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

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

CONTRIBUTION OF XYLAN TO PHYSICOCHEMICAL AND BIODEGRADATION PROPERTIES IN STARCH-BASED BIOPLASTICS.

JOÃO VICTOR CARPINELLI MACEDO

Rio Claro
Julho - 2021

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JOÃO VICTOR CARPINELLI MACEDO

Dissertação apresentada ao Instituto de Biociências do Câmpus de Rio Claro, Universidade Estadual Paulista, como parte dos requisitos para obtenção do título de Mestre em Microbiologia Aplicada.

Orientador: Michel Brienzo

Rio Claro
Julho - 2021

M141c

Macedo, João Victor Carpinelli
Contribution of xylan to physicochemical and biodegradation properties in starch-based bioplastics. / João Victor Carpinelli Macedo. -- Rio Claro, 2021
105 f. : il., tabs.

Dissertação (mestrado) - Universidade Estadual Paulista (Unesp), Instituto de Biociências, Rio Claro
Orientador: Michel Brienzo

1. Ciências biológicas. 2. Biopolímeros. 3. Polissacarideos. 4. Biomassa vegetal. I. Título.

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TÍTULO DA DISSERTAÇÃO: CONTRIBUTION OF XYLAN TO PHYSICOCHEMICAL AND BIODEGRADATION PROPERTIES IN STARCH-BASED BIOPLASTICS

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Rio Claro, 22 de julho de 2021

I dedicate this work to all my family and to everyone who helped me get to where I am.

ACKNOWLEDGEMENT

To my advisor Michel Brienzo, for giving me the opportunity to be part of his students. And trusting me to develop an unprecedented project in his laboratory, which together, we got to develop, starting a new line of research that will generate many fruits for IPBEN and for scientific literature. I acknowledge too all the patience and support offered me throughout the master's, teaching me and helping me to solve the problems related to this project.

To my family, my mother, grandmother, aunts, uncles and cousins for giving me the possibility to graduate and get here. In addition to motivating and strengthening me during all these years of study.

To all the employees of IPBEN for their services that facilitate our lives in the laboratory and colleagues who helped me with so many suggestions, in addition to providing me with good times over these two years.

To Marcia Cristina Branciforti from USP São Carlos, her doctoral student Paula Bertolino Sanvezzo, Renato Grillo from Unesp in Ilha Solteira and the all the technicians for their help in carrying out experiments that we had no access to at IPBEN, in addition to dedicating themselves to clarifying us doubts and give suggestions in carrying out this study.

To the postgraduate program in Applied Microbiology, to all its professors and technical section for their teaching and support.

To CNPq and Fapesp, which despite suffering a reduction in the budget in recent years, is still a competent organization that helps to produce science in the country by investing and providing that works like this are developed. Generating more critical individuals, who know the relevance of science for the well-being and sustainable development of our country.

The present work was carried out with the support of the National Council for Scientific Development and Technological (CNPq)

ABSTRACT

Plastic has served society very well for decades, being able to present itself as a light and moldable material, mechanically and thermally resistant, inert to chemical products, electrical insulator, in addition to having interesting optical characteristics such as its transparency. Such characteristics, associated with the low price of its raw material, a residue from the processing of petroleum until then little used, made it crucial for the industry and the market, which consolidated its presence in society in different countries. However, as it is a resistant material, remaining for centuries without fully decomposing, and for having a large production in order to meet the needs of a consumer society, it began to accumulate in the environment over the years since its creation. Its abundance in the environment causes damage to life in different biomes, especially marine environments, in addition to having residues that can be toxic and reach humans through the food chain. A possible solution is biodegradable materials that use renewable raw materials such as proteins, lipids, and polysaccharides, the so-called bioplastics. In this context, the present study aimed to produce bioplastics based on starch with different proportions of xylan extracted from sugarcane bagasse and glycerol as a plasticizer. For this, their physicochemical properties (solubility, hydrophilicity, moisture, water barrier, opacity, crystallinity, and mechanical resistance) were evaluated. The biodegradation of the bioplastic was determined by buried and CO_2 released. As a result, it was observed that the increase in the proportion of xylan made the bioplastics more soluble in water, susceptible to enzymatic attack by microorganisms, and opaque. Through of the contact angle test, the bioplastic with starch and plasticizer showed lower affinity to water compared to the one including xylan, which among them the proportion of 25 % (w/w of the polysaccharides) was the least hydrophilic. Bioplastic with 5 % (w/w of polysaccharides) xylan showed better crystallinity followed by starch. As for its mechanical strength, the bioplastic with 10 % xylan (w/w of polysaccharides) owned the highest tensile stress (2.56 MPa), but the presence of xylan considerably reduced its elongation at break (ranging from 16 to 37 %) in relation to the starch bioplastic (208.8 %). In general, after 30 days of burial, the bioplastics had practically no fragments visible to the naked eye, and the rate of CO_2 production together with the increase in cell count after the biodegradation period demonstrate that there was an effective catabolic action of the microorganisms in the bioplastics. Thus, the 5 % xylan bioplastic showed the best physicochemical results when obtaining a biodegradable material.

Keywords: Bioplastic, xylan, starch, biomass, biodegradable.

RESUMO

O plástico serviu muito bem à sociedade durante décadas, podendo se apresentar como um material leve e moldável, mecanicamente e termicamente resistente, inerte a produtos químicos, isolante elétrico, além de possuir características ópticas interessantes como sua transparência. Tais características, associada ao baixo preço da sua matéria prima, um resíduo do processamento de petróleo até então pouco utilizado, fizeram com que ele se tornasse crucial para a indústria e o mercado, o que consolidou sua presença na sociedade em diferentes países. Contudo, por ser um material resistente, permanecendo séculos sem se decompor totalmente, e por ter uma larga produção a fim de atender as necessidades de uma sociedade consumista, ele passou a se acumular no meio ambiente ao longo dos anos desde sua criação. Sua abundancia no meio ambiente acarreta prejuízos à vida em diferentes biomas, especialmente os ambientes marinhos, além de possuir resíduos que podem ser tóxicos e chegar ao ser humano através da cadeia trófica. Uma possível solução são os materiais biodegradáveis e que utilizam matéria-prima renovável como proteínas, lipídeos e polissacarídeos, os chamados bioplásticos. Neste contexto, o presente estudo objetivou produzir bioplásticos baseado em amido com diferentes proporções de xilana extraída do bagaço de cana-de-açúcar e glicerol como plastificante. Para isso, suas propriedades físico-químicas (solubilidade, hidrofilicidade, umidade, barreira à água, opacidade, cristalinidade, e resistência mecânica) foram avaliadas. A biodegradaçãodo bioplástico foi determinada por enterramento e liberação de CO_2. Como resultado, foi observado que o aumento na proporção de xilana tornou os bioplásticos mais solúveis em água, susceptíveis ao ataque enzimático de microrganismo, e opacos. Por meio do ensaio de ângulo de contato, o bioplástico apenas com amido e plastificante apresentou menor afinidade à água, comparado aos compostos por xilana, que dentre eles a proporção de 25 % (m/m de polissacarídeos) foi a menos hidrofílica. O bioplástico com 5 % (m/m de polissacarídeos) de xilana apresentou melhor cristalinidade seguido pelo de amido. Quanto à sua resistência mecânica, o bioplastico com 10 % de xilana (m/m de polissacarídeos) foi o que possuiu maior tensão de tração (2,56 MPa), porém a presença de xilana reduziu consideravelmente sua elongação na quebra (variando de 16 a 37 %) em relação ao bioplástico de amido (208,8 %). No geral, após 30 dias enterrados os bioplásticos já não apresentavam praticamente nenhum fragmento visível a olho nú, e a taxa de produção de CO_2 juntamente com o aumento da contagem de células após o período de biodegração demonstram que houve uma efetiva ação catabólica dos microrganimos nos bioplasticos. Sendo assim, a concentração de 5 % de xilana foi a que mostrou melhores resultados físico-químicos ao obter um material biodegradável.

Palavras-chave: Bioplastico, xilana, amido, biomassa, biodegradável.

LIST OF FIGURES

Figure 1 - Polymeric chain models representing a linear polymer and a branched one. 16
Figure 2 - Illustration of a semi-rigid three-dimensional network structure. 27
Figure 3 - Types of copolymers. 28
Figure 4 - Groups of hemicellulose. 34
Figure 5 - Drug-carrying biomaterial applied in tissue regeneration. 36
Figure 6 - Presence of plasticizer in polymers. 39
Figure 7 - Interaction between chitosan and xylan. 42
Figure 8 - Esterification reaction. 45
Figure 9 - Etherification reaction. 46
Figure 10 - Oxidation reaction 46
Figure 11 - Chains crosslinked. 47
Figure 12 - Examples of bioplastics produced from starch and xylan in different proportions in relation to 5 % of polysaccharides (w/w of filmogenic solution). 80
Figure 13 - X-ray diffractograms of bioplastic of starch and xylan (according to Table 3). ... 81
Figure 14 - Relative percentage of contact angle of bioplastics of starch and xylan in relation to starch bioplastics. 84
Figure 15 - Opacity as a function of the composition of xylan in bioplastics, showing the respective photo of each composition 85
Figure 16 - FTIR of starch and xylan bioplastics (according to Table 3). 86
Figure 17 - Scanning electron microscopy images of starch and xylan bioplastics with starch and xylan with different magnitudes. 89
Figure 18 - CO_2 production (mg) from the biodegradation of starch and xylan bioplastics. ... 91
Figure 19 - Decomposition of the bioplastic with 10% of xylan (X10) over 26 days. 92
Figure 20 - Plate growth of soil microorganisms of the mixture of soils used in each bioplastic composition 93

LIST OF TABLES

Table 1 - Evaluation of different proportions of glycerol (G) in 5 % starch (w/w of solution) bioplastics 73
Table 2 - Evaluation of starch gelatinization conditions in bioplastics with 20 % glycerol (w/w of starch) 73
Table 3 - Bioplastic compositions in relation to 5 % (w/w, filmogenic solution) of polysaccharides with glycerol 20 % (w/w, polysaccharides). 74
Table 4 - Xylan extraction yield (%, w/w theoretically present in the bagasse) 78
Table 5 - Lignin content and sugars in biomass and solubilized xylan (%, w/w) 78
Table 6 - Moisture and solubility results of bioplastics with 5 % starch (w/w of solution) and glycerol. 80
Table 7 - Solubility and moisture of bioplastics of starch and xylan (according to Table 3)... 82
Table 8 - Water vapor transmission (WPT) and water vapor permeability (WVP) of bioplastics of starch and xylan (according to Table 3). 83
Table 9 - Tensile stress at maximum load and elongation at break in starch and xylan bioplastics (according to Table 3). 88
Table 10 - Average number of colony-forming units per gram of soil (CFU.g-1) before and after biodegradation of bioplastics (composed of the mixture of soils used in each composition). 93

LIST OF APPENDIX

Appendix A - Representative figure of the setup of the experiment witch a bioplastic 25 % xylan (w/w polysaccharides) 102
Appendix B - Representation of the biodegradation test of bioplastics with variations of xylan and only starch. 103
Appendix C - Interference of gelatinization in xylan and starch bioplastic (left pair), and only starch (right pair). 104
Appendix D - Bioplastics made in different ways and conditions of gelatinization. 105

SUMMARY

CHAPTER I: INTRODUCTION 11
CHAPTER II: OBJECTIVES 13
1. General objective 13
1.1. Specific objectives 13
CHAPTER III: HEMICELLULOSE APPLICATION FOR THE PRODUCTION OF BIOPLASTICS AND BIOMATERIALS 14
1. Introduction 15
2. Plastic 16
2.1. Origin of plastics and their importance for society 16
2.2. Negative impacts caused by an irregular plastics disposal 18
3. Bioplastics 25
3.1. Origin of bioplastics 25
3.2. Bioplastic composition and structure 27
3.3. The bioplastics market 35
3.4. Emerging technologies for bioplastics produced with hemicellulose 35
3.4.1. Importance of plasticizer for hemicellulose films 38
3.4.2. Development of biomolecule blends 40
3.4.3. Crosslinking agents in polymeric chains 47
3.4.4. Functional biopackages 48
3.4.5. Other applications of hemicellulose as a biomaterial 51
4. Concluding remarks 53
REFERENCES 55
CHAPTER IV: DEVELOPMENT OF BIOPLASTICS BASED ON STARCH AND XYLAN: A MECHANICAL PHYSICOCHEMICAL AND BIODEGRADABILITY STUDY 69
1. Introduction 70
2. Material and methods 71
2.1. Raw material 72
2.2. Xylan solubilization 72
2.3. Characterization of biomass and extracted xylan 72
2.4. Gelatinization parameters and plasticizer content 73
2.5. Bioplastic production 73

2.6. Bioplastics characterization 74
2.6.1. Moisture and solubility tests 74
2.6.2. Opacity 74
2.6.3. Hydrophilicity 75
2.6.4. Water vapor transmission (WVT) and water vapor permeability (WVP) 75
2.6.5. Mechanical test 75
2.6.6. Fourier-transform infrared spectroscopy (FTIR) 76
2.6.7. Scanning electron microscopy (SEM) 76
2.6.8. X-ray diffraction (XRD) 76
2.7. Biodegradation 76
2.8. Statistical analysis 77
3. Results and discussion 77
3.1. Biomass composition, xylan solubilization, and characterization 77
3.2. Gelatinization parameters and plasticizer content 79
3.3. Bioplastics characterization 81
3.3.1. X-ray diffraction (XRD) 81
3.3.2. Moisture and solubility tests 82
3.3.3. Water vapor transmission (WVT) and water vapor permeability (WVP) 82
3.3.4. Hydrophilicity 83
3.3.5. Opacity 84
3.3.6. Fourier-transform infrared spectroscopy (FTIR) 85
3.3.7. Mechanical test 86
3.3.8. Scanning electron microscopy (SEM) 88
3.4. Biodegradation 89
4. Conclusions 93
REFERENCES 95
CHAPTER V: CONCLUSION 101
APPENDIX 102

CHAPTER I: INTRODUCTION

The fossil-based plastic, that we conventionally use, assumed an important role in society in a way that it would be impossible to abruptly abolish its use, since it is present in our daily lives from the time we wake up to the time we go to sleep. Although plastic waste management policies can be carried out, the ideal level of recycling to contain the generation of waste, which tends to grow as the world population grows, is a difficult level to be reached. And the reasons for this are the demand for high investment in collection and sorting centers, the problem of the quality of recycled materials in relation to primary plastic and the most important factor, the cooperation of the population, because even if the first two items are resolved, will not be as effective if there is no awareness of the population. This last requirement is a more complex issue, because it is strictly related to the education and civility of each individual.

Biodegradable polymers produced from renewable sources have been seen as a promising strategy to replace (partially) the intensive use of plastic derived from petroleum due to the growing environmental awareness in recent decades, as this synthetic polymer remains in the environment for centuries. The use of polysaccharides has been studied and arouses the interest of researchers as they are molecules capable of forming long chains. The polysaccharides, can form a cohesive network due to inter and intra-molecular bonds, and can also be consumed and degraded by microorganisms resulting in small molecules common to the environment. In addition to being biodegradable, bioplastics have the raw material from renewable sources, and potentially toxic substances are not used in their composition. By relying on several hydroxyl groups, polysaccharides also have the ability to mix with other components (plasticizers and additives) improving their functionality.

Starch is generally used in bioplastic/film production because it is highly available and easy to extract, it has low cost, is biodegradable and biocompatible. It is still widely studied as edible bio-packaging because it has high energy value, in addition to forming films without odor, taste, color, toxicity, showing semipermiability to gases such as CO_2, O_2 and water vapor. However, native starch has a hydrophilic character and tends to form films with poor mechanical properties. Basically formed by two types of molecules, amylose (forms linear chains) and amylopectin (branched chains), both having a large amount of carboxyl groups capable of making hydrogen bonds.

In this context, xylan, a type of hemicellulose composed mostly by pentoses known as xylose, can present itself as a compatible sugar to starch, as it shares practically the same characteristics. Xylan can contribute to form bioplastic with greater mechanical resistance, in addition to theoretically preventing the retrogression process characteristic of starch, which consists of the loss of water molecules causing dryness. The interest in xylan also comes from the fact that it is a polysaccharide with potential for application in bioplastics that is still little used when compared to cellulose, even though it has considerable participation in the composition of plant biomass.

The study of starch in the preparation of biodegradable bioplastic is already well documented. However, from our knowledge, there are not study in the literature dedicated to understanding the contribution and correlation of xylan in bioplastic. In this context, the purpose of this study was to combine starch and xylan (extracted from sugarcane bagasse) to produce bioplastics. The contribution of the xylan concentration was evaluated in properties such as biodegradability, crystallinity, mechanics, opacity, water affinity, and water barrier.

CHAPTER II: OBJECTIVES

1. General objective

The main objective of this study was to evaluate the addition of xylan extracted from sugarcane bagasse in the composition of bioplastics in combination with starch. Physicochemical properties were determined and related to de biodegradation of the bioplastic.

1.1. Specific objectives

- Identify the better starch gelatinization conditions and glycerol concentration;

- Study the contribution of the xylan in the bioplastic compositions on the moisture, solubility, opacity, mechanical, crystallinity, and hydrophilicity, defining the most suitable proportion;

- Analyze the time needed for biodegradation of the bioplastic composed of xylan and starch by burial and CO_2 release.

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CHAPTER III: HEMICELLULOSE APPLICATION FOR THE PRODUCTION OF BIOPLASTICS AND BIOMATERIALS

ABSTRACT

Plastic has become a common material in society's daily life, since it meets industrial needs, due to its ability to be shaped in several ways, providing a relatively light, resistant, and inert product to be processed and manufactured on a large scale and at low costs. However, its environmental consequences over the years have caused several countries to deal with large amounts of residues, which accumulate for centuries without decomposing, thus affecting life in different biomes. An alternative towards the implementation of an efficient collection and recycling system would be its replacement (even if partially) with materials capable of degrading into small elements common to the environment. Hemicellulose, for example, is a polysaccharide highly available in the cell wall of plants, with potential application in the manufacture of biodegradable bioplastics that can replace conventional plastics; however, hemicellulose-based films are hydrophilic and have low mechanical resistance. There are challenges to improve the characteristics and fabrication processes of biodegradable films, which in addition to meeting market demands, must be viable. A great motivation is the strong market for functional materials such as packaging to promote better quality to the food. In addition, consumers are more demanding and concerned with the consumption of environmentally friendly products. In this sense, the objective of this review is to understand the reason for the ubiquity of plastic today, its origin and the various polymers that were developed from its inception to the various types of plastics we have today, also elucidating the environmental consequences caused by its reckless disposal. Thus, understanding the need for bioplastics for society and some of the main difficulties and barriers that bioplastics need to overcome so that they can also be implemented by industry as well as conventional petroleum-derived plastic.

1. Introduction

Plastic has become one of today´s biggest environmental problems, since it can remain undegraded for centuries and, associated with its large worldwide production, results in accumulations in landfills, dumps, and even in the environment. By the end of 2017, 9.2 billion tons of primary plastic was produced worldwide since 1950, and a large portion of this number is already waste (GEYER, 2020). An option for circumventing such an issue would be the use of the so-called bioplastics, which are alternative materials that meet the main industrial requirements and degrade in the environment.

The term "plastic", very widespread and used in our daily lives, does not refer to a single and particular material, just as "metal" does not refer only to iron or aluminum. It is employed for defining a range of materials of different structures, qualities, and compositions, whose common characteristic is their formation from the entanglement or chaining of long molecular chains of high molecular mass, known as macromolecules (MICHAELI et al.,, 1995). Another important characteristic shared by plastics is their deformability, i.e., the possibility of being easily molded under certain conditions of heat and pressure, irreversibly acquiring a new form (CHANDA; ROY, 2008; CHANDA, 2017; MICHAELI et al., 1995; RODRIGUEZ et al., 2014).

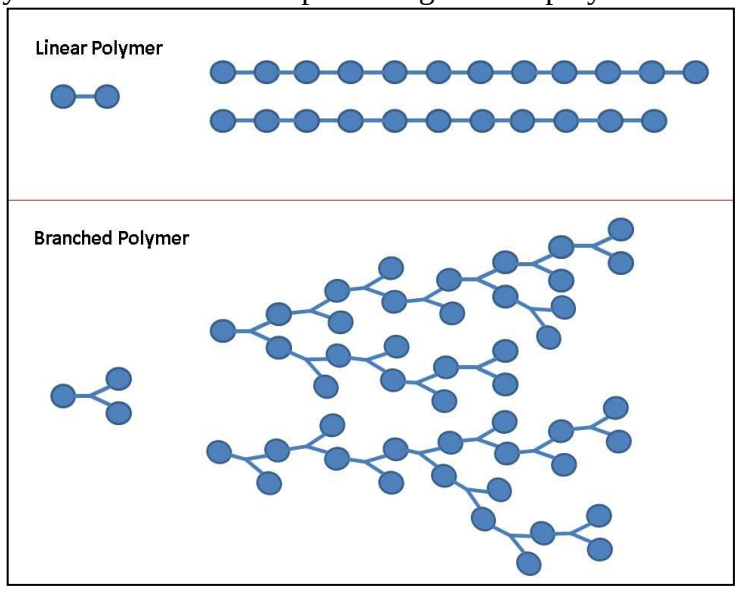
Macromolecules are chemically complex; they are comprised of small molecules, called monomers, which can form sequences of more than 10,000 units. Macromolecular structures are connected and formed through chemical bonds of small units, thus enabling the production of different structures from different monomers and with different arrangements (Figure 1) (HIEMENZ; LODGE, 2007; MANO; MENDES, 1999; MICHAELI et al., 1995; RODRIGUEZ et al., 2014). Macromolecules are formed through chain reactions of those monomers, which start with an initiating agent that promotes the formation of an active center (it can be an ion or a free radical). From this active center, new monomer molecules are added in a fast and successive way, producing a larger chain in continuous growth, with an active center at one of the two ends. Such a process persists until a terminating agent suddenly interrupts, generating a terminal group (HIEMENZ; LODGE, 2007; MANO; MENDES, 1999).

Plastics are the main representatives of “polymers” (from Greek, many parts), which are macromolecules with chemical units repeated in a standardized way along the chain. Therefore, it can be understood that all polymers are macromolecules, but not all macromolecules are polymers (Chanda 2017; HIEMENZ; LODGE 2007; MANO; MENDES

1999). Hemicellulose, a sugar highly available in several biomasses and relatively little used by the industry, is among the various natural raw materials studied in bioplastic compositions.

This chapter explores the reasons why plastics of petrochemical origin are so strongly present in society, and the environmental consequences of the dependence on this material. To then talk about bioplastics, defining what they are, their current market, and studies focused on bioplastics composed of hemicellulose. The main objective of this review is to indicate studies that suggest ways to overcome some of the deficiencies of hemicellulose in its application in the manufacture of bioplastics.

Figure 1 - Polymeric chain models representing a linear polymer and a branched one.



Source: Author

2. Plastic

2.1. Origin of plastics and their importance for society

Natural materials such as wood and several metals have been long used for the production of tools and objects for practical day-to-day tasks and protection, and as weapons. However, since society has evolved and its habits and needs have changed, such materials have become obsolete for certain applications, due to their lack of certain characteristics (e.g., lightness and easy processability). Therefore, new materials and processes of reduced costs have been required.

