biodegradable materials preferably from renewable sources (LACKNER, 2015).

Polymers from plant biomass have shown high potential for use in the development of bioplastics due to their availability, biodegradability and biocompatibility. One of the most studied vegetable polymers for bioplastics production is starch (BERGEL et al., 2018), a polysaccharide capable of blending with many plasticizers and water (BERGEL et al., 2018), which results in thermoplastic starch (TPS) when enough heat is supplied. Hemicellulose, another polysaccharide with strong potential for the production of value-added materials, is the second most abundant biopolymer on Earth. Xylan is a major component of plant hemicellulose and the most abundant renewable polysaccharide in nature found in cereals, grass plants and hardwood (MELATI et al., 2019).

The main objectives of this study were to produce enhanced blends of bioplastics based on xylan and starch and determine their disintegration and biodegradation rate in compost and soil systems. An approach of ecotoxicity assays based on the post-biodegradation samples of bioplastics in soil was included. The latter is of particular interest as different bioplastics have been developed over the past

decades. However, concerns with their physicochemical properties and environmental safety should be a priority and no special attention has been devoted to their effects on organisms - especially on edible vegetables (BALESTRI et al., 2019). To the best of our knowledge, the present study is the first that addresses the formulation, composting, biodegradation and ecotoxicity of xylan-starch blends and their mixture with α -cellulose, holocellulose and xylan extracted from sugarcane bagasse.

2. Materials and methods

2.1. Materials

São João company – Araras-SP supplied sugarcane bagasse and starch (Exôdo científica), glycerin (Synth), glucose (Synth), urea (Neon), H_2O_2 (Synth), glacial acetic acid (Synth), hydrochloric acid (Neon), sodium chlorite (Neon), sodium hydroxide (Neon), $CaCl_2 \cdot 2H_2O$ (Synth) and NaCl (Synth) were supplied in P.A degree. Chloramphenicol and culture media were provided by Sigma and Neogen, respectively. Compost formulation materials (earthworm humus, rabbit feed, sawdust and seed oil) were purchased from a local gardening store and the soil was collected from gardens at São Paulo State University (UNESP) in Rio Claro-SP (coordinates: 22°23'45.18"S 47°32'49.18"W). Low density polyethylene (LDPE), bond paper and seeds (with no chemical additives) were obtained from a local market.

2.2. Extraction of holocellulose, xylan and α -cellulose

Prior to extraction, the bagasse was washed, oven-dried at 60 °C, ground and selected with 20 mesh sieves and stored in plastic bags. The extraction of holocellulose followed an analytical method according to which 0.376 g of sodium chlorite and 0.126 mL of glacial acetic acid were added to each 1 g (dry basis) of the material, over a final 40 mL of distilled water solution. The sample was placed in a water bath at 70 °C and three additional doses of sodium chlorite and glacial acetic acid were added every hour after 1, 2 and 3 h. The reactions were ceased at 4 h and the samples were removed from the bath, cooled, filtered and then washed with deionized water (80 mL of hot water and 200 mL of cold water) until the pH 5 of the filtrate was reached. The insoluble material (holocellulose) was oven-dried at 60 °C and stored in a plastic bag.

Xylan was extracted from 10 g (dry basis) of sugarcane bagasse and the procedure was conducted with hydrogen peroxide (H_2O_2) 6% (w/v), followed by the

addition of 5 mol/L sodium hydroxide (NaOH) until pH 11.6. The yielding water-based solution volume was 200 mL, shaken at 75 rpm at 25 °C for 4 h. After this stage, xylan was obtained according to the procedure described elsewhere (BRIENZO et al., 2009; ALVES et al., 2020).

Afterward, α -cellulose was obtained from the resulting solid insoluble portion from the xylan extraction, during the filtration step after the 4 h reaction with H₂O₂. The filtrate treatment followed the methods published elsewhere (BRIENZO et al., 2015). However, an improvement was made in the substrate that initiated the reaction as the same pretreated material (water insoluble solid), resulting from the xylan extraction step, was used.

2.3. Preparation of bioplastics

Table 1 shows the conditions used to prepare bioplastics based on starch and xylan blends, as well as xylan/holocellulose/cellulose. The main variables were drying temperature (30 and 40 °C) and the total polysaccharide range between 5 and 10% (w/v). A qualitative analysis was based on visual inspection and processability (ease of transfer and spreading on the drying plate) towards an adequate total polysaccharide concentration.

Table 1: Different production conditions for bioplastics based on xylan, starch, holocellulose and α -cellulose.

Filmogenic solution	Polysaccharides (% w/w)	Drying temperature (°C)	Solution volume (mL)	QTP (g)	Gelatinization time (min)
Xylan/starch	10/90 ⁺	30	60	25	3
Xylan/starch	15/85 ⁺	30	60	25	4
Xylan/starch	25/75 ⁺	30	60	25	4
Xylan/starch	25/75 ⁺	40	60	25	4
Xylan/starch	50/50 ⁺	40	60	25	4
Xylan/starch	75/25 ⁺	40	60	25	4
Mixture	15(xy)/5(α)/5(ho)/75(a) ⁺	40	60	25	4

Mixture	15(xy)/5(he)/5(ho)/75 (a) ⁺	30	60	25	4
Xylan/starch	25/75 ⁻	40	60	25	1.15
Xylan/starch	25/75 ⁻	40	60	25	0.83"

⁺=mass based on 5% w/v of total polysaccharides; ⁻=mass based on 10% w/v of total polysaccharides; xy = xylan; α = alpha-cellulose; ho = holocellulose; a = starch; QTP = quantity transferred to the plate; " = equivalent to 50 seconds.

Source: Elaborated by the author

The bioplastics were obtained by the casting method. Xylan was added to 30 mL of deionized water in a 125 mL flask and then solubilized for 30 seconds in a microwave oven (5s intervals for manual agitation). After the solution temperature had stabilized at 25 °C, starch and glycerin (20% w/w of glycerin based on the total polysaccharide content) filled the total volume up to 60 mL. After 30 min stirring at 120 rpm in a shaker, the filmogenic solution was gelatinized at 85 °C for 3 min for the formulation with 10% xylan, 4 min for all formulations whose xylan concentration was above 10% (relative to the total polysaccharide percentage of 5% w/v) and 50 s or 1.15 min for formulations relative to the total polysaccharide percentage of 10% (w/v). The gelatinization time was based on preliminary (not showed) tests from our research group. After gelatinization, 25 g of the solution were transferred to plastic petri dishes (56.71 cm² area) and incubated in an oven to dry (Table 1).

2.4. Solubility, opacity and thickness

Thickness was analyzed by a Mitutoyo micrometer of 0.001 mm resolution and opacity was determined by rectangular bioplastic strips adhered to a glass cuvette and its reading by a spectrophotometer (450 nm). Three strips from different parts of each bioplastic were used and the opacity was calculated dividing the absorbance averages by the average thickness of the different bioplastic formulations.

2.5. Composting (CP)

Bioplastic disintegration measurements were based on the study carried out by Sánchez-safont et al. (2016), adjusted for laboratory scale, changing the temperature to 50 °C and with no starch addition to the compost formulation. CP assays were

performed in duplicate. The soil and possible fragments of bioplastic were sieved (10 and 2 mm meshes sequentially) when disintegration ceased (after 3 days). The rapid disintegration and the material's composition hampered the weighing of the bioplastics, however the disintegration process could be described from observations of the sieved material.

The determination of volatile solids/total solids and pH followed the protocols of Balaguer et al. (2015) and Embrapa (1997), respectively. Morphological evaluations (qualitative ones), disintegration of LDPE plastic (low-density polyethylene (negative control)) and bond paper (cellulose-positive control) were evaluated under the same conditions previously described for the bioplastic. The bioplastic controls were exposed to the same conditions of temperature and composting time, yet not in contact with the compost, so that any disintegration and composting effect could be discarded.

2.6. Disintegration by soil burial process

Disintegration was performed with the 25/75% (xylan/starch, w/w) plastic blend based on 5% (w/v) of total polysaccharides. The disintegration method consisted of burying samples in soil and the resulting mass loss enabled a direct quantification of each material weigh loss. The bioplastics were cut into (3.5 x 3.5) cm squares, dried, and weighed and then inserted into a soil mixture in a plastic container of approximately 64 mm length, 330 mm width and 85 mm depth. The soil was kept at 24.5% humidity and 28-30 °C (DBO incubation). Throughout 3, 5, 10, and 13 days, the samples were removed (duplicates) for weighting. Measurements of disintegration from mass loss proved extremely difficult; therefore, the fragments of bioplastics were separated by sieving the soil (10 and 2 mm sieves) and analyzed by visual inspection.

2.7. Soil analysis and ecotoxicity

After disintegration of the polymeric blends buried in soil, the samples were aliquoted at 0 (soil before disintegration process start), 3, 5, 8, 10 and 13 days for checking the pH (according to the well-established Embrapa method (1997)), colony-forming units (bacteria and fungi), reducing sugars and ecotoxic effects. The microbial population in soil (cultivation-dependent approach) was quantified periodically during the bioplastic disintegration.

Each soil sample (1g) at 0, 3, 5, 8, 10 and 13 days of burial assay was washed with deionized water (5 mL) and then analyzed regarding ecotoxicity and the presence of reducing sugars. The soil toxicity was assessed by 5 mL of the filtered solution transferred to a petri dish through filter paper. Eight cucumber seeds (*Cucumis sativus*) were then placed on top of each filter paper and the plates were covered with film paper (to avoid moisture loss) and dark paper (to avoid photo-induced processes). Incubation occurred in an oven at 22 °C for 120 h and the percentage of germination (% G) and inhibition (% I) was calculated according to Papadimitriou et al. (2008). The ecotoxicity dataset for root and hypocotyl growth was obtained from the same plates used for germination quantification. However, after 120 h, the plates were subjected to freezing as this softens the vegetable tissues and facilitates handling. Root and hypocotyl measurements were calculated for each seedling, according to the recommendation of Papadimitriou et al. (2008). Milli-Q water, rather than soil solution, added to the filter papers was used in the control assays.

Data on microbial ecotoxicity were obtained using *Saccharomyces cerevisiae* (S288C) as a test-organism. The yeast was exposed to the soil before and after biodegradation and ecotoxicity was assessed by counting colony-forming units (CFU) in an YPD medium (1% yeast extract, 1% peptone, 2% sucrose and 1.5% agar). The yeast was first grown in the YPD medium with no agar in a shaker at 30 °C for 24 h at 100 rpm. After cultivation, 5 µL of the inoculum with cells were transferred to a 14 mL tube with 0.5 mL of the soil-based broth at different biodegradation times (0, 3, 5, 10 days), and 5.8 mL of medium YPD were added. In the control assays, 0.5 mL of distilled water was added to replace the soil water content. After 24 h incubation at 30 °C, an aliquot of the solutions with the yeast was diluted and transferred to a petri dish with solid YPD medium. The plates were incubated for 24 h at 30 °C for CFU counting.

Another ecotoxicity analysis checked the cell growth of *S. cerevisiae* and *Bacillus subtilis*, by optical density (OD) analysis performed in Tecan equipment and TM Magellan data analysis software. Yeast was cultivated in the YPD medium (as reported elsewhere), whereas *B. subtilis* was cultivated in a nutrient medium for 24 h at 30 °C. Moreover, 2 µL of the inoculum culture were transferred to a 96-well plate with 100 µL of YPD medium and 100 µL of soil wash (aliquots from each biodegradation time). Controls were also added to the plates containing triplicates of each soil wash with YPD medium with no inoculum. The Tecan device was configured towards OD measurements every 15 min at 600 nm wavelength (660 nm as the reference

wavelength) and after 15 sec shaking. The incubation temperature was 30 °C for 4020 min.

The content of reducing sugars in the soil, at different disintegration times, was determined in aliquots of 0.1 mL of the soil washing samples (previous step) added to test tubes. Afterward, 0.65 mL of distilled water and 0.5 mL of DNS solution were then added to the tubes (MILLER, 1959), which were incubated in boiling water for 10 min and cooled in an ice bath. Then, 3.75 mL of distilled water was added, and the samples were analyzed on a spectrophotometer at 540 nm.

2.8. Statistical analysis

Tukey-ANOVA ($p \leq 0.05$ significance level) assisted by version 5.0 Bioestat software was applied to several treatment groups.

3. Results and Discussion

3.1. Qualitative morphological analysis of bioplastics

The 30 °C drying temperature led to the production of more suitable, continuous and homogeneous bioplastics with no cracks. However, the drying time was longer (3 days). Drying at 40 °C accelerated the production time of the bioplastics (1 day) due to the higher agitation degree of the water molecules (KRISTO et al., 2008; SUDERMAN et al., 2016), and a longer drying period might result in both bonding and conformation optimization between the polysaccharides in the bioplastic matrix (RINDLAVA et al., 1997). The drying temperature of the bioplastic is related to its functional properties (MALI et al., 2010) and cost-effectiveness of the process (SCHULZE et al., 2017).

The 30 °C temperature for drying the bioplastics, shown in the present study, was also used by Yu et al. (2019). In a malleability analysis, PAULINO et al. (2019) observed that starch bioplastics dried at 37 °C for 12 h were less prone to becoming brittle when compared to a higher drying temperature (67 °C). Both drying time and temperature depend on the material or materials of the filmogenic solution (SCHULZE et al., 2017).

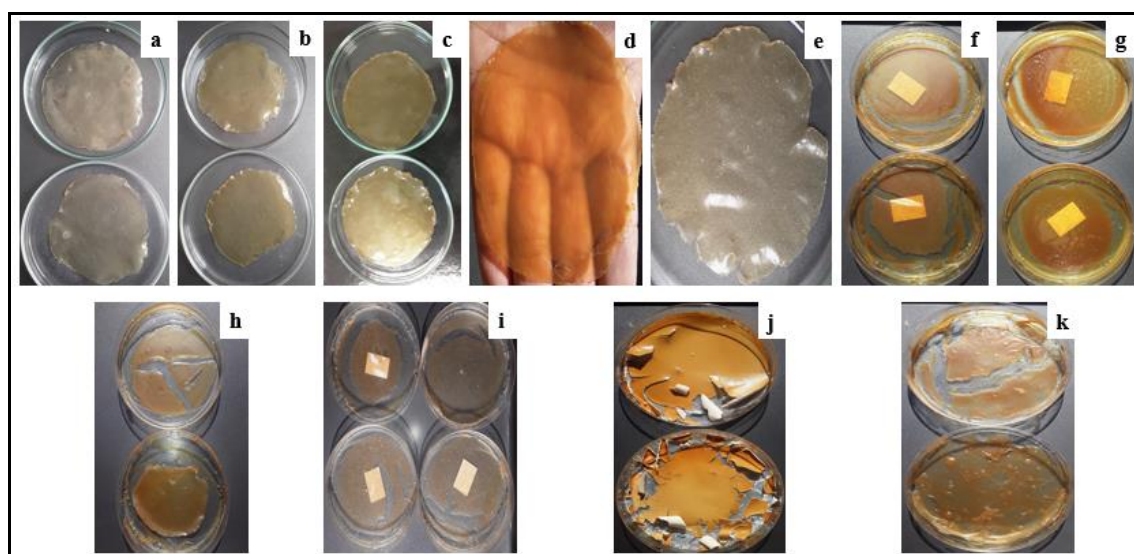
Regarding the hydrophobic character of α -cellulose and holocellulose, these molecules were not distributed equally over the surface of the bioplastic. Therefore, regions of the bioplastic were visually distinct due to their high accumulation. An alternative to using α -cellulose is to obtain nanocellulose as its combination with xylan

in bioplastics can result in continuous materials. A more homogeneous surface can improve the mechanical and barrier properties, reduce the number of cracks and promote bioplastic growth (PENG et al., 2011).

The highest temperature (40 °C) reduced drying time (24 h) and high concentration of xylan in bioplastics made with xylan/starch (75/25%) may have caused clusters of polysaccharides to appear in different zones of the bioplastic film. Thus, increasing the number of bonding between polysaccharides (mostly between xylan chains) and resulting in a bioplastic with an irregular surface and a wrinkled aspect in the accumulation points (darker regions) (Figure 1 (a-k)). Huang et al. (2019) reported that their hemicellulose-based bioplastics (containing arabinoxylan and galactomannan) underwent an intensified formation of hydrogen bonds between the polysaccharide chains. The production process resulted in a material with robust morphology and irregular curves.

Figure 1 (a-k) and Table 2 show the characteristics of the bioplastics developed with different proportions of xylan/starch and dried at 30 °C and 40 °C.

Figure 1: Bioplastics based on 5% and 10% (w/v) of total polysaccharides



(a) 10/90% xylan/starch (w/w) dried at 30 °C; (b) 15/85% xylan/starch (w/w) starch dried at 30 °C; (c,d) 25/75% xylan/starch (w/w) dried at 30 °C; (e) mixture (xylan, α -cellulose/holocellulose/starch) dried at 30 °C; (f) 50/50% xylan/starch (w/w) dried at 40

°C; (g) 75/25% xylan/starch (w/w) dried at 40 °C; (h) 25/75% xylan/starch (w/w) dried at 40 °C; (i) mixture (xylan, α -cellulose/holocellulose/starch) dried at 40 °C; (j) 10% (w/v) polysaccharides with 50 sec gelatinization/dried at 40 °C; (k) 10% (w/v) polysaccharides with 1.15 min gelatinization/dried at 40 °C.

Source: Elaborated by the author

Table 2: Qualitative results of xylan/starch, alpha-cellulose and hemicellulose blends

Bioplastic	Poly (% w/w)	T °C*	GT ^x (min)	Visual analysis results
Xylan/starch	25/75 ⁻	40	0.83"	GT was not suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; not transparent bioplastic with heterogeneous matrix, bubbles, and cracks.
Xylan/starch	25/75 ⁻	40	1.15	GT was suitable for starch gelatinization; difficult transfer of the filmogenic solution to the drying plate; bioplastic with heterogeneous matrix, bubbles, cracks and reduced transparency
Mixture ^o	15/5/5/75 ⁺	30	4	GT was suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; bioplastic with heterogeneous matrix, no bubbles or cracks, and reduced transparency
Mixture ^o	15/5/5/75 ⁺	40	4	GT was suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; bioplastic with heterogeneous matrix, no bubbles, with cracks and reduced transparency
Xylan/starch	25/75 ⁺	30	4	GT was suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; transparent bioplastic with homogeneous matrix, no bubbles or cracks.
Xylan/starch	25/75 ⁺	40	4	GT was suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; transparent bioplastic with homogeneous matrix, no bubbles or cracks.
Xylan/starch	15/85 ⁺	30	4	GT was suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; transparent bioplastics with homogeneous matrix, no bubbles or cracks.
Xylan/starch	10/90 ⁺	30	3	GT was suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; transparent bioplastics with homogeneous matrix, no bubbles or cracks.

Xylan/starch	50/50 ⁺	40	4	GT was suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; transparent bioplastics with heterogeneous matrix, no bubbles or cracks.
Xylan/starch	75/25 ⁺	40	4	GT was suitable for starch gelatinization; easy transfer of the filmogenic solution to the drying plate; bioplastics with heterogeneous matrix, no bubbles or cracks and reduced transparency

Poly=Polysaccharides; °=Xylan, alpha-cellulose, holocellulose and starch, respectively; +=mass based on 5% w/v of total polysaccharides; -=mass based on 10% w/v of total polysaccharides; * = drying temperature of the filmogenic solution; × = gelatinization time; ''= equivalent to 50 seconds.

Source: Elaborated by the author

3.2. Solubility and opacity of bioplastics

An increase in solubility of the formulations with lower xylan content (10% w/w, and mixture) was observed compared to those with higher xylan content (25% and 50% w/w xylan) (Table 3). This result is possibly related to interactions between polysaccharides, which decreased when more xylan was added. In addition to the fact that lignin is in a small proportion, it may have lowered the amount of bonds between starch and xylan and the hydrophilic character of xylan may have resulted in higher solubility degrees.

Table 3: Solubility and opacity of bioplastics in different concentrations of polysaccharides, based on 5% w/v of total polysaccharides.

Bioplastics (% w/w) ⁺	Solubility (%)	Thickness (mm)	Opacity (%)
Xylan/starch 10/90%	17.46±3.6 ^{a*}	0.18±0.024	1.44±0.17
Xylan/starch 15/85%	22.76±0.82 ^{ab}	0.200±0.034	2.77±0.50
Xylan/starch 25/75%	27.93±2.57 ^{bc}	0.16±0.004	5.50±0.70
Xylan/starch 50/50%	32.95±0.54 ^c	...	...
Mixture''	16.40±3.5 ^a	0.22±0.008	2.54±0.03

*Different letters represent the statistical differences in the same column ($p < 0.05$). [†]based on 5% (w/v) of total polysaccharides. ---= values not analyzed. [‡]xylan/ α -cellulose/holocellulose/starch.

