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

PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIAS BIOLÓGICAS
(BIOLOGIA CELULAR, MOLECULAR E MICROBIOLOGIA)

SUGARCANE BAGASSE XYLAN ACETYLATION AND ITS EFFECT ON BIOPLASTIC FORMULATION, PROPERTIES AND BIODEGRADATION

JÚLIA RIBEIRO MARTINS

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Dissertação apresentada ao Instituto de Biociências do Campus de Rio Claro, Universidade Estadual Paulista, como parte dos requisitos para obtenção do título de Mestre em Biologia Celular, Molecular e Microbiologia.

Orientador: Prof. Dr. Michel Brienzo

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TÍTULO DA DISSERTAÇÃO: Sugarcane Bagasse Xylan Acetylation and its Effect on Bioplastic Formulation, Properties and Biodegradation

AUTORA: JÚLIA RIBEIRO MARTINS
ORIENTADOR: MICHEL BRIENZO

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Prof. Dr. MICHEL BRIENZO (Participaçao Virtual)
Laboratorio de Caracterizacao de Biomassa / Instituto de Pesquisa em Bioenergia IPBEN

Prof. Dr. ADILSON ROBERTO GONÇALVES (Participaçao Virtual)
IPBEN / Instituto de Pesquisa em Bioenergia

Prof. Dr. MARIO GUIMARÃES JUNIOR (Participaçao Virtual)
Departamento de Eletromecânica / Centro Federal de Educação Tecnológica de Minas Gerais

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RESUMO

A aplicação de materiais biodegradáveis renováveis em substituição ao plástico é urgente. Devido ao crescimento da população mundial e ao aumento de seus hábitos de consumo, até 23 milhões de toneladas de resíduos plásticos estão sendo descartados em ambientes naturais, como ecossistemas aquáticos, trazendo danos irreversíveis à vida selvagem. Um biopolímero com potencial para a produção de bioembalagens são as hemiceluloses. No entanto, a molécula de hemicelulose apresenta algumas desvantagens, como baixa resistência térmica, e o bioplástico formado pode apresentar fragilidade e baixa resistência mecânica. Assim, modificações químicas de hemiceluloses podem ser aplicadas para superar tais problemas. A acetilação é um tipo de modificação química comumente aplicada às hemiceluloses e pode melhorar algumas das características do bioplástico. No presente estudo, xilana de cana-de-açúcar foi acetilada aplicando ácido sulfúrico como catalisador, e diferentes condições de reação como teor de ácido sulfúrico e tempo de reação foram testadas. Gras de acetilação baixo (0.45) e médio (0.9) foram alcançados, o que resultou em xilana de cana solúvel em água (como vantagem). A reação de acetilação foi responsável pela hidrólise da xilana devido à presença de ácido sulfúrico, que causou grande perda de massa. Isso pode ser observado principalmente em amostras com alto teor de ácido sulfúrico ou com tempo de reação aumentado. Os bioplásticos foram formados utilizando xilana acetilada com baixo e médio DS e xilana não acetilada, aplicando-se amido como copolímero e glicerol como plastificante. Xilana acetilada em blenda com amido na formação de bioplásticos é aqui relatado pela primeira vez. A água foi utilizada como solvente para a formação do bioplástico e o bioplástico à base de amido, sem adição de xilana, foi utilizado para comparação. A acetilação em graus baixos e médios causou um aumento na resistência mecânica e térmica. A acetilação DS de 0,45 aparentemente não afetou a taxa de desintegração do bioplástico, enquanto o DS médio de 0,9 pode ter sido responsável pela diminuição da atividade microbiana, o que foi atestado em análise de ecotoxicidade. Todas as amostras estudadas apresentam propriedade de barreira ao óleo até 30 dias, uma vantagem para aplicação em embalagens. Os resultados indicam que a acetilação em grau moderado trouxe a vantagem de criar xilana solúvel em água, e foi suficiente para melhorar as propriedades dos bioplásticos.