The progress of industrialization has demanded an increased use of electricity, hence, materials such as insulators for the production of electrical equipment and systems. Shellac, a

resin secreted by an insect from Asia, has been widely used by industries as both an insulator and an ideal material for such applications. However, its availability is limited, due to its natural origin and production by insects at a rate lower than that required by the industry. In 1907, Belgian Leo Hendrik Baekeland developed the first synthetic plastic, called bakelite, from phenol and formaldehyde in his laboratory (FRIEDEL, 1984; RODRIGUEZ et al., 2014).

The current idea of the polymer was drawn around 1920, when chemist Hermann Staudinger developed his structural model. Despite the lack of concrete evidence, Staudinger believed materials of chemical structure (unknown until then), such as natural rubber and some synthetic products, were made up of long molecular chains, differently from the idea they were colloidal aggregates of small molecules. Not only was Staudinger awarded the Nobel Prize in 1953, but also new materials started to be designed, thus contributing to the industrial development of the 20th century (MANO; MENDES 1999; MICHAELI et al., 1995).

Several properties (e.g., lightness) are responsible for the unrestrained use of plastics. Because they are lighter than other materials such as metals and ceramics, they are employed in the construction of airplanes and automobiles, and the production of sports equipment and packaging (MICHAELI et al., 1995). Their processing requires lower energy expenditure and is easily conducted at a maximum temperature of 250 ^{o}C; in some cases, it can reach 400 ^{o}C, which is much lower than the 1,400 ^{o}C required for steel, for example. This characteristic enables the integration of substances such as dyes, loads (wood and mineral powder), reinforcement loads (fiberglass or carbon), and foaming additives, responsible for improving the mechanical, thermal conductivity, optical, and insulating properties, as well as the material´s density (CHANDA; ROY, 2008; CHANDA, 2017; MICHAELI, et al., 1995).

Although soluble in organic solvents such as gasoline and alcohol, plastics are good thermal and electrical insulators, since they resist certain chemicals and are less prone to corrosion than metals. They have variable permeability, and may or may not promote the diffusion of substances such as gases. Most of them are highly flexible when compared to natural materials (e.g., metals), and can replace glass, due to their higher resistance to impacts and similar optical properties (they can also be transparent materials) (CHANDA; ROY, 2008; CHANDA, 2017; MICHAELI et al., 1995).

Coal had been the raw material for plastics until the mid-1950s, when it was replaced by naphtha, a portion of the oil refining, thus promoting industrial development, regardless of

some falls over the years (e.g., the oil crisis, in 1973) (NIELSEN et al., 2019; MICHAELI et al., 1995). The success achieved by the alliance between plastics and petrochemical industries has resulted the fact that 99 % of the raw material for the currently plastic production being based on fossil fuels. The plastic production is responsible for approximately 8 to 9 % of global oil and gas consumption - specifically, 4 to 5 % are used as raw materials and 3 to 4 % are destined to power the production (NIELSEN et al., 2019).

2.2. Negative impacts caused by an irregular plastics disposal

Plastic has become an essential material in the infrastructure of modern societies, since it enables the production of several objects with different designs and applications, high resistance, lightness, and bioinertia at low costs (NIELSEN et al., 2019). However, some of such good characteristics have led plastics to be one of the biggest current environmental problems.

Plastic pollution has reached different parts of the world, persisting on surfaces and in abyssal zones of oceans (KRAUSE et al., 2020), soils, freshwater reservoirs, arctic ice (BERGMANN et al., 2019), animal bodies, and the air (WINDSOR et al., 2019). The environmental spread of plastics is due to their persistence, since approximately 450 years are necessary for their disintegration - in some cases, they never reach complete degradation (PARKER, 2018). Another determining factor is their continuous and growing annual production. The worldwide plastic production has increased 200 times since 1950 and has continually grown at a 4 % rate since the year 2000, with a production capacity estimated to grow 40 % by 2030 (WWF, 2019a). In 2018, 359 million tons of products were generated (Plastics Europe 2019). However, according to some reports, this number had already been exceeded in 2016, with 396 million tons (WWF, 2019a).

The three most common worldwide destinations for plastic waste are recycling, incineration, and dumping, either in landfills and dumps, or directly in the natural environment. From the development of the plastic industry in 1950 to the year 2017, 7 billion tonnes of the 9.2 billion produced is waste, in which only 0.7 billion have been recycled while 5.3 billion was discarded in landfills, dumps or natural environment (GEYER, 2020). Barriers have hampered the implementation of an efficient recycling system, hence, a significant share of recycles. One of such obstacles is the wide diversity of materials and formats, since functional innovations beneficial for their application tend to decrease the quality of the recycled material and increase both difficulty and value of the process. Other barriers include

fragmentation and disorganization of the collection and classification system, which hamper a unified, articulated, and more efficient process with a consistent delivery flow of high-quality material to the recyclers (ELLEN MACARTHUR FOUNDATION, 2016b).

In addition to difficulties in the waste management faced by most countries, recycled materials are devaluated on the market, because their quality is sometimes considered lower. Studies have suggested the contamination and mixing of different types of polymers can lead to secondary plastics of lower technical and economic values, thus limiting the reuse of some materials (GEYER et al., 2017). Although recycling is economical in some packaging applications, such as polyethylene terephthalate (PET) bottles, the cost of collection and sorting exceeds the revenue generated (ELLEN MACARTHUR FOUNDATION, 2016b). In other words, the problem goes beyond the arduous exercise of population awareness. Such contexts hamper our devising a reality where the recycling of those wastes, considered the most appropriate way to treat them, can be compared to or even accompany the rate of plastics production. The rate tends to increase over the years towards meeting society´s consumption demands, whereas the percentage of recycled waste will possibly remain unsatisfactory.

Optimistic data collected in the 28 countries of the European Union, Norway, and Switzerland, and presented by Plastics Europe (2019), a trade association representing the plastics industry in Europe, have highlighted a 92 % increase in the recycling of plastic packaging between 2006 and 2018. However, still, only 42 % of the materials are recycled, while worrying 39.5 % are represented as “energy recovery”, a process characterized by the incineration of materials, which can cause other problems to both the environment and the incinerators´ health. Such an increase in the recycling rate is far from being a reality for the vast majority of countries.

In 2014, Europe and China showed high recycling rates of 30 and 25 %, respectively, although incineration rates have also increased 40 and 30 %. This recycling rate is better than those of countries like the United States, which from 2012 to 2014 have remained at the same 9 % (GEYER et al., 2017). The difficulties in achieving an effective management faced by Europe countries and China is due to a complex task that involves waste reduction, adequate waste collection, classification of types of plastics, and improvement in recycling logistics (NIELSEN et al., 2019).

Much of the waste for recycling in Europe is exported for processing (NIELSEN et al., 2019). Although this practice is an environmental solution and offers economic advantages for underdeveloped and developing countries, it is not effective, since such importing

countries have been overburdened. Consequently, China, which had an important function in recycling waste from other countries, restricted the import of waste in 2018 (BROOKS et al., 2018), leaving its role vacant for Southeastern Asian countries that already import waste from some countries of the Organization for Economic Cooperation and Development (OECD). However, many of those Asian countries do not have a proper infrastructure for managing their own wastes (BROOKS et al., 2018).

Some applications for plastics generate more waste and are more alarming. Approximately 42 % of non-fiber plastics, comprised predominantly of polypropylene (PP), polyethylene (PE), and polyethylene terephthalate (PET), have been used for the production of packaging, while 19 % have been employed in construction materials. However, such applications generate 54 % and 5 % of wastes, respectively. Certain products (e.g., disposable objects) are manufactured on a large scale and discarded in the same year of production. On the other hand, plastics used in construction have relatively low production and are generally discarded after decades (GEYER et al., 2017). Therefore, depending on the application and type of plastic, efforts are devoted to solving urgencies considered imminent threats to the environment.

Disposable materials such as packaging, supermarket bags, bottles, straws, containers, cups, and cutlery are the most problematic among plastic wastes (UNEP, 2018), not only because they become waste quickly, but also because they are the most produced plastic materials. Among them, packaging currently represents 26 % of the total volume of plastics used by the industry (ELLEN MACARTHUR FOUNDATION, 2016a). The ubiquity of those materials in the environment is related to a relatively cheap production and the recent demand of society for individual and practical food products. The Brazilian Association of the Food Industry pointed out a 4.9 % increase in sales of ready and semi-ready dishes and frozen and dehydrated foods in 2019.

The effect of the pandemic originated in 2019 due to the SARS-CoV-2 virus, responsible for developing a respiratory crisis in humans that can lead to death, must also be considered. Because the use of personal protective equipment (PPE), such as masks and gloves, that has become an important public health tool to prevent the spread of the virus in the population. As a result, there has been a significant increase in the use and consequent disposal of these equipment that are made of plastic, for example, at King Abdullah University Hospital in Jordan, where it is estimated that ten times more medical waste is produced (approximately 650 kg per day) than in any period prior to the pandemic. The same is reported in other countries, such as Spain and China, which had an increase of 350 and 370

% in the production of hospital waste, respectively. This leads to a particular problem regarding the handling of this potentially infectious plastic waste, because the sorting and recycling of these materials is avoided to ensure the health of employees at recycling facilities. There are only two options for the disposal of this waste, incineration, which ends up being the most practiced by many countries, especially the more developed ones, and disposal in landfills or even dumps (PATRÍCIO SILVA et al., 2021).

Due to the pandemic, the demand for plastic is still expected to grow by 17 % in applications like medical uses and 40 % in packaging due to consumer demand for more packaged fresh food, because they believe that are better protected from SARS-CoV-2 contamination. Thus, the development of PPE from bioplastics, in addition to being an environmentally more suitable alternative, would also prevent the spread of the virus through waste, because viable SARS-CoV-2 persists longer on plastic surfaces than on other materials (PATRÍCIO SILVA et al., 2021).Environmental problems arise when plastic products are incorrectly disposed of. Although the flow of plastic waste among different systems (atmospheric, terrestrial, and freshwater) is multidirectional, marine systems are generally the final destination (WINDSOR et al., 2019). More than 5 trillion plastic particles, i.e., over 250 thousand tons are estimated only on the surface of oceans (ERIKSEN et al., 2014).

Much of the plastic pollution is correlated to human activity in terrestrial environments. Plastic particles can be easily transported by the action of the wind, since they are light materials. Running water also contributes to the distribution of plastic waste; it acts as a conduit that connects terrestrial, freshwater, transition, and marine systems, providing an important long-distance transport route, and can also direct and store waste in benthic, floodplain or riverside habitats. When improperly deposited in the environment, plastics can be carried to river systems by the action of rainfall and through the leaching of the soil, thus representing a risk of contamination in freshwater environments (WINDSOR et al., 2019). Among the main sources of plastic waste in the soil are intensive agricultural practices, which distribute plastics in rural regions through the degradation of machinery, dissemination of garbage, application of sewage sludge in soil conditioning, and plastic coverings. Urban activities also act as a source of plastic in the environment, such as the waste disposal in landfills and dumps and industrial spillage (WINDSOR et al., 2019).

As addressed elsewhere, oceans are considered the endpoint of the plastic flow of hydrographic basins, responsible for a large amount of plastic wastes disposed of in the marine environment. However, a significant quantity is likely to be sent directly into the oceans, since 50 % of the global population reside 31 km from the coast. Industrial activity

and commercial fishing also contribute to the accumulation of plastics in marine ecosystems (WINDSOR et al., 2019). According to an analysis conducted by the Ellen MacArthur Foundation (2016a), if the current ratio of plastic disposal that reaches the oceans remains, more plastics (850-950 million tons) than fish (812-899 million tons) will be found in the ocean (in relation to the mass) by 2050 .

Plastics are encountered even in the air due to their lightness, which enables them to be suspended and transported to the atmosphere. They can come from hydrographic basins, combustion of plastic waste, wind erosion from different media, urban dust (tire wear particles, paint, and synthetic fibers), and waste dispersion (WINDSOR et al., 2019).In the environment, the most obvious impact of plastic pollution on an ecosystem is asphyxiation in large and small animals (WINDSOR et al., 2019). Images of animals trapped in plastic discards are commonly found; such a fact is not exclusive to marine environments, since American crows have shown evidence of strangulation (WINDSOR et al., 2019). More than 690 marine species have ingested some plastic material (PROVENCHER et al., 2017) that can harm them in many ways. For example, the ingestion of some plastic waste can either lead to death by choking, or give a false sense of satiety, reducing the absorption of nutrients, causing changes in the intestinal microbiota, and consequent reduction of energy provisions. All such outcomes lead the animal to exhaustion, reducing important activities for it to stay alive and reproduce (WINDSOR et al., 2019).

Apart from physical impacts, which are more easily observed, indications of chemical impacts from exposure to plastics have also been reported. Because plastics are complex products, they can adsorb contaminants from the environment, or leach their various additives, which act as flame retardants, plasticizers, hardeners, surfactants, and synthetic dyes. These chemical components are released over time and can be potentially toxic to the environment (WINDSOR et al., 2019).

Sea turtles are some of the most affected animals by the impact of plastic waste. Ingestion occurs mainly because they confuse waste with possible food (e.g., plastic bags with jellyfish (CARR, 1987) or seagrass (DUNCAN et al., 2019b), and are attracted by the smell of organic matter from microorganisms that develop and die on the surface of the plastic (PFALLER et al., 2020). In a study with individuals from seven species of sea turtles sampled from three ocean basins (Atlantic, Mediterranean, and Pacific), Duncan et al., (2019a) observed all organisms analyzed had synthetic particles, of which most were fibers, followed by fragments and microspheres. Such particles were found in species that occupy different

trophic levels, indicating those materials can be ingested through multiple routes, including exposure to plastic pollution in the marine ecosystem and trophic transfer.

Plastics of 1 μm to 5 mm are called microplastics (they can be even smaller, and, therefore, called nanoplastics) and are found in different places (e.g., depths of the Mariana trench and the Arctic ice). Most of them result from the degradation of larger plastics, although, in some cases, they are intentionally produced by industries, such as cosmetic ones (NIELSEN et al., 2019). Their presence in the marine ecosystem impairs its oxygen production, interfering with the growth of *Prochlorococcus*, the most abundant photosynthetic bacteria in the oceans. Therefore, their deposit in the oceans can lead to both deficiencies in oxygen production and absorption of carbon from the environment (TETU et al., 2019).

Humans are not exempt from possible damage to health caused by plastic waste, due to evidence of transfer of microplastics through the aquatic food chain. Such a bioaccumulation is a major threat to predators at the top of the food chain, like humans (WANG et al., 2019). The bioaccumulation of plastics was evaluated by Cheikh et al. (2018) in scallop (*Pectenmaximus*), a mollusk commonly appreciated as a refined food. The animal showed rapid uptake of nanoparticles, which accumulated in the intestine and throughout the body after 6 hours of exposure, remaining in the mollusk after 48 days

A study from the University of New Castle, in Australia, revealed an ordinary person can ingest 5 grams of microplastics weekly, which is equivalent to the mass of a credit card. According to the study, such materials are ingested through the consumption of drinking water, beer, seafood, and salt (WWF, 2019b). This finding was corroborated by results achieved by researchers in the Czech Republic, who analyzed water samples and found microplastics at 1,473 to 3,605 particles/L of raw water and 338 to 628 particles/L of treated water. In general, the particles were smaller than 10 μm, with a predominance of fragments and fibers mostly composed of PET (polyethylene terephthalate), PP (polypropylene), and PE (polyethylene) (PIVOKONSKY et al., 2018). Likewise, a Chinese study found 550 to 681 particles/kg in sea salts, 43 to 364 particles/kg in lake salts, and 7 to 204 particles/kg in rock or well salts, mostly characterized by fragments and fibers measuring less than 200 μm. The most common microplastic was PET, followed by PE and cellophane (YANG et al., 2015).

Small particles negatively affect fish's reproductive system (NIELSEN et al., 2019), as well as humans exposed to components used in plastics, such as phthalates, bisphenol A (BPA), polybrominated diphenyl ethers (PBDE), and tetrabromobisphenol A (TBBPA). Phthalates and PBDE act as anti-androgens, BPA has estrogen-like activity, and PBDE and TBBPA can disrupt thyroid hormone homeostasis (essential for normal neurological

development and reproductive function). Such compounds can act on hormonal disorder mainly in childhood; since the child's organism is still under development, it is more sensitive to external interferences. Kovanecz et al., 2014 and Talsness et al., 2009 reported testicular dysgenesis syndrome in male rats after perinatal exposure to phthalates caused by prolonged exposure and accumulation of those compounds in the body, similarly to what is observed in humans.

Evidence has pointed to possible cytotoxic effects of nanoplastics on human blood cells, due to the affinity between plasma proteins and the nanoplastic, leading to conformational changes in the protein, hence, its denaturation and bio-incompatibility. Gopinath et al. (2019) reported indications of genotoxic effects while studying onions (*Allium cepa*), whose root growth was hampered by the exposition to nanoplastics, leading to chromosomal aberrations.

The potential cytotoxicity of micro and nano plastics can be combined with other compounds, forming reactive oxygen species (SCHIRINZI et al., 2017) that transport metals in the marine environment. In some cases, plastic pellets whose concentrations of remaining metals (Cr, Co, Ni, Cu, Zn, Cd, and Pb) exceeded those normally reported for local estuarine sediments (HOLMES et al., 2012) were detected. Another risk is microplastics acting as vectors for the dispersion of pathogenic microorganisms such as *Vibrio spp* adhered to the plastic surface through a biofilm (KIRSTEIN et al., 2016).

Plastic production is potentially polluting. In 2016, it generated approximately 2 billion metric tons of CO_2 emissions, corresponding to 6 % of the emissions of this gas per year, thus intensifying the greenhouse effect (WWF, 2019a). A significant amount of greenhouse gases will still be emitted, since large volumes of plastics are broken down into smaller pieces, also leading to acidification of the oceans, loss of biodiversity, and the ability of this ecosystem to absorb carbon (NIELSEN et al., 2019).

Socio-economic problems could be more effective to alarm society about the problem of waste accumulation on the planet than threats to the environment, to the health of fauna of humans. The fishing activity for both commercial and recreational purposes shows the negative impacts generated by plastic wastes through the reduction of its productivity and damage caused to fish (WINDSOR et al., 2019). According to Mouat et al. (2010), the activity of 86 % of Scottish fishing vessels had been harmed by marine litter. Despite the relatively low concentration of contamination, the ingestion of microplastics by fish and seafood can also exert a negative economic impact through the bad impression conveyed by the products to consumers (WINDSOR et al., 2019).

Plastic waste also affects tourism in natural environments, since pollution impairs the visual appeal of the place and represents a risk to the well-being of tourists. Approximately 70 % of marinas and ports for leisure reported their users had already suffered an incident with solid waste (MOUAT et al., 2010). Water treatment systems also suffer financial losses due to plastics improperly discarded, which end up in the pipes and equipment, damaging them and causing obstructions. Treated water suppliers are forced to invest and look for solutions that adapt their infrastructure to this current problem (WINDSOR et al., 2019).

Modern society has assumed a certain dependence on plastics, as in the case of food packaging, which protects and maintains the desirable qualities of a product for the consumer and increases its both longevity and hygiene (NIELSEN et al., 2019). However, the problem caused by the unrestrained use and irresponsible disposal of that material is evident. Environmental awareness and the adequate handling of plastics through an efficient recycling system have proven the most prudent and thoughtful solution, although it is still a difficult reality and very far from being reached. Consequently, the replacement of part of plastics with biodegradable materials has motivated studies on the use of biomaterials instead of conventional plastics.

3. Bioplastics

3.1. Origin of bioplastics

Evidence has shown man has used natural materials obtained from plants from the very beginning. Gums, for example, are substances formed by polysaccharides and their derivatives, characterized by colorless, odorless, tasteless, non-toxic, and capable of forming viscous solutions or even gels. (MANO; MENDES, 1999; PEREIRA et al., 2012). They were used for years to join pieces of wood in buildings or to waterproof boat surfaces (LACKNER, 2015). Gum Arabic, a secreted resin from Acacia trees used by the Egyptians in 2000 B.C. as an adhesive in the mummification process and mineral paints is still used mainly by the food and pharmaceutical industry (MUSA et al., 2018).

There is no doubt about the importance of the industrialization process for the development of new materials. In the beginning, once the understanding of chemistry was still relatively limited, the industry took its first steps using and studying completely natural materials. The progress of chemistry, combined with the application of those organic materials, has promoted the development of new bio-based products with increasingly

interesting properties. One of the major findings is attributed to Charles Goodyear, who, in 1839, discovered the process of vulcanization of natural rubber, a polymer derived from a milky colloidal suspension called latex and found in certain tree species. The process enables the addition of sulfur to the polymeric rubber chain at high temperatures, making it more resistant and elastic (COSTA et al., 2003; LACKNER, 2015). The discovery of this thermoset material, which can be molded only once after being heated and cooled, encouraged the search for new polymers, resulting in the creation of thermoplastic materials, which can be remodeled several times.

The 1862 London International Exhibition presented parkesine, the first plastic material, produced by English Alexander Parkes. It was biobased, due to its formation from cellulose nitrate derived from cotton, in which the cotton cellulose was treated with nitric and sulfuric acid and then mixed with vegetable oil and organic solvents (LACKNER, 2015; LINTSEN et al., 2017; QUYE, 2017; VINCENT, 2006). In summary, the polymer is formed because the cellulose has hydroxyl side groups (-OH) that are replaced by nitrate groups (NO_3-) through an esterification reaction with an aqueous acid mixture. Consequently, the acid concentration of the mixture determines the degree of substitution of the groups, and plastics with different properties are produced. For example, moldable plastics were obtained with 10.5 % nitrogen content of the final product, and films were made with 11.5 %. However, a material with explosive characteristics could be obtained (QUYE, 2017) with a slightly higher content, i.e., approximately 13.5 %.

Thermoplastics were a great novelty for that time, and their consistency was similar to that of dough, which could be shaped in different ways when subjected to heat and pressure. Parkesine was described as "hard as a horn, flexible as leather, capable of being cast or printed, painted, dyed or sculpted" (VINCENT, 2006), thus showing the dependence on the referenced materials (e.g., horn, leather, ivory), currently considered more rustic, and the novelty thermoplastics represented, as well as the greater possibility of producing materials of different shapes and colors, important for the industry. However, parkesine was still relatively fragile and brittle; its production was impaired and interrupted after two years due to its high costs, forcing manufacturers to produce a lower quality material (LINTSEN et al., 2017; QUYE, 2017). Despite the failure of parkesine, researchers continued to look for new materials, and some of them, such as celluloid, caught the attention of the industry (LINTSEN et al., 2017; QUYE, 2017; VINCENT, 2006).

The origin of celluloid is related to a contest held by American company Phelan and Collander in the middle of 1870, towards finding a cheaper substitute for ivory, extracted

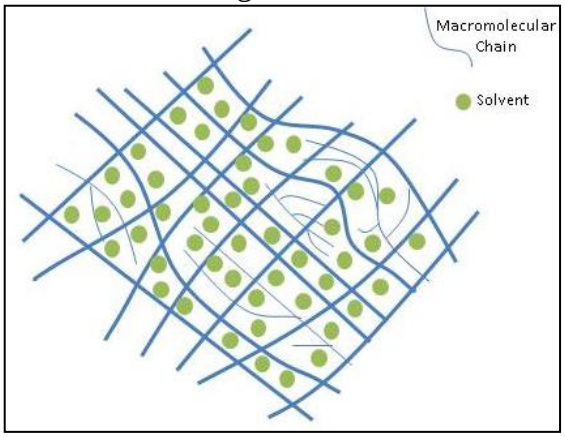
from elephants, for the production of its billiard balls. American researcher John Wesley Hyatt applied the same cellulose nitrate technique used by Parkes, but adding camphor as a plasticizer and ethyl alcohol as a solvent. Although the use of flammable reactants, a more stable than parkesine and ideal material for the industry was created (CANTO, 2004; LINTSEN et al., 2017; QUYE, 2017; VINCENT, 2006; RODRIGUEZ et al., 2014).