Source: Elaborated by the author

Considering that the reduction in solubility is a desired property, our findings showed improved solubility properties compared to studies involving bioplastics based on hemicellulose. Pereira et al. (2017) obtained bioplastics based on wheat straw hemicellulose of approximately 95% solubility (4.51 g of insoluble mass/100 g). However, solubility was approximately 57% with the addition of 4% nanocellulose and 30% citric acid (42.57 g of insoluble mass/100g). Sabiha-Hanim and Siti-norsafurah (2012) reported that bioplastics made with hemicellulose from sugarcane bagasse showed 36.9 to 67.1% solubility. However, comparisons among different studies must consider the conditions of processing, composition, and thickness of biomaterials since they affect several properties of bioplastics such as solubility.

Cellulose bioplastics (on a nanoscale) show reduced water solubility as cellulose has high crystallinity and hydrophobicity and forms inter and intramolecular interactions through hydrogen bonds (RHIM and NG, 2007; PERREIRA et al., 2017). Our solubility results (Table 3) may be a consequence of its use on a macro scale; therefore, further studies aimed at decreasing the solubility of bioplastics by decreasing the size of cellulose particles are encouraged.

The opacity of the bioplastics increased with the amounts of xylan (Table 3). As addressed by Pineros-hernandez et al. (2017), a reduction in transparency due to the presence of phenolic compounds is interesting to obtain bioplastics with a photoprotective effect (in relation to UV). A dark biopackaging can protect a product against photooxidative effects such as lipid oxidation. However, it can also exert a negative consumption effect as the consumer prefers seeing the product wrapped in plastic when purchasing it. Regarding medical applications, a dark material can hinder the observation of healing processes (AHMAD et al., 2020). Therefore, according to the desirable application, different bioplastics can be developed with different polymers.

3.3. Composting of bioplastics (disintegration)

All bioplastic formulations (xylan/starch and mixture) disintegrated in less time than that indicated by the ASTM D6400-19 standard adopting the composting technique. No distinguishable fragments were found in less than 84 days, and the separation of fragments of all biomaterials by a sieve (2 mm) was unfeasible after 3-day composting. As a negative control, the bioplastic samples were exposed to 50 °C in a BOD with no compost. After the 3-day composting (bioplastic and compost), the controls with no compost were unchanged in relation to mass loss and morphology/integrity of the bioplastics. The result proved that the bioplastics developed are disintegrable in a short time.

The accelerated disintegration time of xylan/starch bioplastics can be justified by the increase in the microbial population, compost temperature (which favors the disintegration process), and hydrophilicity of the bioplastic matrices. Both solubility and diffusion of water in the bioplastics may have favored disintegration and biodegradation. Similar results were reported by Balaguer et al. (2015), developing bioplastics based on wheat gluten (gliadins monomers) modified with cinnamaldehyde. They fully disintegrated in 4 days of compost burial, and the control (microcrystalline cellulose) showed 100% biodegradation in 14 days. This was a result close to that found in the present study (12 days for disintegration and total biodegradation of the bond paper). However, after 3-day composting, the positive control (bond paper) showed no loss of mass but only a change in color (yellowing).

The presence of fungal hyphae is a qualitative indication of disintegration and biodegradation. Microbial growth was observed in regions of the compost close to the bioplastic. However, no fungal growth was detected in the negative control of composting (low-density polyethylene). The plastic mass also remained unchanged during the composting test. Balaguer et al. (2015) also reported the presence of hyphae in the composting material, after exposure of the bioplastics to compost.

The total disintegration time (3 days) of the bioplastics produced in this study was shorter than that of several other starch bioplastics reported in the literature (TORRES et al., 2011; XIONG et al., 2008). According to Jaramillo et al. (2016), bioplastics made from starch and an addition of yerba mate extract completely disintegrated in 12 days, and Pineros-Hernandez et al. (2017) reported a 14-day period for a complete

disintegrate/biodegrade of bioplastics from thermoplastic starch. Apart from differences in processing and composition of bioplastics and compost, Pineros-Hernandez et al. (2017) and Jaramillo et al. (2016) performed composting at room temperature, which may be the main factor for the reduced time of disintegration and biodegradation shown in the present study. Among other factors (enzymatic activity, community of microorganisms, and humidity), the temperature at which composting is carried out is of vital importance since heat weakens the starch chains (PINEROS-HERNANDEZ et al., 2017).

According to the reduced composting time of the bioplastics in this study, the proposed biomaterial can potentially replace synthetic plastic packaging (when only composting time is taken into account for some applications). These bioplastics are an alternative to reducing environmental impacts, volume of plastic wastes, and governmental expenditures on plastic waste treatments (JARAMILLO et al., 2016). Table 4 shows the ash content, pH, volatile solids, and total solids of the compost before and after composting.

Table 4: Compost properties before and after composting the different bioplastics.

Compost [×]	Ash content (% w/w) ⁺	Volatile solids (% w/w) ⁺	Total solids (% w/w) ⁺	pH
Xylan/starch 10/90% (w/w)	20.18±0.15 ^{a*}	79.81±0.15 ^a	46.82±0.04 ^{acd}	8.23
Xylan/starch 15/85% (w/w)	21.65±0.55 ^a	78.34±0.55 ^a	45.54±0.20 ^{acd}	8.31
Xylan/starch 25/75% (w/w)	21.43±0.52 ^a	78.56±0.52 ^a	47.02±0.17 ^c	8.14
Mixture	20.87±1.35 ^a	79.12±1.35 ^a	47.26±0.15 ^{cd}	8.29
Bond paper	33.2±1.9 ^b	66.81±1.9 ^b	47.68±0.46 ^{cd}	8.39
LDPE	20.16±0.70 ^a	79.83±0.70 ^a	43.29±0.30 ^b	8.03
CBC	19.91±5.9 ^a	80.08±5.9 ^a	44.41±1.85 ^{ab}	8.23

[×] Properties of the compost before and after (3 days) composting and exposed to different materials; CBC = Compost before the composting process; ⁺ = Based on a dry basis;

*Different letters represent statistical difference between the lines in the same column (p <0.05).

Source: Elaborated by the author

Most results of volatile solids showed that the compost did not vary significantly before and after 3-day composting with the tested bioplastics, indicating that the priming effect probably did not occur after the inclusion of the bioplastics (composed basically of organic matter prone to microbial metabolism). Therefore, the presence of the bioplastics did not stimulate the consumption of the organic material of the compost. These organic compounds are probably inaccessible before and after the start of composting.

The priming effect in biodegradation in soil and composting systems is often detected by respirometry, in which the amount of CO₂ produced during material biodegradation is converted to the percentage of mineralization and used as an indicator of the polymer biodegradation. Respirometric assays infer the priming effect when biodegradation is above 100%. The absence of a significant variation between the composts (before and after composting), in relation to volatile solids, indicating no priming effect was exerted. However, it is worth highlighting the importance and relevance of future respirometry tests for confirming the results.

Another factor to be considered is the analysis time of volatile solids. Three days of composting was a short time for observations of the priming effect, because, statistically, no reduction in volatile solids compared to the control was verified. In this period, microorganisms prioritize the consumption of organic matter from bioplastics. After a longer time of analysis, the consumption of the organic matter of the compost, after the stimulus of the bioplastic, might be verified. Bher et al. (2019) observed the priming effect in composts exposed to PLA/starch bioplastics in periods longer than 15 days.

No statistically significant variation was detected in the total solids content of the compost exposed to bioplastics (10/90 and 15/85% w/w xylan/starch) and LDPE compared to the compost at time zero (before composting). However, the concentration of total solids varied for the compost exposed to the mixtures, to 25/75% w/w of xylan/starch blend, and to bond paper. The compost exposed to such biomaterials was significantly different from the initial compost in terms of the total solid count. The increase in total solids in the

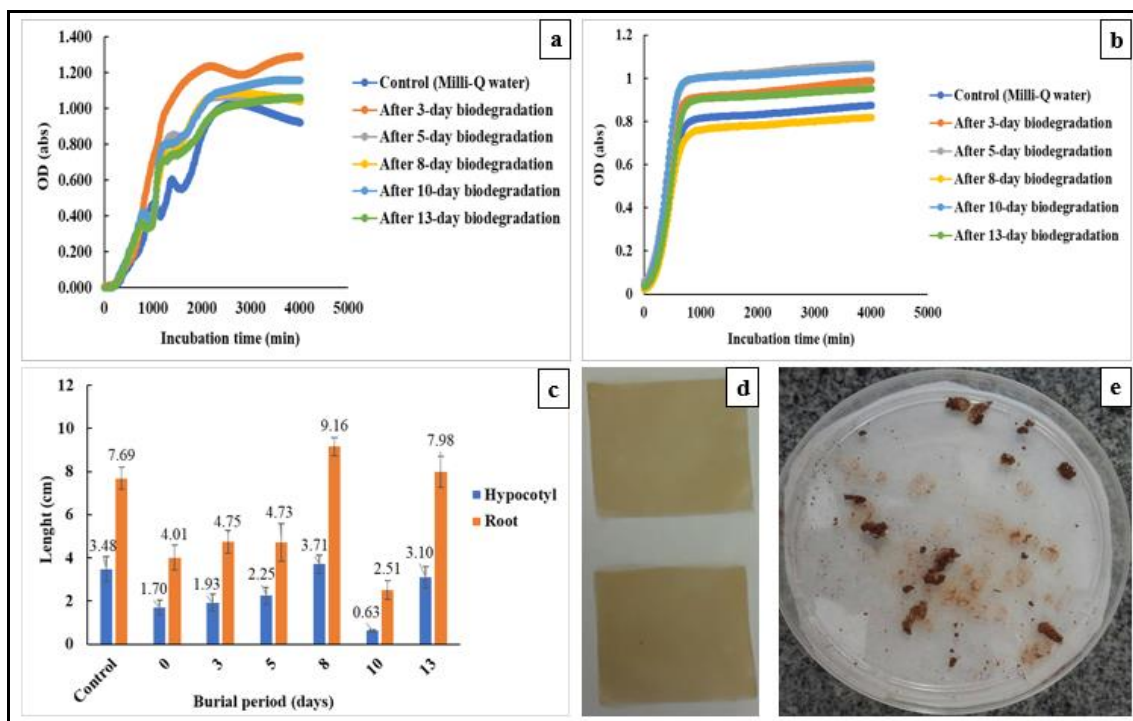
compost, exposed to bond paper and mixture, was probably due to not fully degraded cellulosic fibers in 3-day composting. Therefore, the fibers are difficult to be differentiated from the composting material and may be responsible for the observed mass gain in the compost.

Total and volatile solids before and after composting (Table 4) differ from those reported by Balaguer et al. (2015) (67.20 and 58.31% total dry and volatile solids, respectively) and Gómez et al. (2013) (24.3 and 88.9% total dry and volatile solids, respectively), in relation to the pre-composting stage. The contents of total dry solids were in accordance with the standards (close to 45%), indicating the compost used was suitable for composting compared to the literature (SARASA et al., 2009), and the levels of volatile solids showed a high percentage of organic matter (80.08% (Table 4)). The pH values (Table 3) varied as the compost was exposed to different formulations of bioplastics (xylan/starch and mixture) in a 3-day period and due to the production and release of acids and alkaline substances (SARASA et al., 2009).

3.4. Disintegration of bioplastics by burial in soil

The bioplastic (25/75% xylan/starch blend, w/w) vanished in soil within 13 days. During this period, no disintegration or fragmentation of LDPE (control), a non-biodegradable plastic derived from petroleum, was observed. In 3 days of burial, discoloration and fragmentation were noticeable; prior to soil disintegration, the bioplastics showed a red/orange color, but after 3 days, the fragments were whitish. Moreover, the bioplastic blends had a 50% greater mass loss. No mass variation was observed in other sampling times due to sample-handling issues as it is difficult to clean the bioplastic and separate it from the soil. Washing also resulted in fragmentation and loss of material for weighing. However, disintegration was accompanied by a visual analysis of the soil and the presence of fragments of the blend after sieving (2 mm mesh). Figure 2 (d,e) shows the xylan/starch bioplastic before and after 3-day biodegradation.

Figure 2: Results of biodegradation and ecotoxicity tests



(a) ecotoxicity assessment with *B. subtilis*; (b) ecotoxicity assessment with *S. cerevisiae*; (c) phytotoxicity test with seed of *Cucumis sativus*; (d) bioplastics before biodegradation in the 25/75% xylan/starch (w/w) proportion based on 5% (w/v) total polysaccharide; (e) bioplastics after biodegradation in the 25/75% xylan/starch (w/w) proportion based on 5% (w/v) total polysaccharide; OD= optical density.

Source: Elaborated by the author

The total fragmentation and bioplastic disappearance (absence of fragments of bioplastics after sieving and visual analysis) based on xylan/starch occurred after 13 days of burial in the soil and in only 3 days during composting. Such a difference can be explained mainly by the growth and microbial activity promoted by a nutrient-rich compound. The composting system probably promoted better microbial growth compared to the soil (Table 5).

In general, at the beginning and during composting, a higher number of microbial cells develop in the compost compared to the soil, favoring biodegradation and disintegration. Similar results and the same explanation were provided by Kim et al. (2006), Accinelli et al. (2012), and Nguyen et al. (2016).

Humidity and temperature are other factors to be considered in the biodegradation process, and which may have influenced biodegradation by burial in the soil (compared to composting) (NGUYEN et al., 2016; ACCINELLI et al., 2012; EMADIAN et al., 2017; FOLINO et al., 2020). The moisture used in the present study (24.5%) for soil disintegration was lower than that of the composting process (55%). Soil moisture close to real field conditions (approximately 24%) should be considered since it better represents soil moisture in different environments where most plastic waste accumulates.

The development of bioplastics of low biodegradation time shortens the life cycle of plastic materials in landfills, thus minimizing their environmental impacts (DATTA and HALDER, 2019). Datta and Halder (2019) produced bioplastics ($(146 \pm 10.52) \mu\text{m}$ and $(117 \pm 9.26) \mu\text{m}$) of starch from two plant sources, namely potato and corn, which fully biodegraded between 12 and 15 days after burial in soil (18.67% soil moisture and biodegradation at room temperature). According to LUCENA et al. (2017), the blends of bioplastics made with xylan and gelatin showed 100% biodegradation after 15 days of burial in soil. The authors argued that, due to the non-toxicity of degradation products and the rapid biodegradation, bioplastics based on xylan and gelatin are considered non-polluting materials and can potentially be used in biodegradable packaging applications. Wahyuningtyas and Suryanto (2017) produced starch bioplastics that showed total biodegradation in 9 days after burial in soil. Such fast biodegradation was probably related to the glycerol content used, which influenced the microbial activity due to greater water absorption.

3.5. Soil analysis

Table 5 shows the number of microbial cells (bacteria and fungi), pH and amount of reducing sugars (RS) in the soil before and after (0, 3, 5, 8, 10, and 13 days) disintegration of bioplastics elaborated with 25% xylan and 75% starch.

Table 5: Colony forming unit (CFU), pH and amount of reducing sugars (RS) in the soil before and after disintegration of 25/75% xylan/starch bioplastics.

Assay	Soil	3 rd day	5 th day	8 th day	10 th day	13 th day
pH	4.78	4.83	4.8	5.03	4.94	5.07
RS content (g/g of soil)	0	0	0	0	0	0
Colony forming unit (CFU/g soil)-Bac	8*10 ³	1.38*10 ⁶	2.1*10 ⁵	***	4.1*10 ⁵	2.7*10 ⁴
Colony forming unit (CFU/g soil)-Fung	2.9*10 ²	4.3*10 ²	3.8*10 ²	***	2.8*10 ³	3.3*10 ²

***= analysis not performed.

Source: Elaborated by the author

The soil pH increased during the 13 days of disintegration compared to the soil before burial assays, due to the production of alkaline substances (SARASA et al., 2009). Moreover, due to the increase in the number of bacterial colonies, this increase in soil pH was expected since bacteria generally develop better in environments of pH close to neutrality. However, an increase in fungus colony forming units was observed during disintegration, which is not significant for the reduction in soil pH, i.e., the increase in fungal colonies is more discreet in comparison to that in the number of bacterial cells, since a reduction in soil pH is expected with an increase in the count of fungi (GONÇALVES, 2009). Therefore, the disintegration and biodegradation of bioplastic formulated with 25% xylan and 75% starch may have been influenced by the increase in the number of microbial cells due to the availability of organic matter in the soil.

An increase in the bacterial population during biodegradation is expected in studies on the biodegradation of bioplastics in the soil, as is the case of the present study. Altaee et al. (2016) reported an increase in the microbial population in soil subjected to biodegradation of bioplastics from PHB/TiO₂ (polyhydroxybutyrate/titanium dioxide) over 1 (approx. Log₁₀ (4 CFU/mL)) to 7 weeks (approx. log₁₀ (13 CFU/mL)). Adhikari et al. (2016) claimed the degradation products of the bioplastic blend (poly (butylene

succinate/starch)) did not affect microbial biomass; however, the bacterial population increased more sharply than fungi in relation to biodegradation time (28 days).

The absence of RS in the soil samples (Table 5) indicates disintegration occurred with simultaneous consumption of the sugars released from the bioplastic (glucose and xylose) through microbial activity.

3.6. Ecotoxicity analysis

S. cerevisiae and *B. subtilis* exposition to soil washing samples (50% (v/v) soil washing liquid concentration) did not inhibit their growth before or after the disintegration of bioplastics based on xylan and starch (Figure 2 (a,b)). In general, *S. cerevisiae* cultures exposed to soil washing samples increased from 3, 5, 10, and 13rd disintegration days ($p < 0.05$) (Figure 3e). The only exception was observed on the eighth day when the yeasts were exposed to the washing soil sample ($p > 0.05$). Therefore, the disintegration of bioplastic in soil did not inhibit the growth of *S. cerevisiae*. The same increase in *S. cerevisiae* cell count was observed in colony-forming units, whose treatments (0, 3, 5, 8, 10 disintegration days) showed a CFU/mL (6.9×10^6 ; 8×10^6 ; 9.2×10^6 ; 7.2×10^6 ; 7.2×10^6 , respectively) higher than the control (6.6×10^6) ($p < 0.05$).

Compared to the control (soil sample at time 0), the microbial growth of *B. subtilis* exposed to samples from different days of disintegration showed an increase, which was more significant on the third day. However, the *B. subtilis* cell growth did not vary significantly among days 5, 8, 10, and 13 of disintegration ($p > 0.05$). The fluctuation in the bacterial cell growth (Figure 2a), compared to yeast growth (Figure 2b) resulted from the formation of biofilms and biosurfactants that probably prevented a complete homogenization of *B. subtilis* suspension during the analysis.

Both microbial cells tested (*S. cerevisiae* and *B. subtilis*) may have increased due to microbial substances and metabolites produced throughout the disintegration process of xylan/starch-based bioplastics (Table 5). No sugars from bioplastic disintegration were found in the soil; therefore, the RS from bioplastics did not increase *S. cerevisiae* and *B. subtilis*. Further experiments for a complete determination of the chemical composition of the soil samples might provide additional insights. The increase in microbial cells (Table 5)

can also lead to changes in soil properties and impact microbial diversity and abundance due to the production of metabolites, specific interactions, and pH changes.

The evaluation of ecotoxic effects on plants is also relevant in studies of biodegradation as plants play vital roles in the development and maintenance of soil structure, ecosystem and microbial community functions (BEARE et al., 1995, KUZUYAKOV and BLAGODATSKAYA, 2015; BALESTRI et al., 2019). The ecotoxicity tests with seeds of *Cucumis sativus* analyzed germination, root size, and hypocotyl. The control was germinated only in Milli-Q water. The germination rate in the tests was 100% ($p>0.05$) and no germination inhibition was observed. Both the root and hypocotyl development were more sensitive to the treatments. Since the initial stage of germination requires no substrate, plant tissues are more sensitive to toxic substances than germination (MILBERG and LAMONT, 1997; BALESTRI et al., 2019).

Compared to the controls (Figure 2c), the size (cm) of *Cucumis sativus* hypocotyl indicates the tissue development of the treated seeds was inhibited, except on the eighth (hypocotyl and root) and the thirteenth days (root) ($p>0.05$) of treatment. However, on the other days, the results show a pattern of reduced inhibition of *C. sativus* tissues when exposed to different treatments ($p<0.05$). Disintegration and possible biodegradation process exerted a positive effect on the tissue development, probably due to the production of metabolites that stimulated plant cell division. According to the phytotoxicity results of the soil at day 0 (Figure 2c), toxic substances present in the soil may have also been consumed by microorganisms. The inhibition in the development of *C. sativus* hypocotyl exposed to soil washing at different disintegration times (0, 3, 5, and 13 respectively) ($p<0.05$) was reduced (51.07%, 44.6%, 35.25%, 10.8%).

Regarding the root development, the washing at different biodegradation times - except on the eighth ($p<0.05$) and the thirteenth days ($p>0.05$) - showed inhibition ($p<0.05$), when compared to the control. The root inhibitions were 47.80%, 38.21%, 38.53%, related to the 0, 3, 5 disintegration day, respectively.

