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UNIVERSIDADE ESTADUAL PAULISTA
"JÚLIO DE MESQUITA FILHO"
INSTITUTO DE BIOCIÊNCIAS – RIO CLARO

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

Disintegration evaluation of bioplastic elaborated with polysaccharides from plant biomass

MATEUS MANABU ABE

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Dissertation presented to the Institute of Biosciences of the Campus of Rio Claro, Universidade Estadual Paulista, as part of the requirements for obtaining the title of Master in Applied Microbiology.

Advisor: Prof. Dr. Michel Brienzo

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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 físicoquimico 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.

LIST OF FIGURES

Chapter II

Chapter III

Chapter IV

Chapter V

LIST OF TABLES

Chapter II

Chapter III

Chapter IV

Chapter V

SUMMARY

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 resitence to degradation and slow biodegradation of plastics. Therefore, the accumulation of plastic waste is a concern due to the ingestion of formeds 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 CO_2 (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 CO_2, 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.

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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 opaquest. 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.