Industries have always aimed at larger, cheaper, and higher-quality productions, and, because of the discoveries related to cellulose nitrate plastic, have developed more and more materials synthetically and based on fossil fuels. Like naphtha, a cheap raw material, that enabled a massive production of petrochemical polymers in the 1940s and 1950s. Due to these circunstances, the industry was moving towards a more synthetic route similar to what occurred with bio-based fuels, which were replaced by fossils such as gasoline and diesel (LACKNER, 2015).

3.2. Bioplastic composition and structure

Similarly to plastics of fossil origin, the structure of bioplastics is comprised of chains of macromolecules formed by monomers. Such chains are connected to each other resulting in a semi-rigid three-dimensional network structure, with the solvent trapped and immobilized between the bonds, as illustrated in Figure 2. The degree of cohesion of the structure depends directly on the structure of the polymer (the polymeric chains that make up the network), the solvent used, the drying temperature, and the presence of other molecules, such as plasticizers. Polysaccharides of linear structure (e.g., cellulose, amylose, or chitosan) generate more resistant, flexible, and transparent polymers, and are an efficient barrier to fat and oils (THARANATHAN, 2003).

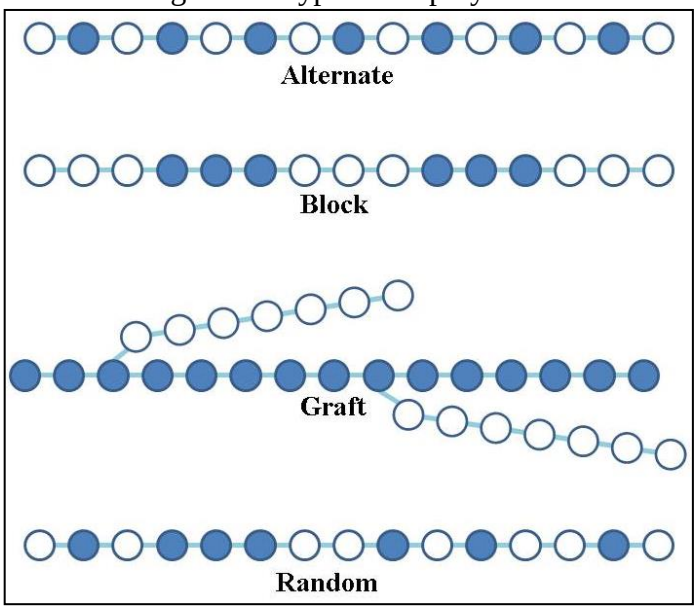
Figure 2 - Illustration of a semi-rigid three-dimensional network structure.



Source: Author

This network of biomolecules, in many cases called a polymer, can be classified according to the “meros” (from the Greek, meaning “parts”) that form it. If made from a single type of unit, they are homopolymers; however, the concept here of pure polymers is different from that applied to chemistry in general, due to the difficulty in obtaining fractions of absolute molecular uniformity with biomolecules. On the other hand, polymers formed from more than one type of units are called copolymers. Copolymers are characterized as alternate, in case of perfect sequencing regularity, block, if, instead of a single chemical unit, there are sequences of equal chemical units alternating (such specific blocks as polymeric branches are known as graft or grafted copolymers), and random copolymers, which, as the name implies, are formed by units with randomly arranged sequencing (MANO; MENDES, 1999), as illustrated in Figure 3. Hemicellulose, which will be further addressed, is an example of random copolymer, due to its both complex and random composition and sequence (IMRE et al., 2019).

Figure 3 - Types of copolymers.



Source: Author.

The European Bioplastics Industry Association characterizes bioplastic as being biobased or biodegradable or both. The European Committee for Standardization also brings as a criterion to bioplastics the biocompatibility of these materials, which allows them to be applied in medical therapy (IMRE et al., 2019). They are biobased materials, if their constitutional units are originated from biomass totally or partially. They can be natural,

synthesized by living organisms, or even biobased synthetics, whose monomers are derived from biological sources. Another characteristic of bioplastics is their ability to be biodegraded in the environment. The biodegradation process transforms organic matter into final smaller inorganic molecules such as CO_2 and H_2O, a process known as mineralization. The process takes place from the action of enzymes released by living cells (usual microorganisms), and is often accompanied and promoted by physical-chemical phenomena (IMRE; PUKANSZKY, 2013; IMRE et al., 2019; LACKNER, 2015).

The bioplastic decompositions by microorganism action occur with a pool of enzymes that act on different types of hemicellulose (and its substituents) with different chain sizes, producing monomeric sugars, uronic and acetic acids. Such enzymes with different functions act synergistically in specific regions of the polysaccharide, such as endo-1,4-β-xylanase, which is used hydrolyzes xylan into oligosaccharides, and 1,4-β-xylosidase, which releases xylose monomers from oligosaccharides. Accessory enzymes (e.g., xylanesterases, ferulic acid esterases, p-coumaric-esterases, α-1-arabinofuranosidases, and α-4-O-methyl glucuronosidases) generally act breaking the binds between the side groups and the main chain composed of xylan.

Must be considered the bioplastics behavior towards the action of the enzymes, because it is important to estimate the time and conditions required for the material to be fully mineralized, proving its biodegradability. Although few studies have addressed the biodegradation of hemicellulose bioplastics, Lucena et al., (2017) proved bioplastics based on xylan blended with gelatin are fully biodegradable after 15-day conditioning in a mixture of soil and manure. However, the rate of biodegradation depends on the proportion of hemicellulose and the component it is mixed with. After buried for 30 days, films produced with beechwoodxylan and polyvinyl alcohol showed 42.2 % and 56 % biodegradtion degrees, and 25 and 50 % xylan concentrations, respectively, indicating xylan is more prone to enzymatic attack (WANG et al., 2014). In the same study, the authors observed the presence of citric acid in the bioplastics interfered with the degree of biodegradation, which decreased from 42.2 to 33.5 %, due to the ester bonds formed when the crosslinker was present, hampering the attack of microorganisms, in comparison to hydrogen bonds (WANG et al., 2014).

Xylan bio-composites produced with poly-(ε-caprolactone) (PCL), and a high biodegradation degree between 95.3 and 99.7 % after 28 days of analysis was identified (FARHAT et al., 2018). However, the biodegradation kinetics was different between films composed only of hemicellulose and those with PCL. The materials showed slower

biodegradability kinetics when the PCL content was increased, probably due to the fact that this component has a higher degree of polymerization and substituition rate compared to hemicellulose.

Some types of raw material processing, such as chemical modification through acetylation, can also change the biodegradability degree of bioplastics. Fitch-Vargas et al., (2019) produced films based on acetylated starch and lignocellulosic fibers that showed an approximately 30 % level of biodegradability in 5 weeks, suggesting, according to the authors, the bioplastic maintained reasonable stability. They also observed an increase in the fiber increased both crystallinity and recalcitrance of the bioplastic, hindering the access and action of degrading enzymes. However, all such results provide an estimate of the time required for bioplastics comprised of hemicellulose to degrade, since the diversity of microorganisms responsible for degradation and the conditions to which bioplastics are subjected can change the degradation rate. In all cases, hemicellulose proved capable of being biodegraded, and, depending on the desired application of the bioplastic, the addition of some polymers or chemical modifications can extend the time for the material to be converted into simpler compounds in nature (GU, 2003).

The characteristics that define bioplastics do not necessarily present themselves as adjuncts. In some cases, the material may be of biological origin, but not biodegradable, as is the case of biobased polyethylene terephthalate (PET), polyamides, polyurethanes, natural rubber, and highly substituted cellulose acetate. On the other hand, bioplastics of fossil origin, such as polybutylene succinate, poly-ε-caprolactone, and polyvinyl alcohol can be biodegradable (IMRE; PUKANSZKY 2013; IMRE et al., 2019; LACKNER, 2015).

Biobased plastics are comprised of renewable materials, and can be produced from derivatives of organic molecules (e.g., biomass-based PET, formed through the polycondensation of ethylene terephthalate monomers, which are products of reactions between terephthalic acid (esterification reaction) or dimethyl terephthalate (transesterification reaction) with ethylene glycol). Based on this principle, Lackner (2015) and Mohsenzadeh et al., (2017) developed a PET using monoethylene glycol (MEG) derived from sugarcane ethanol. However, biobased products can also be natural (e.g., polylactic acid (PLA) and polyhydroxybutyrate (PHB)). They are thermoplastic polyesters secreted by microorganisms, and enable large-scale production through fermentation in bioreactors (IMRE et al., 2019; PACHEKOSKI et al., 2014). Chitosan is also a macromolecule of biological origin widely used in the production of biodegradable films. Its excellent film-forming property, due to its numerous hydroxyl and amine groups, enables the formation of

several hydrogen bonds. Obtained by the deacetylation of chitin present mainly in the cell wall of fungi and the exoskeleton of arthropods, it is biodegradable and non-toxic, with antioxidant and antimicrobial activity (COSTA et al., 2015; XU et al., 2019). Among natural materials are the macromolecules produced by plants, which have the advantage of being raw material obtained by an inexpensive way, since it requires only the ideal conditions for the development of plants. A wide diversity of plants rich in starch, lignocellulose, and pectin can also be applied in bioplastics production (IMRE et al., 2019).

Most of the studies on biodegradable films are focused on the use of cellulose and starch in the composition of such films (IMRE et al., 2019). Cellulose is the most abundant biopolymer on Earth, present in the cell wall of plants, along with two other main components, namely hemicellulose, and lignin. Its structure is built from β (1-4) glycosidic bonds between D-glucopyranosyl units, forming long, linear polymer chains that, due to the hydroxyl groups in their structure, are grouped into microfibrils through intramolecular and intermolecular hydrogen bonds. Despite the partial presence of amorphous regions, the chain arrangement results in a material of high crystallinity degree (MANO; MENDES, 2013; Shackelford 2004) that guarantees the characteristic resistance of cellulose (COMA, 2013; IMRE et al., 2019; MANO; MENDES, 2013; MELATI et al., 2019).

Starch is a vegetable storage polysaccharide, widely available in nature, found in cereals, tubers, pods, and roots (BOTHAM, 1995; DENARDIN; da SILVA, 2009; KEETELS et al., 1996; MANO; MENDES, 2013; SOUZA; ANDRADE, 2000), and which displays two types of α-D-glucopyranose polysaccharides structures. One is amylose, a linear macromolecule joined by α(1-4) glycosidic bond, and generally found in lower quantity and mass than the second type, i.e., branched amylopectin, also characterized by α-type bonds (1-6) at branch points and α (1-4) (DENARDIN; da SILVA, 2009; IMRE et al., 2019; KEETELS et al., 1996; SOUZA; ANDRADE, 2000).

Hemicellulose has been gaining attention of researchers in recent decades for composing between 15 and 35 % of plant biomass (NAIDU et al., 2018). It is a polysaccharide of partial solubility in water, but quite soluble in diluted alkaline medium (ALVES et al., 2020; FREITAS et al., 2019; BRIENZO et al., 2016). It is associated with cellulose in the plant cell wall and can vary according to its composition and primary molecular structure, showing 80 to 200 sugar units polymerization degree. Its high complexity causes its composition to vary not only between plant species, but also between tissues and developmental stages in a same species (FERREIRA et al., 2009; FREITAS et al., 2019; MELATI et al., 2019).

The structure of hemicellulose is comprised of different types of monosaccharides/compounds, including pentoses (D-xylose and α-L-arabinose), hexoses (D-galactose, D-glucose, and D-mannose), and uronic acids such as α-D-glucuronic, α-D-4-O-methylgalacturonic and α-D-galacturonic. Like cellulose, its main chain is composed of monosaccharides (mainly glucose, mannose, and xylose) with β (1-4) bonds and branches of neutral sugars and uronic acids (FERREIRA et al., 2009; FREITAS et al., 2019; IMRE et al., 2019; MELATI et al., 2019). Due to its diversified composition and structure, hemicellulose has low crystallinity, characterized by its amorphous state and lower polymerization degree. Thus, showing less chemical and thermal stability compared to cellulose (STEPAN et al., 2012). Hemicellulose whose main chain is formed by β (1-4) bonds of D-pyranose residues (hemiacetal sugars) is classified into three main groups, namely mannans, xylans, and xyloglucans (Figure 4) (NAIDU et al., 2018).

The main chain of mannans is formed by mannose units. Mannans are divided into four subgroups, namely linear mannans, galactomannans, glucomannans, and galactoglucomannans. The first subgroup is comprised solely of mannose residues and can be found in the endosperm of some plants, such as ivory nut and species of the Leguminosae family. Galactomannans are found in legume seeds, and their main chain consists of mannose units with lateral groups of galactose making α-1,6 bond at an above 5 % rate – the higher the rate, the higher the hydrophilicity of the polysaccharide. Glucomannans are abundant in the secondary cell wall of woody species (mainly softwood), and their main chain is formed by β (1-4) bonds of mannose and glucose, whose rate substantially varies according to the source. They usually form chains with few branches, starting from the mannose units. Finally, Galactoglucomannans are also found in softwood, and their main chain is formed by mannose and glucose, with branches of galactose units. Similarly to galactomannans, galactose content and its degree of branching increase its solubility in water (NAIDU et al., 2018; STEPAN et al., 2012).

Xylan is the most common type of hemicelluloses (FREITAS et al., 2019), present in hardwoods, grasses, cereals, and herbs (EBRINGEROVÁ; HEINZE, 2000; STEPAN et al., 2012). Its main chain is formed by D-xylose units through β (1-4) glycosidic bonds to which branch groups of L-arabinose, acetic acid, and uronic acids are attached (DEUTSCHMANN; DEKKER, 2012; NAIDU et al., 2018). It also has subgroups determined by the source. The first is comprised of homoxylans, found in seaweed, and formed only by xylose residues, which may be linear or branched; therefore, they may have both β-1-4 and 1-3 bonds, as well as a mixture of them. The second group is composed of arabinoxylans, found in cereals. Their

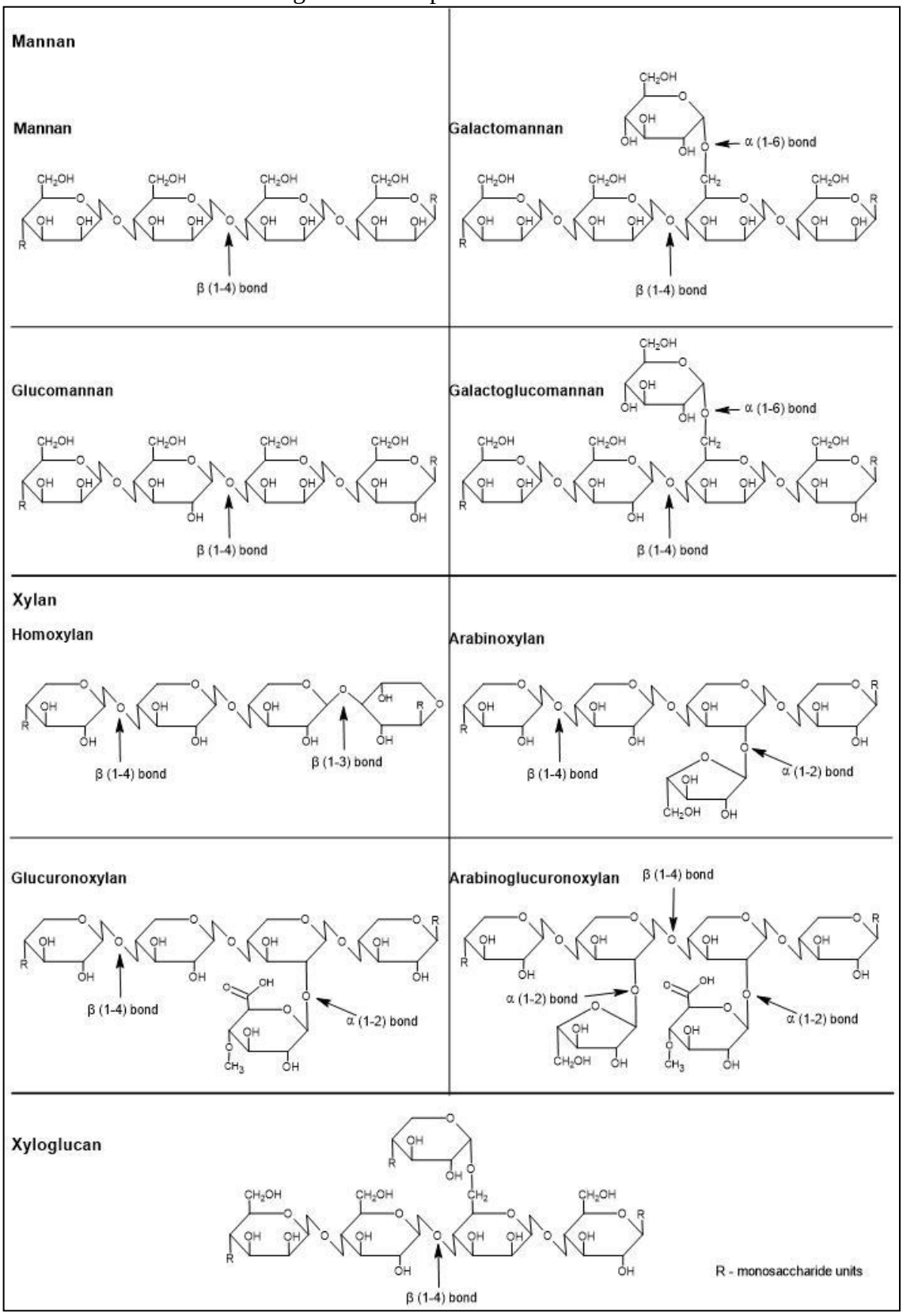
backbone is formed by xylose, with arabinose units being the main side group, attached to the carbon 2 or 3 positions of xylose units. However, carbon atoms in the same positions can be linked to acetyl groups. The rate of arabinose in relation to xylose is an important factor; since it influences the degree of sugar branching that will influence the polymerization degree.

The third subgroup is formed by glucuronoxylans, present in hardwood trees and whose main chain is composed of xylose residues, replaced every 10 units by 4-O-methyl-D-glucuronic acid. The chain also has partial acetylation on carbons 2 and 3, and these acetyl groups collaborate for the solubility of xylan. The next subgroup of xylans is called arabinoglucuronoxylan, found in non-woody plants, such as grasses and softwood. Its structure is characterized by the binding of arabinofuranose and glucuronic acid in the carbon of positions 2 or 3 of xylose that makes up the main chain. Approximately, substitutions with glucuronic acid and arabinofuranose occur every 5-6 and 5-12 xylose units, respectively, and the presence of ferulic and coumaric acids is associated with arabinose residues through esterifications (NAIDU et al., 2018; STEPAN et al., 2012).

The last subgroup is comprised of xyloglucans which, except grasses, are the most abundant hemicellulose in many plants. Their structure is similar to that of cellulose, i.e., formed by glycosidic bonds β-1-4 with xylose residues linked in position 6 of some glucose residues. They are highly branched, and arabinose and galactose units can be linked to xylose residues, forming di or triglycosyl side chains. This group substantially contributes to the structural integrity of the cell wall by making hydrogen bonds with cellulose (NAIDU et al., 2018).

The presence of several side groups in the main chain of hemicellulose prevents molecules from forming a tight packaging, as it occurs with cellulose, influencing its amorphous characteristics, solubility in water, and interactions with other components in a film. In a hypothetical composition formed by hemicellulose and cellulose, the region of hemicellulose with least degree of substitution will closely interact with cellulose and form a less soluble region, also influencing other properties such as mechanical performance (STEPAN et al., 2012). The side groups play an important role in the solubilization of hemicellulose. A high substitution degree chemically induced with acetyl groups also results in the removal of hydrophilic substituents, enabling polysaccharides to become more hydrophobic (STEPAN et al., 2012).

Figure 4 - Groups of hemicellulose.



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3.3. The bioplastics market

The origin of plastics is related to the biobased polymers, since parkesine (considered the first plastic) and later celluloid are both obtained from cellulose. However, the cheaper alternative raw materials and new technologies that emerged, such as bakelite in 1907, provided the achievement of synthetic materials with their peak in the mid-1950s. Mainly because the plastic synthetic was more efficient, meeting the massive production of plastics required by the market. However, since the 1980s, bioplastics have become more interesting for society, due to the growing environmental awareness and the oil crisis of the 1970s, which alarmed the industry regarding its dependence on a finite and limited source (LACKNER 2015).

The global production of bioplastics has increased steadily from the 1980s, reaching 2.11 million tons in 2019, and the production capacity is estimated to reach approximately 2.43 million in 2024. However, such a growth is still modest; the share of bioplastics in the market has not exceeded 1 % of the more than 359 million tons of conventional plastics produced annually. And the growth can potentially increase due to the emergence of new products, applications of more sophisticated technologies, instability in the price of petrol, and demand of a group of consumers of greater environmental awareness (EUROPEAN BIOPLASTICS & NOVA-INSTITUTE, 2019; IMRE and Pukánszky 2013; IMRE et al., 2019).

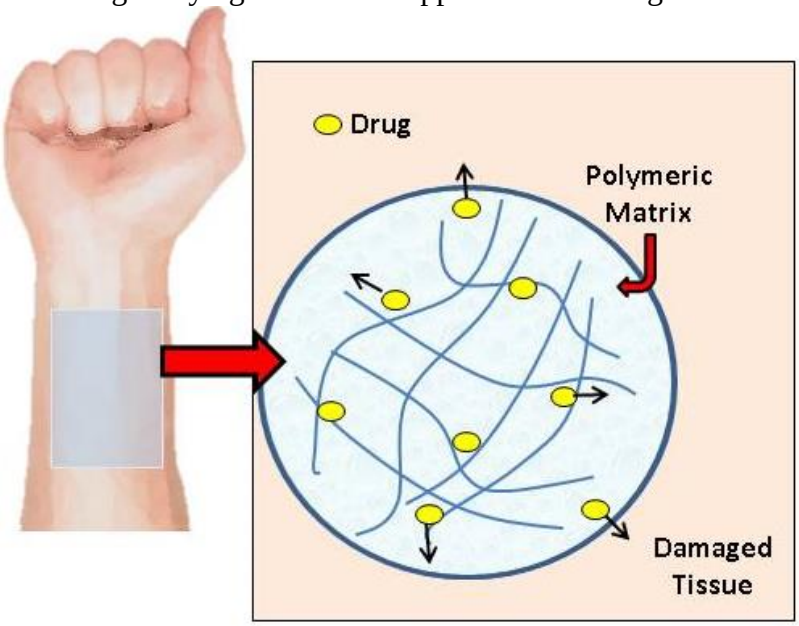
3.4. Emerging technologies for bioplastics produced with hemicellulose

The concept of biorefinery can support the production of bioplastics by the industry, since a single raw material can yield several products of high value, and the integration of the various processes involved would reduce production costs (LACKNER, 2015). A good example is sugarcane, which, after being processed in a sugar and alcohol plant for the extraction of its sucrose used in alcoholic fermentation, results in bagasse, considered a by-product of low value. However, the considerable content of lignocellulosic molecules, such as hemicellulose, in the bagasse can potentially be applied for the bioplastics production (BRIENZO et al., 2016). In other words, the addition of a structure and methods that can process such “wastes” and obtain important molecules to be applied in new products would guarantee a greater use of that initial raw material.