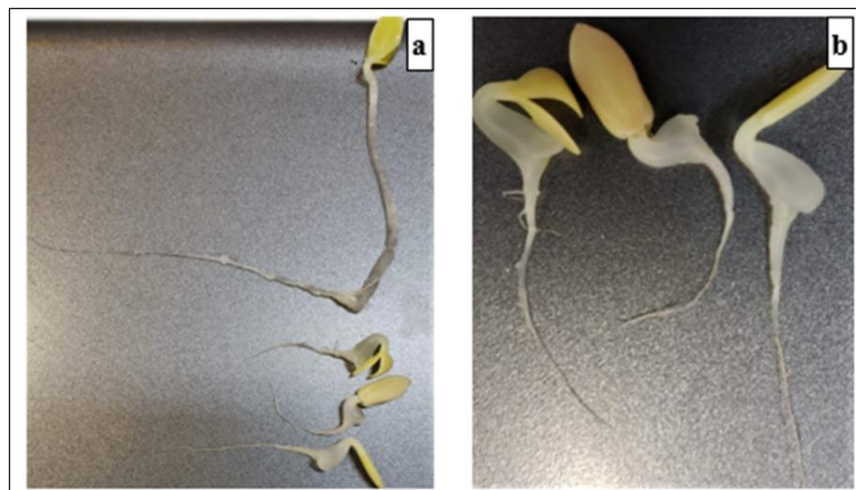
The exposure of the seeds to soil washing on the tenth day clearly inhibited both root and hypocotyl growth (Figures 2c and 3) ($p<0.05$) of *C. sativus*. Compared to the growth at time 0 ($p<0.05$), this result may be related to the production of toxic microbial metabolites for the development of plant tissues, especially due to the increase in microbial

biomass and soil pH change during the disintegration of bioplastics (Table 5). However, this inhibition was not observed in seeds exposed to soil washing on the 13th day, which led to temporary phytotoxicity due to the presence of intermediate metabolic steps with toxic substances (CLOYD and CYCHOLL, 2002) and illustrates the importance of bioplastic ecotoxicity studies. Although temporary, the ecotoxic effects can be relevant for the development of some organisms, with implications for further trophic stages.

Balestri et al. (2019) claimed bioplastics based on starch-vinyl alcohol (Master-bi) and HDPE (high density polyethylene) were toxic to *Lepidium sativum* L. The root was the tissue most affected by the bioplastic, whereas the tested materials did not affect germination. The authors justified the ecotoxic effects with the leaching of toxic substances from bioplastics and common plastics. However, in a scenario of real environmental pollution, metabolites produced by microorganisms from the soil or from the aquatic environment, resulting from biodegradation of such materials, can also exert ecotoxic effects (LUCAS et al., 2008).

Although cucumber seeds are not sensitive to ecotoxicity tests based on germination, they are sensitive to phytotoxicity tests. As observed by Wang et al. (2001), environmental characteristics, such as pH, must be considered in such tests. The authors observed that the pH of soil washing at different biodegradation times of bioplastics (Table 5) was above 3 and below 8. These values are known as germination inhibitors (MALHOTRA, 1930; JANSEN and CRONIN, 1953; BALESTRI et al., 2019). Another relevant factor for seedling development is the availability of nutrients, mainly micronutrients, present in the substrate since they influence plant growth (HANDRECK and BLACK, 1999), which is a factor that pH can influence.

Figure 3: Images of the hypocotyl and root of *Cucumis sativus*



(a) exposed to the liquid of 13-day biodegradation (above)/exposed to the liquid of 10-day biodegradation (below); (b) exposed to the liquid of 10-day biodegradation.

Source: Elaborated by the author

As a series of future follow-up experiments, we suggest analyzing the possible impacts of bioplastics on the environment. Besides biodegradation tests with a wide variety of environmental samples, tests of chemical modifications of polysaccharides that constitute those bioplastics can be prioritized towards the optimization of their properties. Quantitative assays of mechanical and thermal resistances, crystallinity, FTIR, scanning electron microscopy, properties of barrier to different gases, and formulation of bioplastic blends (with xylan, starch and nanocellulose) are also desirable. Other plants and microorganisms shall also be applied towards the continuity of this research, hence a better understanding of ecotoxicity and environmental safety.

Conclusions

Xylan from sugarcane bagasse represents a renewable source to obtain disintegrable bioplastics, which are an interesting alternative for reducing the production and disposal of non-biodegradable plastic wastes. The results of bioplastics ecotoxicity showed the need and importance of studies on impacts of bioplastics on the environment considering the different organisms present in the soil and its quality for sustainable production and disposal of such biomaterials. Although bioplastics are an alternative to petroleum-derived

plastics and benefit from the green industry brand, the accumulation and disposal of any mass-produced residue, regardless of the source material, are known to result in environmental impacts. However, the inadequate management of bioplastics is less likely to harm the environment compared to their petroleum-based counterpart as they are organic materials that are easily metabolized by microorganisms. This study has attested xylan-starch blends and mixtures with α -cellulose and holocellulose as safely adoptable formulations for the production of biodegradable bioplastics. Both disintegration and composting time were significantly shorter than those from petroleum and xylan-starch showed no ecotoxicity in the organisms tested. Further studies must ensure the full-scale application of those materials in different sectors of society and improve their mechanical and gas-barrier properties.

References

- ACCINELLI, C., SACCÀ, M. L., MENCARELLI, M., & VICARI, A. (2012). Deterioration of bioplastic carrier bags in the environment and assessment of a new recycling alternative. *Chemosphere*, 89(2), 136–143. doi:10.1016/j.chemosphere.2012.05.028
- ADHIKARI, D., MUKAI, M., KUBOTA, K., KAI, T., KANEKO, N., ARAKI, K. S., & KUBO, M. (2016). Degradation of Bioplastics in Soil and Their Degradation Effects on Environmental Microorganisms. *Journal of Agricultural Chemistry and Environment*, 5, 23-34. <http://dx.doi.org/10.4236/jacen.2016.51003>
- AHMAD, N., TAYYEB, D., ALI, I., ALRUWAILI, N. K., AHMAD, W., REHMAN, A. UR, & IQBAL, M. S. (2020). Development and Characterization of Hemicellulose-Based Films for Antibacterial Wound-Dressing Application. *Polymers*, 12(3), 548. doi:10.3390/polym12030548
- ALTAEE, N., EL-HITI, G. A., FAHDIL, A., SUDESH, K., & YOUSIF, E. (2016). Biodegradation of different formulations of polyhydroxybutyrate films in soil. *SpringerPlus*, 5(1). doi:10.1186/s40064
- ALVES, R. C., MELATI, R. B., CASAGRANDE, G. M. S., CONTIERO, J., PAGNOCCA, F. C., & BRIENZO, M. (2020). Sieving process selects sugarcane bagasse with lower recalcitrance to xylan solubilization. *Journal of Chemical*

- ASTM D6400-19. 2019. Standard Specification for Labeling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities, ASTM International, West Conshohocken, PA.
- BALAGUER, M. P., VILLANOVA, J., CESAR, G., GAVARA, R., HERNANDEZ-MUNOZ, P. (2015). Compostable properties of antimicrobial bioplastics based on cinnamaldehyde cross-linked gliadins. *Chem. Eng. J.*, 262, 447–455. <https://doi.org/10.1016/j.cej.2014.09.099>
- BALESTRI, E., MENICAGLI, V., LIGORINI, V., FULIGNATI, S., RASPOLLI GALLETTI, A. M., & LARDICCI, C. (2019). Phytotoxicity assessment of conventional and biodegradable plastic bags using seed germination test. *Ecological Indicators*, 102, 569–580. <https://doi.org/10.1016/j.ecolind.2019.03.005>
- BEARE, M. H., COLEMAN, D. C., CROSSLEY, D. A., HENDRIX, P. F., & ODUM, E. P. (1995). A hierarchical approach to evaluating the significance of soil biodiversity to biogeochemical cycling. *Plant and Soil*, 170(1), 5–22. doi:10.1007/bf02183051
- BERGEL, B. F., DIAS OSORIO, S., DA LUZ, L. M., & SANTANA, R. M. C. (2018). Effects of hydrophobized starches on thermoplastic starch foams made from potato starch. *Carbohydrate Polymers*, 200, 106–114. <https://doi.org/10.1016/j.carbpol.2018.07.047>
- BHER, A., UNALAN, I. U., AURAS, R., RUBINO, M., & SCHVEZOV, C. E. (2019). Graphene modifies the biodegradation of poly(lactic acid)-thermoplastic cassava starch reactive blend films. *Polymer Degradation and Stability*. doi:10.1016/j.polymdegradstab.2019.04.014
- BRIENZO, M., SIQUEIRA, A. F. & MILAGRES, A. M. F. (2009). Search for optimum conditions of sugarcane bagasse hemicellulose extraction. *Biochem Eng J.*, 46, 199–204.
- BRIENZO, M., TYHODA, L., BENJAMIN, Y., & GÖRGENS, J. (2015). Relationship between physicochemical properties and enzymatic hydrolysis of sugarcane bagasse varieties for bioethanol production. *New Biotechnology*, 32(2), 253–262. <http://dx.doi.org/10.1016/j.nbt.2014.12.007>
- CLOYD, R. A., & CYCHOLL, N. L. (2002). Phytotoxicity of selected insecticides on

- greenhouse grown herbs. *HortScience*, 37, 671–672.
<https://doi.org/10.21273/hortsci.37.4.671>
- DATTA, D., & HALDER, G. (2019). Effect of media on degradability, physico-mechanical and optical properties of synthesized polyolefinic and PLA film in comparison with casted potato/corn starch biofilm. *Process Safety and Environmental Protection*, 124, 39–62. doi:10.1016/j.psep.2019.02.002
- EDGE, M., HAYES, M., MOHAMMADIAN, M., ALLEN, N. S., JEWITT, T. S., BREMS, K., & JONES, K. (1991). Aspects of poly(ethylene terephthalate) degradation for archival life and environmental degradation. *Polymer Degradation and Stability*, 32(2), 131–153. [https://doi.org/10.1016/0141-3910\(91\)90047-U](https://doi.org/10.1016/0141-3910(91)90047-U)
- EMADIAN, S. M., ONAY, T. T., & DEMIREL, B. (2017). Biodegradation of bioplastics in natural environments. *Waste Management*, 59, 526–536. doi:10.1016/j.wasman.2016.10.006
- EMPRESA BRASILEIRA DE PESQUISA AGROPECUARIA (EMBRAPA). 1997. Manual de métodos de análise do solo; SNLCS: Rio de Janeiro, Brazil.
- FOLINO, A., KARAGEORGIOU, A., CALABRÒ, P. S., & KOMILIS, D. (2020). Biodegradation of Wasted Bioplastics in Natural and Industrial Environments: A Review. *Sustainability*, 12(15), 6030. doi:10.3390/su12156030
- GEYER, R., JAMBECK, J. R., & LAW, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances*, 3(7), e1700782. <https://doi.org/10.1126/sciadv.1700782>
- GÓMEZ, E. F., & MICHEL, F. C. (2013). Biodegradability of conventional and bio-based plastics and natural fiber composites during composting, anaerobic digestion and long-term soil incubation. *Polymer Degradation and Stability*, 98(12), 2583–2591. doi:10.1016/j.polymdegradstab.2013.09.018
- GONÇALVES, S. P. C. (2009). Biodegradação de filmes de PHBV, PCL, PP e blendas pela ação de microorganismos de solo, Tese (Doutorado), Universidade Estadual Paulista “Júlio de Mesquita Filho” (UNESP), Instituto de Biociências, Rio Claro (2009).
- HANDRECK, K., & BLACK, N. (1999). Growing media for ornamental plants and turf. University of New South Wales, Sydney.

- HUANG, C., FANG, G., TAO, Y., MENG, X., LIN, Y., BHAGIA, S., WU, X., YONG, Q., & RAGAUSKAS, A. J. (2019). Nacre-inspired hemicelluloses paper with fire retardant and gas barrier properties by self-assembly with bentonite nanosheets. *Carbohydrate Polymers*, 115219. doi:10.1016/j.carbpol.2019.115219
- JAMBECK, J. R., JI, Q., ZHANG, Y.-G., LIU, D., GROSSNICKLE, D. M., & LUO, Z.-X. (2015). Plastic waste inputs from land into the ocean. *Science*, 347(6223), 768–771. <https://doi.org/10.1126/science.1260879>
- JANSEN, L. L.; CRONIN, E. H. (1953). Halogeton on trial. *Farm & Home Science*, 14, 38-39.
- JARAMILLO, M. C., GUTIÉRREZ, T. J., GOYANES, S., BERNAL, C., & FAMÁ, L. (2016). Biodegradability and plasticizing effect of yerba mate extract on cassava starch edible films. *Carbohydrate Polymers*, 151, 150–159. doi:10.1016/j.carbpol.2016.05.025
- KAZA, S., YAO, L. C., BHADA-TATA, P., & VAN WOERDEN, F. (2018). What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050. In *Urban Development Series. World Bank*: <http://hdl.handle.net/10986/30317>
- KIM, H.-S., KIM, H.-J., LEE, J.-W., & CHOI, I.-G. (2006). Biodegradability of bio-flour filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil. *Polymer Degradation and Stability*, 91(5), 1117–1127. doi:10.1016/j.polymdegradstab.2005.07.002
- KRISTO, E., KOUTSOUMANIS, K. P., & BILIADERIS, C. G. (2008). Thermal, mechanical and water vapor barrier properties of sodium caseinate films containing antimicrobials and their inhibitory action on *Listeria monocytogenes*. *Food Hydrocolloids*, 22(3), 373-386.
- KUZYAKOV, Y., & BLAGODATSKAYA, E. (2015). Microbial hotspots and hot moments in soil: Concept & review. *Soil Biology and Biochemistry*, 83, 184–199. doi:10.1016/j.soilbio.2015.01.025
- LACKNER, M. (2015). Bioplastics-biobased plastics as renewable and/or biodegradable alternatives to petroplastics. In: *Kirk-Othmer Encyclopedia of Chemical Technology*, 6, 1–41. <https://doi.org/DOI:10.1002/0471238961.koe00006>
- LUCAS, N., BIENAIME, C., BELLOY, C., QUENEUEDEC, M., SILVESTRE, F., &

- NAVA-SAUCEDO, J. E. (2008). Polymer biodegradation: Mechanisms and estimation techniques - A review. *Chemosphere*, 73, 429–442. <https://doi.org/10.1016/j.chemosphere.2008.06.064>
- LUCENA, C. A. A., DA COSTA, S.C., ELEAMEN, G. R. D. A., MENDONÇA, E. A. D. M., OLIVEIRA, E. E. (2017). Development of xylan and xylan/gelatin biofilms for production of biodegradable packages. *Polimeros*, 27, 35–41. 1034 <https://doi.org/10.1590/0104-1428.2223>
- MALI, S., GROSSMANN, M. V. E., YAMASHITA, F. (2010). Filmes de amido: produção, propriedades e potencial de utilização. *Semina: Ciências Agrárias*, Londrina, 31(1), 137-156.
- MALHOTRA, R. C. A. (1930). new method of germination and the influence of hydrogen-ion concentration on the germination and growth of *Helianthus annuus* and *Lycopersicum (sic) esculentum*. *Journal Indian Botanical Society*, 9, 218-239.
- MELATI, R. B., SHIMIZU, F. L., OLIVEIRA, G., PAGNOCCA, F. C., DE SOUZA, W., SANT'ANNA, C., & BRIENZO, M. (2019). Key Factors Affecting the Recalcitrance and Conversion Process of Biomass. *Bioenergy Research*, 12(1), 1–20. <https://doi.org/10.1007/s12155-018-9941-0>
- MILBERG, P., & LAMONT, B. B. (1997). Seed/cotyledon size and nutrient content play a major role in early performance of species on nutrient-poor soils. *New Phytol*, 137, 665–672. <https://doi.org/10.1046/j.1469-8137.1997.00870.x>
- MILLER, G. L. (1959). Use of dinitrosalicylic acid reagent for determination of reducing sugar. *Analytical Chemistry Washington*, 31, 3, 426-428.
- MOORE, C. J. (2008). *Synthetic polymers in the marine environment : A rapidly increasing* ., 108, 131–139. <https://doi.org/10.1016/j.envres.2008.07.025>
- NGUYEN, D. M., DO, T. V. V., GRILLET, A.-C., HA THUC, H., & HA THUC, C. N. (2016). Biodegradability of polymer film based on low density polyethylene and cassava starch. *International Biodeterioration & Biodegradation*, 115, 257–265. doi:10.1016/j.ibiod.2016.09.004
- PAPADIMITRIOU, C. A., HARITOU, I., SAMARAS, P., & ZOUBOULIS, A. I. (2008). Evaluation of leaching and ecotoxicological properties of sewage sludge–fly ash mixtures. *Environmental Research*, 106(3), 340–

348. doi:10.1016/j.envres.2007.04.007

- PAULINO, G. S., PEREIRA, J. S., RIBON, A. O. B., EVELINE TEIXEIRA CAIXETA, E. V., & MENDES, T. A. O., (2019). Produção de bioplástico a partir de resíduos de café e seu uso como matriz de liberação de antimicrobianos. *X Simpósio de Pesquisa dos Cafés do Brasil*. ISSN: 1984-9249.
- PENG, X., REN, J., ZHONG, L., & SUN, R. (2011). Nanocomposite Films Based on Xylan-Rich Hemicelluloses and Cellulose Nanofibers with Enhanced Mechanical Properties. *Biomacromolecules*, 12(9), 3321–3329. doi:10.1021/bm2008795
- PEREIRA, P. H. F., WALDRON, K. W., WILSON, D. R., CUNHA, A. P., BRITO, E. S. D., RODRIGUES, T. H. S., ROSA, M. F., & AZEREDO, H. M. C. (2017). Wheat straw hemicelluloses added with cellulose nanocrystals and citric acid. Effect on film physical properties. *Carbohydr. Polym*, 164, 317-324.
- PIÑEROS-HERNANDEZ, D., MEDINA-JARAMILLO, C., LÓPEZ-CÓRDOBA, A., & GOYANES, S. (2017). Edible cassava starch films carrying rosemary antioxidant extracts for potential use as active food packaging. *Food Hydrocolloids*, 63, 488–495.
- RHIM, J. W., & NG, P. K. W. (2007). Natural biopolymer-based nanocomposite films for packaging applications. *Critical Reviews in Food Science and Nutrition*, 47, 411–433.
- RINDLAVA, Å., HULLEMAN, S. H. D., & GATENHOLMA, P. (1997). Formation of starch films with varying crystallinity. *Carbohydrate Polymers*, 34(1-2), 25–30. doi:10.1016/s0144-8617(97)00093-3
- ROWE, R. K., RIMAL, S., & SANGAM, H. (2009). Ageing of HDPE geomembrane exposed to air, water and leachate at different temperatures. *Geotextiles and Geomembranes*, 27(2), 137–151. <https://doi.org/10.1016/j.geotexmem.2008.09.007>
- SÁNCHEZ-SAFONT, E. L., GONZÁLEZ-AUSEJO, J., GÁMEZ-PÉREZ, J., LAGARÓN, J. M., & CABEDO, L. (2016). Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate)/Purified Cellulose Fiber Composites by Melt Blending: Characterization and Degradation in Composting Conditions. *Journal of Renewable Materials*, 4(2), 123-132. doi:10.7569/jrm.2015.634127
- SABIHA-HANIM, S., & SITI-NORSAFURAH, A. M. (2012). Physical Properties of Hemicellulose Films from Sugarcane Bagasse. *Procedia Engineering*, 42, 1390–1395. doi:10.1016/j.proeng.2012.07.532