Palavras-chave: Bioplástico, Bagaço de Cana-de-açúcar, Xilana, Acetilação, Solúvel em Água, Modificação Química

ABSTRACT

The application of renewable biodegradable materials replacing plastic is urgent. Due to world population growth and an increase in its consuming habits, up to 23 million metric tons of plastic wastes are being disposed of in natural environments, such as aquatic ecosystems, bringing irreversible damage to wildlife. A potential biopolymer for biopackaging production is hemicelluloses. However, hemicelluloses molecule presents some disadvantages such as low thermal resistance, and the bioplastic formed may present brittleness and low mechanical strength. Therefore, chemical modifications of hemicelluloses can overcome such issues. Acetylation is a common chemical modification applied to hemicelluloses, and can enhance some of the bioplastic features. In the present study, sugarcane xylan was acetylated applying sulfuric acid as catalyst, and different reaction conditions such as sulfuric acid content and reaction time were tested. Low (0.45) and medium (0.9) acetylation degrees substitution (DS) were achieved, which resulted in water-soluble sugarcane xylan (as an advantage). Acetylation reaction was responsible for xylan hydrolysis due to the presence of sulfuric acid, which caused for high mass loss. This could be seen specially in samples with high sulfuric acid content or with increased reaction time. Bioplastics were formed using acetylated xylan with low and medium DS and non-acetylated xylan, applying starch as copolymer and glycerol as a plasticizer. Acetylated xylan blended with starch in bioplastics formation is here reported for the first time. Water was used as a solvent for bioplastic formation, and starch-based bioplastic, without the addition of xylan was used for comparison. Acetylation in both low and medium degrees caused an increase in mechanical and thermal resistance. Acetylation DS of 0.45 apparently didn't affect the disintegration rate of the bioplastic, while medium DS of 0.9 may have been responsible for decreasing microbial activity, which was attested in ecotoxicity analysis. All of the samples studied present oil barrier property up to 30 days, an advantage for package application. The results indicate that acetylation in a moderate degree brought the advantage of creating water-soluble xylan, and it was sufficient for enhancing bioplastics properties.

Keywords: Bioplastic, Sugarcane Bagasse, Xylan, Acetylation, Water-soluble, Chemical Modification

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SUMMARY

CHAPTER I: INTRODUCTION AND OBJECTIVES

1. Introduction

The world population is growing significantly, and the current average population increase is estimated at 81 million people per year (WORLDOMETER, 2022). That, associated with its increasing consumption habits, resulted in an increase in the production of plastic materials. It is estimated that 19 to 23 million metric tons of plastic waste entered aquatic ecosystems in 2016, which represents 11 % of plastic waste generated globally in that year (BORRELLE et al., 2020). Synthetic polymers degradation is a slow process, as they are not directly consumed by microorganisms. They are initially degraded by environmental factors, such as light, heat, moisture, and chemical conditions, which rupture the bonds of macromolecules (SINGH et al., 2021; WILKES et al., 2017). In this process, micro and nanoplastics are created, resulting in radical sites, which are essential for the action of microorganisms.

With increasing worldwide concerns over such problematics, much effort has been directed to the application of biopolymers in the production of bioplastics, such as cellulose and hemicelluloses. Hemicelluloses are a group of polysaccharides with highly diversified structures incorporating various sugars, usually presenting an amorphous structure. It accounts for 20 ~ 35 percent of plant biomass and is the second most abundant biopolymer after cellulose (LING et al., 2020). In sugarcane bagasse, xylose content represents up to 80 % of hemicelluloses (ALVES et al., 2021).

Acetyl group is a common substituent found on hemicelluloses in their natural state, usually connected to its backbone or ramification through ester linkages (GILLE; PAULY, 2012). It is thought that hemicelluloses acetylation was obtained through an evolutionary process, adjusting the plant biological functions, such as flexural properties of wood, polysaccharide interaction, plant growth, and stress resistance (GAO et al., 2017; GRANTHAM et al., 2017; JOHNSON et al., 2017; PAULY; RAMÍREZ, 2018; VOGEL et al., 2004; YAN et al., 2018; ZHANG et al., 2017; ZHU et al., 2014). However, for industrial processing, hemicelluloses are deacetylated during separation from other biomass polymers, due to alkaline solubilization frequently applied (PENG et al., 2012). Therefore, there is a great amount of free hydroxyl groups on hemicellulosic backbones, specifically two per xylose unit. The free hydroxyl groups present an opportunity for chemical modifications, which may be used to hinder the molecule drawbacks such as poor solubility in common

organic solvents and low thermal stability during sample processing (HUDA et al., 2005; LÖNNBERG et al., 2006). Among the modification strategies are esterification, including acetylation, oleoylation, lauroylation, fluorination, crosslinking, and etherification, including methylation, carboxymethylation, and benzylation (ALEKHINA et al., 2014; MARTINS; ABE; BRIENZO, 2022; PENG; REN; SUN, 2010; REN; SUN; PENG, 2008).