A higher implementation of biodegradable bioplastics by the industry requires the development of new technologies so that their production becomes feasible and competes with conventional plastics. Therefore, researchers have been looking for more resistant, inert, and biodegradable materials worldwide, which must also be easily deployed on an industrial scale.

Some plant polysaccharides are noteworthy for having several highly polar hydroxyl groups in their chains, with the potential to form strong intermolecular and intramolecular hydrogen bonds and provide, in some cases, considerable crystallinity to the macromolecular network. Due to its concentration in plant biomass, high availability (agro-industrial residues), biocompatibility, bioactivity, and biodegradation, hemicellulose can be employed in biotechnology, for the manufacture of biomaterials (BRIENZO et al., 2016; CHERUBINI 2010; FREITAS et al., 2019; GABRIELLI et al., 2000; OLIVEIRA et al., 2010; URTIGA et al., 2020) with different applications (e.g., food packaging, tissue engineering, bio-devices and drug delivery systems (Figure 5) (URTIGA et al., 2020).

Figure 5 - Drug-carrying biomaterial applied in tissue regeneration.



Source: Author.

The challenges for the application of film based on hemicellulose are related to its heterogeneity, low mechanical properties, difficulty in forming continuous/homogeneous bioplastics, and hydrophilic property (CHEN et al., 2016; ESCALANTE et al., 2012; GOKSU et al., 2007). Hydrophilicity, in particular, can provide structural benefits because the polar hydroxyl groups are able to form hydrogen bonds with other hydrophilic molecules, and these

same molecules end up interacting with more water molecules from the ambient, making the film more sensitive to humidity.

Therefore, depending on the humidity and temperature conditions to which they are subjected, they can contain a large amount of water, leading to significant hydrolysis, decrease in mass, and instability in their properties during application (IMRE et al., 2019). Based on these characteristics, hemicelluloses have good properties to be used in packaging for foods that do not interact with water like fatty foods (NAIDU et al., 2018).

This chapter focuses on the manufacture of films since there is a recurring need to find a substitute for synthetic plastics used in packaging production. Hemicellulose has gain attention as a feedstock to film/biomaterial production. Materials based on biopolymers and biomolecules are an alternative to plastic films from non-renewable sources that persist in the environment. Such biomaterials have drawn attention mainly from the pharmaceutical industry, which sees them as promising drug-carrying systems, and from the food industry, which is the largest consumer of films for the packing of their products, representing 70 % of the application of bioplastics (NAIDU et al., 2018; URTIGA et al., 2020).

Regarding food, those packages must meet several safety and quality requirements, as to preserve the food and prevent any type of toxic contamination. The main function of packaging films is to protect products from external factors, such as effects of gases, water vapor, odors, microorganisms, dust, mechanical shocks, vibrations, and compressive forces; they can also serve as a vehicle for the incorporation of food additives (e.g., antioxidant, antimicrobial, flavoring and coloring agents) (MIKKONEN; TENKANEN, 2012; THARANATHAN, 2003).

Oxygen gas exerts a relevant impact on the properties of packaged food, changing the shelf life of a product. It can favor microbial growth, changes in color in fresh and cured meats, oxidation of lipids and consequent rancification, and senescence of fruits and vegetables, since compounds generated through an oxidative process can affect the texture, ability to store water, nutritional characteristics, and quality of food (AKRAM et al., 2019; MIKKONEN; TENKANEN, 2012). The presence of water or moisture should still be considered because the film must have good properties of barrier to water outlet and inlet since an increase in the water activity can generate chemical reactions, enzymatic changes, and microbial growth in the food (MIKKONEN; TENKANEN, 2012).

Bioplastics must meet those requirements to be accepted on the market. The composition and formulation of a biopolymer vary according to the raw material used. Agricultural products or residues can form combinations and be processed in the manufacture

of polymers, which, with the addition of plasticizers or other additives, improve their capacity to form films with the desirable characteristics (THARANATHAN, 2003). However, Urtiga et al., (2020) claimed the ability of hemicelluloses (e.g., xylan) to form films is unsatisfactory due to the size of their chains, presence of branches, low molecular mass, relative high glass transition temperature, and low water solubility - unless they undergo heat treatment. In this sense, several procedures have been studied for overcoming those deficiencies, being the use of hemicelluloses in biodegradable films, as well as in composite films, a good alternative. Therefore, modifications in the different types of hemicellulose (chemical, enzymatic and cross-linked ones) and/or addition of other polymers and fillers to the polymeric matrix are an alternative for obtaining bioplastics with better properties and characteristics for different applications (URTIGA et al., 2020).The response of the different methods used is influenced by the characteristics of each hemicellulose. Due to the heterogeneity of the polysaccharide, its use depends on its degree and type of substitution, degree of polymerization, and extraction process (URTIGA et al., 2020).

Using xylan extracted from sugarcane bagasse, Jin et al., (2019) analyzed the effect of molecules of different molecular weights (8,200-26,800) and different amounts of lignin (1.6-9.5 %) and observed hemicelluloses of higher molecular weight and low number of branches and lignin content provided films with better mechanical properties. Lignin in films with hemicellulose of low molecular mass acted as a reinforcing agent for the polysaccharide; however, it might be an impurity in hemicellulose of high molecular weight, thus impairing the mechanical properties of the film. Using xylan extracted from cotton stalk and birchwood, GOKSU et al. (2007) corroborated the possibility of lignin promoting the formation of films based on xylan, because when lignin was present with at least 1 % (w/w) it acted as a plasticizer in these films.

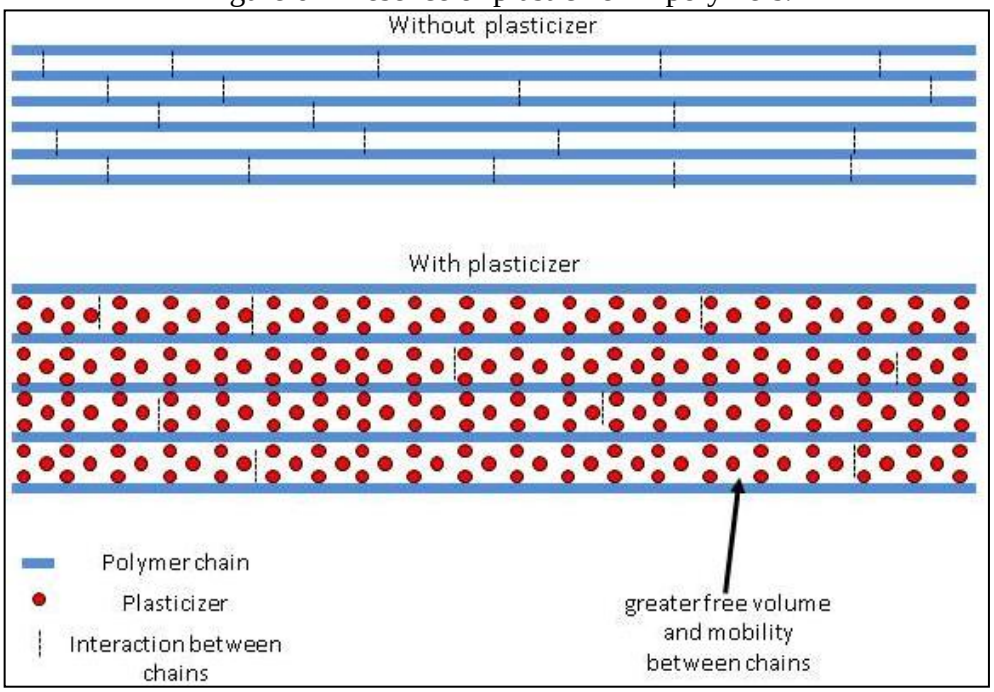
3.4.1. Importance of plasticizer for hemicellulose films

The addition of plasticizers to films produced with biomolecules aims to increase the plasticity of the material, altering its ability to change shape, through changes in rheological and mechanical properties (BERTUZZI et al., 2012; IMRE; PUKÁSZNKY, 2013). Plasticization improves flexibility and elongation, enabling the film to undergo greater deformation until it reaches the breaking point. However, the addition of a plasticizer in the composition of a film can reduce its mechanical strength (BERTUZZI et al., 2012; XU et al.,

2019). The mechanical properties of films are strongly influenced by the plasticizer's nature and its concentration (IMRE; PUKÁSZNKY 2013; LI; HUNEAULT,2011).

Many biomolecules (e.g., polysaccharides) have low deformability and resistance to impact due to the conformation of their chains, which have limited mobility. The use of plasticizers reverses this situation, since they can weaken the hydrogen bonds between the polymer chains and increase the free volume and chain mobility, as illustrated in Figure 6, changing some of the film´s properties (IMRE; PUKÁSZNKY, 2013; XU et al., 2019).

Figure 6 - Presence of plasticizer in polymers.



Source: Author.

Was addressed by Bertuzzi et al. (2012), Imre and Pukásznky (2013), Li and Huneault (2011), and Xu et al. (2019) the use of polar molecules or compounds of relatively low molecular mass in the plasticization of films (e.g., water, glycerol, sorbitol, propylene glycol, urea, and formamide). Although water has proven an efficient plasticizer, the use of compounds of higher boiling point, such as glycerol, is often preferred, since they decrease sensitivity to water and make some of their properties more stable (IMRE; PUKÁSZNKY 2013; LI; HUNEAULT, 2011).

A comparison of the effects of two plasticizers (sorbitol and glycerol) on films based on arabinoxylan revealed the plasticizers proportion can lead to different consequences in the mechanical properties of the films. Films with concentration of 10 % (w/w) in glycerol resulted in higher tensile strength than those containing 10 % of sorbitol. However, the films

exhibited an opposite behavior when the plasticizers concentration was 40 % (w/w), the film with sorbitol was more resistant. Although the presence of 10 % of sorbitol has resulted in films with low tensile strength, these films showed lower water vapor permeability, 1.1 g mm/ (m2.d.kPa) (at a relative humidity gradient of 0-54 %) while the corresponding films with glycerol showed permeability value equal to 3.3 g mm/ (m2.d.kPa). Films containing 10 % (w/w) of glycerol or sorbitol showed similar values of oxygen permeability of 3 cm3.μm/(m2.d.kPa) at 50–75 % of relative humidity. However, when the plasticizer concentration was 40 %, the films with sorbitol proved a better barrier to oxygen than glycerol (7.4 and 4.7 cm^3.μm/(m^2.d.kPa, respectively). In both cases, the increase in the plasticizer content increased the permeability of the films to water and oxygen (MIKKONEN et al., 2009).

Xu et al., (2019) compared the influence of three different plasticizers, namely glycerol, xylitol, and sorbitol on the composition of films based on hemicellulose and chitin reinforced with cellulose nanofibers. The authors observed a 10 to 40 % variation in the plasticizer concentration slightly increased the water vapor permeability, oxygen permeability, transparency, solubility, and low contact angle of the plasticized films, in comparison to non-plasticized ones. Among the plasticizers studied, glycerol generated a greater tension in the break (7.8-18.53 %), while the films in which sorbitol was used showed higher tensile strength (23.14-48.96 MPa).

An often overlooked problem is the tendency of some plasticizer compounds to migrate to the surface of the products, altering the macroscopic properties of the biofilm. In this way, plasticizer can diffuse out of material causing environmental and health problems depending on the released concentration (IMRE; PUKÁSZNKY, 2013). To minimize this effect, plasticizer with higher molecular weight are generally used, as they diffuse more slowly, and as a result the migration rate of plasticizer to out of the material is reduced. However, such an application decreases the efficiency of the plasticizer in increasing the mobility of polymer chains (BERTUZZI et al., 2012; IMRE; PUKÁSZNKY, 2013).

3.4.2. Development of biomolecule blends

Films are usually produced with the addition of different compounds, forming blends, or composites, whose performance is dependent on the control of the structure and the interfacial adhesion, for facilitating the transfer of tension among the different phases of the

material. An alternative to reduce hydrophilicity in some vegetable polysaccharides would be to mix them with a more hydrophobic matrix (IMRE et al., 2019).

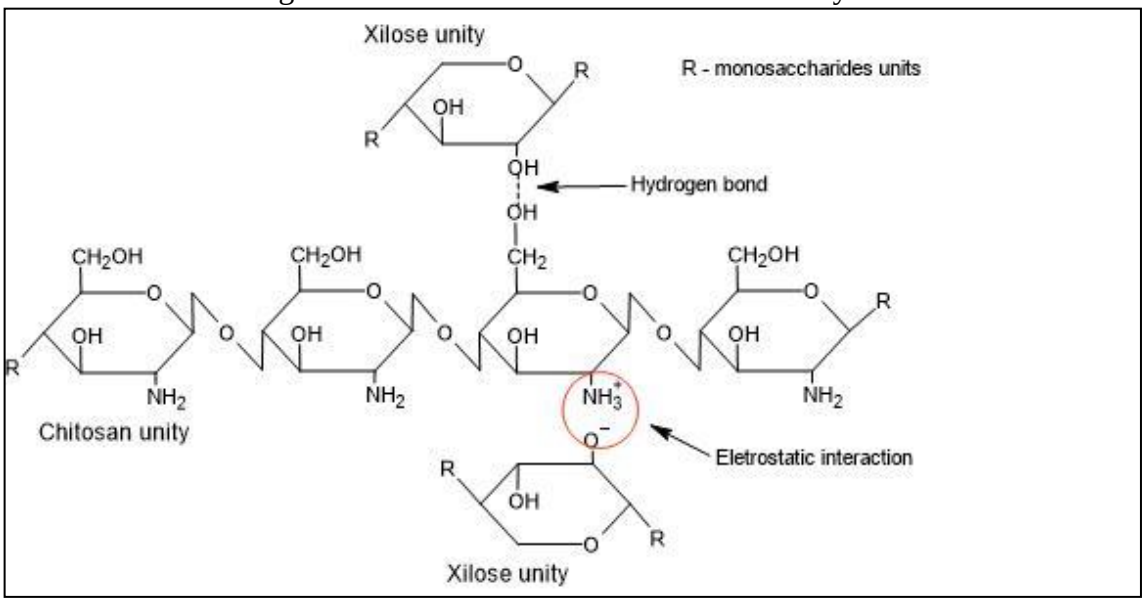
Examples of polymers good for blending are proteins and polysaccharides, like cellulose. Cellulose is a natural resource highly available, has hydrophobic character, chemical compatibility with other polysaccharides, crystallinity, and has been used to improve mechanical, thermal resistance, and water vapor barrier properties of bioplastics (HANSEN et al., 2012). However, the dimensions and amount of cellulose in bioplastics are important factors, since cellulose can be used with different dimensions and high concentrations can generate fiber agglomerations, thus, reducing the properties of bioplastics (CHEN et al., 2009ab; do LAGO et al., 2020; GUIMARÃES et al., 2016; XIE et al., 2014). Several studies have confirmed the improvement in the properties of hemicellulose-based bioplastics with the addition of cellulose nanofibers (AZEREDO et al., 2010; GORDOBIL et al., 2014; LONG et al., 2019; LOPEZ-RUBIO et al., 2007; MIKKONEN et al., 2012; MIKKONEN et al., 2011; PLACKETT et al., 2010; STEVANIC et al., 2011; SVAGAN et al., 2007; SVAGAN et al., 2008). Peng et al., (2011) observed nanocellulose reinforcement promoted mechanical resistance in films composed of hemicellulose (xylan). In bioplastics made with 5, 10, 15 and 20 % (w/t) nanocellulose, both tensile strength properties (15.5, 20.2, 28.9 and 39.5 MPa, successively) and Young's modulus (1,322, 1,578, 2,355 and 3,404 MPa, successively) increased, thus reducing elongation (2.9, 2.6, 1.8, 1.4 %, successively). The authors also reported an increase in the thermal stability of xylan-based bioplastics with the addition of nanocellulose. Such an improvement and the mechanical properties may be related to the linear and homogeneous structure of cellulose, optimization of hydrogen bonds (high aspect ratio), and increased crystallinity of bioplastics with nanocellulose. The addition of nanocellulose to xylan-based bioplastics can also increase barrier properties (reduced water vapor and oxygen permeability) (HANSEN et al., 2012) due to the formation of tortuous paths of nanofibers in the bioplastic matrix, hampering the passage of water vapor through the bioplastic (SAXENA et al., 2011).

Chitosan is another promising compound for application in films with hemicellulose due to its various hydroxyl and amine groups capable of forming hydrogen bonds with hemicellulose (Figure 7), showing good miscibility between the two polysaccharides (XU et al., 2019). Investigating the gel-forming capacity of films made with chitosan and xylan with the use of FTIR, Gabrielli and Gatenholm (1998) observed possible interactions between the functional glucuronic acids of xylan and the amino groups of chitosan, and suggested the formation of a three-dimensional network. The proportion of those polysaccharides can affect

their miscibility. Dynamic mechanical and a microscopic atomic force analyses revealed films homogeneous composed of 10 % chitosan and 90 % hemicellulose, however when was employed 70 % of chitosan and 30 % of hemicellulose, a two phases system was identified.

Arabinoxylan (AX) and arabinoxylooligosaccharides (AXOS) of different molecular masses were combined to produce edible films based on chitosan (COSTA et al., 2015). Films composed of high molecular mass AXs (3,670 and 3,503 degrees of polymerization) slightly improved the mechanical properties of chitosan-based films. The authors concluded films could be made with those constituents due to the prebiotic benefits of XOS.

Figure 7 - Interaction between chitosan and xylan.



Source: Author.

The reinforcement with nanofibers of cellulose also substantially improved the tensile strength of films composed of hemicellulose and chitosan. With no reinforcement, the tensile strength of the films was 16.24 MPa with the addition of 5 to 20 % cellulose (based on the dry weight of chitosan and hemicelluloses), and the tensile strength increased to 53.75 and 69.16 MPa, respectively (XU et al., 2019).

The correlation between hemicellulose and chitosan can still provide some benefits for food preservation (LI et al., 2011). Products from the Maillard reaction, which occurs between an amino group and reducing sugar aldehydes or ketones exposed to high temperature, can show excellent antioxidant and antimicrobial activity. This was evidenced in this study, which used chitosan (rich in amino groups) and xylan (source of reducing sugars). The latter is composed of xylose, which has high reactivity, thus increasing the reaction speed and

showing promising in obtaining complexes with antioxidant and antimicrobial properties (SHIBAO; BASTOS, 2011).

In some cases, the blend components do not interact well. In such cases, a series of chemical and physical modifications can improve the integration among different materials, making them more compatible. Although compatibility and miscibility are not completely independent terms, they are often confused. Miscibility describes the number and composition of phases in a mixture of polymers and is determined by a thermodynamic factor called enthalpy free from the mixture as showed in Equation 1 (IMRE et al., 2019).

$$\Delta Gmix = \Delta Hmix - T\,\Delta Smix \quad (1)$$

Where, ΔG, ΔH, T, and ΔS represent variation in free enthalpy, variation in enthalpy, temperature, and variation in entropy, successively. When blends are formed by components of high molar mass, the contribution of entropy becomes highly negligible, and the resulting morphology is determined by enthalpy (IMRE et al., 2019). If this factor is negative, the mixture is homogeneous and, therefore, shows no formation of separate phases. The free enthalpy of a mixture is correlated with the intramolecular and intermolecular interactions between the compounds of the mixture. A completely miscible mixture is rarely found, due to the lack of some specific interactions. Therefore, in practice, most constituent pairs of a mixture are at most partially miscible, containing two different phases with an abundance of a certain constituent and a small fraction of another (IMRE et al., 2019).

Compatibility is a technical term that refers to the property profile of a mixture in relation to its mechanical characteristics, processability, transparency, permeability, surface quality, or degradability. The degree of compatibility of a mixture can be measured, for example, by the relative tensile strength. In this case, blends with greater miscibility will show higher resistance, differently from blends based on immiscible compounds which, due to their more complex morphology, undergo consequent micromechanical deformation processes. Compatibility is generally given as a function of interfacial adhesion between two or more phases, which is dependent on the strength and number of interactions, often determined by the chemical structure of macromolecular chains (IMRE et al., 2019).

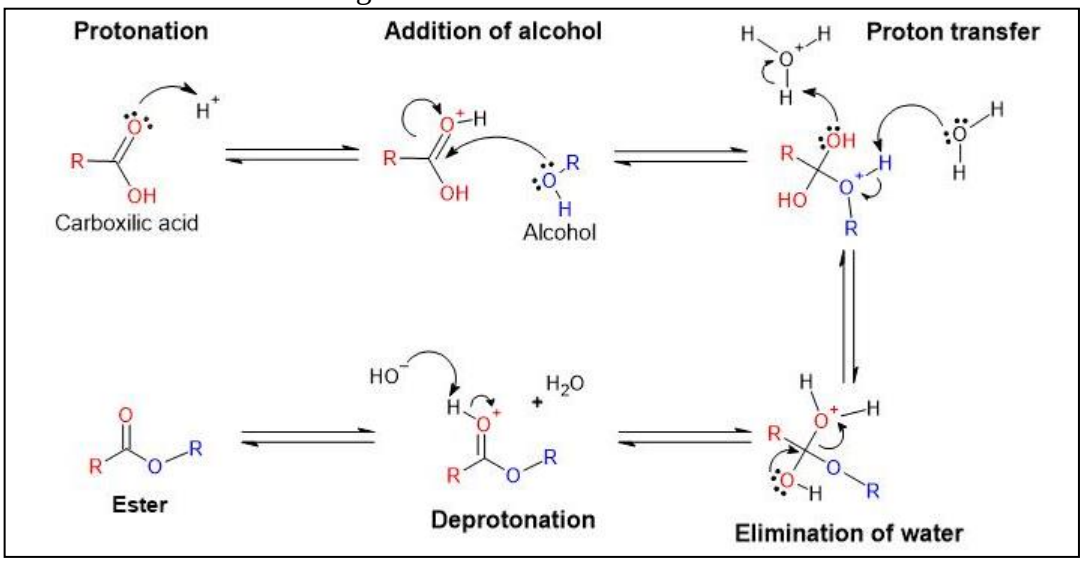
The most common compatibility techniques involve the addition of additives that will act at the interface of the constituents of the mixture, promoting adhesion between them. In this case, non-reactive compatibilization occurs (a compatibilizing agent is used and characterized by an amphiphilic compound). Its structure usually has a copolymer block prefabricated and inserted in theblend, which has a polar portion and a nonpolar one. The

other possibility in this technique is reactive compatibilization, in which an amphiphilic structure is formed in situ during mixing. Reactive compounds of low molar mass are normally used, and act as coupling agents forming covalent bonds between the phases. Reactive methods are generally more efficient, especially in polysaccharides such as hemicellulose, since they show several hydroxyl groups that can potentially undergo reactive modifications. Numerous bifunctional compounds can form covalent bonds with polysaccharides (e.g., organic bi and trifunctional acids, malic and succinic anhydride, and silane and diisocyanate compounds). Several studies have reported promising results on the use of citric, malic, and tartaric acids, which are more environmentally appropriate, non-toxic, and non-volatile alternatives. Moreover, they are abundant and relatively more accessible, since they are obtained from inexpensive biological routes (IMRE et al., 2019).

Chemical modifications can not only guarantee better crystallinity and compatibility among hemicellulose and other components of a mixture, but also make the film/biomaterial more hydrophobic (CUNHA; GANDINI, 2010; GORDOBIL et al., 2014; SODERQVIST-LINDBLAD; ALBERTSSON, 2004). Such reactions aim to replace the hydroxyl group with a hydrophobic one. Therefore, an increase in its hydrophobicity improves the water-resistance of the films, their thermal stability, thermoplastic properties, and solubility in organic solvents (FARHAT et al., 2016). Reactive methods commonly used are esterification, etherification, or oxidation.