- SARASA, J., GRACIA, J. M., & JAVIERRE, C. (2009). Study of the biodisintegration of a bioplastic material waste. *Bioresource Technology*, 100(15), 3764–3768. doi:10.1016/j.biortech.2008.11.049
- SCHULZE, C., JURASCHEK, M., HERRMANN, C., & THIEDE, S. (2017). Energy Analysis of Bioplastics Processing. *Procedia CIRP*, 61, 600–605. doi:10.1016/j.procir.2016.11.181
- SUDERMAN, N., ISA, M. I. N., & SARBON, N. M. (2016). Effect of drying temperature on the functional properties of biodegradable CMC-based film for potential food packaging. *International Food Research Journal*, 23(3), 1075-1084.
- THOMPSON, R. C., MOORE, C. J., SAAL, F. S. V., & SWAN, S. H. (2009). Plastics, the environment and human health: Current consensus and future trends. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526), 2153–2166. <https://doi.org/10.1098/rstb.2009.0053>
- TORRES, F. G., TRONCOSO, O. P., TORRES, C., DÍAZ, D. A., & AMAYA, E. (2011). Biodegradability and mechanical properties of starch films from Andean crops. *International Journal of Biological Macromolecules*, 48(4), 603–606.
- XIONG, H., TANG, S., TANG, H., & ZOU, P. (2008). The structure and properties of a starch-based biodegradable film. *Carbohydrate Polymers*, 71(2), 263–26.
- WAHYUNINGTYAS, N., & SURYANTO, H. (2017). Analysis of Biodegradation of Bioplastics Made of Cassava Starch. *J. Mech. Eng. Sci. Technol*, 1, 24–31.
- WANG, X., SUN, C., GAO, S., WANG, L., SHUOKUI, H. (2001). Validation of germination rate and root elongation as indicator to asses phytotoxicity with *Cucumis sativus*. *Chemosphere*, 44, 1711-1721.
- WRIGHT, S. L., THOMPSON, R. C., & GALLOWAY, T. S. (2013). The physical impacts of microplastics on marine organisms: a review. *Environmental Pollution (Barking, Essex : 1987)*, 178, 483–492. <https://doi.org/10.1016/j.envpol.2013.02.031>
- YU, J., ZHU, Y., MA, H., LIU, L., HU, Y., XU, J., WANG, Z., & FAN, Y., (2019). Contribution of hemicellulose to cellulose nanofiber-based nanocomposite films with enhanced strength, flexibility and UV-blocking properties. *Cellulose*, 26, 6023–6034. <https://doi.org/10.1007/s10570-019-02518-6>

CHAPTER V: Holistic analysis of the biomass polysaccharide-based bioplastics development

Abstract

The large population growth and the current consumption habits impacting the environment due to the extraction of natural resources and waste generation. The production and disposal of plastic materials accumulates for a considerable time in the environment and negatively impacts the flora, fauna, and the entire biota of the environment. Therefore, the objective of this study was to elaborate starch-based bioplastics with different concentrations of xylan extracted from sugarcane bagasse, in addition to the inclusion of holocellulose and alpha-cellulose. Ecotoxicity tests of the soil exposed to the bioplastic were performed, with *Saccharomyces cerevisiae* and *Lactuca sativa*. All bioplastic compositions resulted in homogeneous and bubble-free materials, and there was no difference in transparency at 600 nm (except for bioplastic with alpha-cellulose and hemicellulose). However, between 200-400 nm of the wavelength, bioplastics with higher concentrations of xylan reduced the transmittance, probably due to the presence of lignin. The bioplastic with 25% xylan showed a small photoprotective capacity against the yeast *S. cerevisiae* when exposed to UVC light. Solubility increases in acidic simulants with plastics with higher xylan concentration (25% w/w). However, in fatty food simulants the solubility of the bioplastic with 25% (w/w) of xylan was negligible. The disintegration occurred in 16 days in soil with 32.6% of moisture, in the composting system. Due to the higher solubility and reduced crystallinity, the 25% xylan composition resulted in the most efficient disintegration. The addition of xylan, alpha-cellulose, and holocellulose reduced the thermal resistance in relation to the pure starch-based bioplastic, as well as reduced crystallinity with higher concentrations of xylan, except for the addition of alpha-cellulose and holocellulose. The highest tensile strength was with the composition 15/25% (w/w) of xylan/starch (2.99 MPa). The bioplastics disintegration in the soil, after 15 days resulted in the complete inhibition of germination of *L. sativa* seeds. Therefore, this study demonstrated the importance of analysis of bioplastics impacts in different environments.

Keywords: Bioplastic, disintegration, ecotoxicity, solubility, mechanical properties

1. Introduction

Non-biodegradable plastics from petroleum derivatives currently surpassed the production volume of 8.3 billion tons since 1950, of which 6.3 billion tons became waste (GEYER et al., 2017). The plastics annual production is approximately 300 million tons (LEBRETON et al., 2017), with disposal and management generally performed inadequately or inefficiently (CHEN et al., 2021; ROBAINA et al., 2021). The environmental impacts are diverse for fauna, flora, water, and soil, ranging from behavioral alterations (PALANZA et al., 2020), influence on abnormal protein and liver dysfunction (LANG et al., 2008; PROSHAD et al., 2018), plant development (RILLIG et al., 2019; IQBAL et al., 2020), physicochemical and biological soil/water changes (HUERTA-LWANGA et al., 2017; MACHADO et al., 2018; WAN et al., 2019) and overrun of membranes of biological barriers (PRÜST et al., 2020; RAGUSA et al., 2021). All these factors and the ubiquity of plastics in almost all regions of the planet can characterize these materials as a landmark of the unofficial "anthropocentric" era (HARRISON et al., 2018).

The plastic problem that society is currently trying to overcome encourages the development of biodegradable materials and/or of biological origin (KJELDSEN et al., 2018; ZHANG et al., 2019). In such a scenario, the bioplastics elaboration stands out in addition to the possibility of being renewable and biodegradable. The production of this technology does not compete with the use of arable land, reduces the ecological and water footprint when waste is used (KOROL et al., 2020).

Polysaccharides such as starch, cellulose, and hemicellulose are widely used in research on bioplastics elaboration, in addition to the industrial application that is already present. These polysaccharide-based bioplastics show adequate barrier properties to certain gases (CO₂ and O₂) (CAZÓN et al., 2017; KOCIRA et al., 2021), are renewable, and generally biodegradable and biocompatible. Nevertheless, the use of polysaccharides to achieve synthetic plastic characteristics such as mechanical properties, hydrophobicity, solubility, and formation of continuous and homogeneous bioplastics are difficult (GOKSU et al., 2007; LIU et al., 2009; DANG and YOKSAN, 2015; SABETZADEH et al., 2015; SHAH et al., 2016). This difficulty is highlighted for hemicellulose-based bioplastics, mainly of the xylan type (HANSEN et al., 2012). Even with the characteristics of optical,

biodegradable, and soluble in water, obtaining bioplastic with xylan is laborious due to its chemical composition heterogeneity and represents a highly branched polymer.

A critical problem related to plastics is the population perception of these materials, which when consolidated in a general and mistaken way, can result in the accumulation of bioplastics in natural environments and public misinformation (CHOE et al., 2021). It is often common to come across bioplastic development studies that use the terms "Biodegradable", "Biocompatible", "Ecofriendly", "Environmentally safe" and "Non-toxic". This label given to bioplastic may be related to the equality of the terms bioplastic and biodegradable, which is generally considered synonymous (ADAMCOVÁ et al., 2019; DILKES-HOFFMAN et al., 2019). Many of these statements may result from different simulations of environmental conditions because considering the sensitive ecosystem balance between the organisms and the discrepancy of environmental and laboratory variables. Bioplastic cannot be considered biodegradable, environmentally safe, and non-ecotoxic in any environment and bioplastic composition (ADAMCOVÁ et al., 2019; BALESTRI et al., 2019; ZIMMERMANN et al., 2020; CHOE et al., 2021; ABE et al., 2022).

Other approaches that need to be explored to enable the viability and sustainability of bioplastics are the applications and management of possible waste from bioplastics. Even if the annual production volume of bioplastics is approximately 1% (in relation to synthetic plastic) (GEYER et al., 2017), studies show that for the next few years, the bioplastic production projection will increase (MOSHOO et al., 2021). Therefore, the generation of bioplastic residues composed of organic matter of easy microbial assimilation may become a common and problematic residue in the future. Thus, the discussion of possible applications for this waste should be started, in order to financially stimulate the planning and management of bioplastic waste. Similar approaches are applied to plastic and agro-industrial waste. The bioplastic waste recycling approach is still in its embryonic development stage.

In the context aforementioned and the growing social acceptance, there is a need for studies in the area of bioplastic development and application in a holistic way, in which the problem posed on synthetic plastic is not inevitably transferred to bioplastics, thus guiding decision-makers policies (GERASSIMIDOU et al., 2021). This study aimed to develop

bioplastics as a way of reusing agro-industrial plant residues. Mechanical, physicochemical properties as well as whether this material disintegrates in soil and composting systems were verified. However, to develop a sustainable and viable bioplastic, ecotoxicity tests, photoprotective agent, and food coating were addressed in this study.

2. Materials and methods

2.2. Materials

The company São João – Araras-SP supplied sugarcane bagasse, and starch (Exodo científica), glycerin (Synth), glucose (Synth), urea (Neon), H_2O_2 (Synth), glacial acetic acid (Synth), hydrochloric acid (Neon), sodium chlorite (Neon), sodium hydroxide (Neon), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Synth) and NaCl (Synth), PCA medium (NEOGEN) were reagents in P.A degree. Compost formulation materials (vegetable soil, rabbit feed, sawdust, and seed oil) were purchased from a local gardening store. The seeds were supplied by ISLA company.

2.3. Extraction of holocellulose, xylan and α -cellulose

The polysaccharides used in this research (holocellulose, xylan, and α -cellulose), with the exception of starch, were extracted from sugarcane bagasse following the method described elsewhere (ABE et al., 2022).

2.4. Bioplastics elaboration

Xylan and starch-based bioplastics were developed by the casting method (Abe et al., 2022). Xylan was solubilized in microwaves (30 s approximately, with short cycles and agitation), and after the starch addition, the filmogenic solutions were gelatinized for 4 min at 85 °C, and oven-dried at 30 °C for 3 days. The total polysaccharides concentration was 5% (w/v, mass of polysaccharides per volume), in the proportion relation of 10/90; 15/85; 25/75 (% w/w) xylan/starch. We also developed a bioplastic composed of xylan/holocellulose/ α -cellulose/starch (15/5/5/75, % w/w), hereafter mentioned as “mixture”.

2.5. Solubility in food simulants, opacity, and thickness of bioplastic

The solubility in food simulants (test to simulate the behavior of bioplastic in different foods) was tested for xylan and starch-based bioplastics. The simulant acidic (3% acetic acid) and fatty (90% ethanol) solutions were tested in 125 mL flasks with a 30 mL of working volume. Strips of bioplastics were prepared (2.5 x 1 cm) and immersed in the simulating solutions for 24 h at 25 °C. The solubility was determined by relation to the initial mass (previously oven-dried at 50 °C) and the final mass (after 24 h).

Thickness was analyzed by a Mitutoyo micrometer (0.001 mm) reading 6 points (random) on each strip. Opacity was determined by rectangular bioplastic strips adhered to a glass cuvette and read by spectrophotometer (600 nm). Three strips from different parts of each bioplastic formulation were used and the opacity was calculated by dividing the mean absorbance by the mean thickness. Furthermore, the light transmittance through bioplastics was analyzed in 200-800 nm wavelength intervals. Thickness and opacity tests were performed for all bioplastics formulations. All assays (solubility, opacity, and thickness) were performed in triplicate.

2.6. Analysis of the bioplastic as a photoprotector for *Saccharomyces cerevisiae*

The bioplastic with the composition of 25/75% (w/w) xylan/starch was used in the analysis of the photoprotector of the yeast *S. cerevisiae*. This procedure was carried out in a Tecan configured for an assay of 24 h, the wavelength of 600 nm in polystyrene plates (96 wells), 15 min for each recording of optical density with shaking for 15 s before recording. The experiment was set up in three groups, (1) yeast exposed for 2 h to UVC light-uncoated, (2) yeast exposed for 2 h to UVC light-covered by the bioplastic, and (3) yeast not exposed to UVC light. After treatments, the inoculum was transferred to the 96-well plate in triplicate with YPD medium (1% yeast extract, 1% peptone, and 2% sucrose) at a temperature of 30 °C.

2.7. Soil and compost disintegration of bioplastics

The first disintegration test was carried out with the bioplastic of 25% xylan (w/w) and 75% (w/w) of starch in different soil moistures (14.3% and 32.6%). For that same

bioplastic composition (25/75% xylan/starch), the disintegration on the surface of compost was analyzed (ABE et al., 2022). The soil disintegration assay for others bioplastics compositions (10% xylan, 15% xylan, mixture, and pure starch) was performed with the moisture fixed at 32.6%. The incubation temperature was adjusted to 30 °C (soil assay) and 50 °C (composting assay) and the loss of integrity was performed with the photo recording.

2.8. Soil ecotoxicity

20 g of bioplastic pieces (approximately 1.5 x 1.5 cm) were mixed with 200 g of soil (32.6%). The soil was incubated with bioplastics for 5 and 15 days, at a temperature of 30 °C. After sampling times, the soil was washed with water in a solid-liquid ratio of 1:5 (g/mL). Controls were formulated with incubation of the soil without bioplastics exposure. Considering a possible variation in the compositions of bioplastics that can be found on the market, the 20 g of bioplastics was prepared with all the compositions developed in the present study. The soil pH was measured in phmeter equipment.

An aliquot of 4.5 mL of the washes from soils exposed and not exposed to bioplastics was transferred to plate Petri with filter paper and 20 *Lactuca sativa* seeds. The tests were performed in triplicate. Plates were incubated at 22 °C for 5 days. After germination, G% (germination percentage), I% (germination and tissue development inhibition) were calculated based on Papadimitriou et al. (2008).

Cell growth of *S. cerevisiae* was analyzed for 26 h in a Tecan set as reported in Abe et al. (2022). The environmental controls were soil washing after 5 and 15 days without bioplastic in addition to the positive control (inoculum and YPD medium only) and negative control (YPD medium without inoculum). Soil washings with bioplastic was employed to verify the possible impact on yeast growth.

2.9. Morphological analysis, crystallinity, mechanical properties, and thermal resistance

Thermogravimetric analysis was performed in a TGA model Q500 equipment (TA instruments). The thermal profile was made with the mass of bioplastics between 9-11 mg, the initial temperature of 30 °C, the final temperature of 720 °C, the heating rate of 10

°C/min, nitrogen atmosphere and flow of 50 mL/min and environmental conditions of 22 °C and 50% relative humidity.

Dynamic-mechanical analysis for the study of stress curves as a function of the deformation of the samples (item 2.4), were made in DMA equipment (model EXSTAR 600 brand SII Nanotechnology). The analysis conditions were temperature of 30 °C, grip load of 0 to 9.8 N, force rate of 1 N/min, nitrogen atmosphere of 50 mL/min the with bioplastics dimensions of length x width x thickness of 20 mm x 8-10 mm x 0.14-0.21 mm respectively. The ambient conditions were 24 °C and 55% relative humidity. All analyzes were developed in triplicate.

Images of the surface of the bioplastics were obtained by scanning electron microscopy (SEM, EVO-LS-15, Carl Zeiss) operating at 10 kV in a 10.5 to 11.5 mm working distance. Prior to observation, the samples were gold-sputtered.

DSC analyzes were conducted on a PerkinElmer brand DSC model 8500 with an Intracooler II type cooling accessory. The temperature range studied was from 20°C to 250°C at a heating rate of 10°C/min under a nitrogen atmosphere of 20 mL/min. Samples with a mass between 5 to 7 mg were placed in a hermetically sealed aluminum sample holder. The degree of crystallinity (X_c) of starch in the bioplastic was calculated according to the following equation (PILLA, et al., 2010; REIS et al., 2016):

$$X_c(\%crystalinidade) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{w}$$

Where ΔH_m is the enthalpy of fusion obtained in the DSC analysis, ΔH_m^0 is the enthalpy of fusion of 100% crystalline starch (this value is not found in the consulted literature or with a lot of divergence between the authors) and w is the percentage of starch in the bioplastic. In this way, to proceed with the calculations of the crystallinity of the starch/xylan-based bioplastic and of the mixture, the enthalpy value obtained for the pure starch bioplastic was taken as a reference, being this one of 197 J/g. In this way, the calculation of the percentage (%) of crystallinity in the studied bioplastics was performed relative to starch.

2.10. Statistical analysis

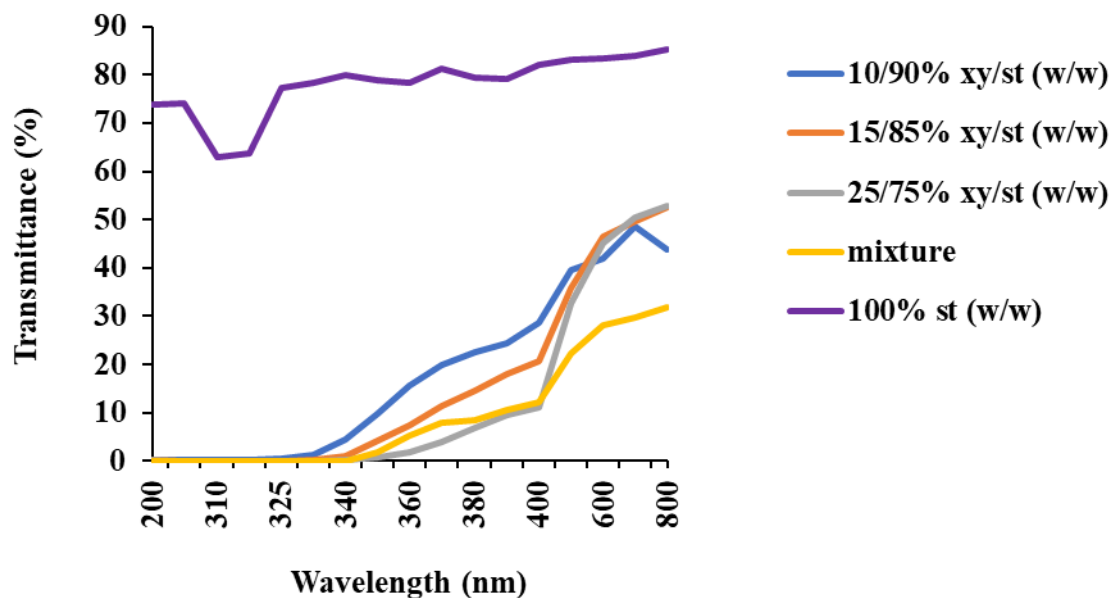
For the enzymatic activity, optical properties, mechanical properties, solubility properties, photoprotector properties, CFU in water, and anaerobic digestion assays, the statistical test used was one-way ANOVA (test Turkey, significance $p < 0.05$) in the Bioestat 5.0 program. Seed ecotoxicity data were evaluated using the R software (R Core Team, 2021). For analysis of normality and homogeneity, the Shapiro-Wilk and Bartlett tests were used respectively. The data did not show a normal and homogeneous distribution and they were submitted to the nonparametric Kruskal-Wallis test, followed by the Dunn post test at 95% significance.

3. Results and Discussions

3.1. Photoprotection property of xylan-starch-based bioplastics

Bioplastics produced from the xylan-starch-based blends showed UV light absorption properties in the three different classes (UV-A (315-400 nm), UV-B (280-315 nm), and UV-C (100-280 nm), (Figure 1). This property is probably due to the presence of phenolic macromolecules (lignin) associated with xylan. Yu et al. (2019) exhibited the same observation regarding the influence of phenolic compounds bond to xylan. Based on our knowledge, this is the first study to develop a bioplastic with UV light blocking properties from xylan mixed with starch.

Figure 1: Light transmittance at 200-800 nm wavelength through bioplastic.



xy= Xylan. st= Starch

Source: Elaborated by the author

The starch-based bioplastic elaborated with 10% xylan showed a large difference in the transmittance results when compared then pure starch-based bioplastic. Accordingly, the property of reducing the transmittance and greater absorbance of light at the UV wavelength was attributed to the xylan addition in the bioplastic composition. A xylan higher concentrations bioplastic resulted in a reduction in UV light transmittance (Figure 1). The same result was observed by Yu et al. (2019) from the increased load of xylan in nanocellulose composites.

The developed bioplastic showed potential for applicability in fresh food packaging, due to protection against UV light, which is responsible for reducing the quality of foods such as milk (MESTDAGH et al., 2005; YANG et al., 2020) and its derivatives, among other fatty foods. This detriment to the quality of food by the action of light is the result of the lipid oxidation process (development of aromas, flavors, color change, and nutritional value impairment) (ADDIS, 1986). The lipid peroxidation mechanism or lipid oxidation occurs through the formation of free radicals and their action on the lipid molecules, extracting electrons from them (FALOWO et al., 2014).

Xylan is reported in other studies as a polysaccharide with potential for photoprotective applications. In the study of Yu et al. (2019), the increase in xylan concentration from up to 50% (wt) resulted in a reduction in transmittance (325 nm) from 75.1% to 28.2%. In the same study, the addition of another type of hemicellulose (glucomannan) depicted a reduction in transmittance at 325 nm. However, less marked than the nanocellulose and xylan-based bioplastics. In the study of Yang et al. (2020), the bioplastic of carboxymethyl-xylan and heat-treated xylan (carbon dots derived from xylan) presented a higher transmittance in the range of 200 nm and 400 nm, when compared to the results obtained in the present study. The use of xylan (reagent) without lignin by Yang et al. (2020) can justify this difference in the results.