Chemical acetylation is an esterification reaction that substitutes hydroxyl groups in the hemicelluloses backbone with relatively hydrophobic acetyl groups (compared to the hydroxyl groups). Such modification influences the molecule properties, such as hydrophobicity, solubilization in different solvents, and thermal degradation. However, such properties will depend on the degree of acetylation obtained, as acetyl groups will be responsible for impeding hydroxyl groups to create hydrogen bonds with water and spontaneous intra-molecular hydrogen bonding, keeping the xylan chains from aggregating (STEPAN et al., 2013; ZHU et al., 2020). Also, relatively hydrophobic acetyl groups present good affinity with some organic solvents such as chloroform, dimethylsulfoxide, and tetrahydrofuran (SUN; HUGHES, 1999).

Numerous methods for hemicelluloses acetylation have been reported to achieve varying degrees of substitution and controlled hemicelluloses properties (AKKUS; OZKAN; BAKIR, 2018; MORAIS DE CARVALHO et al., 2019; REN; SUN; LIU, 2007; SUN; HUGHES, 1999; YILMAZ-TURAN et al., 2020; ZHU et al., 2020). Hemicelluloses may be acetylated by varying reaction conditions such as the solvents and catalysts applied, as well as reaction time and temperature, which will also influence the molecule degradation in the process. Therefore, this study evaluated the sugarcane bagasse xylan acetylation reaction conditions, applying acetic anhydride as an acetylation agent, and sulfuric acid as a reaction catalyst. The conditions were applied to produce xylan with different acetylation degrees, which were employed in starch/xylan-based bioplastics formulation. Bioplastic properties such as mechanical resistance, thermal degradation, water-solubility, oil barrier, and disintegration were evaluated.

2. General Objective

The focus of the present study was to investigate a chemical acetylation reaction of the sugarcane bagasse xylan with different acetylation degrees. The xylan acetylation was evaluated as an influence on bioplastic physicochemical, thermal, and biodegradation properties.

2.1. Specific objectives

- To evaluate the chemical acetylation reaction parameters of xylan, resulting in different degrees of substitution (DS);
- To identify the influence of xylan degree of acetylation on the methods for bioplastics formation, such as solvent and affinity with other components;
- To describe the influence of xylan acetylation DS on the mechanical and thermal properties of the bioplastic;
- To identify the influence of xylan acetylation DS on the disintegration and ecotoxicity.

3. Study presentation and dissertation organization

This study was presented in chapters, elucidating materials already published and prepared for submission. In addition to this Chapter I - Introduction, this dissertation is composed of:

- Chapter II – Review chapter published in the Springer book “Hemicelluloses Biorefinery: A Sustainable solution for value addition to bio-based products and bioenergy”. This chapter aims to elucidate and bring a critical review on studied and applied hemicellulose chemical modifications.
- Chapter III – Review article about hemicelluloses acetylation for industrial application. This chapter aims to gather information about hemicellulose acetylation, from naturally occurring acetylation to chemical acetylation, and its implication for bioplastics formation.
- Chapter IV – Results compilation in a paper. This chapter elucidates the discoveries of a research project which studied a hemicelluloses acetylation reaction, and the influence of such modification on bioplastics properties, such as thermal and mechanical resistance and water vapor and oil barrier.
- Chapter V – General conclusion of the dissertation.

The objective of this dissertation organization is to encourage and simplify material publication and, as all of the chapters complement themselves in terms within the same subject, it is possible that repetitions of information may occur.

CHAPTER II: CHEMICAL MODIFICATION STRATEGIES FOR DEVELOPING FUNCTIONALIZED HEMICELLULOSES: ADVANCED APPLICATIONS OF MODIFIED HEMICELLULOSES

ABSTRACT

Hemicelluloses are highly hydrophilic homo or heteropolysaccharides with a branched structure. These polysaccharides exhibit great potential as a feedstock material, and a derivatization results in the formation of better feedstock material. Hemicelluloses can be used as a bio-polymeric material as they are biodegradable. They also exhibit the advantage of being renewable and available in residues/waste. The backbone of the hemicelluloses and the side chains contain a large number of hydroxyl groups. Esterification, etherification, graft copolymerization, and other reactions can be conducted to chemically modify these hydroxyl groups. The chemical modifications help tune various properties such as hydrophobicity, thermal stability, and solubility (in different solvents). The free hydroxyl groups present in the macromolecules can be chemically modified to other functional groups to address the drawbacks. The modified compounds can find applications in various fields and their novel properties can be exploited.