Esterification involves the reaction between an alcohol and a carboxylic acid towards forming an ester, conventionally with the use of anhydride or acyl chloride as esterifying reagents (Figure 8) (IMRE et al., 2019; ZHANG et al., 2020b). Several esterification processes, such as acetylation, propionylation, and oleylation, have been adopted for the generation of hydrophobicity in hemicellulose (FARHAT et al., 2016). Acetylation is a chemical modification that links an acetyl group to the hemicellulose chain. When conducted prior to film formation, this process reduces water solubility and increases its thermal stability, also improving its mechanical properties such as flexibility, and its hydrophobicity, which is essential for maintaining the barrier property of packaging based on hemicellulose under high humidity (STEPAN et al., 2012; AYOUB et al., 2013; GORDOBIL et al., 2014; GRÖNDAHL et al., 2003).

Figure 8 - Esterification reaction.

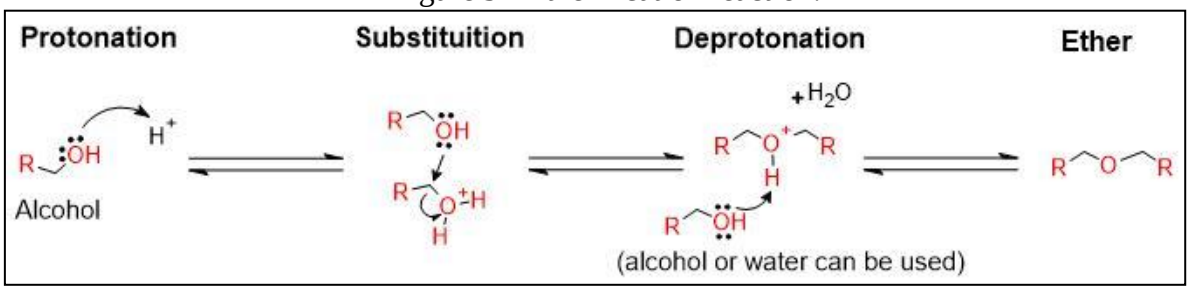


Source: Author.

However, some of such esterification processes tend to form by-products from the severe acidic degradation of hemicellulose. Therefore, processes based on transesterification with vinyl ester can be an alternative to a milder acylation method, avoiding the formation of decomposition products. Zhang et al., (2020b) studied the transesterification process using vinyl laurate to chemically modify hemicellulose and evaluate the films produced. The films showed an approximately 120 ^{o} water contact angle, hence, excellent hydrophobicity and improved mechanical properties, like tensile strength (33.94 ± 3.09 MPa) and elongation at break (22.41 ± 2.87 %). Moreover, the modified hemicellulose films showed a good barrier to water and oxygen, with permeability values ranging from 1.59 ± 0.07 to 2.23 ± 0.11 (10^{-10}·g/m·s·Pa) and 1.21 ± 0.04 to 4.24 ± 0.30 (cm^3·μm/m^2·d·kPa), respectively.

Hemicellulose can also be altered by etherification, which consists of a reaction between an alcohol and an alkylating agent, such as alkyl halides (chlorides, bromides, and iodides), alkyl sulfonates, vinyl monomers, and epoxides (Figure 9). Carboxymethylation is an example of etherification and involves the reaction between hemicellulose and sodium monochloroacetate in alkaline conditions. Such modifications can potentially improve the thermal stability of the formed films and reduce their hydrophilicity (REN et al., 2008). Benzylation, a type of etherification, also replaces the hydrogen atoms of the hydroxyl group with benzyl groups, in a reaction with benzyl chloride (SERESHTI; MOHAMMADI-ROVSHANDEH, 2003). Such a process increases the hydrophobicity of the film as well as its oxygen barrier and thermal stability (HARTMAN et al., 2006; REN et al., 2012).

Figure 9 - Etherification reaction.

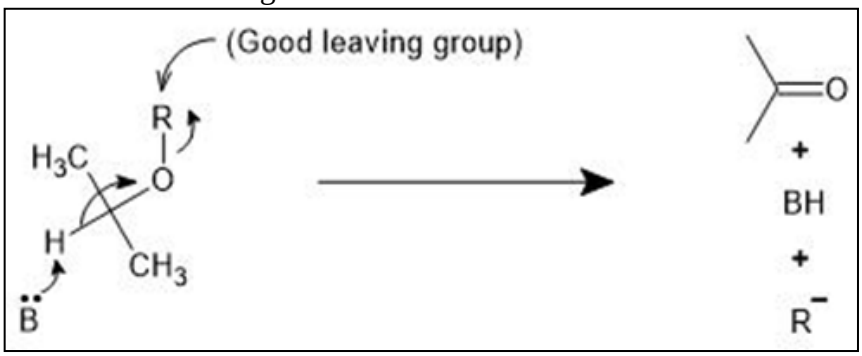


Source: Author.

Fluorination is a process that can be applied after the formation of hemicellulose-based films, in a reaction, for example, with trifluoroacetic anhydride. It provides unique chemical and surface properties such as high hydrophobicity, chemical resistance, and thermal stability. Films that undergo fluorination have a strong barrier to gases and liquids, a low friction coefficient, and low humidity (FARHAT et al., 2016; GRÖNDAHL et al., 2006; TRESSAUD et al., 2007; WOODWARD et al., 2003).

Oxidation, another reactive approach, is based on redox reactions between the -OH groups of polysaccharides and ions (Figure 10). Using this method, Kochumalayil et al., (2013) chemically modifiedxyloglucan towards reducing its glass transition temperature, so that it became more malleable and moldable from a milder heat treatment. Periodate ion oxidized the hydroxyl groups present in xyloglucan, resulting in the breaking of the xylose ring and formation of dialdehyde groups, which were subsequently modified through a reduction reaction with sodium borohydride in alcohols, as well as perturbations in the packing of modified xyloglucan chains, changes in intermolecular interactions, and increased molecular mobility.

Figure 10 - Oxidation reaction.



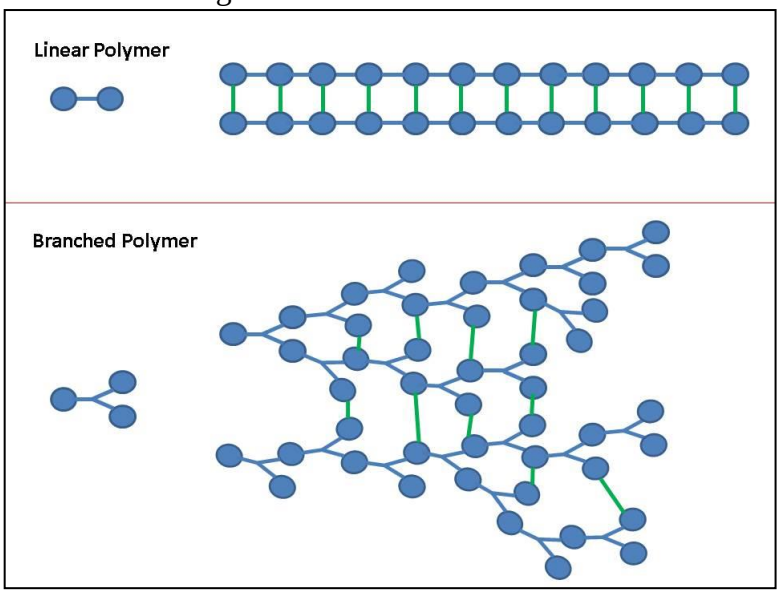
Source: Author.

3.4.3. Crosslinking agents in polymeric chains

Crosslinking agents are additives that act on one or more phases of the polymer providing cross-links between its chains (Figure 11). Such a process increases the barrier to oxygen and water vapor, the hydrophobicity of the formed films, (AZEREDO et al., 2015; ZOLDNERS; KISELEVA, 2013), their tensile strength and elongation, as well as other properties such as transparency and surface homogeneity (GUAN et al., 2016; SHAO et al., 2019).

Crosslinking generally involves the reaction between a polysaccharide and a carboxylic acid (e.g., oxalic acid, citric acid, or succinic acid) and can be influenced by both crosslinker content and reaction temperature (CHEN et al., 2015; GUAN et al., 2016; MIKKONEN et al., 2013). Ammonium zirconium carbonate (AZC) is a cross-linker effectively evaluated in different hemicellulose-based films to improve their mechanical resistance (CHEN et al., 2015). The use of epichlorohydrin has also been studied in films made of quarternized hemicellulose and chitosan, which display a uniform porous structure, good optical transparency, and excellent mechanical resistance (GUAN et al., 2016). However, epichlorohydrin shows carcinogenic potential (U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 2016), therefore, its application and proportion are limited in the production of biodegradable plastics.

Figure 11 - Chains crosslinked.



Source: Author.

Some acids (e.g., citric acid) act as both a crosslinking agent, due to di-ester intermolecular bonds between the hydroxyl groups of the polysaccharide with two of its carboxylic groups, and a plasticizer, as reported by Shi et al. (2008). However, their quantity must be moderate, since their excess can lead to a thermosetting behavior of the material.

3.4.4. Functional biopackages

Several studies have focused on the development of functional bioplastics for use as food packaging that can change the conditions of the packaged product, improving its quality, increasing its life span, safety for consumption, and sensory properties, and providing a better nutritional value. Among such technologies, those aiming at preventing contamination or oxidation processes in packaged foods through active compounds have excelled (COMA, 2013; MEDINA-JARAMILLO et al., 2017; VALDÉS et al., 2014). The active compounds may be too volatile to be applied directly to the food; therefore, an advantage of functional biopackages is their potential for a controlled release of those active agents, ensuring the quality of the food for longer time (COMA, 2013; VALDÉS et al., 2014). Moreover, the slower release of the agents prevents their concentration beyond the limit allowable in food (MUGWAGWA; CHIMPHANGO, 2020).

The use of antimicrobial substances in packaging is intended to solve problems of contamination in food, since they inhibit the growth or even cause the death of pathogenic and/or deteriorating microorganisms. However, one of the great challenges for their application is to find the limit between their resistance to the attack of microorganisms during their useful life and their degradation at the end of their cycle (COMA 2013; VALDÉS et al., 2014). Essential oils, organic acids, nisin, chitosan, microparticles, and nanoparticles (silver, gold, copper, titanium dioxide, magnesium oxide, calcium oxide, and zinc oxide) can be used for this purpose. The latter compounds interact with the bacterial cell wall destroying its integrity. The use of titanium dioxide (TiO_2) in functional films not only improves their mechanical properties, but also shows antibacterial performance in functional chitosan-based films incorporated with hemicelluloses (ZHANG et al., 2020a). However, inorganic additives are not biodegradable and slow down the biodegradation of the material when exposed to the environment (CAMPOS et al., 2010; CAPELEZZO et al., 2018; SILVA et al., 2014).

Several studies have focused on natural extracts from plants, essential oils, or agricultural residues. The antimicrobial and antioxidant capabilities of, for example, extracts of grape seed, green tea, raspberry, among other natural products that have relevant

compounds for such an application (e.g., low molecular weight phenolic acids, tannins, proanthocyanidins, flavonoids, and others) are known (VALDÉS et al., 2014).

Mango peel polyphenol extract was incorporate into acetylated hemicellulose-nanocellulose films coated with polycaprolactone. The films were immersed in polyphenol extract for 1 min, and the amount of the mango polyphenols absorbed was 2.89 mg/g Gallic acid equivalent. The antioxidant activity of polyphenol extract was efficient in packaging food, because it increased temperature and time, hence, their release into the food. The greatest release of antioxidants occurred in fatty foods, since mango polyphenolics are recognized as hydrophobic (MUGWAGWA; CHIMPHANGO, 2020).

Essential oils can be easily incorporated into aqueous polymeric solutions for the obtaining of film. In general, they reduce water permeability, often due to its hydrophobicity, since the impact of lipid on the microstructure of emulsified films is a determining factor regarding efficiency as a water barrier. In turn, such microstructures are affected by other factors (e.g., physical state of the oil and its distribution in the polymer). However, they can also affect the structural, physical, and bioactive properties of the biofilm, thus triggering discontinuity in the polymeric network. The use of essential oils is more limited to the formation of films by casting, which hinders their application in the industry, which prefers compression molding or extrusion, in which high temperature is applied to the material (ATARÉS; CHIRALT, 2016).

The use of linoleic acid in films made from carboxymethylated-xylan resulted in films of weaker mechanical properties, probably due to the presence of a large number of hollow regions and thickness. However, such films showed less permeability to water vapor and oxygen, and antimicrobial activity against gram-positive bacteria (QUEIRÓS et al., 2017). The outer membrane of gram-negative bacteria may explain the low susceptibility of such microorganisms to the action of lipidic antimicrobial agents, which limits the diffusion of hydrophobic compounds through the lipopolysaccharide membrane. The antimicrobial activity of fatty acids is related to the size of the aliphatic chain and number of double bonds so that long unsaturated chains tend to be more effective against gram-positive bacteria than gram-negative ones (AKRAM et al., 2019; QUEIRÓS et al., 2017). Antioxidant and antibacterial properties of licorice essential oil into carboxymethyl-xylan films were evaluate, even after being stored for 20 days at 25 ^{o}C. Discs of the films (10 mm diameter) were placed on the surface of seeded agar plates and showed antibacterial activity against two recognized foodborne pathogens, namely *Enterococcus faecalis* and *Listeria monocytogenes* (both Gram-positive), of 8.53 and 17.31 mm inhibition zones diameters, respectively. The antioxidant

activity inhibited approximately 20 % of free radicals after 5 hours. Moreover, films with essential oils significantly inhibited lipid peroxidation, unlike the control films (LUÍS et al., 2019).

Phenolic and terpenoid compounds are generally responsible for the antimicrobial activity of essential oils. Oregano and thyme exert an effective action against the development of gram-negative and potentially pathogenic bacteria such as *E. coli* and several *Salmonella* subspecies, due to phenolic components (e.g., thymol and carvacrol) in their composition (AKRAM et al., 2019). Apart from the antibacterial effect, some of those essential oils display antioxidant properties, limiting lipid peroxidation by decreasing the formation of free radicals or sequestering them. They can neutralize them using chelating transition metals capable of extinguishing oxygen singlets and triplets from the decomposition of peroxides. Lately, there is a greater interest in natural antioxidants, due to consumer preference and possible toxicity of synthetics (AKRAM et al., 2019).

Although essential oils are registered as safe food additives, they can cause some allergic reactions and dermatitis (e.g., orange, lemon, and *Litsea cubeba* oils provoke phytotoxic reactions after frequent use). The Information Network of Departments of Dermatology (IVDK) is a multicentric project founded in 1988, comprised of more than 50 skin clinics in Germany, which record and develop scientific analyses of contact allergies. Between 2,000 and 2,008, it registered 637 cases of hypersensitivity caused by oils of ylang-ylang, lemongrass, jasmine, sandalwood, and cloves. The use of essential oils in the composition of biofilms can promote several beneficial characteristics; however, depending on the application, attention must be paid to the more than 80 oils registered as causing contact allergies (AKRAM et al., 2019).

Naturally, hemicellulose is not an antioxidant, but chemical modifications can give it such a property. When modified by transesterification with vinyl laurate, hemicelluloses howed an improved antioxidant activity (reaching a radical scavenging activity of approximately 38 %), due to the introduction of laurate chains in its hydroxyl groups (ZHANG et al., 2020b). Moreover, the effect of the combination of hemicellulose and chitosan during the Maillard reaction generated products with antioxidant activities (LI et al., 2011).

Smart packaging has also drawn the attention of researchers, since this system performs functions that enable the detection of deterioration processes and temperature fluctuations during storage, and indicate whether a fruit is ripe, providing information and alerts on the quality of packaged products. This technology also seeks natural compounds that

can fulfill this function, since synthetics can have relatively greater toxic and mutagenic potential. Such composites can be found in vegetables, fruits, grains, herbs, and flowers (BHARGAVA et al, 2020; MEDINA-JARAMILLO et al., 2017; VEDOVE et al., 2021).

Food contamination and deterioration are usually related to pH modification. Natural pigments, like chlorophyll and carotenoids, can be found in several natural extracts and change color when exposed to changes in pH. For example, when incorporated in a film-forming starch matrix, extracts of green tea and basil can improve their mechanical properties, impermeability to water vapor, and antioxidant activity. Moreover, they are stable at high temperatures, resisting those above 240 ^{o}C without degrading. However, the presence of natural pigments makes them suitable for applications in smart packaging (MEDINA-JARAMILLO et al., 2017).

Anthocyanin from grape is a natural pigment that can be incorporated into bioplastics. Food spoilage processes release ammonia, lowering pH and changing the color of anthocyanin from purple to blue. However, the major obstacle for the industrial application of this material is its thermal stability (VEDOVE et al., 2021).

Several studies have focused on other natural compounds such as curcumin, tannins, betalain, quercetin, basiline, and their application as indicators of other properties (e.g., temperature change, an essential factor that can affect both safety and quality of food). Those indicators provide such information through a continuous, clear, and irreversible reaction in response to temperature changes. The duration of their exposure to temperature variations is represented by variations in color and corresponds to the stability of the food product stored. Sensitivity to the levels of CO_2 and O_2 is also used in evaluations of the quality of packaged products, since carbon dioxide is generated during the metabolism of microorganisms. For that, can be used visual sensors based on luminescent pigments, which when exposed to CO_2 emit fluorescence; and pH indicators that respond with color variation when exposed to CO_2 (BHARGAVA et al, 2020).

3.4.5. Other applications of hemicellulose as a biomaterial

Hemicellulose has attracted attention and been studied in the area of food packaging. However, this biomolecule can also potentially form hydrogels, which are polymeric networks with cross-links that absorb large amounts of water without losing their structure. Such an ability to retain water is similar to that of living tissues, thus making hydrogels

suitable for biomedical applications (e.g., drug distribution) (NAIDU et al., 2018; URTIGA et al., 2020).

Hydrogels based on polysaccharides such as hemicellulose have been developed for different purposes apart from drug distribution (e.g., as cell immobilizing matrix and in tissue engineering). Hemicelluloses are not toxic, and are biocompatible, biodegradable, and widely available from renewable sources, and display a variety of promising structures for the production of macromolecular networks (NAIDU et al., 2018; URTIGA et al., 2020). Urtiga et al. (2020) proposed the use of xylan-based hydrogel as a controlled distributor of medicines in the colon region, since this polysaccharide is not digested by the human gastrointestinal system, but can be degraded by bacteria present in a certain region of the intestines. Such hydrogels are obtained mainly by inducing physical or chemical reticular reactions, for example, they can be produced through chemical cross-linking and the use of horseradish peroxidase and hydrogen peroxidase enzymes as catalysts. Hydrogel loaded with caffeine demonstrated efficient diffusion in both distilled water and 0.1 mol/L HCl solution (IRAVANI et al., 2011). Sun et al., 2013, used xylan from wheat straw for the production of hydrogel with acrylic acid and N,-N-methylene-bisacrylamide as crosslinkers, and observed the release of compounds was influenced by pH - the greater release had duration of 5-6 hours with a pH of 7.4.

As in film production, the development of hydrogels with xylan can consider adding other compounds. Regarding synthetic compounds, the composition with acrylic derivatives is the most common. Xylan hydrogels were mixed with N-isopropylacrylamide and acrylic acid, and with methacrylate acid (GAO et al., 2016; SUN et al., 2015). However, hydrogels with other functionalities can also be obtained (e.g., a photosensitive hydrogel based on xylan with azobenzene as a copolymer for the selective release of vitamin B12 promoted a better release at neutral pH and with UV irradiation (CAO et al., 2014).

The use of blends with synthetic polymers can eventually incur risks, since the literature has reported some cytotoxicity. Such negative aspects can be related to their molecular mass, electrical charge (cationic polymers are generally more toxic than anionic ones), ramifications, concentration, and exposure time (URTIGA et al., 2020). Hydrogels can also be manufactured from only natural macro-molecules such as chitosan associated with xylan (GABRIELLI; GATENHOLM, 1998; GABRIELLI et al., 2000). Another approach is the use of blends with natural and synthetic molecules (e.g., Kappa-carrageenan followed by mixing with polyvinyl-pyrrolidone associated with xylan of different origins) (MEENA et al., 2013).

Xylan-based hydrogels can be employed in several applications, including tissue regeneration. Tests performed on rats with bone problems revealed hydrogels with xylan improved the recovery rate compared to those with only chitosan (BUSH et al., 2016), and was reported their potential for application in the remediation of water-absorbing heavy metals (PENG et al., 2012). In the present study, xylan was combined with acrylic acid – 859 mg, 495 mg, and 274 mg of palladium, cadmium, and zinc, successively, were removed for each hydrogel gram. Moreover, a subsequent easy hydrogel regeneration and metal recovery were obtained. Another interesting approach is obtaining magnetic hydrogel through the addition of acrylic acid and Fe_3O_4 to hydrogel based on xylan. Tests with blue methylene showed the hydrogels presented a maximum value of absorption equal to 438.6 mg/g of hydrogel (SUN et al., 2015). Still using magnetic Fe_3O_4, acetylated xylan hydrogel was synthesized to detect hydrogen peroxide. The produced hydrogel showed peroxide sensitivity to a concentration of 5 µmol/L (DAI et al., 2016).

Xylan hydrogel can immobilize microorganisms and enzymes (e.g., *Propionibacterium acidipropionici)* to produce propionic acid via fermentation (WALLENIUS et al., 2015). Lipase was also immobilized showing more tolerance to higher pH and temperature than when it was free (PARK et al., 2015). The properties of hemicellulose also enable its use as an wood adhesive, although little research has been developed in this area (NORSTRÖM et al., 2015). Adhesives must wet, drain and penetrate the wood surface tobeying a limit for an adequate e adhesion. Hemicellulose can be used as adhesive altering their properties by adding of xylan dispersing agents such as polyvinyl-alcohol or polyvinyl-amine, and crosslinkers such as glyoxal or hexamethyl-oxymethyl melamine.

4. Concluding remarks

Environmental pollution caused by plastics has affected life in different biomes and can potentially impact human health. Over the past few decades, it has been a matter of concern for many countries. However, since the number of plastic residues found in nature is significant, the measures adopted may have been unsatisfactory. At least part of the traditional plastics must be replaced with a biodegradable version preferably from renewable sources. Hemicellulose biomolecule is a good example for such an application, since it is abundant in nature and has numerous hydroxyl groups capable of making hydrogen bonds. Hemicellulose is biocompatible with other biomolecules, and studies have shown its efficiency as a barrier to

oxygen and its promising antioxidant effect when complexed to certain protein molecules. However, some challenges must be overcome so that the hemicellulose based-material can be more suitable for film-formation. Depending on the desired application, the hemicellulose hydrophobicity must be modified. Solutions are based on chemical modifications of hemicellulose, addition of additives such as plasticizers and cross-linkers, formation of biocomposites with other polymers, among other procedures that improve its miscibility in polymeric matrices, mechanical resistance, and action of water. Hemicellulose-based materials can meet the requirements of industrial large-scale production through the functionalization of their structure. From the first versions of the plastics used by the industry (biobased-ones) to the various types currently used (mostly synthetic ones), profit and financial losses have dictated the industry's preference for the material to be implemented. However, consumers´ increasing awareness is a new factor to be considered, since such consumers desire products that do no harm the environment. In this sense, bioplastics have become more attractive to the industry as more sustainable alternatives of viable production.