The transmittance results of the present study (bioplastic with 25% xylan) at the wavelength 200 nm (0.17%), 350 nm (0.7%), and 400 nm (11.16%) were lower than the results of Araújo et al. (2018), at the same wavelength range (0.50%, 78.73%, and 80.3%) from protein-based bioplastics derived from fish. Thus, aforementioned the bioplastic developed with xylan and starch showed greater potential about the barrier against UV light. Other studies of bioplastics developed with starch and different materials, addressed the bioplastics ability to act as a cover/mulch and photoprotective material to foods, in addition to medical applications due to the harmful effects of UV light on human skin (SHIKU et al., 2004; SIREROL et al., 2015; TEE et al., 2016; NARAYANAN et al., 2017; YANG et al., 2020). The present study showed that the bioplastic developed has a lower transmittance in the length of UV light compared to polyethylene (SHIKU et al., 2004; TEE et al., 2016). Thus, characterizing the superiority of xylan-starch-based bioplastics with disintegration, biocompatibility, renewable, and photoprotection property.

Contrary to what is desired with the bioplastic concerning the transmittance in the range of UV light (200-400 nm), related to visible light length, it is interesting to obtain transparent bioplastics, that is, a high transmittance is required. The transparency of the bioplastic is interesting for medical healing applications, allowing to visualize the injured tissues and the healing process (AHMAD et al., 2020). Another important factor that transparent bioplastics have is the possibility of viewing packaged products, meeting a commercial need. The passage of light through the biomaterial also has advantages in applications in agriculture. Considering the need for plants to capture visible radiation, such

as blue and red light, light stimulates the growth of plants and the synthesis of chlorophyll (POUDEL et al., 2007; YANG et al., 2020).

The bioplastics developed are transparent, and xylan higher concentrations insertion did not increase the transparency value (Figure 2, Table 1). Bioplastic with alpha-cellulose and holocellulose (mixture), was the composition that resulted in the least transparent bioplastic, a characteristic that probably comes from lignin associated with hemicellulose and cellulose fibers.

Figure 2: Bioplastics elaborated with xylan and starch.



(a)= 10/90% (w/w) xylan/starch, (b)= 15/85% (w/w) xylan/starch, (c)= 25/75% (w/w) xylan/starch.

Source: Elaborated by the author

Table 1: Transparency value of xylan and starch-based bioplastics

Bioplastic (% w/w)	Transparency value (Abs _{600nm} /thickness)	Thickness (mm)
10/90 xylan/starch	1.63 ± 0.19 ^{a*}	0.18 ± 0.01
15/85 xylan/starch	1.73 ± 0.06 ^a	0.19 ± 0.01
25/75 xylan/starch	1.72 ± 0.11 ^a	0.20 ± 0.01
Mixture	2.58 ± 0.06 ^b	0.21 ± 0.01

*= Different letters represent statistical difference (p<0.05).

Source: Elaborated by the author

Figure 3b depicts the effect of UV light (UV-C) on the growth of the yeast *S. cerevisiae* exposed or protected by the blend of 25/75% xylan/starch (w/w). Even though the difference in the sample exposed to UV light without protection and the one exposed with protection was small, there was a statistical difference ($p < 0.05$). The control experiment (not exposed to UV) and the exposure with the bioplastic protection did not present a significant difference ($p > 0.05$). These results, together with the transmittance between 200-400 nm, highlight the possible photoprotective role of the bioplastic elaborated in the present study.

According to the results, xylan-starch-based bioplastics and those developed with alpha-cellulose and holocellulose show potential for food protection blocking UV light. In addition, bioplastic showed potential for applications in agriculture, such as covers applications. UV light, especially UV-B, is widely studied concerning soil health and different environments (PIERISTÈ et al., 2020). It can affect the microbial community through damage to the genetic material of microorganisms, which occurs through the formation of cyclobutane pyrimidine dimers and pyrimidine (6–4) pyrimidinone photoproducts. That is, DNA replication and microbial RNA transcription are affected (PIERISTÈ et al., 2020; PULLERITS et al., 2020).

Reduction of fungal hyphae and spore germination may be the result of exposure to high doses of UV light (MOODY et al., 1999; VERHOEF et al., 2000). In the study of Lin et al. (2015), microbial respiration was reduced when organic matter was exposed to UV light in the summer period, which may be related to the nitrogen reduction in the litter. Therefore, the bioplastics application in agriculture can be beneficial since UV light can cause changes in the processes of nutrient cycling, microbial decomposing activity, and composition of the microbial community (JACOBS et al., 2001; LIN et al., 2015; PIERISTÈ et al., 2020).

3.2. Solubility in food simulants

The blend of bioplastics based on xylan and starch showed high solubility in the solution of simulating acidic foods (Figure 3a). The acid simulant may have solubilized the xylan and starch polymers, thus solubilizing the organic material in the solution. In

addition, the hydrophilic acid solution, through the polar groups, reacts with the hydroxyl groups of the polymers (MUGWAGWA and CHIMPHANGO, 2020), and these solubilize part of the mass in bioplastic.

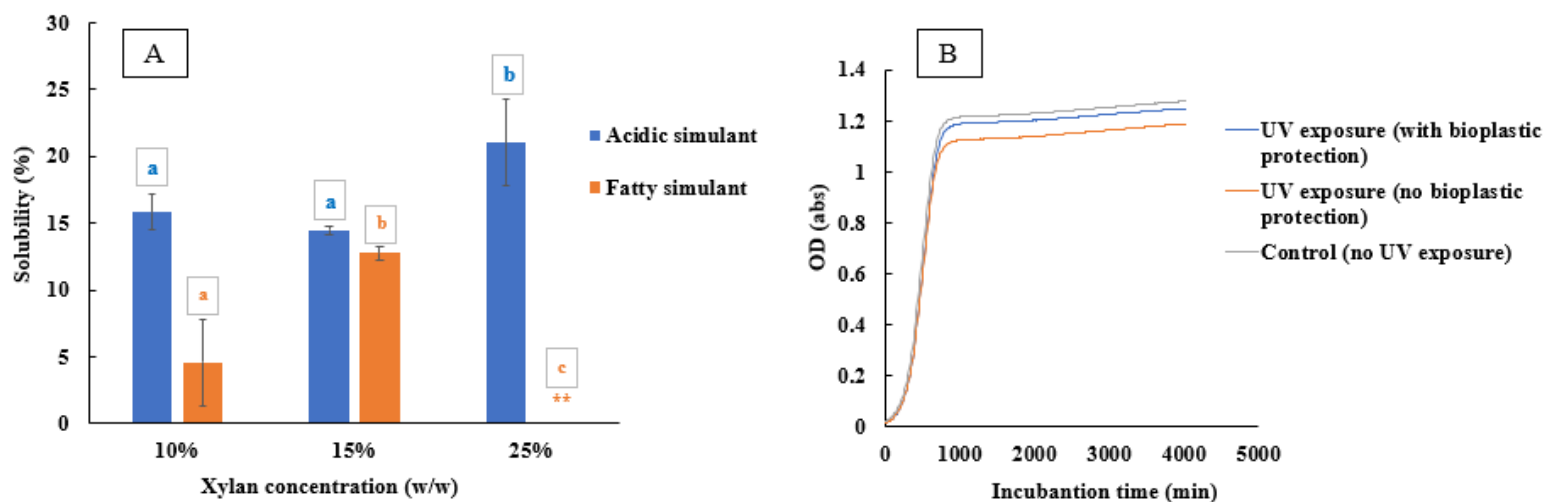
The increase in the bioplastic solubility in acidic simulants with higher concentrations of xylan may be due to the addition of higher loads of hydrophilic polysaccharides in the polymeric matrix. The pure starch-based bioplastic was not tested for solubility in food simulants, however, even though it represents a hydrophilic polymer, the interactions between the starch chains were stronger, as indicated by TGA tests. Thus, the interactions between xylan and starch may also have influenced the solubility in simulants food assays. The interactions between polymers are indicated in the literature as an influence on the solubility property (MUGWAGWA and CHIMPHANGO, 2020). Therefore, to reduce solubility, the optimization of bonds between polymers should be studied.

Regarding solubility in fatty food simulants, the bioplastic elaborated with xylan and starch showed potential for application in the packaging and coverage of these types of foods. In relation to bioplastics formulated with 10 % (w/w) and 25 % (w/w) of xylan, the increase in the hemicellulose load resulted in a reduction of bioplastic solubility in fatty simulants (in relation to the higher concentration of xylan (Figure 3b), no alteration in the bioplastic mass was detected). However, even the bioplastic with 10 % xylan showed low solubility in the simulant in question (4.6%). The reason for the low bioplastic solubility in the fatty simulant in comparison to the acidic simulant, in the present study, is probably due to the reduction of hydroxyl groups in the fatty simulant (FORTUNATI et al., 2012; MUGWAGWA and CHIMPHANGO, 2020). This reduction in the polar character consequently reduces the interactions between the food simulant with the bioplastic matrix.

In the study of Mugwagwa and Chimphango, (2020), the arabinoxylan-based bioplastic showed lower solubility in fatty food simulants (approx. 24%), compared to solubility in acidic simulant (approx. 32%). The addition of acetylated nanocellulose is an alternative to mixing with hemicellulose to reduce the solubility of bioplastics in fatty, acidic, and alcoholic simulants (MUGWAGWA and CHIMPHANGO, 2020). The bioplastic developed in the present study may be studied in the future in applications of biosachet or biopouch, as approached by Mulyono et al., (2015) in the elaboration of

starch-based bioplastics. Based on Mulyono et al., (2015), cassava and tapioca starch-based bioplastics proved to be suitable for packaging vegetable oils and sweet soy sauce.

Figure 3: Cell growth of *S. cerevisiae* exposed to UV light and bioplastic solubility in food simulant.



A= Bioplastic solubility in different food simulants; B= Growth of *S. cerevisiae* after exposure to UV light with and without protection *= Different letters represent statistical difference ($p < 0.05$).

Source: Elaborated by the author

3.3. Mechanical, morphological, and thermal properties of bioplastics

The xylan addition to the bioplastics at any concentration reduced the thermal stability of the material when compared with the pure starch formulation (Table 2). Even the bioplastic named mixture (xylan/holocellulose/ α -cellulose/starch), which due to the cellulose presence (high crystallinity) was expected to depict greater thermal resistance, presented a T_{max} lower than the pure starch-based bioplastic. The T_{max} refers to the temperature at which the thermal disintegration is maximum or related to the heat needed to overcome the energy bond in the carbon net (FARIVAR et al., 2021). Therefore, due to the need for thermal stability of thermoplastics during processing, and considering the same

measure was used for xylan-cellulose-based bioplastics (GORDOBIL et al., 2014) and starch (OLUWASINA et al., 2021), in this study the $T_{\max}$ was used for the measurements.

The lower crystallinity due to xylan branches (arabinoxylan), in addition to the interaction reduction between polysaccharides, may justify the reduced thermal resistance of xylan and starch-based bioplastics. A possible plasticizing effect of hemicelluloses in reducing thermal stability is known (ILYAS et al., 2018; NORDIN et al., 2018). The higher $T_{\max}$ value in the bioplastic with 25% (w/w) xylan can be a result of the better interaction between the starch and the xylan polymers, which was not evident in the tensile strength. However, it could be confirmed due to the formation of a surface without cracks, voids, and smoother (Table 2). Although lignin (present as a residue in the xylan) shows a wide thermal degradation range (250-600 °C) and is generally more thermally stable than polysaccharides (XIAO et al., 2001), a lignin state “hydrolyzed lignin” (by means of alkaline processes), can show the maximum degradation at 250 °C, and thus reduce the $T_{\max}$ of polysaccharides such as xylan (TEDESCHI et al., 2020). As in the studies of Xiao et al. (2001) and Tedeschi et al. (2020), Table (2) shows that the xylan present in bioplastics increases charcoal at 600 °C, probably due to the lignin content.

As in the case of thermal stability, and demonstrated in scanning electron microscopy images, the reduced interaction between the polymers may have resulted in a reduction in the tensile strength of starch-based bioplastics with xylan, in addition, it can be also understood for the called mixture formulation. Similar to the results in Table (2), Gáspár et al. (2005) and Chen et al. (2009) observed that starch-based bioplastics with cellulose depict lower tensile strength than pure starch ones. This impact on starch-based bioplastic from lignocellulosic components, such as cellulose, is a result of the reduction in the aspect ratio (width-to-thickness), which is related to the optimization of hydrogen bonds between the polysaccharides and allows the homogeneous dispersion of fillers in the matrix (XIE et al., 2015).

The results of the tensile strength of the present study were similar to the results by Goksu et al. (2007), which used 8-14 % (w/w) of xylan (from cotton stalk), glycerol (14.2-25 %), and obtained elongation and tensile strength between 45.56-56.76 % and 1.08-1.39 MPa, respectively. Freitas et al. (2021) obtained starch-based bioplastic with lignin (2-8% w/w) and 30 % plasticizer varying the tensile strength from 0.55-0.75 MPa approximately.

Another similar result was found in the study by Sabiha-Hanim and Siti-Norsafurah. (2012), in which sugarcane bagasse xylan resulted in bioplastic with the tensile strength of 0.31-1.72 MPa. However, the results obtained (Table 2) are low than polyethylene plastic, hydroxypropyl cellulose, and methylcellulose bioplastic, ranging between 15 and 60 MPa (THARANATHAN, 2003). Apparently, 15 % xylan together with 85 % starch (w/w) resulted in a higher tensile strength composition, however, elongation did not follow the trend (increased tensile strength and reduced elongation). More studies should be carried out with xylan and starch considering their heterogeneity and moisture absorption, as greater water particles uptake intertwined with the polymers network results due to plasticizer effect (PEROTTO et al., 2020).

Figure 4a shows the DSC curve of the pure starch-based bioplastic obtained in the first heating of the sample. There is a broad endothermic peak between 70 °C and 160 °C, which may be related to sample melting. The onset temperature was 81°C, with a peak temperature of 107 °C and an enthalpy of 197 J/g. In the literature, there is no consensus on such an endothermic event, and many studies treat it as a starch gelatinization process. Gelatinization is defined as an order-disorder transition that involves the disruption of the molecular organization within starch granules, under heating and in the presence of plasticizers (water, for example). By comparison with synthetic polymers, it can be proposed that the temperature dependence of this loss of crystallinity varies with the botanical origin of the starch, the polymorphism of the crystals, its degree of perfection, the chain length involved in the crystalline unit, and the amount of plasticizer used. Such an event is reported to occur over a wide temperature range of 15 to 145 °C with an average enthalpy of 113 J/g (SCHLEMMER, et al., 2010). However, it should be noted that the starch analyzed in the present study was already in the form of bioplastic, that is, it was a processed starch subjected to shear and temperature in the presence of water, transforming it into a molten material also known as thermoplastic starch (TPS). As a DSC analysis was performed on this material, it must be that the endothermic event, similar to synthetic polymers, is in fact the fusion of the semi-crystalline structure of thermoplastic starch.

The crystallinity of starch is mainly attributed to amylopectin (TESTER et al., 2004). In this way, with heating, the crystalline parts of the starch change from the ordered crystalline solid-state to the departed liquid state (melting of amylopectin crystals). Figure

4b shows the DSC curves for the starch bioplastic samples; mixture; starch/10% xylan; starch/15% xylan; starch/25% xylan. All of them are found to have an endothermic peak in their thermal profile. Table 4 shows a summary of the data obtained from the DSC curves of the bioplastics studied in the present study.

The increase in the xylan concentration decreased the initial temperature, peak temperature, final melting temperature as well as melting enthalpy value, and crystallinity (Figure 4b, Table 3). One possible explanation is that xylan, through the formation of new hydrogen bonds in starch-based bioplastic, hinders the mobility of the polymer chain, generating more amorphous regions in the starch-based bioplastic (ABDULKHANI, et al., 2019). The literature (ABDULKHANI, et al., 2019; LUCENA, et al., 2017; GOKSU, 2007) reports that pure xylan has a high value of glass transition temperature, mentioning the value of approximately 240 °C. On the other hand, it is known that the addition of plasticizers in filmogenic solutions of xylan induces changes in the three-dimensional organization of molecules and, therefore, in their functional properties, such as the reduction of their Tg. Such phenomenon was confirmed in the DSC curves with the presence of xylan. It can be observed in the DSC curve of the bioplastic with 10% xylan, a small deviation from the baseline towards the endotherm in the region of 171 °C, which may be related to the Tg of the xylan. This phenomenon is not observed for the 15% xylan bioplastic. However, for the 25% xylan bioplastic, there was also the presence of a deviation from the baseline in the endothermic direction right after the starch melting peak, and the measured Tg was 126 °C. For the mixture bioplastic, there was an increase in the initial, onset and peak temperatures in relation to the sample of pure thermoplastic starch and bioplastic with xylan. The measured crystallinity was also higher for mixture bioplastic than the xylan ones. In this case, it can be stated that, despite the fact that xylan reduces the bioplastic crystallinity, the presence of cellulose contributed to a little increase in the crystallinity of the film obtained.

Considering that hemicellulose-based bioplastic, such as xylan, has a high degree of ramifications, amorphous regions, and hydroxyl groups, the performance of this material in relation to thermal and mechanical resistance can be compromised when they are applied in their unmodified form (ZHAO et al., 2020). Furthermore, the type and botanical source

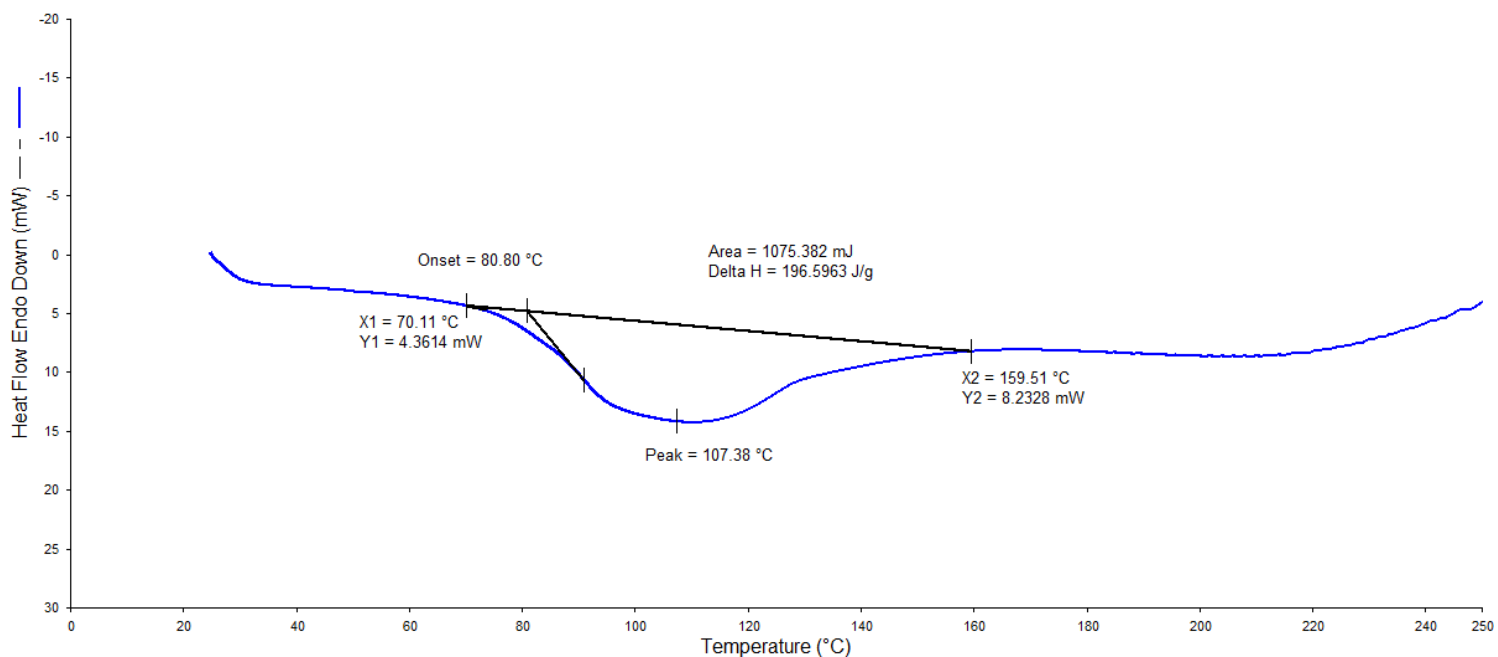
from which hemicellulose is extracted also influence the properties of the bioplastic (SHAO et al., 2019; ZHAO et al., 2020).

The modifications of the xylan, from the specific enzymatic tailoring, such as the arabinose removal (arabinoxylan), result in an increase in crystallinity (HÖJE et al., 2008; HEIKKINEN et al., 2013). Thus, a bioplastic with polysaccharides that is more difficult to face thermal degradation can be achieved. Acetylated nanocellulose and acetylated bleached xylan formed bioplastics with improved mechanical and thermal properties compared to non-acetylated and unreinforced polymers (GORDOBIL et al., 2014).