Keywords: Esterification, Etherification, Bioplastic, Hydrophobicity, Thermal Stability, Solubility

1. Introduction

Hemicelluloses are renewable and widely available polysaccharides associated with cellulose present in lignocellulosic biomass. They account for approximately 20–35 % of plant biomass such as corn stalk (30.3 %) (DONG et al., 2018), empty fruit bunch (26.64 %) (NASIR et al., 2018), meadow grass (28.14%) (TSAPEKOS; KOUGIAS; ANGELIDAKI, 2015), sorghum straw (32.57 %) (HERNÁNDEZ-BELTRÁN; HERNÁNDEZ-ESCOTO, 2018), sugarcane bagasse (23.27 %) (FERNANDES et al., 2020), elephant grass (23.93 %) (SANTOS et al., 2018), spent coffee ground (28.12 %) (CHIYANZY et al., 2015), and wheat straw (26.9 %) (SHAH; ULLAH, 2019). The hemicelluloses in their natural states are amorphous and branched polymers of low molecular weight. The structural characteristics of the hemicelluloses can be attributed to the heterogeneous chemical constituents. The degree of polymerization is reported in the range of 80–200 (SUN; LAWTHER; BANKS, 1996). Hemicelluloses can be potentially used in various fields. These polysaccharides can be used as alternatives to the natural energy sources that are getting constantly depleted. They can also be used in their native or modified forms to form biocomposite films for the development of packaging materials (LI; PAN, 2018). The chemically modified polysaccharide can potentially find use in various industries.

Hemicelluloses exhibit poor solubility in common organic solvents and low thermal stability during sample processing. These properties result in poor compatibility between the hydrophilic hemicelluloses chain and the hydrophobic polymeric matrix (HUDA et al., 2005; LÖNNBERG et al., 2006). Hemicelluloses can be chemically modified as a large number of hydroxyl groups are present in the hemicelluloses backbones. Esterification (acetylation, oleoylation, lauroylation, fluorination) and crosslinking (PENG; REN; SUN, 2010) reactions can be carried out with the hemicelluloses. The compounds can also be chemically modified by carrying out etherification (methylation, carboxymethylation, benzylation) and hydrolysis (ALEKHINA et al., 2014; REN; SUN; PENG, 2008) reactions. The biodegradability, biocompatibility, and structural backbone characteristics are retained (KONG et al., 2018; LIU; LUAN; LI, 2019).

Hemicelluloses are isolated from the cell walls of plant biomass prior to carrying out the chemical modification reactions. The difficulty in solubilizing hemicelluloses, present in biomass, can be attributed to biomass recalcitrance (especially the interaction between the hemicelluloses and cellulose (and/or lignin) components of the cell wall) and biomass heterogeneity (MELATI et al., 2021). The alkaline solubilization and enzymatic solubilization

processes can be used to isolate hemicelluloses. Hemicelluloses can also be isolated using peroxide-based reagents in an alkaline medium (ALVES et al., 2021). The isolation methods can potentially affect the properties (such as the degree of polymerization) of hemicelluloses. The side groups present in the backbone can also be affected by reacting in the isolation process altering the properties of the hemicelluloses (BRIENZO et al., 2016; DE FIGUEIREDO et al., 2017).

The specific properties exhibited by hemicelluloses post chemical modifications depend on the functional groups introduced, types of linkages formed, substitution patterns produced, and degree of substitution achieved. The modified hemicelluloses can be used in a wide range of fields and for the preparation of materials with specific features (SALAM et al., 2011).

The hydrophobicity, thermal stability, viscosity, and solubility (in various solvents such as chloroform, dimethylsulfoxide, and tetrahydrofuran) of hemicelluloses can be tuned by derivatizing hemicelluloses compounds. The biocompatibility, water resistance, and stability of the compounds against microorganisms were considered during derivatization. These properties make the modified hemicelluloses molecules suitable for application in various industrial fields. They can be potentially used for the development of biodegradable films, hydrogels, medical implants, etc.