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CHAPTER IV: DEVELOPMENT OF BIOPLASTICS BASED ON STARCH AND XYLAN: A MECHANICAL PHYSICOCHEMICAL AND BIODEGRADABILITY STUDY

Abstract

Plastic tends to accumulate and remain in the environment for centuries without degrading, leading to the need for the development of biodegradable materials from renewable and inexpensive raw materials. This study investigates the influence of xylan from sugarcane bagasse on the mechanical and chemical properties of bioplastics composed of starch and glycerol as a plasticizer. Bioplastics were produced from a combination of starch and xylan, representing 5 % of the total mass of the filmogenic solution, in which 0 to 50 % (w/w) proportions of xylan were used complementary with starch content (100 to 50 %, w/w). Glycerol was used as plasticizer at a 20 % concentration (w/w of total polysaccharides) and the bioplastic-forming solutions were gelatinized and dried by the casting method. Both bioplastic solubility in water and its opacity increased as the xylan content increased – the former ranged between 20.31 and 44.16 %, and the latter ranged between 0.44 and 9.77 %, with only starch and 50 % w/w xylan, respectively. The presence of xylan also made the bioplastics more hydrophilic and less crystalline, and interfered with their mechanical proprieties. Whereas xylan bioplastics with 5 and 10 % (w/w) showed higher tensile stress of 2.35 and 2.56 MPa, respectively. The elongation at break was greater in bioplastics composed of only starch (208.8 %), and a reduction in elongation to 15.8 and 19.3 % was detected when the amount of xylan was 25 and 50 % w/w, respectively. The bioplastics were completely biodegraded after being buried for 30 days. The starch and xylan combination with lowest xylan proportions (5 and 10 %) improved the mechanical properties of the film causing no significant changes in its solubility, producing less opaque bioplastics and biodegradable.

Keyword: Bioplastic, Xylan, Starch, Glycerol, Biodegradable

1. Introduction

The ubiquity of plastics has caused environmental concerns, because they are already found in uninhabited environments or composed of small groups of human beings like the Mariana's trench and arctic ice (NIELSEN et al., 2019). Plastics are inexpensive and versatile materials (they can be molded in different shapes), with good mechanical resistance and transparency, and can meet several needs of industry, commerce, and agriculture (ALI et al., 2021; MACARTHUR, 2017). However, their inadequate disposal and poor waste management, as well as society's lack of awareness of recycling, have caused them to accumulate in the environment, compromising the lives of several beings, since they take centuries to decompose (NIELSEN et al., 2019; MACARTHUR, 2017; WINDSOR et al., 2019). Over the past years, the impact of micro and nanoplastics and studies of other biodegradable materials that can replace them have been extensively discussed worldwide (MITRANO et al., 2021). Bioplastics, for instance, are an option, since they are biodegradable and manufactured from renewable raw materials (e.g. vegetable biomass) (IMRE et al., 2019).

Starch is a polysaccharide widely used and studied for the production of bioplastics, and the presence of amylose (a linear chain of sugars that together with amylopectin compose the starch grain) provides it with reasonable mechanical resistance (PRABHU;PRASHANTHA, 2018; SANYANG, 2015). Two characteristic processes of starch are gelatinization and retrogradation. The former is related to the breakdown of the granule in an aqueous medium at 60-70 ^{o}C, and the latter occurs when, at low temperatures, the chains of starch molecules reestablish connections, expelling water molecules. Therefore, starch retrogradation makes the bioplastics more brittle, such rigidity can be avoided or reduced by adding water-soluble polymers (PRABHU; PRASHANTHA, 2018; STEENEKEN; WOORTMAN, 2009).

Hemicellulose, lignin, and cellulose are part of the lignocellulosic material present in the plant cell wall, being the second most abundant polysaccharide in the biosphere representing 20-35 % of the lignocellulosic mass. It is recognized as amorphous due its structure highly branched, in addition, it is characterized by having low molecular mass, being formed by pentoses and hexoses molecules (BRODIN et al., 2017; FARHAT et al., 2018; ZHAO et al., 2020). Its various hydroxyl groups are responsible for its greater affinity for water, thus influencing solubility and resistance to the passage of steam in biomaterials composed of this sugar. On the other hand, such a hydrophilic characteristic provides it with a

higher greater degree of barrier to gases such as CO_2 and O_2 (KOCHUMALAYIL et al., 2013).

The hemicellulose structure is heterogeneous, being composed by diverse molecules that originate different types of hemicellulose, that present themselves in a varied way among the different species of plants even between tissues of the same individual. It is commonly composed of D-xylose, D-glucose, D-mannose, D-glucuronic acid, and 4-O-methyl-D-glucuronic acid, forming different types of sugars, of which the most common is xylan (BRAGA; POLETTO, 2020; BRODIN et al., 2017; FARHAT et al., 2018; FELPUCI et al., 2021;ZHAO et al., 2020). Hemicellulose is represented mainly by xylan in most biomasses and grasses such as sugar cane (ALVES et al., 2020; BRIENZO 2009). Xylan is a cheap raw material for the development of products with high added value (ABE et al., 2021; FARHAT et al, 2018; ZHAO et al, 2020). It is found in large amounts in residual biomass, which is generated from agricultural activities, food processing, sugar and alcohol industries, and timber industries (ALVES et al., 2020; MELATI et al., 2021; PEREIRA et al., 2021; RESHMY et al., 2021).

Despite producing brittle and hydrophilic bioplastics, both xylan and starch are biocompatible, fully biodegradable, and highly available. Several studies have aimed at a more viable applicability of xylan to bioplastics through chemical modifications (FARHAT et al., 2018; HANSEN and PLACKETT, 2008; RESHMY et al., 2021; ZHAO et al., 2020); however, the use of certain chemical agents can cause hemicellulose degradation during its modification (ZHAO et al., 2020). This article addresses changes made to xylan from sugarcane bagasse towards the evaluation of its influence on the combination with starch for the bioplastics production. To the best of our knowledge, no study has focused on the understanding of the correlation between starch and xylan in bioplastics. The mechanical, physicochemical and biodegradation properties of starch and xylan bioplastics were determined. The biodegradation was characterized by soil burial and CO_2 quantification. Our findings suggest an eco-friendly and simple route for the production of a bioplastic that can potentially be used in packaging and coating, drug distribution, and in other applications, contributing to the sustainable development of the planet.

2. Material and methods

2.1. Raw material

The xylan used in this study was extracted from sugarcane bagasse supplied by the company São João (Araras - SP), commercial starch from Êxodo científica was used and glycerol (commercially known as glycerin) from Synth 99.5 % pure.

2.2. Xylan solubilization

The xylan solubilization from sugarcane bagasse was based on an optimized methodology (ALVES et al., 2020; BRIENZO et al., 2009). The bagasse was milled in a knife mill (Marconi, MA 580), selected and sieved through a 20 mesh sieve. 100 g of ground bagasse were mixed in 2 L of a 6 % (w/v) hydrogen peroxide solution with pH adjusted to 11.6 in a NaOH solution. This mixture was kept under stirring in a mechanical stirrer (ENGCO) for 24 h at room temperature and 500 rpm and filtered in filter paper after the reaction. The liquid fraction (consisting of xylan) had the pH changed to 6 with the addition of 5 mol/L HCl, and this fraction proceed to the concentration stage in an oven at 50 °C until it reached about one-third of its initial volume. The liquid fraction concentrated was precipitated with 3 volumes of ethanol 92 %. After precipitation/sedimentation of xylan, the supernatant was removed and an ethanol solution (70 %) was added, this step was repeated until a clear supernatant had been obtained. The precipitate xylan was dried at 50 °C for 24 h, milled and sieved (with a 40 mesh sieve). .

2.3. Characterization of biomass and extracted xylan

The characterization of biomass and xylan were conducted according to the methodology described by ABNT (2018), Brienzo et al. (2009) and Alves et al. (2020). In which, in the case of sugarcane bagasse, an extractive removal step was carried out in a soxhlet using alcohol as a solvent and then water. The samples were subjected to acid treatment (using 72 % sulfuric acid, w/w) and thermal through of an autoclave (Stermax box digital) in order to break the structure of the polysaccharides, making them available for later analysis (mass difference, spectrophotometry and High performance liquid chromatography).

2.4. Gelatinization parameters and plasticizer content

The glycerol proportion was evaluated on starch films according to Table 1. In addition, a study of the best gelatinization conditions was performed in starch bioplastics with 20 % glycerol (w/w of starch). In the a-f tests presented in Table 2, gelatinization conditions were changed such as, temperature, time, starch concentration, and evaluated if the solution was better gelatinized in an Erlenmeyer or directly on the Petri dish.

Table 1 - Evaluation of different proportions of glycerol (G) in 5 % starch (w/w of solution) bioplastics

	Glycerol (%, w/w of starch)
G40	40
G20	20
G10	10

Source: Author

Table 2 - Evaluation of starch gelatinization conditions in bioplastics with 20 % glycerol (w/w of starch)

	Bioplastic					
	a	b	c	d	e	f
Starch (%, w/w)	10	10	10	10	10	5
Gelatinization temperature (^{o}C)	80	80	80	80	75	75
Gelatinization time (min)	25.0	25.0	1.0	2.0	2.5	2.5
Gelatinization directly on a Petri dish	yes	no	no	no	no	no

a-f: individual experimental condition.

Source: Author

2.5. Bioplastic production

The bioplastics were produced using polysaccharides in a concentration of 5 % (w/w of polysaccharides in relation to the total mass of the filmogenic solution)according the Table 3, and 20 % of glycerol (w/w of polysaccharides). The xylan was solubilized in destilled water heating the solution in a microwave oven in several alternating cycles between a short heating time (e.g. 10 seconds) and manual agitation of Erlenmeyer flask containing the

solution. The procedure was repeated until xylan solubilization, and starch and glycerol were added after cooling. The constituents were homogenized in a shaker (Solab, SL - 222), at room temperature, at 110 rpm constant agitation for 1 h. After homogenization, the solution was gelatinized in a thermostatic bath at 75 ^{o}C for 3 min, and transferred to a Petri dish. The bioplastics were dried according to the Casting technique and using a Petri dish (area of 56.71 cm^2) containing 0.4 $g.cm^{-2}$ of a filmogenic solution that remained in an oven (Solab, SL-100) for 20 h at 40 ^{o}C.

Table 3 - Bioplastic compositions in relation to 5 % (w/w, filmogenic solution) of polysaccharides with glycerol 20 % (w/w, polysaccharides).

	SB	X5	X10	X25	X50
Xylan (%,w/w)	0	5	10	25	50
Starch (%,w/w)	100	95	90	75	50

Source: Author

2.6. Bioplastics characterization

2.6.1. Moisture and solubility tests

Samples of 0.9 x 1.5 cm were weighed and oven-dried at 105 ^{o}C for 24 h. The procedure was repeated until a constant mass had been obtained, and its moisture percentage was then determined from the difference in masses before and after drying, which represents the water content present in the bioplastic (JARAMILLO et al, 2017). The same samples were inserted into a beaker containing 50 mL of distilled water, and stirred at 110 rpm, at room temperature for 24 h. After this period, they were again oven-dried at 105 ^{o}C until the obtaining of the final dry mass (AZEREDO et al, 2015; FAKHOURI et al., 2007; JARAMILLO et al, 2017).

2.6.2. Opacity

The opacity of the bioplastic was determined by a spectrophotometer (Biospectro, SP-22). The samples were cut into 3.0 x 0.9 cm^2 rectangles, supported on the wall of a glass

cuvette, and different parts of the bioplastic were read in triplicate at a 450 nm wavelength. The calculation was performed by the division between the absorbance and the thickness of the film bioplastic (GOUNGA et al., 2007).

2.6.3. Hydrophilicity

The affinity of the bioplastics with water was measured in contact angle tests by CAM 101 (KSV Instruments), and the images were analyzed by CAM 2008 software version 4.04 (KSV Instruments). A Hamilton syringe deposited drops of water in three specimens for each sample, and images were captured by a DMK 21AF04 camera (Imaging Source) in a 16 ms interval with 40 images.

2.6.4. Water vapor transmission (WVT) and water vapor permeability (WVP)

These tests were based on E96/E96M – 05: Standard Test Methods for Water Vapor Transmission of Materials. A flask of 1.2 cm base diameter and 3.5 cm height was used, having a lid with opening of 1.15 cm diameter in its center where the bioplastic was attached (Figure S1). The flask was filled with 4 mL of distilled water and placed in a desiccator with silica gel dried at 105 ^{o}C for 1 day. A ruler attached to the flask measured the water level over the days, and the desiccator with the whole set remained for 10 days at 30 ^{o}C.

2.6.5. Mechanical test

Tensile stress at maximum load and elongation at break of the bioplastic were measured by an Instron model 5969 universal testing machine. Specimens of 2 cm in length and 0.6 cm in width had their thickness previously measured in different and random regions by a digital micrometer 0-25 mm with 0.001 mm resolution (Mitutoyo 293-230). The samples remained stored at 65 % relative humidity and were then fixed in the claws of the device. The test was conducted at a 1 mm.min^{-1} displacement speed.

2.6.6. Fourier-transform infrared spectroscopy (FTIR)

Fourier transform infrared spectrometer (Shimadzu IRAffinity-1S) was used. The FTIR spectra were recorded according to an attenuated total reflection (ATR) method, with 32 scans at ± 4 cm^{-1} resolutions in a 400 – 4000 cm^{-1} spectral range. The samples were directly placed onto ZnSe crystal.

2.6.7. Scanning electron microscopy (SEM)

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.

2.6.8. X-ray diffraction (XRD)

A Rigaku Ultima IV diffractometer equipped with a Cu anode was used. It operated at 40 kV and 30 mA voltage in a 10 ^{o} to 100 ^{o} normal scan at of 2 $^{o}.min^{-1}$ speed, and X-ray diffractograms of the samples were recorded for 2θ.

2.7. Biodegradation

The bioplastics were exposed to microorganisms, and the biodegradation rate was obtained from measurements of the CO_2 production. Hermetic containers with a sealing system and 1 L volume (Yazi) were used (Figure S2). Were deposited 100 g of soil and samples of 3x3 cm^2 dimensions were buried approximately 2 cm from the surface. A pot with soil and no bioplastic was used as a control for further calculations. A 50 mL beaker was also kept inside the container with 10 mL of 0.3 $mol.L^{-1}$ KOH solution that was titrated for measurements of the CO_2 content produced during the biodegradation of the bioplastic and sequestered by the solution. From time to time, the solution with KOH was titrated and another beaker with a new solution was put in place to be analyzed in a next titration. The titration consisted of the addition of 1 mL of 0.1 $mol.L^{-1}$ BaCl to KOH solution, for precipitating the sequestered CO_2, and three drops of phenolphthale in solution; the previously standardized 0.2 $mol.L^{-1}$ HCl was used as the titrant. Equation (1) provided the

mass of CO_2 produced over time - A represents the volume of titrant spent on the control, B is the volume of titrant spent on the sample, 50 is the conversion factor equivalent in µmol of CO_2, 0.044 is the conversion factor of µmol of CO_2 to mg of CO_2, and fHCl is the titrant correction factor.

$$mgCO_2 = (A - B) * 50 * 0.044 * fHCl \quad (1)$$

After the biodegradation period, the microorganisms present in the soil were suspended in distilled and autoclaved water with 0.85 % NaCl which was used to inoculate the microorganisms in Petri plates with Potato Dextrose Agar (PDA) medium (Neogen). The colony-forming units were counted on plates with PDA with antibiotics to promote the growth of filamentous fungi and without antibiotics to count single-celled microorganisms.

2.8. Statistical analysis

Statistical treatment was carried out for some of the results obtained through the analysis of variance (ANOVA) with a single criterion by Tukey's method using the BioEstat software (version 5.3).

3. Results and discussion

3.1. Biomass composition, xylan solubilization, and characterization

The mass of hemicellulose recovered varied between batches of extraction, with an average of 4.9 g of extracted xylan for every 100 g of bagasse (90 g of dry mass). Considering that the average amount of hemicellulose present in the sugarcane bagasse is 25 % (BRIENZO et al., 2009), the extractions yielded of hemicellulose potentially present in sugarcane bagasse was 21.77 % (Table 4). In comparison with the results of hemicellulose extraction yield obtained by Alves et al. (2020), Brienzo et al. (2009), and Melati et al. (2021) under the same conditions (Table 4), the average extraction yield was below the one expected (between 70-80 %), probably due to a natural variation in the bagasse's properties, such as its recalcitrance.. Another possible explanation is the volume of extraction, which was 10 times greater than reported in other studies and may have impaired the mixture of oxidizing agents

with the bagasse, due to the greater possibility of generating “dead zones”, where the agitation was not effective.

Table 4 - Xylan extraction yield (%, w/w theoretically present in the bagasse)

	Mean of extractions	Brienzo et al. (2009)	Alves et al. (2020)	Melati et al. (2021)
Extraction yield (%, w/w)	21.77 ±11.07	86	71.43	86.25

Source: Author

Table 5 - Lignin content and sugars in biomass and solubilized xylan (%, w/w)

	Lignin total	Glucan	Arabinan	Xylan	Acetyl	Sum
Sugarcane bagasse (%, w/w)	21.41 ± 0,17	46.77 ± 1.44	2.49± 0.51	23.48 ± 1.39	1.21± 1.15	95.36
Xylan (%, w/w)	12.87 ± 0.79	4.11± 0.92	6.87± 3.78	37.03± 13.39	1.69± 2.42	62.57

Source: Author

The residual lignin content in xylan was 12.9 % (Table 5); however, Alves et al. (2020), Brienzo et al., (2009) and Melati et al. (2021) reported values among 4.4, 5.9, and 7.6 %, respectively. The presence of residual lignin adhered to xylan can exert positive effects on the formation of films, as claimed by Goksu et al. (2007). Bioplastics produced with hemicellulose extracted from birchwood were more continuous as the lignin concentration increased from 0.86 to 1.13 % (w/w of hemicellulose). The extracted xylan (Table 5) was mostly composed of xylose, despite being present in a smaller amount compared to the proportion obtained by Brienzo, which, under the same extraction conditions, xylan presented 80.9 % of xylose (dry weight of hemicelluloses, w/w). The Arabinose content was above that obtained by the author (3.8 %), and acetyl groups were below (3.9 %). Such small differences in relation to acetyl and arabinose may be related to possible variations between bagasse; however, as for xylose, this large difference can be exclusively attributed to a deficient xylan extraction, corroborated by the aforementioned low yield. Regarding the lignin content, cellulose and hemicellulose (represented by xylan, arabinan, and uronic acids) bagasse showed values close to the literature equal to 20, 45 and 25 %, respectively (ALVES et al., 2020; BRIENZO et al., 2009; MELATI et al., 2021).

3.2. Gelatinization parameters and plasticizer content

Gelatinization helped in the bioplastics formation, making them less brittle, more continuous, and less fragmented (Figure S3). Regarding the two procedures for gelatinization , in Erlenmeyer to be then transferred to a petri dish or directly conducted in the Petri dish, this last one produced irregular bioplastics after drying, with regions where gelatinization was not effective (Figure S4 - a), probably due to the lack of agitation and spillage of solution from the plate. The lower heat transfer of the plastic in comparison to glass may also have hampered gelatinization as a whole. Concerning bioplastic b (Figure S4), due to the gelatinization conditions, like time exposed to heat, temperature and starch concentration, the solution became too viscous after gelatinization, thus reducing its spreading capacity and hampering the transfer of its proper mass to the Petri dish. Bioplastics c and d (Figure S4) were produced decreasing the gelatinization time. With the time of 1 minute (c) gelatinization was not effective, represented by a white bioplastic, completely opaque, more rigid and thick, and with 2 minutes (d), gelatinization was more visible, but the solution was not distributed equally across the plate, and showed numerous bubbles.

E and f tests were applied at lower temperature, for longer time in relation to c and d, and with lower starch concentration (5 %, w/w) in f, towards reaching the gelatinization point with no loss of the spreading capacity of the solution. Bioplastic e showed the same characteristics as d (10 % starch w/w and 2 min of gelatinization). On the other hand, bioplastic f had better distribution on the plate, without the formation of bubbles. Probably because it has half of starch concentration in relation to another tests, in which the higher proportion of polysaccharides consequently made the medium more viscous hampering to spread evenly and to disperse the gases present. Therefore, gelatinization in an Erlenmeyer flask with subsequent transfer of the appropriate mass to the plate was considered a more efficient method, and the concentration of 5 % of polysaccharides was the best result.

The highest proportion of glycerol, denoted by G40, produced a more soluble bioplastic with higher humidity (Table 6). On the other hand, the values of G20 and G10 were close. The plasticizer can increase the bioplastic hidrofilicity as reported by Mehyar and Han (2004), in which films with 50 % glycerol (w/w of starch) based on starch from rice and pea showed 44.4 and 32 % solubility , respectively, while without plasticizer the solubility was 1.5 %. This result was corroborated by Peressini et al. (2004) and Bertuzzi (2007), who reported the solubility of starch-based films remained in the same range with the use of glycerol, also observed by Mehyar and Han. Such hydrophilic property of glycerol is even

reported in the literature (MALI et al, 2004), due the hydroxyl groups of plasticizer that facilitated its interaction with water, increasing humidity and solubility in bioplastics.

Glycerol improved the handling of the G20 bioplastic presenting less rigid than G10. However, the increase in the proportion of glycerol in G40 decrease stiffness and high adhesiveness of bioplastic, thus it presented greater difficulty to be removed from the plate without tearing/breaking the bioplastic. This same characteristic was observed by Shimazu et al. (2007), in the same proportion of 40 % glycerol in relation to starch. Therefore, because for having lower solubility and better handling, the glycerol concentration of G20 (20 % glycerol, w/w of starch) was selected for the tests carried out in the sequence.

Table 6 - Moisture and solubility results of bioplastics with 5 % starch (w/w of solution) and glycerol.

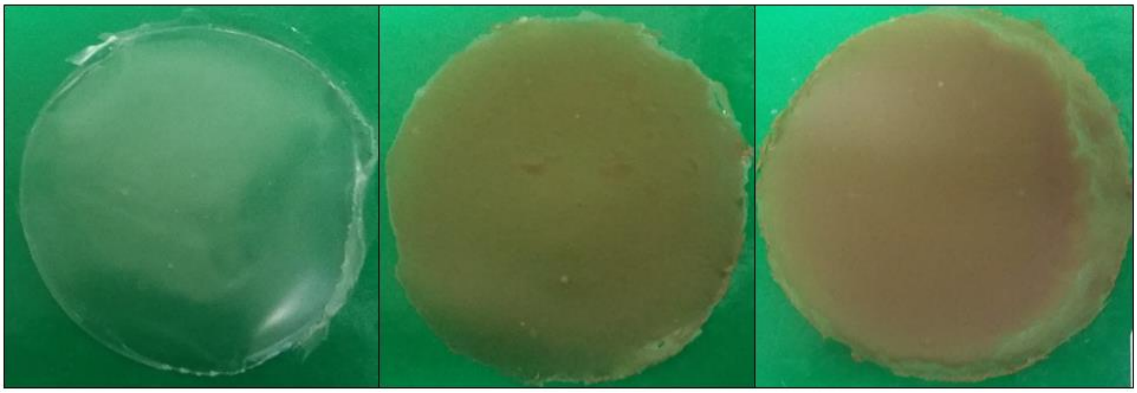
	Glycerol (%, w/w of starch)	Moisture (%)	Solubility (%)
G40	40	24.34 ± 1.88	22.57 ± 3.15
G20	20	10.66 ± 2.83	14.58 ± 2.66
G10	10	8.65 ± 2.50	16.64 ± 0.62

Source: Author

.

From the best conditions of gelatinization and proportion of plasticizer achieved above, reasonably continuous and flexible bioplastics produced according to the formulations in Table 3 were easily detach from the plate, as identified in the examples in Figure 12.