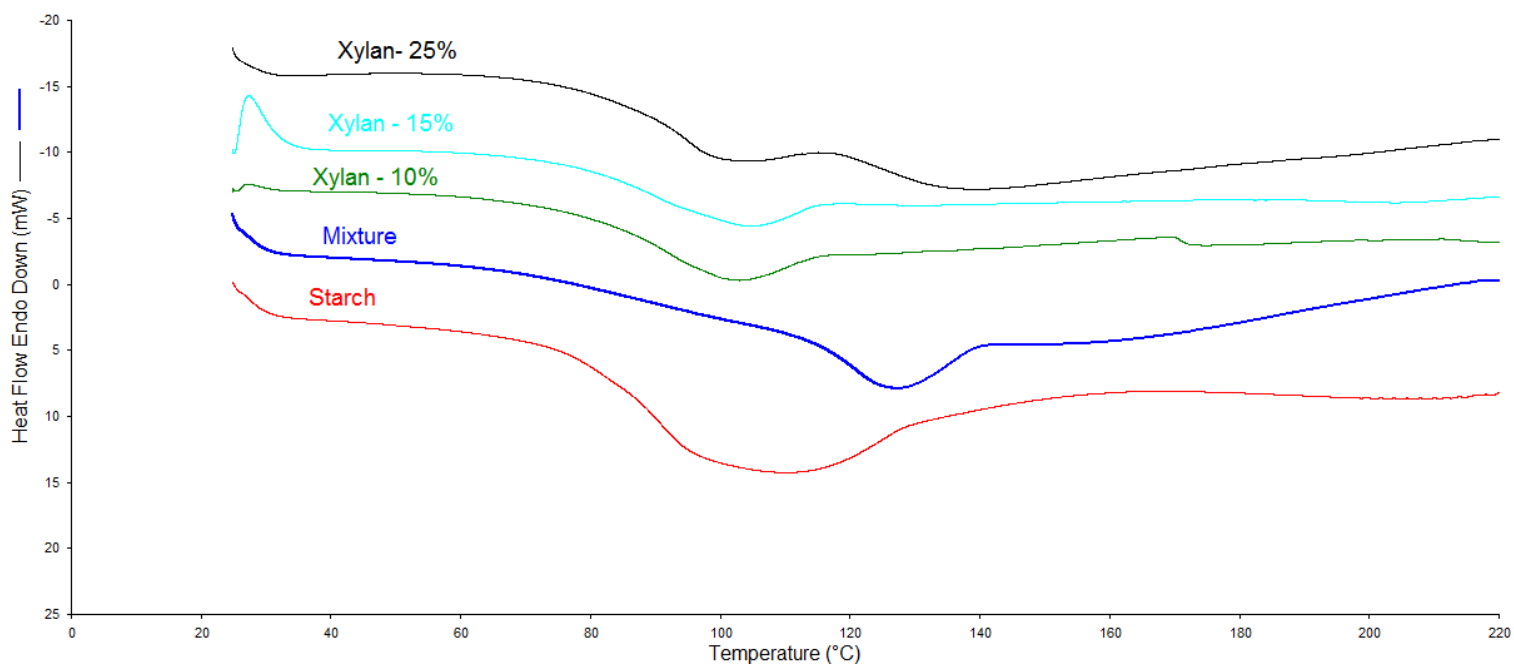
In addition to optimizing the gelatinization process (time and or temperature), due to the presence of non-gelatinized starch granules (Table 2), these approaches to improve the physicochemical properties of bioplastics must take into account the biodegradation characteristic of these materials, as such changes impact solubility, crystallinity and steric hindrance. All these changes influence the process of biodegradation and enzymatic degradation (MITCHELL et al., 1990; GLASSER et al., 1995; RIVARD et al., 1995; TSERKI et al., 2006; ŠÁRKA et al., 2011; ARNLING BÅÅTH et al., 2018; NEVORALOVÁ et al., 2019; OLUWASINA et al., 2021).

Figure 4: Thermal behavior of bioplastics by DSC analysis

a



b



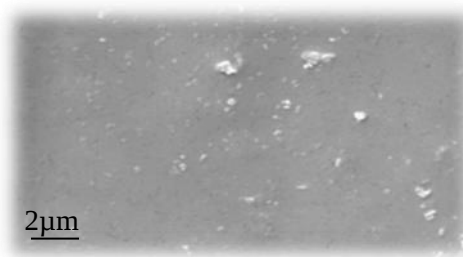
a= Thermal behavior of pure starch bioplastic, b= Thermal behavior of different bioplastic compositions.

Source: Elaborate by the author

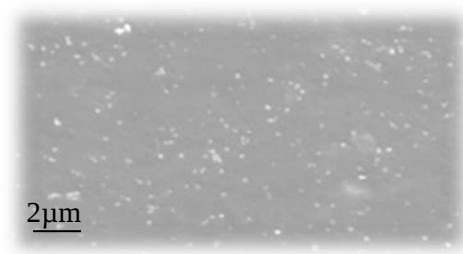
Table 2: Mechanical, morphological, and thermal properties of bioplastics

Bioplastic composition (%, w/w)	Tensile strength (MPa)	Elongation (%)	T ₅₀ (°C)	T _{max} (°C)	Residue 600 °C (%)	SEM
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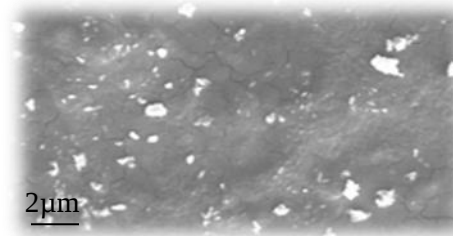
Pure starch 1.21^{a*}±0.09 11.06^a±2.74 297.9 324.85 1.55



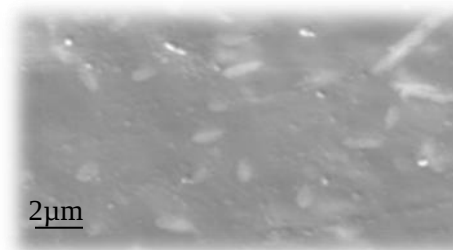
10/90
xylan/starch 0.89^a±0.09 27.58^b±6.17 289 287.40 16.33



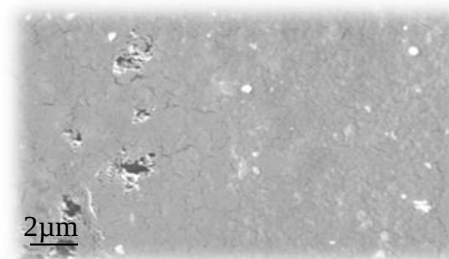
15/85 2.99^b±1.6 18.30^a±1.74 290.18 287.40 16.89
xylan/starch



25/75 0.89^a±0.12 13.52^a±1.94 289.09 295.80 19.42
xylan/starch



Mixture 0.82^a±0.06 10.24^a±0.9 297.10 287.68 18.22



*= Different letters represent statistical difference (p<0.05).

Source: Elaborated by the author

Table 3: Data obtained from DSC curves of starch bioplastics as well as relative crystallinity.

Bioplastic composition (%, w/w)	T _{initial} (°C)	T _{onset} (°C)	T _{peak} (°C)	T _{final} (°C)	ΔH (J/g)	X _c (%)
Pure starch	70	81	107	160	197	-
10/90 Xylan/starch	66	84	101	118	35	20
15/85 Xylan/starch	65	83	104	120	35	21
25/75 Xylan/starch	72	89	100	117	16	11
Mixture	84	111	126	144	38	26

Source: Elaborated by the author

3.4. Soil moisture influence on bioplastic disintegration and composting system

Xylan and starch-based bioplastics (25/75% w/w) disintegrated in the soil and a composting system (Figure 5). The bioplastics elaborated in the present study showed application potential when it is desired to obtain disintegratable (and possible biodegradable) and renewable materials. Based on this conception, the present results follow the trend of the bioeconomy, mainly regarding the mitigation or reduction of the

problems resulting from synthetic plastics accumulation (JARAMILLO et al., 2016; FREITAS et al., 2021) with the use of agro-industrial waste.

Abe et al. (2022), showed that the bioplastic resulted in a total disintegration in 13 days, featuring faster disintegration than in the present study (using the same bioplastic composition and soil disintegration temperature). This result can be justified by the bioplastic burial process applied by the last study cited, in which the results of the present study refer to the bioplastic exposure to the soil surface, thus reducing the contact surface of the bio-based material with the soil. Starch-based bioplastics in the study by Datta & Halder, (2019) depict different rates of biodegradation when exposed to simulants from different environments.

Based on the aforementioned, the present study evaluated the disintegration (visual analysis) of the xylan/starch-based bioplastic at different moistures. After the 16th day of biomaterial exposure on the soil surface with 32.6% moisture, it was not possible to detect bioplastic fragments. However, even after the 40th day of exposure (soil with 14.3% moisture), the bioplastic did not show total fragmentation and disintegration. The study of different factors that influence the biodegradation/deterioration of bioplastics (or common plastics), such as different environments, pH, temperature, humidity, microbial community, chemical agents, the addition of nutrients, the polymer's chemical structure, among other biotic and abiotic factors, is necessary to understand the materials disintegration and biodegradation process (KIM et al., 2006; LUCAS et al., 2008; NGUYEN et al., 2016; DATTA et al., 2019). In relation to moisture, it is known that the different groups of microorganisms, such as fungi and bacteria, have a varied range of moisture for growth, therefore, processes such as polymer disintegration and biodegradation are influenced by moisture, as water acts as a solubilizer and is necessary for microbial metabolism.

Even in both soil moistures, it is noted that on the 2nd day and mainly on the 5th day of exposure, there was microbial growth in the peripheral soil to the bioplastic (Figure 5). With accentuated yellowish spots on the bioplastic surface. However, on the 2nd day and 5th day of bioplastics on the soil surface with higher moisture, a more gelatinous and solubilizing appearance is observed. Probably, the greater solubilization of the bioplastic in soil with 32.6% moisture allowed a greater fragmentation degree, and thus an increase in the contact surface of biotic and abiotic factors with the bioplastic. Such changes in surface

and bioplastic integrity, i.e., erosion and fragmentation processes, were also observed in starch-based bioplastics with Kraft lignin (FREITAS et al., 2021).

It is worth mentioning that based on the solubility (27.93) of the 25% w/w xylan bioplastic in water (ABE et al., 2022), it is possible that higher solubilization in soil with a moisture content of 32.6%, resulted in greater availability of carbohydrates in the soil. Therefore, similar to the composting effect, higher soil moisture may have stimulated microbial growth, and thus a faster disintegration than in soil with lower moisture.

Composting system assay resulted in faster bioplastic disintegration of 25/75% w/w xylan/starch composition (Figure 5). In addition to the higher humidity (55%), the temperature of 50 °C is a factor that results in the weakening of the bonds between the polymer chains, and thus, accelerating the bioplastic disintegration. Another factor of composting that may have influenced the accelerated disintegration in relation to the soil would be the greater number of microbial cells. The addition of nutrients in the composting system results in a stimulus for microbial proliferation at the beginning and during the composting process (KIM et al., 2006; ACCINELLI et al., 2012; NGUYEN et al., 2016).

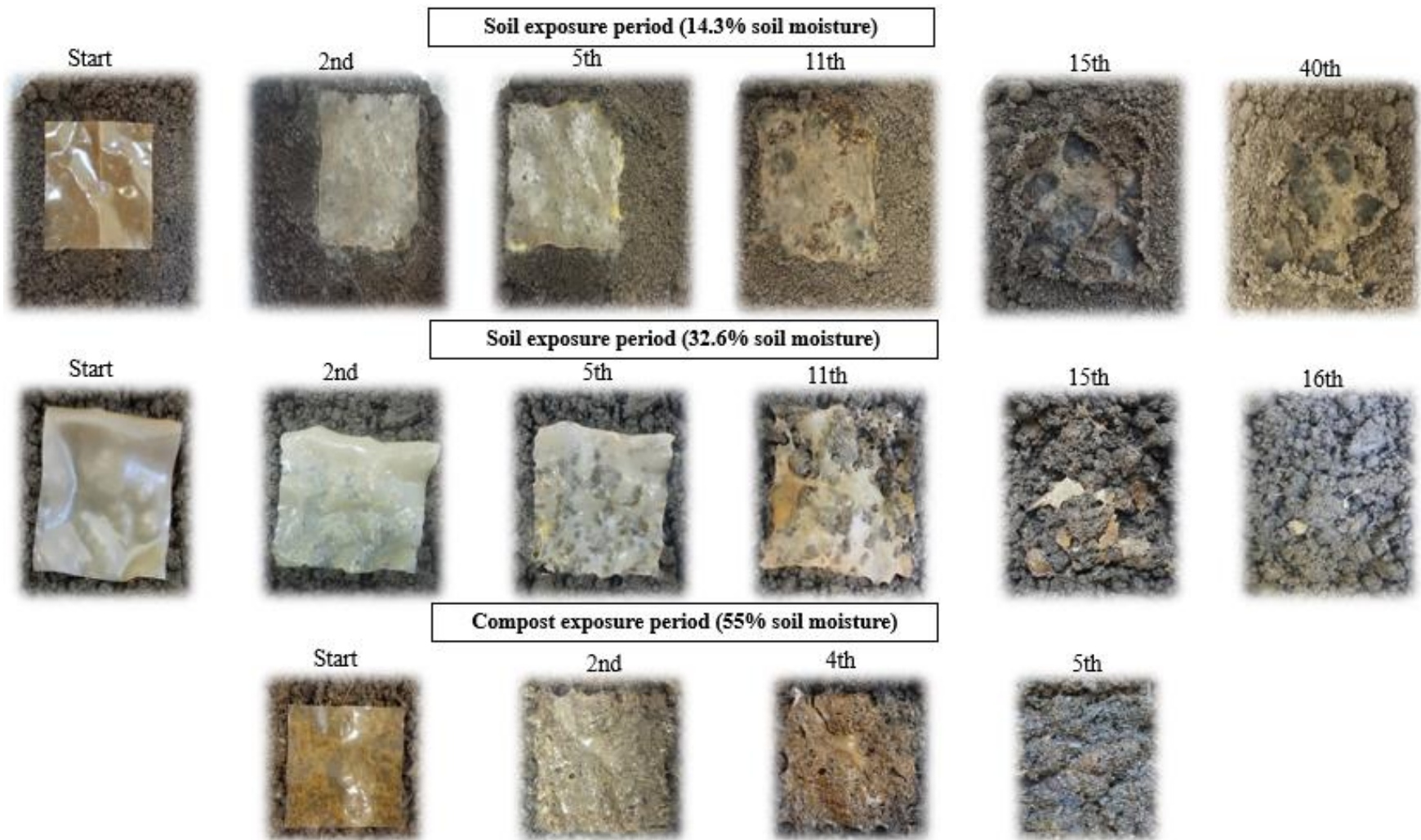
It is important to emphasize the impact of moisture on biodegradation, as in the polysaccharide's biodegradation, it is also related to polymers chemical composition. Corn starch-based bioplastics show a degradation rate in water medium of 94.23%, while potato starch-based bioplastics were 79.64% biodegraded (DATTA et al., 2019). This difference was due to the higher solubility/hydrophilicity of starch with higher amylose contents. Based on Rivard et al. (1995), due to xylan and starch-based bioplastics acetylation (starch and xylan chemical derivatization) there was a reduction in bioplastic hydrophilicity, and consequently a delay in biodegradation. Therefore, future studies encompassing different compositions and structures of polymers will be necessary for a deeper understanding of bioplastics' biodegradation profile.

The disintegration of the bioplastic (25/75% xylan/starch) showed that the environment influences in disintegration/biodegradation process, although the results of the present study used three different temperatures of the soil and composting system. Therefore, in-depth studies mitigating the different environmental conditions must be carried out as many of the laboratory experiments do not reflect the natural environment (CHOE et al., 2021). In the laboratory, the application of isolates and condensation of

microbial cells usually occurs, a factor that accelerates biodegradation (DUSSUD et al., 2018), which differs from the natural environment in which there is competition for different substrates and heterogeneity of decomposers (ANDRADY, 1994).

Other factors that oscillate in natural environments and influence the disintegration/biodegradation rate, weakening of chemical bonds, and bioavailability of the bioplastics are temperature (HENTON et al., 2005; KARAMANLIOGLU et al., 2017), radiation (LUCAS et al., 2008; SADI et al., 2010), mechanical shear (LUCAS et al., 2008; WRIGHT et al., 2020), moisture (LUCAS et al., 2008), and bioplastic chemical properties (DATTA et al., 2019). These factors should be considered *in situ* and *ex-situ* approaches in evaluating the biodegradation and disintegration of bioplastics (CHOE et al., 2021).

Figure 5: Moisture influence on bioplastic disintegration



Source: Elaborated by the author

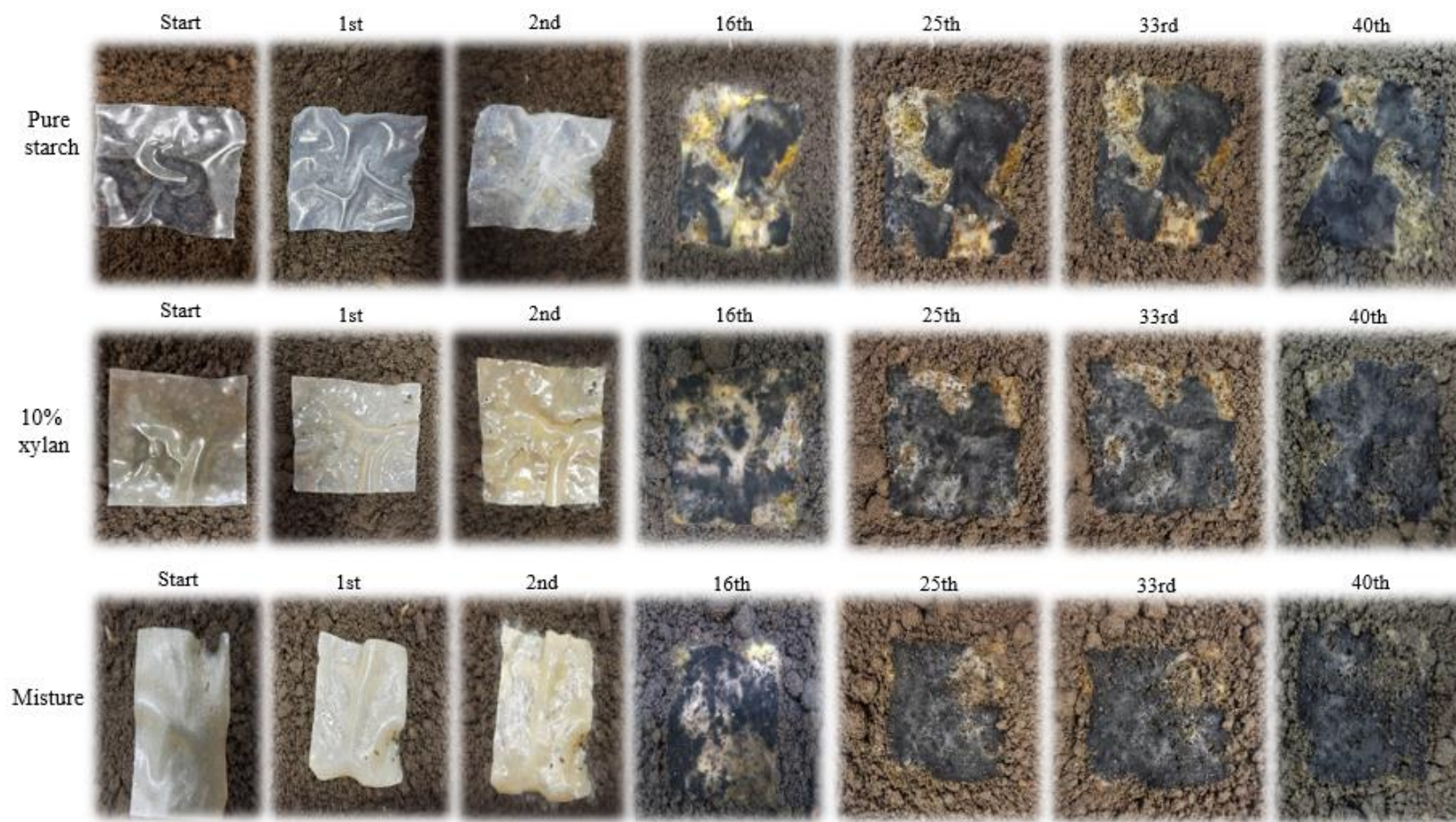
3.4. Effect of xylan addition on the bioplastics disintegration

Similar to 25/75% (w/w) xylan/starch-based bioplastic (Figure 5), all formulations showed microbial growth and yellowing spots on the 2nd day of soil exposure (32.6% moisture) (Figure 6). The alteration in color and integrity of bioplastics changed during 40 days of the bioplastic exposure to the soil. However, unlike the bioplastic composed of 25% xylan, the pure starch, 10% xylan and blend formulations took longer to disintegrate. Even after 40 days of exposure to the soil at 32.6% moisture, the bioplastics did not completely disintegrate (Figure 6). Precisely, the greater integrity of the pure starch-based bioplastic and crystallinity (Table 3) was one of the factors that resulted in reduced disintegration capacity after 40 days of soil surface exposure. Due to the diffusion of oligomers via water and the enzymatic impermeability through the dense polymer structure, crystallinity may delay biodegradation (PANTANI and SORRENTINO, 2013).

The difference in disintegration time for bioplastics with lower xylan contents (10/80% xylan/starch and mixture) can also be explained by the low water solubility (17.46 and 16.4%, respectively), when compared to the reported solubility of 27.93% of bioplastics 25/75% xylan/starch (ABE et al., 2022). Starch-based bioplastics with lower degrees of solubility in water (8.97% and 42.53%) present lower rates of biodegradation (12.07% and 49.48%) when compared to the more soluble ones (85.17% and 85.57%), impacting the efficiency of biodegradation (69.96% and 81.41%) (SHAFQAT et al., 2021). The absorption of water affects microbial growth (MAULIDA et al., 2016; SHAFQAT et al., 2021), and the addition of polymers/polysaccharides can lead to greater microbial adhesion and crack formation on the surface. These cracks were observed on mixture bioplastics (Table 2).

In addition to increased solubility, surface for microbial adhesion, and bioplastic matrix failures, adding fibers such as from husks (KIM et al., 2006; SHAFQAT et al., 2021) can stimulate fungal growth (MASTALYGINA et al., 2017) and bioplastic oxidation processes (SHAFQAT et al., 2021).

Figure 6: Xylan content influence on bioplastic disintegration



Source: Elaborated by the author

3.6. Soil ecotoxicity

From the exposure of vegetable soil (used for planting vegetables) to xylan-starch-based bioplastic (10% w/w bioplastics, based on dry soil) was possible to verify the changes in a few characteristics of this substrate. The assessment of ecotoxic effects from organisms defined as primary producers, i.e vegetables (in soil), represent vital importance as they make up an essential trophic level for ecosystems (HOFFMAN ET AL., 2003; KUZYAKOV and BLAGODATSKAYA, 2015; BALESTRI et al., 2019; LIWARSKA-BIZUKOJC, 2021). For this reason, the present study contributes to studies on the impacts of bioplastics on soil since the verification of physical-chemical impacts is limited when arising from bioplastics, thus limiting the understanding of bioplastics impacts on soil biota (LIWARSKA-BIZUKOJC, 2021).

The germination was only inhibited in relation to soil exposed to bioplastics for 15 days (Table 4). The total inhibition of germination (lethal effect-embryo death) was similar to the positive control (zinc sulfate heptahydrate (0.05 M)). In root development, only the 15-day soil control and the 15-day bioplastic treatment showed a statistical difference from the negative control (distilled water). Therefore, it is possible that the soil itself presented slight phytotoxicity without the influence of the bioplastic. However, as the germination in the 15-day control was similar to the negative control, the relevance of the addition of the bioplastic in the soil as an enhancer of phytotoxicity was highlighted. The hypocotyl data show that the soil exposed to the bioplastic for 15 days was phytotoxic and compared to the positive control. In other words, the results of the present study demonstrate the importance of verifying phytotoxicity in soils exposed to bioplastic, as they represent an organic matter of easy microbial assimilation. Thus, influencing the abundance and microbial richness of the soil, pH, enzyme activity, porosity, and absorbent agents of toxic substances.

Qi et al. (2018) found that bioplastic for agricultural application in the mulching scheme was more harmful to wheat development than polyethylene. Despite the reduction in root biomass and no effect on germination with polyethylene and starch mulching (biodegradable), soil with starch-based bioplastic showed a greater inhibitory effect on shoots development (QI et al., 2018). Balestri et al. (2019) demonstrated that Mater-Bi bioplastic (based on starch and vinyl-alcohol copolymers) caused more damage to the *Lepidium sativum* L radicle with the formation of abnormalities in that organ. In the present study, despite the temporary phytotoxicity presented by the soil after 10 days of burial of the bioplastic (xylan/starch), the biodegradation process was positive for the reduction of phytotoxicity in the soil (ABE et al., 2022).

Table 4: Soil bioplastic disintegration impact on *L. sativa* germination and phytotoxicity.

Test	pH	Germination (%)	Radicle growth (mm)	Hypocotyl growth (mm)
Negative control	-	85±0 ^{ab*}	11.55±2.28 ^a	8.2±0.65 ^b
Positive control	-	0±0 ^c	0±0 ^b	0±0 ^c
Soil control 5 day	6.81	86.66±7.63 ^{ab}	12.73±1.70 ^a	15.14±0.99 ^a
Soil treat 5 day	5.31	95±7.63 ^a	9.77±0.42 ^a	10.41±1.75 ^{ab}
Soil control 15 day	5.6	68.33±16.07 ^{ab}	0.069±0.12 ^b	5.17±1.10 ^b
Soil treat 15 day	4.91	0±0 ^c	0±0 ^b	0±0 ^c

*= Different letters represent statistical difference (p<0.05).

Source: Elaborated by the author

Soil reaction (pH) changed in the soil after 5 days and 15 days of disintegration of the bioplastics (Table 4). The reduction in pH can differ by variation in the concentration of bioplastic in the soil, microbial community, soil moisture, exposure time, and other factors. The reduction in pH from the biodegradation of the bioplastic was probably due to the production of cationic acids by microorganisms (BALESTRI et al., 2019). Soil reaction is an important factor for plant development since this characteristic includes microbial activity, solubility, and nutrient availability (GENTILI et al., 2018). For example, essential micronutrients for the development of plants may be available to plants due to the low pH

(LONČARIĆ ET AL., 2008), however, the large accumulation of these nutrients can generate a toxicity effect (GENTILI et al., 2018). Even though the 15 days of soil exposure to bioplastic had a pH below the range of 5.5-6.5 or of 5.5-8.5 (PRIAC et al., 2017; GENTILI et al., 2018), which are the suitable range for different cultivars and lettuce (genus *Lactuca*). The identification of microbial compounds and metabolites should be performed for an in-depth understanding of soil bioplastic influence after disposal.

The difficulty in inferring the real ecotoxic effect of bioplastics on soil and water is due to the heterogeneity of their compositions, forms, chemical structure, physical-chemical and biological properties of the soil (or water). Furthermore, the dose-dependent factor must also be studied, which represents a limiting factor in the current literature (LIWARSKA-BIZUKOJC, 2021).

Conclusions

In addition to the biomass residues valorization, the development of starch-based bioplastics with xylan resulted in a material with optical barrier, and covering fatty foods properties. More studies must be carried out to optimize the interactions between the polymeric chains and the dispersion in the matrix, thus increasing the mechanical, thermal, and crystallinity resistance of the material. The mechanical and thermal properties were disadvantaged with the addition of xylan, however, the chemical modification of the polysaccharides constituting the bioplastic can improve these properties. Complete disintegration in soil took 16 days at 32.6% moisture, however, at 14.6% moisture disintegration was slow. The total composting of the bioplastic was 5 days. Due to the addition of xylan and reduced crystallinity, the formulation with 25% xylan was shown to degrade faster. Seed germination in soil washes after 5 days of disintegration was not influenced, as for the 15-day wash, there was complete inhibition. Another important factor to be analyzed in the development of bioplastic is the integrity of the materials exposed to natural environmental conditions because due to the chemical differences of bioplastics, abiotic and biotic factors in the environment and the discrepancy of laboratory tests, the process of disintegration and biodegradation can occur with different efficiencies.

Reference

ABE, M. M., BRANCIFORTI, M. C., NALLIN MONTAGNOLLI, R., MARIN MORALES, M. A., JACOBUS, A. P., & BRIENZO, M. (2022). Production and assessment of the biodegradation and ecotoxicity of xylan- and starch-based bioplastics. *Chemosphere*, 287, 132290. <https://doi.org/10.1016/j.chemosphere.2021.132290>

- ABDULKHANI, L., MAZHAR, A. N., HEDJAZI, S., HAMZEH, Y. (2019). Preparation of xylan bio-composite films reinforced with oxidized carboxymethyl cellulose and nanocellulose. *Polymer Bulletin*. <https://doi.org/10.1007/s00289-019-03075-5>
- ACCINELLI, C., SACCÀ, M. L., MENCARELLI, M., & VICARI, A. (2012). Deterioration of bioplastic carrier bags in the environment and assessment of a new recycling alternative. *Chemosphere*, 89, 2, 136–143. doi:10.1016/j.chemosphere.2012.05.028
- ADAMCOVÁ, D., ZLOCH, J., BRTNICKÝ, M., & VAVERKOVÁ, M. D. (2019). Biodegradation/Disintegration of Selected Range of Polymers: Impact on the Compost Quality. *J Polym Environ*, 27, 892–899. <https://doi.org/10.1007/s10924-019-01393-3>
- ADDIS, P. B. (1986). Occurrence of lipid oxidation products in foods. *Food and Chemical Toxicology*, 24, 10-11, 1021–1030. doi:10.1016/0278-6915(86)90283-8
- AHMAD, N., TAYYEB, D., ALI, I., K. ALRUWAILI, N., AHMAD, W., UR REHMAN, A., IQBAL, M. S. (2020). Development and Characterization of Hemicellulose-Based Films for Antibacterial Wound-Dressing Application. *Polymers*, 12, 3, 548. doi:10.3390/polym12030548
- ANDRADY, A. L. (1994). Assessment of Environmental Biodegradation of Synthetic Polymers. *J. Macromolecular Sci. C: Polym. Rev*, 34, 1, 25–76. doi:10.1080/15321799408009632
- ARAÚJO, C. S., RODRIGUES, A. M. C., PEIXOTO JOELE, M. R. S., ARAÚJO, E. A. F., & LOURENÇO, L. F. H. (2018). Optimizing process parameters to obtain a bioplastic using proteins from fish byproducts through the response surface methodology. *Food Packaging and Shelf Life*, 16, 23–30. doi:10.1016/j.fpsl.2018.01.009
- ARNLING BÅÅTH, J.; MARTÍNEZ-ABAD, A., BERGLUND, J., LARSBRINK, J., VILAPLANA, F., & OLSSON, L. (2018). Mannanase hydrolysis of spruce galactoglucomannan focusing on the influence of acetylation on enzymatic mannan degradation. *Biotechnol. Biofuels*, 11, 1.
- BALESTRI, E., MENICAGLI, V., LIGORINI, V., FULIGNATI, S., RASPOLLI GALLETTI, A. M., & LARDICCI, C. (2019). Phytotoxicity assessment of conventional and biodegradable plastic bags using seed germination test. *Ecological Indicators*, 102, 569–580. <https://doi.org/10.1016/j.ecolind.2019.03.005>
- CAZÓN, P., VELAZQUEZ, G., RAMÍREZ, J. A., & VÁZQUEZ, M. (2017). Polysaccharide-based films and coatings for food packaging: A review. *Food Hydrocolloids*, 68, 136–148. doi:10.1016/j.foodhyd.2016.09.009

- CHEN, Y., LIU, C., CHANG, P. R., ANDERSON, D. P., & HUNEALULT, M. A. (2009). Pea starch-based composite films with pea hull fibers and pea hull fiber-derived nanowhiskers. *Polymer Engineering & Science*, 49, 2, 369–378. doi:10.1002/pen.21290
- CHEN, X., CHEN, X., LIU, Q., ZHAO, Q., XIONG, X., & WU, C. (2021). Used disposable face masks are significant sources of microplastics to environment. *Environmental Pollution*, 285, 117485. doi:10.1016/j.envpol.2021.117485
- CHOE, S., KIM, Y., WON, Y., MYUNG, J. (2021). Bridging Three Gaps in Biodegradable Plastics: Misconceptions and Truths About Biodegradation. *Frontiers in Chemistry*, 9, 334. doi:10.3389/fchem.2021.671750
- CORRADINI, E., LOTTI, C., MEDEIROS, E. S., CARVALHO, A. J. F., CURVELO, A. A. S., MATTOSO, L. H. C. (2005). Estudo comparativo de amidos termoplásticos derivados do milho com diferentes teores de amilose. *Revista Polímeros: Ciência e Tecnologia*, 15, 4, 268-273.
- DANG, M. K., & YOKSAN, R. (2015). Development of thermoplastic starch blown film by incorporating plasticized chitosan. *Carbohydr. Polym*, 115, 575–581.
- DATTA, D., & HALDER, G. (2019). Effect of media on degradability, physico-mechanical and optical properties of synthesized polyolefinic and PLA film in comparison with casted potato/corn starch biofilm. *Process Safety and Environmental Protection*, 124, 39– 62. doi:10.1016/j.psep.2019.02.002
- DILKES-HOFFMAN, L., ASHWORTH, P., LAYCOCK, B., PRATT, S., & LANT, P. (2019). Public Attitudes towards Bioplastics - Knowledge, Perception and End-Of-Life Management. *Resour. Conservation Recycling*, 151, 104479. doi:10.1016/j.resconrec.2019.104479
- DUSSUD, C., HUDEC, C., GEORGE, M., FABRE, P., HIGGS, P., BRUZAUD, S. (2018). Colonization of Non-biodegradable and Biodegradable Plastics by Marine Microorganisms. *Front. Microbiol*, 9, 1571. doi:10.3389/fmicb.2018.01571
- FALOWO, A. B., FAYEMI, P. O., & MUCHENJE, V. (2014). Natural antioxidants against lipid–protein oxidative deterioration in meat and meat products: A review. *Food Research International*, 64, 171–181. doi:10.1016/j.foodres.2014.06.022
- FARIVAR, F., YAP, P. L., KARUNAGARAN, R. U., & LOSIC, D. (2021). Thermogravimetric Analysis (TGA) of Graphene Materials: Effect of Particle Size of Graphene, Graphene Oxide and Graphite on Thermal Parameters. *C*, 7, 41. <https://doi.org/10.3390/c7020041>

- FORTUNATI, E., PELTZER, M., ARMENTANO, I., TORRE, L., JIMÉNEZ, A., & KENNY, J. M. (2012). Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohydrate Polymers*, 90, 2, 948–956. doi:10.1016/j.carbpol.2012.06.025
- FREITAS, D. S. M., RODRIGUES, A., MACIEL, J. S., PIRES, C. C., LEMES, A. A. F., FERREIRA, A. P., & BOTARO, V. R. (2021). Improvements in thermal and mechanical properties of composites based on thermoplastic starch and Kraft Lignin. *International Journal of Biological Macromolecules*, 184, 863–873. doi:10.1016/j.ijbiomac.2021.06.153
- GERASSIMIDOU, S., MARTIN, O. V., CHAPMAN, S. P., HAHLADAKIS, J. N., & IACOVIDOU, E. (2020). Development of an integrated sustainability matrix to depict challenges and trade-offs of introducing bio-based plastics in the food packaging value chain. *Journal of Cleaner Production*, 125378. doi:10.1016/j.jclepro.2020.125378
- GÁSPÁR, M., BENKŐ, Z., DOGOSSY, G., RÉCZEY, K., & CZIGÁNY, T. (2005). Reducing water absorption in compostable starch-based plastics. *Polymer Degradation and Stability*, 90, 3, 563–569. doi:10.1016/j.polymdegradstab.2005.03.012
- GENTILI, R., AMBROSINI, R., MONTAGNANI, C., CARONNI, S., & CITTERIO, S. (2018). Effect of Soil pH on the Growth, Reproductive Investment and Pollen Allergenicity of *Ambrosia artemisiifolia* L. *Frontiers in Plant Science*, 9. doi:10.3389/fpls.2018.01335
- GEYER, R., JAMBECK, J. R., & LAW, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances*, 3, 7, e1700782. <https://doi.org/10.1126/sciadv.1700782>
- GLASSER, W. G., RAVINDRAN, G., JAIN, R. K., SAMARANAYAKE, G., TODD, J. (1990) Comparative Enzyme Biodegradability of Xylan, Cellulose, and Starch Derivatives. *Biotechnol. Prog*, 11, 552–557.
- GOKSU, E. I., KARAMANLIOGLU, M., BAKIR, U., YILMAZ, L., & YILMAZER, U. (2007). Production and Characterization of Films from Cotton Stalk Xylan. *Journal of Agricultural and Food Chemistry*, 55, 26, 10685–10691. doi:10.1021/jf071893i
- GORDOBIL, O., EGÜÉS, I., URRUZOLA, I., & LABIDI, J. (2014). Xylan–cellulose films: Improvement of hydrophobicity, thermal and mechanical properties. *Carbohydrate Polymers*, 112, 56–62. doi:10.1016/j.carbpol.2014.05.060

- HANSEN, N. M. L., BLOMFELDT, T. O. J., HEDENQVIST, M. S., & PLACKETT, D. V. (2012). Properties of plasticized composite films prepared from nanofibrillated cellulose and birch wood xylan. *Cellulose*, 19, 6, 2015–2031. doi:10.1007/s10570-012-9764-7
- HARRISON, J. P., BOARDMAN, C., O'CALLAGHAN, K., DELORT, A.-M., & SONG, J. (2018). Biodegradability standards for carrier bags and plastic films in aquatic environments: a critical review. *Royal Society Open Science*, 5, 5, 171792. doi:10.1098/rsos.171792
- HEIKKINEN, S. L., MIKKONEN, K. S., PIRKKALAINEN, K., SERIMAA, R., JOLY, C., TENKANEN, M. (2013). Specific enzymatic tailoring of wheat arabinoxylan reveals the role of substitution on xylan film properties. *Carbohydr. Polym*, 92, 733–740.
- HENTON, D. E., GRUBER, P., LUNT, J., & RANDALL, J. (2005). Polylactic Acid Technology. *Nat. Fibers, Biopolymers, Biocomposites*, 16, 527–577. doi:10.1002/1521-4095(200012)12:233.O.CO;2-E
- HOFFMAN, D. J., RATTNER, B. A., BURTON, G. A. L., CAIRNS JR., J. (2003). Handbook of Ecotoxicology. *Lewis Publishers*, 2, Boca Raton
- HÖLJE, A., STEMEMALM, E., HEIKKINEN, S., TENKANEN, M., GATENHOLM, P. (2008). Material properties of films from enzymatically tailored arabinoxylans. *Biomacromolecules*, 9, 2042–2047.
- HUERTA-LWANGA, E., GERTSEN, H., GOOREN, H., PETERS, P., SALANKI, T., VAN DER PLOEG, M, BESSELING, E., KOELMANS, A.A., GEISSEN, V. (2017). Incorporation of microplastics from litter into burrows of *Lumbricus terrestris*. *Environmental Pollution*, 220, 523–531.
- IQBAL, S., XU, J., ALLEN, S.D., KHAN, S., NADIR, S., ARIF, M. S., (2020). Unraveling consequences of soil micro- and nano-plastic pollution on soil-plant system: implications for nitrogen (N) cycling and soil microbial activity. *Chemosphere*, 260, 127578. <https://doi.org/10.1016/j.chemosphere.2020.127578>
- ILYAS, R. A., SAPUAN, S. M., & ISHAK, M. R. (2018). Isolation and characterization of nanocrystalline cellulose from sugar palm fibers (*Arenga Pinnata*). *Carbohydrate Polymers*, 181, 1038-1051. <https://doi.org/10.1016/j.carbpol.2017.11.045>
- JACOBS, J. L., & SUNDIN, G. W. (2001). Effect of Solar UV-B Radiation on a Phyllosphere Bacterial Community. *Applied and Environmental Microbiology*, 67, 12, 5488–5496. doi:10.1128/aem.67.12.5488-5496.2001