Figure 12 - Examples of bioplastics produced from starch and xylan in different proportions in relation to 5 % of polysaccharides (w/w of filmogenic solution).



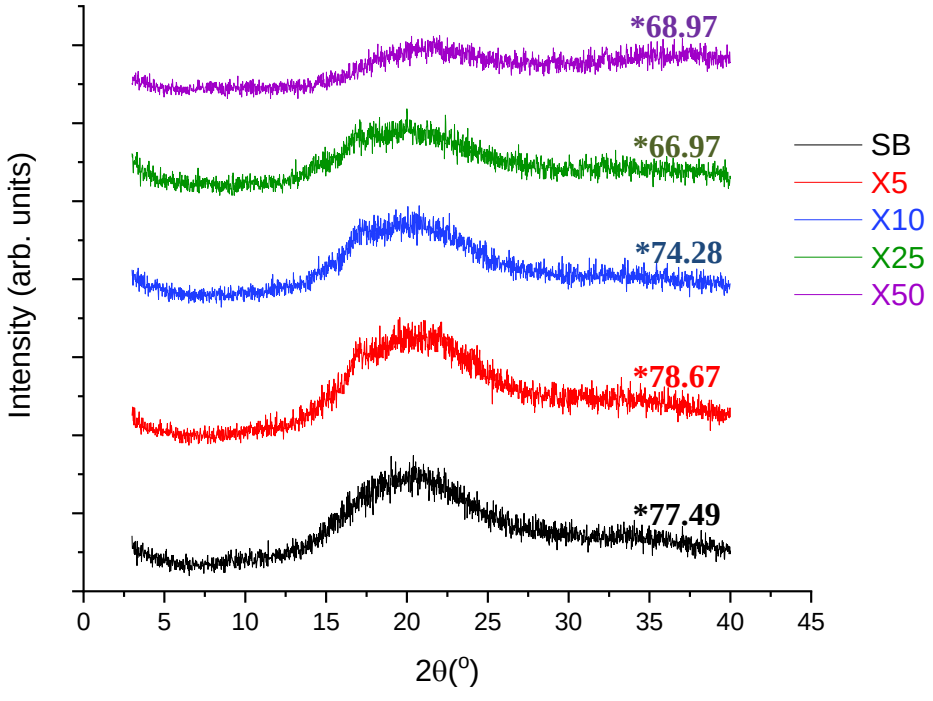
From left to right: SB, X25, and X50.
Source: Author

3.3. Bioplastics characterization

3.3.1. X-ray diffraction (XRD)

The X-ray diffraction showed a similar pattern for all bioplastics analyzed, with slight difference between the intensity of the detected signals. . Figure 13 shows a single peak at 20°, similarly to the pattern reported by Li et al. (2019) for waxy starches with a type-V structure characterized by disruption of the double helix conformation of starch and establishment of stable single chain V-conformations helices. This phenomenon might be due to the addition of glycerol to the filmogenic solution, forming glycerol-amylose complexes (SANYANG et al., 2016). As proposed by Li, those complexes can form regions with an efficient encapsulation capacity because they contain six, seven, or eight glucose residues per turn in helix, being possible to load small molecules like CO_2 in these spaces; however, the low crystallinity of this structure can affect that efficiency as a carrier of small molecules. The increase in the proportion of xylan in the bioplastic formulation decreased the intensity of diffraction peaks. This behavior was reported previously comparing the diffraction of the PVA/xylan blends in the proportion of 3/1 to 1/1, which can be explained by the heterogeneous and branched structure of xylan (GAO et al., 2014).

Figure 13 - X-ray diffractograms of bioplastic of starch and xylan (according to Table 3).



* respective crystallinity index

Source: Author

3.3.2. Moisture and solubility tests

The proportion of xylan was an interferring factor in the solubility of the bioplastics in distilled water (Table 7) - xylan concentration above X5 (5 %, w/w of total polysaccharides) showed a gradual increase in their solubility. Similar results were reported by Wang et al (2014) by increasing the proportion of polyvinyl alcohol per xylan resulting in a decrease in the solubility of the films. Therefore, the solubility of bioplastics was related to the side groups present in hemicellulose and abundant in hydroxyl groups (XU et al., 2019, WANG et al., 2014; NAIDJONOKA et al. 2020). For humidity results, the X5 bioplastic had lower water content than the others and this slight difference in water content may be related to loss during the drying process or to an uneven the crystallinity of the bioplastics, , because according to Figure 13, X5 showed higher cristalinity and water sorption is related to disordered regions of the material. For instance, xylan can contribute to the spread of such regions in bioplastics, because shows high levels of ramifications (GRÖNDAHL et al., 2004; NAIDU et al, 2018; PENG et al., 2011).

Table 7 - Solubility and moisture of bioplastics of starch and xylan (according to Table 3).

	SB	X5	X10	X25	X50
Solubility (%)	20.31 ± 2.15^{a}	20.25 ± 0.48^{a}	$25.49 \pm 1.63^{a,b}$	31.02 ± 1.37^{b}	44.16 ± 4.13
Moisture (%)	16.27 ± 1.21^{a}	13.34 ± 0.31^{b}	$14.43 \pm 0.39^{a,b,c}$	$18.49 \pm 1.05^{a,d}$	$16.44 \pm 1.19^{a,c,d}$

Equal letters indicate that there was no significant difference ($p < 0.01$).
Source: Author

3.3.3. Water vapor transmission (WVT) and water vapor permeability (WVP)

The water barrier property of bioplastics is an important factor to be studied, since several applications, especially food packaging, require a greater control of the passage of water through the material for preventing its exit or entry (GOKSU et al., 2007; MIKKONEN; TENKANEN, 2012). The bioplastics showed a similar water vapor transmission (WVT) rate (31.19-36.86 g/hm^2) between the treatments (see Table 8). However, when compared to the test with no barrier, they were much more efficient in controlling the amount of water transferred between the different locations.

Bioplastics show a more remarkable difference since the permeability calculation (according to ISO E96/E96M – 05: Standard Test Methods for Water Vapor Transmission of

Materials) takes into account vapor pressure and thickness (Table 8), probably due to the thickness of each bioplastic (MALI et al., 2004) - the water vapor permeability (WVP) of bioplastic with starch from yam was influenced by the linear effects of thickness. One of the hypotheses for the WVP increase in function of the increase in thickness is the transport of films containing hydrophilic polysaccharides is highly complex due to the non-linear isotherms of water sorption and water content-dependent diffusivities - the vapor flow of water through them does not vary linearly with the water vapor pressure gradient (MALI et al., 2004). The WVP values were below those reported by Kechichian et al. (2010), who measured the permeability of starch films (5 %, w/w) with sucrose (0.7 %, w/w) and inverted sugar (1.4 %, w/w) additives, obtaining 2.65 g mm/d m^2KPa. The value achieved in the presented study may have been lower due to the presence of xylan which absorbed and maintained the water vapor trapped between the polymer chains of the bioplastic

Table 8 - Water vapor transmission (WPT) and water vapor permeability (WVP) of bioplastics of starch and xylan (according to Table 3).

	No bioplastic	SB	X5	X10	X25	X50
WVT (g/h m^2)	104.91	34.03	39.70	36.86	34.03	36.86
WVP (g mm/d m^2KPa)	-	0.56	0.43	0.52	0.71	0.49
Thickness (mm)	-	0.21	0.14	0.18	0.27	0.17

Source: Author

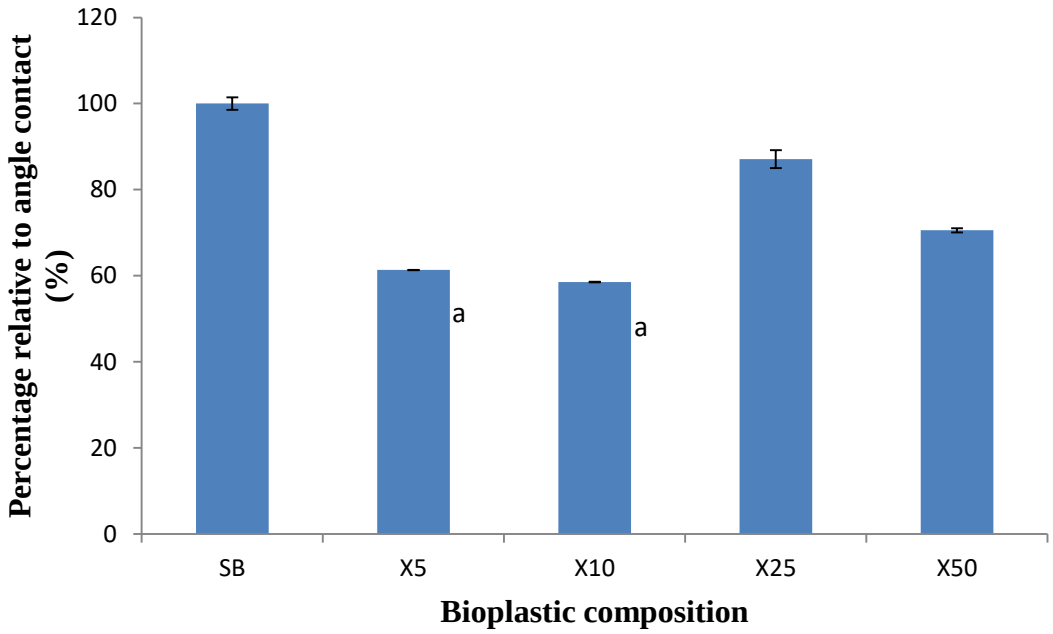
3.3.4. Hydrophilicity

The hydrophilicity was measured by contact angle test and a percentage relation of the angle degree of each samples (X5, X10, X25 and X50) with the SB sample (without xylan) is presented in Figure 14,. in which the high degree of contact angle between the drop and the bioplastic indicates greater hydrophobicity of the sample (FARHAT et al., 2017; XU et al., 2019). The bioplastics X5 and X10 were less hydrophobic than SB , indicating xylan increased the hydrophilicity of the film. The difference was smaller for X25, demonstrating a possible better interaction between the hydrophilic groups present in the side groups of xylan and starch with the plasticizer.

Films of hemicellulose/chitosan also showed a reduction in the contact angle as the percentage of glycerol increased, due to the hydroxyl groups present in the plasticizer (XU et

al., 2019). In the case of this study an increase in the hydrophilicity of the material would be expected to accompany the increase in the proportion of xylan, as obtained by Luo et al. (2014) studying polymers with chitosan and xylan, . However, for some reason, the molecular chains organized in a way that the hydrophilic groups were less exposed at X25 and X50.

Figure 14 - Relative percentage of contact angle of bioplastics of starch and xylan in relation to starch bioplastics.



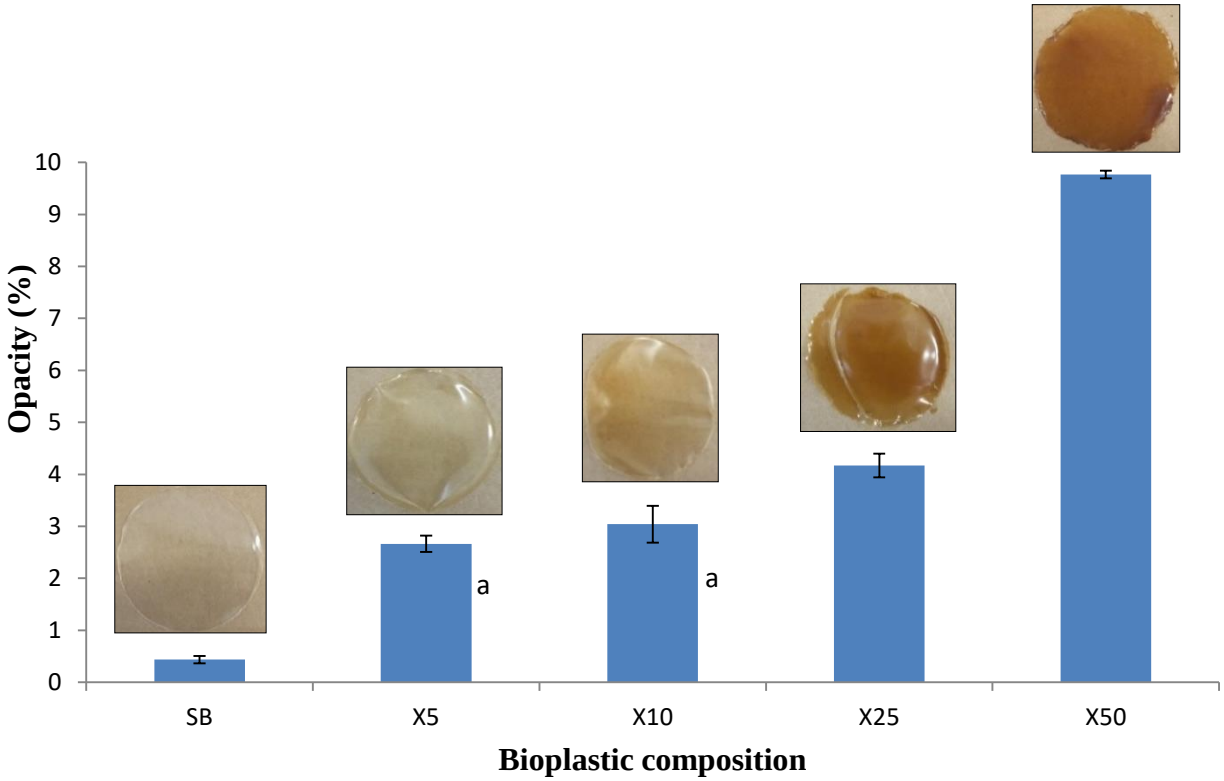
Equal letters indicate no significant difference according to ANOVA.
Source: Author

3.3.5. Opacity

Opacity increased as the proportion of xylan increased (Figure 15), showing a statistically significant difference among the tests ($p < 0.01$), except for samples X5 and X10, which showed no difference between the treatments. The same was observed by Lucena et al. (2017) and Ruiz et al. (2013) in films produced with hemicellulose extracted from corn cob and wheat straw, respectively. Such a behavior can be explained by the presence of residual lignin in the extracted hemicellulose – the chromophores of such lignin are represented mainly by quinoids, catechols, aromatic ketones, stilbenes, conjugated carbonyls with phenolics, and metal complexes, promoting the brown coloration in bioplastics as shown in the photos in Figure 15 (ZHANG et al., 2020). Transparency in plastics is more preferable in certain applications, such as food packaging, as the consumer feels more secure by being able

to view the packaged product. However, the chromophores present in lignin are able to absorb ultraviolet radiation (ZHANG et al., 2020). Thus, in addition to promoting an amber coloration to the bioplastic they also result in a barrier, protecting products sensitive to light.

Figure 15 - Opacity as a function of the composition of xylan in bioplastics, showing the respective photo of each composition



Equal letters indicate no significant difference according to ANOVA.
Source: Author

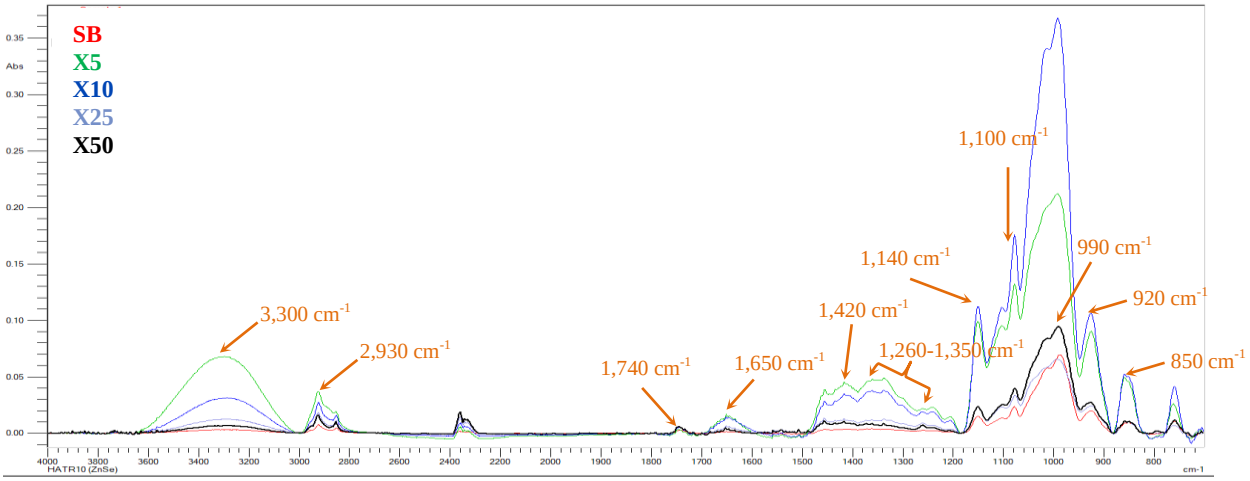
3.3.6. Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectroscopy of the samples was performed to identify the main functional groups present in the bioplastic and showed similarity among the bands found (Figure 16), just varying the intensity of absorption between the specimen. The observed bands coincide with the main functional groups found in polysaccharides and glycerol. For example, the band at 3,300 cm^{-1} represents stretches of hydroxyls (–OH) associated with the polymer (ABDULKHANI et al., 2020; DANISH et al., 2017; GAO et al., 2014; LIANG;WANG, 2017; SABIHA-HANIM;AZIATUL-AKMA, 2016) and is present in all samples because both the polysaccharides and the plasticizer used are rich in hydroxyl side groups. The band at 2,930 cm^{-1} region indicates –CH bonds (ABDULKHANI et al., 2020; LIANG; WANG, 2017;

PALANIAPPAN et al., 2017) due to the common carbon skeleton in polysaccharides. At 1,740 cm^{-1}, a small band can be attributed to the presence of acetyl groups and ester in hemicelluloses C=O (SABIHA-HANIM; AZIATUL-AKMA, 2016), and the presence of a carbonyl (C=O) is observed at 1,650 cm^{-1} (DANISH et al., 2017; LIU et al., 2018). However, Mendes et al. (2017) attributed the region between 1,600 to 1,700 cm^{-1} to the presence of residual water in polysaccharide films such as starch and hemicellulose. At around 1,420 cm^{-1}, the −CH and −OH groups are generally identified (GAO et al., 2017; LIANG; WANG, 2017; LIU et al., 2018; SABIHA-HANIM;AZIATUL-AKMA, 2016), while the regions of 1,260-1,350 cm^{-1} and close to 1,100 cm^{-1} can be related to the C-O bond in primary and secondary alcohols (DANISH et al., 2016; LIU et al., 2018; MENDES et al., 2017), confirming the hydrocarbon structure rich in hydroxyl side groups.

Bands between 990 and 1,140 cm^{-1} are typical of xylan, since they are overlapping vibrations with elongation vibration of (C-OH) side groups and glycosidic bonding vibrations (C-O-C) (ABDULKHANI et al., 2020; LIANG; WANG, 2017; PALANIAPPAN et al., 2017). Another alcohol-related band can be seen at 920 cm^{-1}, representing an axial C-OH of C-4 (DANISH et al 2016; MENDES et al., 2017) and finally, β-glycosidic bonds are showed at 850 cm^{-1} (LIU et al., 2018; PALANIAPPAN et al., 2017).

Figure 16 - FTIR of starch and xylan bioplastics (according to Table 3).



Source: Author

3.3.7. Mechanical test

Higher tensile strength was observed in the X10 film (Table 17), followed by X5 and starch bioplastic (SB) (values of 2.56, 2.35 and 1.83 MPa, respectively). Bioplastic X50 was statistically the lowest value in all tests, probably due to the disorganization generated by the

xylan chains, and the relatively low mechanical strength of X25 and X50 was attributed to their characteristic of form brittle bioplastics with molecular organization amorphous. The tensile stress dropped from 22.4 MPa to close to 10 MPa in films produced with xylan and Polivinyl alcohol (PVA), when the PVA/xylan ratio changed from 3: 1 to 1: 2, respectively (GAO et al., 2014). The crystallinity studied (Figure 13) can be correlated with the tests, since X50, which showed the lowest degree of crystallinity, also had reduced tensile stress, whereas SB, X5, and X10 demonstrated higher crystallinity and consequently higher mechanical resistance. The up to 10% addition of xylan led to a slight increase in resistance to tensile stress. However, it was not a statistical significant improvement in relation to the bioplastic with starch.

Regarding elongation at break (Table 9), no relevant difference was observed between the bioplastics with xylan, however their values were drastically lower than SB bioplastics, which have only starch and glycerol. The formation of bioplastics with xylan extracted from sugarcane bagasse was also studied by Braga and Polleto (2020), however without the addition of starch and plasticizer. In this way, the authors achieved higher tensile stress values compared to the present study: 9.2, 12.4 and 22.3 MPa, witch concentrations of 2, 3 and 4 % (w/v) of xylan, respectively. However, the elongation at break results (1.3, 0.8 and 0.7%) obtained by them were below those presented in Table 9, probably due to the absence of starch and glycerol.

The interference of glycerol in the mechanical properties of bioplastics was evidenced in tests performed with corn starch films with glycerol (25 %, w/w of starch), which showed a 38.24 to 5.6 MPa reduction in tensile stress, whereas elongation at break considerably increased from 6.48 to 52.37 % with the plasticizer (NORDIN et al., 2020). This may be due to the better interaction between the plasticizer and the starch chain, since the increased plasticization effect generates greater mobility between the polymer chains allowing the bioplastic to have greater elongation. On the other hand, the lower elongation with xylan may be due to a strong intermolecular hydrogen bond (FARHAT et al., 2018; LAOHAKUNJIT; NOOMHORM, 2004; NORDIN et al., 2020).

Table 9 - Tensile stress at maximum load and elongation at break in starch and xylan bioplastics (according to Table 3).