- JARAMILLO, M. C., GUTIÉRREZ, T. J., GOYANES, S., BERNAL, C., & FAMÁ, L. (2016). Biodegradability and plasticizing effect of yerba mate extract on cassava starch edible films. *Carbohydrate Polymers*, 151, 150–159. doi:10.1016/j.carbpol.2016.05.025
- KARAMANLIOGLU, M., PREZIOSI, R., & ROBSON, G. D. (2017). Abiotic and Biotic Environmental Degradation of the Bioplastic Polymer Poly(lactic Acid): A Review. *Polym. Degrad. Stab*, 137, 122–130. doi:10.1016/j.polymdegradstab.2017.01.009
- KIM, H. S., KIM, H. J., LEE, J. W., & CHOI, I. G. (2006). Biodegradability of bio-flour filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil. *Polymer Degradation and Stability*, 91, 5, 1117–1127. doi:10.1016/j.polymdegradstab.2005.07.002
- KJELDSSEN, A., PRICE, M., LILLEY, C., GUZNICZAK, E., ARCHER, I. A. (2018). Review of Standards for Biodegradable Plastics. *Ind. Biotechnol. Innov. Cent*, 33, 1.
- KOCIRA, A., KOZŁOWICZ, K., PANASIEWICZ, K., STANIAK, M., SZPUNAR-KROK, E., HORTYŃSKA, P. (2021). Polysaccharides as Edible Films and Coatings: Characteristics and Influence on Fruit and Vegetable Quality—A Review. *Agronomy*, 11, 813. <https://doi.org/10.3390/agronomy11050813>
- KOROL, J., HEJNA, A., BURCHART-KOROL, D., & WACHOWICZ, J. (2020). Comparative Analysis of Carbon, Ecological, and Water Footprints of Polypropylene-Based Composites Filled with Cotton, Jute and Kenaf Fibers. *Materials*, 13, 16, 3541. doi:10.3390/ma13163541
- KUZYAKOV, Y., & BLAGODATSKAYA, E. (2015). Microbial hotspots and hot moments in soil: concept & review. *Soil Biol. Biochem*, 83, 184–199. <https://doi.org/10.1016/j.soilbio.2015.01.025>
- LANG, I.A., GALLOWAY, T.S., SCARLETT, A., HENLEY, W.E., DEPLEDGE, M., WALLACE, R.B., DAVID, M. (2008). Association of urinary bisphenol A concentration with medical disorders and laboratory abnormalities in adults. *JAMA* 300: 1303-1310.
- LEBRETON, L., VAN DER ZWET, J., DAMSTEEG, J.W., BOYAN, S., ANTHONY, A., & JULIA, R. (2017). River plastic emissions to the world's oceans. *Nat Commun*, 8, 15611. <https://doi.org/10.1038/ncomms15611>
- LIN, Y., SCARLETT, R. D., & KING, J. Y. (2015). Effects of UV photodegradation on subsequent microbial decomposition of *Bromus diandrus* litter. *Plant and Soil*, 395, 1-2, 263–271. doi:10.1007/s11104-015-2551-0

- LIU, H., XIE, F., YU, L., CHEN, L., & LIN, L. (2009). Thermal processing of starch-based polymers. *Prog. Polym. Sci*, 34, 1348–1368.
- LIWARSKA-BIZUKOJC E. (2021). Effect of (bio)plastics on soil environment: *A review*. *Sci Total Environ*, 15, 795, 148889. doi: 10.1016/j.scitotenv.2021.148889.
- LUCAS, N., BIENAIME, C., BELLOY, C., QUENEUDEC, M., SILVESTRE, F., & NAVASAUCEDO, J. E. (2008). Polymer biodegradation: Mechanisms and estimation techniques - A review. *Chemosphere*, 73, 429–442. <https://doi.org/10.1016/j.chemosphere.2008.06.064>
- LUCENA, C. A. Z., COSTA, S. C., ELEAMEN, G. R. A., MENDONÇA, E. A. M., E ELQUIO ELEAMEN OLIVEIRA, E. E. (2017). Desenvolvimento de biofilmes à base de xilana e xilana/gelatina para produção de embalagens biodegradáveis. *Polímeros*, 27, 35-41. <http://dx.doi.org/10.1590/0104-1428.2223>
- MACHADO, A. A. S., LAU, C. W., TILL, J., KLOAS, W., LEHMANN, A., BECKER, R., & RILLIG, M. C. (2018). Impacts of microplastics on the soil biophysical environment. *Environmental Science & Technology*, 52, 9656–9665.
- MASTALYGINA, E. E., POPOV, A. A., & PANTYUKHOV, P. V. (2017). Effect of biobased fillers nature on biodeterioration of hybrid polyethylene composites by mold fungi. *IOP Conf. Ser.: Mater. Sci. Eng*, 213, 012011.
- MAULIDA, SIAGIAN, M., & TARIGAN, P. (2016). Production of Starch Based Bioplastic from Cassava Peel Reinforced with Microcrystalline Cellulose Avicel PH101 Using Sorbitol as Plasticizer. *J. Phys.: Conf. Ser*, 710, 1, 012012.
- MESTDAGH, F., MEULENAER, B. D., CLIPPELEER, J. D., DEVLIEGHERE, F., HUYGHEBAERT, A. (2005). Protective Influence of Several Packaging Materials on Light Oxidation of Milk. *Packag. Technol. Sci*, 32, 9.
- MITCHELL, D., GROHMANN, K., HIMMEL, M., DALE, B., & SCHROEDER, H. (1990). Effect of the degree of acetylation on the enzymatic digestion of acetylated xylans. *J. Wood Chem. Technol*, 10, 111–121.
- MOODY, S. A., NEWSHAM, K. K., AYRES, P. G., & PAUL, N. D. (1999). Variation in the responses of litter and phylloplane fungi to UV-B radiation (290–315 nm). *Mycol Res*, 103, 1469–1477. <https://doi.org/10.1017/S0953756299008783>
- MOSHOD, T. D., NAWANIR, G., MAHMUD, F., MOHAMAD, F., AHMAD, M. H., ABDUL GHANI, A. (2021). Expanding Policy for Biodegradable Plastic Products and

- Market Dynamics of Bio-Based Plastics: Challenges and Opportunities. *Sustainability*, 13, 6170. <https://doi.org/10.3390/su13116170>
- MUGWAGWA, L. R., & CHIMPHANGO, A. F. A. (2020). Enhancing the functional properties of acetylated hemicellulose films for active food packaging using acetylated and polycaprolactone coating nanocellulose reinforcement. *Food Packaging and Shelf Life*, 24. 10.1016/j.fpsl.2020.100481
- MULYONO, N., SUHARTONO, M. T., & ANGELINA, S. (2015). Development of bioplastic based on cassava flour and its starch derivatives for food packaging. *J. Harmoniz. Res. Appl. Sci*, 3, 2, 125-132.
- NARAYANAN, M., LOGANATHAN, S., VALAPA, R. B., THOMAS, S., & VARGHESE, T. O. (2017). UV protective poly(lactic acid)/rosin films for sustainable packaging. *International Journal of Biological Macromolecules*, 99, 37–45. doi:10.1016/j.ijbiomac.2017.01.152
- NEVORALOVÁ, M., KOUTNÝ, M., UJČÍČ, A., HORÁK, P., KREDITUSOVÁ, J., ŠERÁ, J., RŮŽEK, L., RŮŽKOVÁ, M., KREJČÍKOVÁ, S., & ŠLOUF, M. (2019). Controlled biodegradability of functionalized thermoplastic starch based materials. *Polym. Degrad. Stab*, 170.
- NGUYEN, D. M., DO, T. V. V., GRILLET, A. C., HA THUC, H., & HA THUC, C. N. (2016). Biodegradability of polymer film based on low density polyethylene and cassava starch. *International Biodeterioration & Biodegradation*, 115, 257–265. doi:10.1016/j.ibiod.2016.09.004
- NORDIN, N., OTHMAN, S. H., KADIR-BASHA, R., & ABDUL-RASHID, S. (2018) Mechanical and thermal properties of starch flms reinforced with microcellulose fbres. *Food Res*, 2, 555–563.
- OLUWASINA, O. O., AKINYELE, B. P., OLUSEGUN, S. J., OLUWASINA, O., & MOHALLEM, N. D. S. (2021). Evaluation of the effects of additives on the properties of starch-based bioplastic film. *SN Appl. Sci*, 3, 421.
- PALANZA, P., PATERLINI, S., BRAMBILLA, M. M., RAMUNDO, G., CAVIOLA, G., GIOIOSA, L., & PONZI, D. (2020). Sex-Biased Impact of Endocrine Disrupting Chemicals on Behavioral Development and Vulnerability to Disease: Of Mice and Children. *Neuroscience & Biobehavioral Reviews*. doi:10.1016/j.neubiorev.2020.11.015
- PANTANI, R., & SORRENTINO, A. (2013). Influence of crystallinity on the biodegradation rate of injection-moulded poly(lactic acid) samples in controlled composting conditions.

- Polymer Degradation and Stability*, 98, 5, 1089–1096. doi:10.1016/j.polymdegradstab.2013.01.005
- PAPADIMITRIOU, C. A., HARITOU, I., SAMARAS, P., & ZOUBOULIS, A. I. (2008). Evaluation of leaching and ecotoxicological properties of sewage sludge–fly ash mixtures. *Environmental Research*, 106, 3, 340–348. doi:10.1016/j.envres.2007.04.007
- PARKER, R. & RING, S. G. J. (2001). *Cereal Sci.*, 34, 1.
- PENG, X., REN, J., ZHONG, L., & SUN, R. (2011). Nanocomposite Films Based on Xylan-Rich Hemicelluloses and Cellulose Nanofibers with Enhanced Mechanical Properties. *Biomacromolecules*, 12, 9, 3321–3329. doi:10.1021/bm2008795
- PEROTTO, G., SIMONUTTI, R., CESERACCIU, L., MAURI, M., BESGHINI, D., & ATHANASSIOU, A. (2020). Water-induced plasticization in vegetable-based bioplastic films: A structural and thermo-mechanical study. *Polymer*, 122598. doi:10.1016/j.polymer.2020.122598
- PIERISTÈ, M., FOREY, E., LOUNÈS-HADJ SAHRAOUI, A., MEGLOULI, H., LARUELLE, F., DELPORTE, P., & CHAUVAT, M. (2020). Spectral Composition of Sunlight Affects the Microbial Functional Structure of Beech Leaf Litter During the Initial Phase of Decomposition. *Plant and Soil*. doi:10.1007/s11104-020-04557-6
- PILLA, S., KIMB, S. G., AUER, G. K., GONG, S., & PARK, C. B. (2010). Microcellular extrusion foaming of poly(lactide)/poly(butylenes adipate-co-terephthalate) blends. *Materials Science and Engineering*, 30, 255–262.]
- POUDEL, P. R., KATAOKA, I., & MOCHIOKA, R. (2007). Effect of red- and blue-light-emitting diodes on growth and morphogenesis of grapes. *Plant Cell Tiss. Org. Cult*, 92, 147–153.
- PRIAC, A., BADOT, P. M., & CRINI, G. (2017). Treated wastewater phytotoxicity assessment using *Lactuca sativa*: Focus on germination and root elongation test parameters. *Comptes Rendus Biologies*, 340, 3, 188–194. doi:10.1016/j.crv.2017.01.002
- PROSHAD, R., KORMOKER, T., ISLAM, M. S., HAQUE, M. A., RAHMAN, M. M., & MITHU, M. M. R. (2017). Toxic effects of plastic on human health and environment: A consequences of health risk assessment in Bangladesh. *International Journal of Health*, 6, 1, 1. doi:10.14419/ijh.v6i1.8655
- PRÜST, M., MEIJER, J. & WESTERINK, R. H. S. (2020). The plastic brain: neurotoxicity of micro- and nanoplastics. *Part Fibre Toxicol*, 17, 24. <https://doi.org/10.1186/s12989-020-00358-y>

- PULLERITS, K., AHLINDER, J., HOLMER, L., SALOMONSSON, E., ÖHRMAN, C., JACOBSSON, K., & RÅDSTRÖM, P. (2020). Impact of UV irradiation at full scale on bacterial communities in drinking water. *Npj Clean Water*, 3, 1. doi:10.1038/s41545-020-0057-7
- QI, Y., YANG, X., PELAEZ, A. M., HUERTA LWANGA, E., BERIOT, N., GERTSEN, H., & GEISSEN, V. (2018). Macro- and micro- plastics in soil-plant system: Effects of plastic mulch film residues on wheat (*Triticum aestivum*) growth. *Science of The Total Environment*, 645, 1048–1056. doi:10.1016/j.scitotenv.2018.07.229
- RAGUSA, A., SVELATO, A., SANTACROCE, C., CATALANO, P., NOTARSTEFANO, V., CARNEVALI, O., & GIORGINI, E. (2021). Plasticenta: First evidence of microplastics in human placenta. *Environment International*, 146, 106274. doi:10.1016/j.envint.2020.106274
- REIS, M. M. S, SANTOS, Z. I. G., UEKI, M. M., BRITO, G. F. (2016). Avaliação do tipo de plastificante nas propriedades de blendas de polietileno/amido termoplástico. *Revista Eletrônica de Materiais e Processos*, 11, 3, 130–135.
- RILLIG, M. C., LEHMANN, A., DE SOUZA MACHADO, A. A., & YANG, G. (2019). Microplastic effects on plants. *New Phytologist*. doi:10.1111/nph.15794
- RIVARD, C., MOENS, L., ROBERTS, K., BRIGHAM, J., KELLEY, S. (1995). Starch esters as biodegradable plastics: Effects of ester group chain length and degree of substitution on anaerobic biodegradation. *Enzyme Microb. Technol*, 17, 848–852.
- ROBAINA, M., MURILLO, K., ROCHA, E., & VILLAR, J. (2020). Circular economy in plastic waste - Efficiency analysis of European countries. *Science of The Total Environment*, 730, 139038. doi:10.1016/j.scitotenv.2020.139038
- SABETZADEH, M., BAGHERI, R., MASOOMI, M. (2015). Study on ternary low-density polyethylene/linear low-density polyethylene/thermoplastic starch blend films. *Carbohydr. Polym*, 119, 126–133.
- SABIHA-HANIM, S., & SITI-NORSAFURAH, A. M. (2012). Physical Properties of Hemicellulose Films from Sugarcane Bagasse. *Procedia Engineering*, 42, 1390–1395. doi:10.1016/j.proeng.2012.07.532
- SADI, R. K., FECHINE, G. J. M., & DEMARQUETTE, N. R. (2010). Photodegradation of Poly(3-Hydroxybutyrate). *Polym. Degrad. Stab.* 95 (12), 2318–2327. doi:10.1016/j.polymdegradstab.2010.09.003

- ŠÁRKA, E., KRULIŠ, Z., KOTEK, J., RŮŽEK, L., KORBÁŘOVÁ, A., BUBNÍK, Z., RŮŽKOVÁ, M. (2011). Application of wheat B-starch in biodegradable plastic materials. *Czech J. Food Sci*, 29, 232–242.
- SCHLEMMER, D., SALES, M. J. A., RESCK, I. S. (2010). Preparação, Caracterização e Degradação de Blendas de PS/TPS Usando Glicerol e Óleo de Buriti como Plastificantes. *Polímeros: Ciência e Tecnologia*, 20, 1, 6-13.
- SHAFQAT, A., AL-ZAQRI, N., TAHIR, A., & ALSALME, A. (2021). Synthesis and characterization of starch based bioplastics using varying plant-based ingredients, plasticizers and natural fillers. *Saudi Journal of Biological Sciences*, 28, 3, 1739–1749. doi:10.1016/j.sjbs.2020.12.015
- SHAO, H., SUN, H., YANG, B., & ZHANG, H. J. (2019). Latest Research Progress in Hemicellulose Films. *China Plastics*, 33, 126–136.
- SHAH, U., NAQASH, F., GANI, A., & MASOODI, F. A. (2016). Art and Science behind Modified Starch Edible Films and Coatings: A Review. *Compr. Rev. Food Sci. Food Saf*, 15, 568–580.
- SHIKU, Y., YUCA HAMAGUCHI, P., BENJAKUL, S., VISESSANGUAN, W., & TANAKA, M. (2004). Effect of surimi quality on properties of edible films based on Alaska pollack. *Food Chemistry*, 86, 4, 493–499. doi:10.1016/j.foodchem.2003.09.022
- SIREROL, J. A., FEDDI, F., MENA, S., RODRIGUEZ, M. L., SIRERA, P., AUPÍ, M., PÉREZ, S., ASENSI, M., ORTEGA, A., & ESTRELA, J. M. (2015). Topical treatment with pterostilbene, a natural phytoalexin, effectively protects hairless mice against UVB radiation-induced skin damage and carcinogenesis. *Free Radic. Biol. Med*, 85, 1–11.
- TEE, Y. B., WONG, J., TAN, M. C, & TALIB, R. A. (2016). Development of Edible Film from Flaxseed Mucilage. *BioResources*, 11, 4, 10286-10295.
- TEDESCHI, G., GUZMAN-PUYOL, S., CESERACCIU, L., PAUL, U. C., PICONE, P., DI CARLO, M., & HEREDIA-GUERRERO, J. A. (2020). Multifunctional Bioplastics Inspired by Wood Composition: Effect of Hydrolyzed Lignin Addition to Xylan–Cellulose Matrices. *Biomacromolecules*, 21, 2, 910–920. doi:10.1021/acs.biomac.9b01569
- TESTER, R. F., KARKALAS, J. & QI, X. J. (2004). *Cereal Sci.*, 39, 151.
- THARANATHAN, R. N. (2003). Biodegradable films and composite coatings: past, present and future. *Trends Food Sci. Technol*, 14, 71– 78

- TSERKI, V., MATZINOS, P., & PANAYIOTOU, C. (2006). Novel biodegradable composites based on treated lignocellulosic waste flour as filler. Part II. Development of biodegradable composites using treated and compatibilized waste flour. *Compos. Part A Appl. Sci. Manuf*, 37, 1231–1238.
- VERHOEF, H. A., VERSPAGEN, J. M. H., & ZOOMER, H. R. (2000). Direct and indirect effects of ultraviolet-B radiation on soil biota, decomposition and nutrient fluxes in dune grassland soil systems. *Biol Fertil Soils*, 31, 366–371. <https://doi.org/10.1007/s003749900181>
- XIAO, B., SUN, X., & SUN, R. (2001). Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw. *Polymer Degradation and Stability*, 74, 2, 307–319. doi:10.1016/s0141-3910(01)00163-x
- XIE, F., AVÉROUS, L., HALLEY, P. J., & LIU, P. (2015). Mechanical performance of starch-based biocomposites. *Biocomposites*, 53–92. doi:10.1016/b978-1-78242-373-7.00011-1
- WAN, Y., WU, C., XUE, Q., & HUI, X. (2019). Effects of plastic contamination on water evaporation and desiccation cracking in soil. *Science of the Total Environment*, 654, 576–582.
- WRIGHT, R. J., ERNI-CASSOLA, G., ZADJELOVIC, V., LATVA, M., & CHRISTIE-OLEZA, J. A. (2020). Marine Plastic Debris: A New Surface for Microbial Colonization. *Environ. Sci. Technol*, 54, 19, 11657–11672. doi:10.1021/acs.est.0c02305
- YANG, Y., ZHAO, Y., HU, Y., PENG, X., & ZHONG, L. (2020). Xylan-Derived Light Conversion Nanocomposite Film. *Polymers*, 12, 1779. <https://doi.org/10.3390/polym12081779>
- YU, J., ZHU, Y., MA, H., LIU, L., HU, Y., XU, J., & FAN, Y. (2019). Contribution of hemicellulose to cellulose nanofiber-based nanocomposite films with enhanced strength, flexibility and UV-blocking properties. *Cellulose*, 26, 6023–6034. <https://doi.org/10.1007/s10570-019-02518-6>
- ZHANG, C., WANG, C., CAO, G., WANG, D., & HO, S. H. (2019). A sustainable solution to plastics pollution: an eco-friendly bioplastic film production from high-salt contained *Spirulina* sp. residues. *Journal of Hazardous Materials*, 121773. doi:10.1016/j.jhazmat.2019.121773

- ZHAO, Y., HUI, S., BIAO, Y., & YUNXUAN, W. (2020). Hemicellulose-Based Film: Potential Green Films for Food Packaging. *Polymers*, 12, 8, 1775. <https://doi.org/10.3390/polym12081775>
- ZIMMERMANN, L., DOMBROWSKI, A., VÖLKER, C., & WAGNER, M. (2020). Are bioplastics and plant-based materials safer than conventional plastics? In vitro toxicity and chemical composition. *Environment International*, 106066. doi:10.1016/j.envint.2020.106066

Chapter VI: Conclusions and next steps

The results obtained in this study showed that the addition of xylan in bioplastics enabled the formation of a continuous and homogeneous plastic matrix. The best conditions of bioplastics formulations were drying temperature of 30 °C and a total polysaccharide concentration of 5% (m/v). All xylan concentrations (w/w) resulted in continuous (no cracks) and homogeneous bioplastics. The increase of xylan amount resulted in an increase in water solubility, possibly due to the hydrophilic character of the xylan, in addition to the possibility of reduced interaction between polysaccharides. The opacity at 450 nm increased with the addition of xylan, with a bioplastic composition of 25% (w/w) of xylan being the opaqueness. Total composting time was three days, while disintegration by burial in soil took 13 days. In addition to the effect of temperature and humidity, the addition of nutrients possibly resulted in bioaugmentation at the beginning and during composting. Under the conditions tested, biodegradation of the bioplastic with 25% xylan (w/w) was positive for the development of *C. sativus* seeds, however, temporary phytotoxicity in the soil with 10 days of exposure to bioplastics shows the importance of such analyses. In addition to the results regarding phytotoxicity, the increase in the density of microbial cells and the change in soil pH are indicative of the need to incorporate analyzes of environmental impacts in the development and application of bioplastics. The results of thermal resistance and mechanical properties showed that the addition of xylan reduced these properties and in-depth studies on the chemical modification of polysaccharides and concentration should be studied to optimize the interactions between the polymers. The rate of disintegration and composting on the surface of soil and compost proved to be dependent on contact with the substrate, moisture, and crystallinity, that is, for a better understanding of the disintegration process of bioplastics, studies in different simulations of environments are needed.