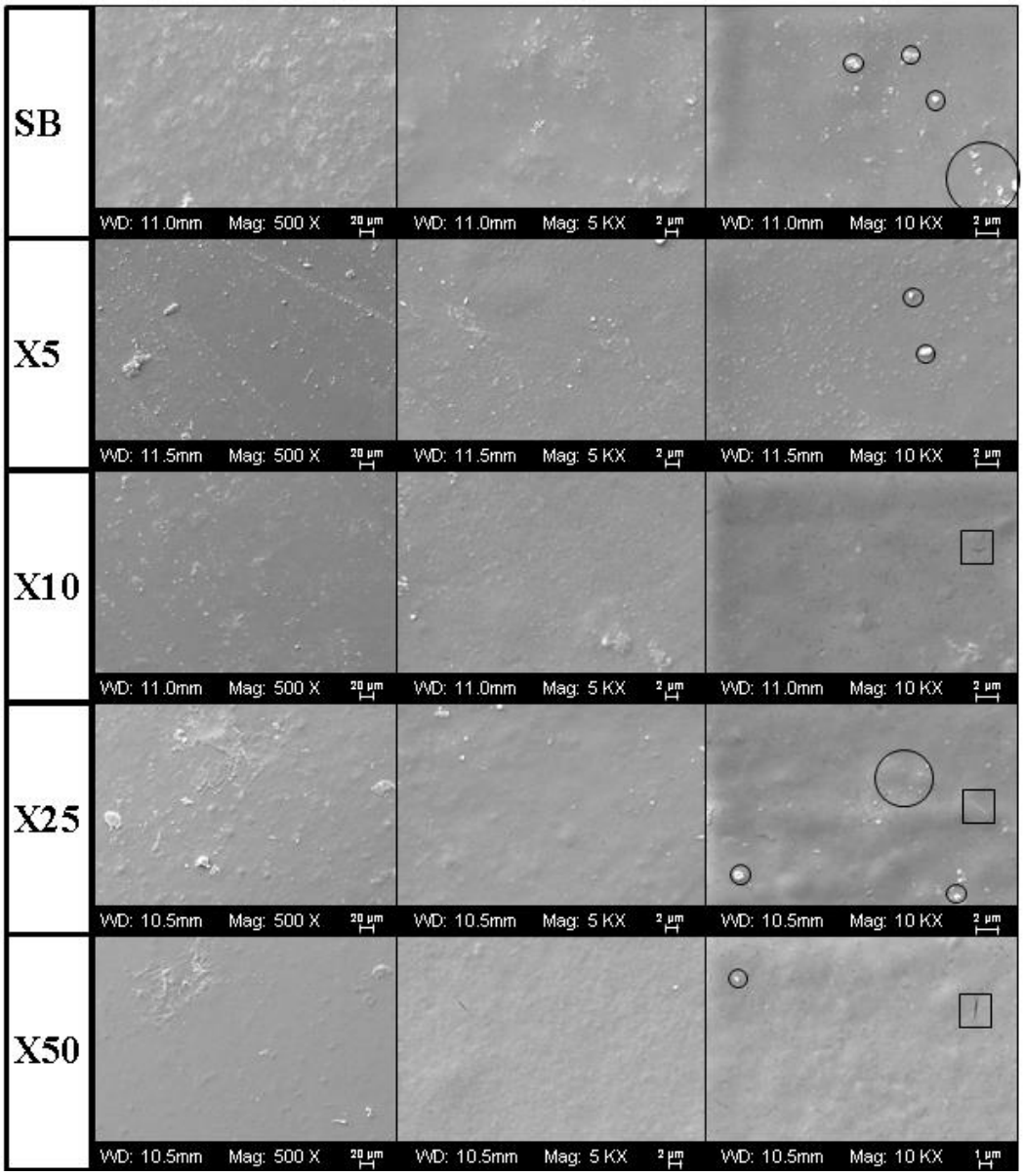
	SB	X5	X10	X25	X50
Tensile stress (MPa)	1.83 ± 0.1^{a}	$2.35 \pm 0.44^{a,b}$	$2.56 \pm 0.33^{a,b}$	$0.96 \pm 0.55^{a,b,c}$	0.06 ± 0^{c}
Elongation at break (%)	209 ± 42.28	37 ± 11.77^{a}	36 ± 0.20^{a}	16 ± 15.08^{a}	19 ± 4.21^{a}

Equal letters indicate that there was no significant difference according to ANOVA
Source: Author

3.3.8. Scanning electron microscopy (SEM)

The bioplastics showed a slightly rough surface, with unevenness probably due to drying by casting, in which the face that remains in contact with the air is uneven due to the absence of any mold (Figure 17). The images show some structures similar to grains (circle identified in the figure), possibly from starch having persisted to gelatinization or even restructured as a grain during the reverse retrogradation process. In addition, it was possible to notice the presence of some cracks along the bioplastic presented in the image below (square identified).

Figure 17 - SEM images of starch and xylan bioplastics with different magnitudes.



Circles: structures similar to grains; square: cracks in the structure.
Source: Author

3.4. Biodegradation

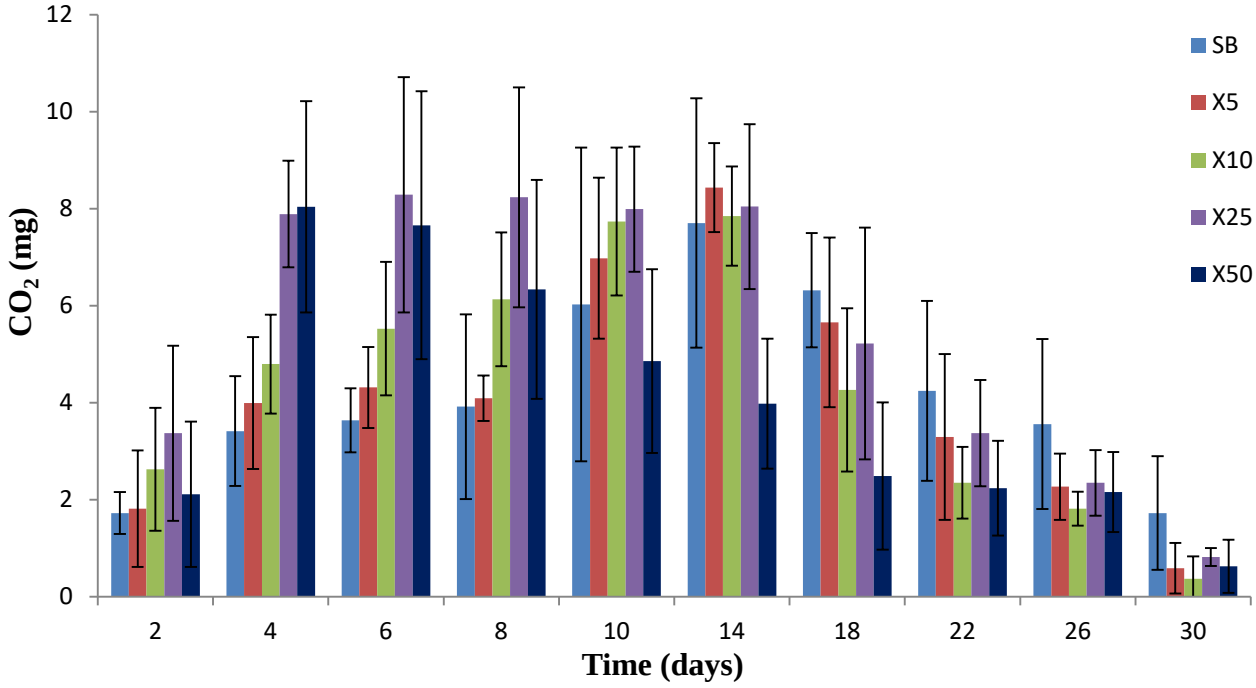
The different compositions of the bioplastics showed certain patterns in relation to the content of xylan. The bioplastics with a higher proportion of xylan, X25 and X50, resulted in a higher production of CO_2 (Figure 18) when biodegraded. The CO_2 generation is a product of the catabolic activity of the bioplastic decomposing microorganisms (ABE et al., 2021), leading to the inference of a faster decomposition of the bioplastics in shorter time when compared to X5 and SB. The biodegradation peaks can be seen on the fourth and sixth days

for X25 and X50, while those with lower sugar content had the CO_2 production peak only on the fourteenth day.

Such a possible effect of xylan on the decomposition of bioplastics may be due to the recalcitrance of the material, since those of faster degradation in shorter time coincide with less crystalline bioplastics (X25 and X50, as shown in Figure 13) (ABE, et al. 2021). On the other hand, another hypothesis is related to the set of enzymes used by microorganisms during the catabolic process of sugars. The growing microorganism may be deficient in amylolytic enzymes, or have more enzymes that catalyze hemicellulose breakdown reactions, such as endo-1,4-β-xylanase and 1,4-β-xylosidase, which degrade xylan into oligosaccharides and monosaccharides, respectively. The complete xylan hydrolysis is achieved with accessory enzymes such as xylan-esterases, ferulic and p-coumaric-esterases, α-L-arabinofuranosidases, and α-4-O-methyl glucuronidase, generally responsible for breaking the side groups (ABE et al., 2021; FARHAT et al., 2018).

An efficient biodegradation was attributed to the presence of hemicellulose in the buried films, between 95.3 and 99.7 % biodegradability (FARHAT et al., 2018) after 28 days of analysis for both unmodified hemicellulose and its derivatives. For films produced with xylan extracted from corn cob and gelatin, the time taken for total biodegradation was even shorter than that reported by Farhat. Such films decompose completely in 15 days, probably due to the gelatin, which provided the film with a more fragile and soluble structure in water and less recalcitrance (LUCENA et al., 2017). Therefore, increasing the proportion of xylan tends to improve the biodegradation of bioplasticss in soil (WANG et al., 2014).

Figure 18 - CO_2 production (mg) from the biodegradation of starch and xylan bioplastics.



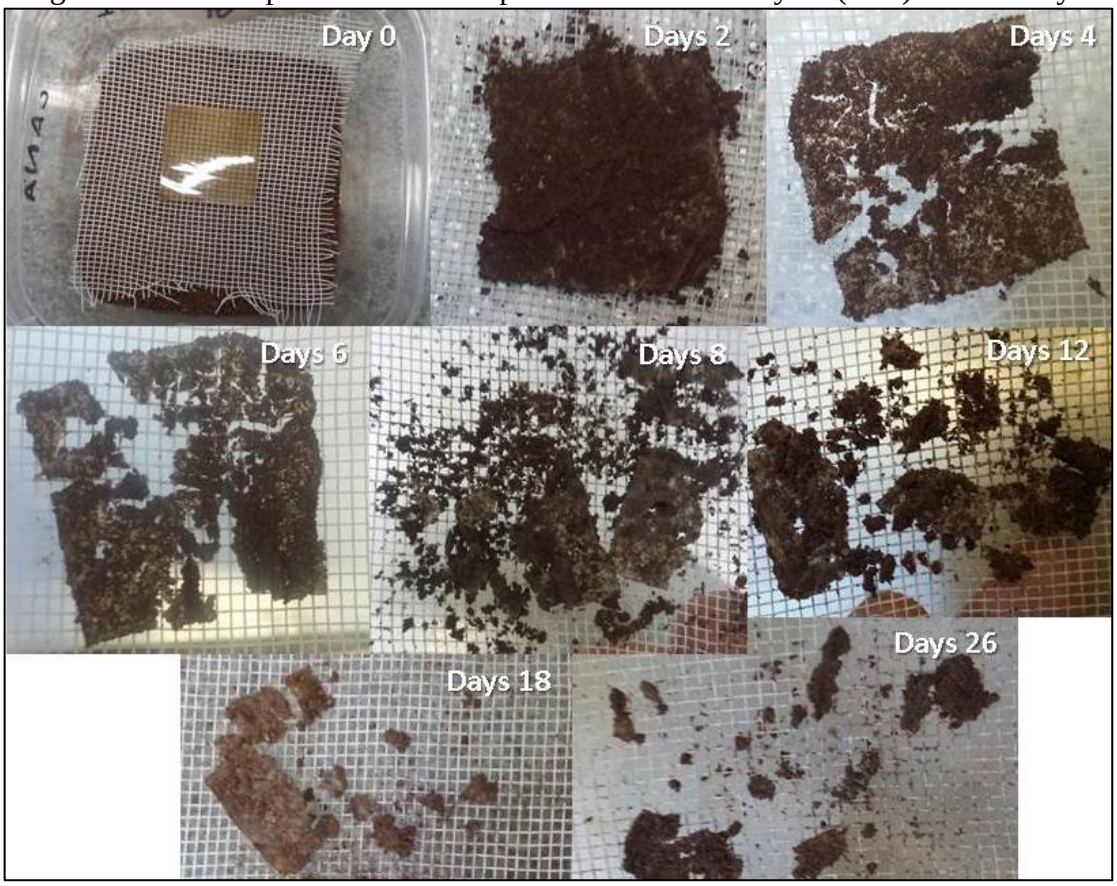
Source: Author

After the second day of biodegradation, X10 began to undergo fragmentation (Figure 19); it was highly fragmented after 8 days and its structure was reduced. At day 26, only a few pieces of the film remained in the soil. The presence of xylan in the bioplastic may contribute to the decomposition of the material, because in other studies, such as that carried out by Campagner et al. (2014), the time required for degradation was greater when using only starch and lignin in lignosulfonate form. Being reported fragments still visible after 35 days, in addition to showing slower decomposition as increased proportion of starch in bioplastics.

The microorganism's growth was evaluated in the soil before and after the bioplastic biodegradation. The influence of bioplastics produced in this study in the microbiological growth is evidenced due to a higher number of colony-forming units (CFU) per gram of soil (Table 10) after the period in which bioplastics were buried. It is possible to morphologically characterize the colonies of microorganisms showed in Figure 20 (based on visual observation), in which what is probably a filamentous fungus showed rapid growth stands out taking the entire plate in a short time, having characteristics of *Aspergillus fumigatus* and *Penicillium digitatum* for possessing colonies green in the center and white in the border (F in Figure 20) and to show coloration in their conidia, specific spores of these genera, and not in their hyphae (LAFUENTE; ALFÉREZ, 2015; MESQUITA-ROCHA, 2019; SIDRIM et al., 2004; TORTORA et al., 2017). However, the chances of being *A. fumigatus* are greater, as *P.*

digitatum is a fungus that commonly develops in citrus fruits (LAFUENTE; ALFÉREZ, 2015). It was still possible to observe, like presented in Figure 20, small colonies represented by a circular type, with a smooth margin, umbilical elevation, and brown color (A); a white colony with a jagged, opaque, floury margin, with a raised and peaked surface (B); a convex circular shape, with a gelatinous texture, smooth margin and brown (C); opaque, irregular shape, flat, with wavy margin, gelatinous texture and brown color (D); finally, a white, cotton-like filamentous fungus was observed (E). These microorganisms represent a variety of yeasts; however, the morphological characterization by itself is not very conclusive as they can vary in the same genus depending on the cultivation conditions, requiring a complementary genetic study to identify exactly which microorganisms they are.

Figure 19 - Decomposition of the bioplastic with 10% of xylan (X10) over 26 days.



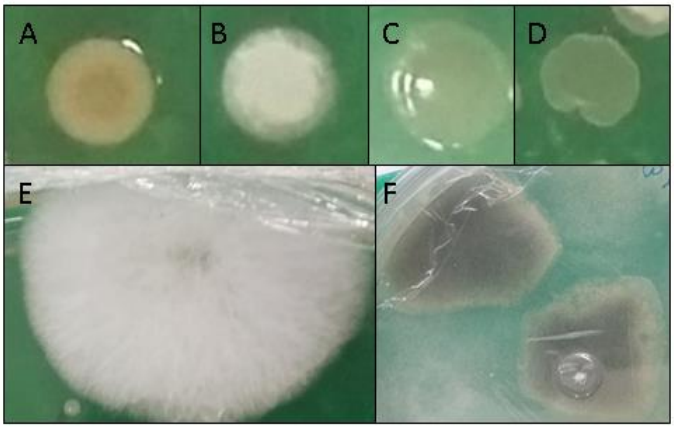
Source: Author.

Table 10 - Average number of colony-forming units per gram of soil (CFU.g-1) before and after biodegradation of bioplastics (composed of the mixture of soils used in each composition).

	PDA+ (CFU.g^{-1})	PDA- (CFU.g^{-1})
Before biodegradation	$2.11x10^3 \pm 0.00$	$1.05x10^5 \pm 4.24x10^4$
After biodegradation	$7.69x10^4 \pm 7.07x10^3$	$3.66x10^6 \pm 7.89x10^5$

(+) and (-) denote presence or absence of antibiotics in the Potato Dextrose Agar (PDA) medium, respectively.
Source: Author.

Figure 20 - Plate growth of soil microorganisms of the mixture of soils used in each bioplastic composition



A, B, C, D and E: PDA with no antibiotic and witch serial dilution 10^{-3}; F: PDA with antibiotic and 10^{-2} serial dilution.
Source: Author.

4. Conclusions

The effect of xylan on bioplastics with starch was identified, in which the increase in its proportion raised solubility and opacity, however reduced crystallinity of the bioplastic. Such alterations occurred probably due to the xylan hydrophilic characteristic and its heterogeneous and branched structure rich in hydroxyl groups. However, this relation was not seen in hydrophilicity and water barrier tests, probably because of the way in which macromolecules organized in the polymer matrix exposing more or less its hydrophilic groups. Bioplastic X10 showed a higher tensile stress compared to SB, however, increasing the proportion of xylan from 10 % did not generate mechanical benefits to the bioplastic, which is corroborated by the reduction in the crystallinity of these materials. The films showed an efficient degradation, not remaining visible fragments after a month buried, and the influence of xylan in the bioplastics was evidenced when it was more present (X25 and X50) by the increase in the rate of CO_2 production by microorganisms. The combination of

starch and xylan in the bioplastics showed appropriate for applications whose objective is the degradation of the material.

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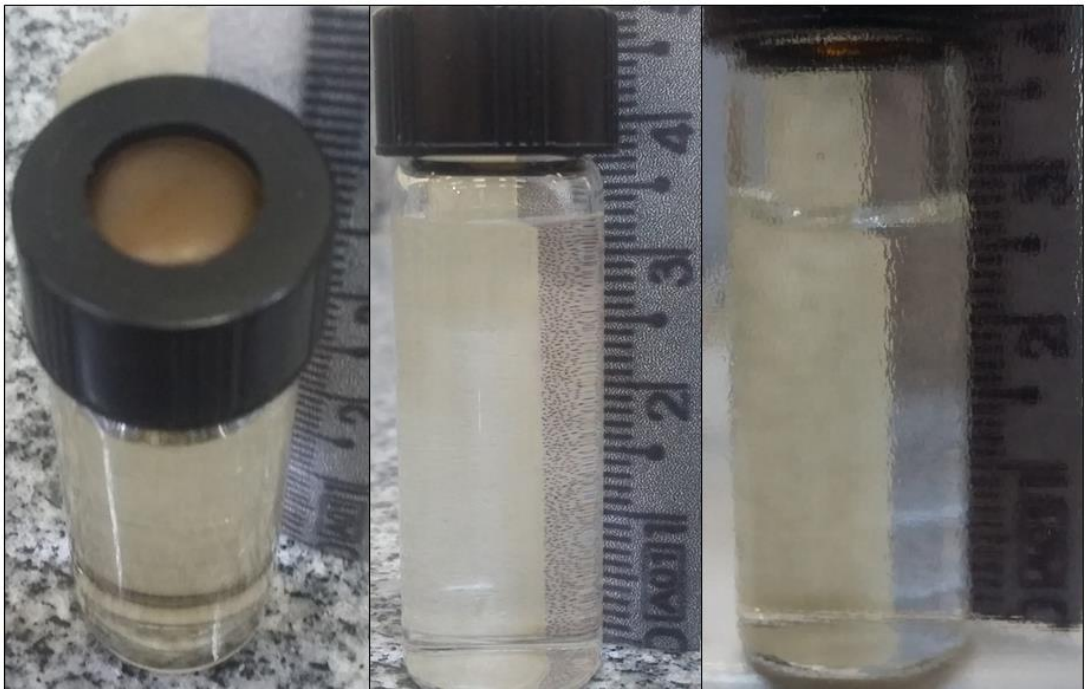
CHAPTER V: CONCLUSION

Researchers from companies and governmental initiatives around the world are trying to develop a material that is similar to plastic but that can be completely degraded. In this sense, the use of biopolymers/biomolecules from plant biomass is a renewable and environmentally beneficial option in the production of bioplastics, as in the case of the xylan used in this study together with starch. In relation to the bioplastic production, the gelatinization process contributed to its integrity, as well as its flexibility, which was also favored when the glycerol content was 20 % (w/w of polysaccharides), resulting in films that were easier to handle and remove from the drying plate. The association of polysaccharides generated homogeneous and intact bioplastics, indicating a good association between them. Moreover, xylan tended to increase the opacity, solubility, and hydrophilicity of bioplastics reducing their crystallinity and elongation at break. When buried, the bioplastics were almost completely degraded within a month, and in those where xylan was more present, CO_2 production peaked in fewer days, indicating an even more accelerated decomposition. Its properties may not make xylan bioplastics ideal candidates for use in food packaging and bags, for example, but in applications that do not require high mechanical strength but rather a fast biodegradation rate, they are an efficient option, such as in agricultural applications where some products or even the cultivation itself needs a covering that preferably can be degraded over time without generating potentially toxic waste and plastic waste.

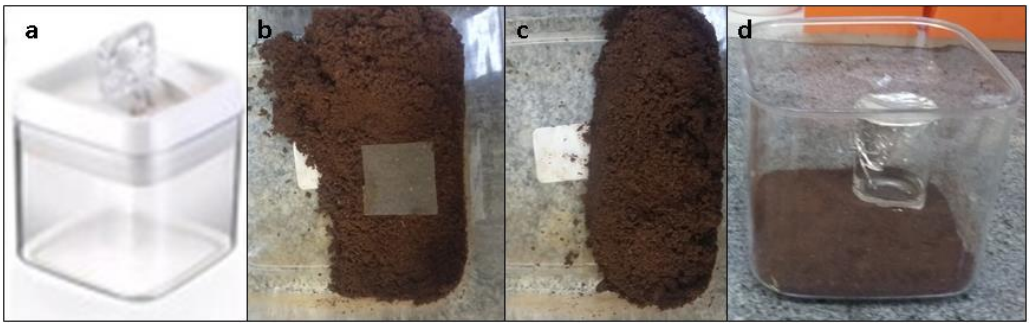
APPENDIX

Appendix A - Representative figure of the setup of the experiment witch a bioplastic 25 % xylan (w/w polysaccharides)



Left: insertion of the bioplastic in the bottle cap; center and right: water level at the beginning and after 8 days, respectively.
Source: Author.

Appendix B - Representation of the biodegradation test of bioplastics with variations of xylan and only starch.

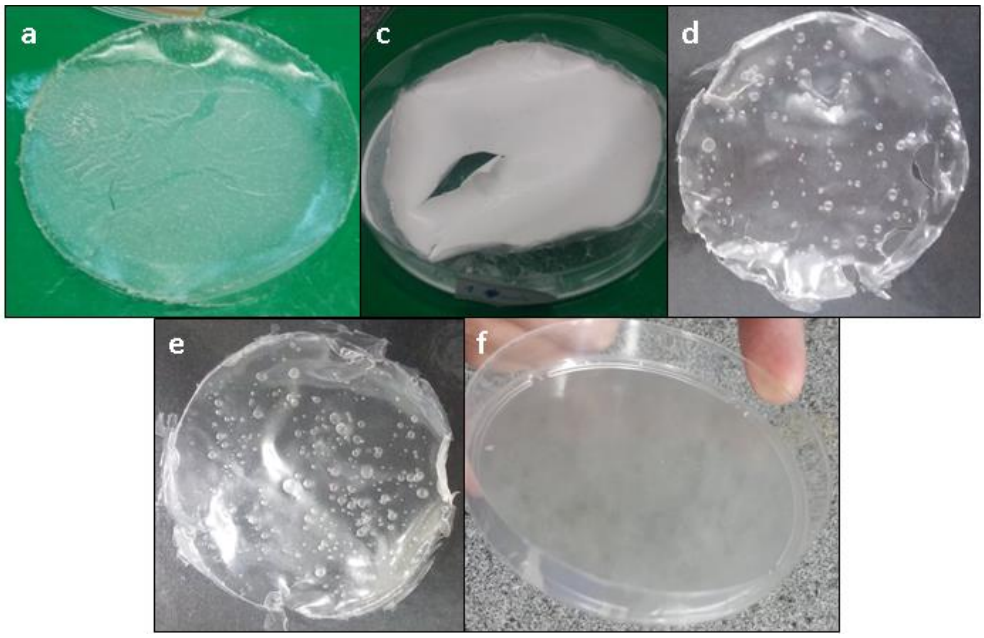


a: illustrative image of the used hermetic pot; b and c: bioplastic before and after being buried; d: Pot with soil and the beaker containing KOH solution protected by aluminum foil until the beginning of the experiment. Source: Author.

Appendix C - Interference of gelatinization in xylan and starch bioplastic (left pair), and only starch (right pair).

1 and 3: with gelatinization; 2 and 4: without gelatinization.
Source: Author.

Appendix D - Bioplastics made in different ways and conditions of gelatinization.



Source: Author.