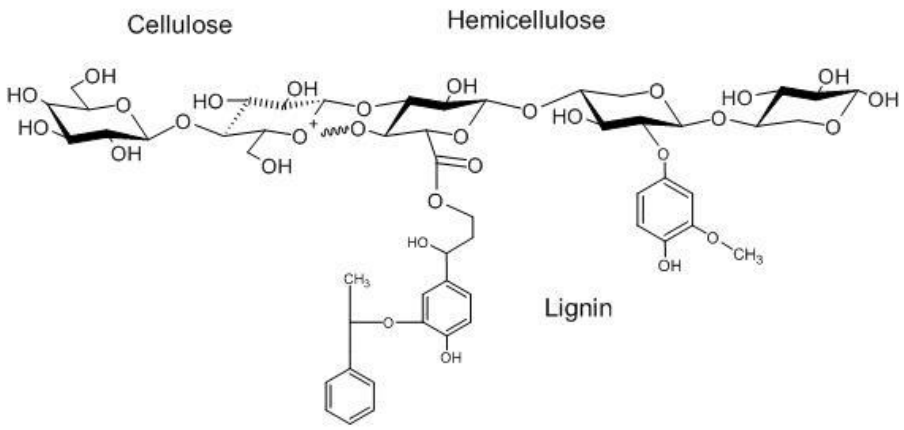
Solubilization of hemicelluloses results in the isolation of macromolecules. Partial hydrolysis of the compounds results in the formation of oligomers while total hydrolysis of hemicelluloses results in the formation of monosaccharides. Chemically modified hemicelluloses exhibit new properties that make the modified compounds suitable for specific applications. This review aims to investigate the possible chemical modifications that can be introduced into the structure of hemicelluloses. The advantages and disadvantages of the methods used to chemically modify hemicelluloses molecules have also been presented. The potential applications (based on the chemical modifications) of the molecules have also been discussed.

2. Solubilization of hemicelluloses

Hemicelluloses are extracted from the lignocellulosic biomass (agro and industrial waste). Hemicelluloses are tightly bound to lignin and cellulose present in the plant cell wall. This results in the formation of microfibrils, which organize to form stable macrofibrils (LIU et al., 2016). Hemicelluloses interact with lignin through covalent bonds to form lignin–carbohydrate complexes that contain phenyl glycoside bonds, ester groups, and benzyl ether

moieties (CHRISTOPHER, 2012; SCHMATZ; TYHODA; BRIENZO, 2020). It is believed that hydrogen and/or glycosidic bonds are formed between hemicelluloses and cellulose (Figure 1) (LODISH et al., 2000).

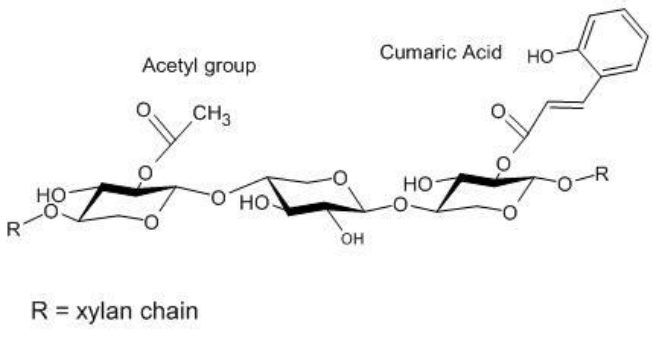
Figure 1 - Hemicelluloses-cellulose and hemicelluloses-lignin linkages



Source: author

Ester linkages are formed between acetyl units and hydroxycinnamic acids in hemicelluloses (Figure 2) (PENG et al., 2012). The diverse nature of the bonds present in the molecules makes the isolation of hemicelluloses from the plant cell wall difficult. Structural modifications (e.g., the reduction in the degree of polymerization) help in the efficient extraction of hemicelluloses from plant cell walls (BRILLOUET et al., 2002; SUN; SUN; SUN, 2004).

Figure 2 - Hemicelluloses containing pendant acetyl and cumaric acid groups



Source: author

The chemical composition and morphology of the wood matrix dictate the choice of the hemicelluloses solubilization method. The use of the obtained carbohydrates and their potential for further valorization help in identifying the solubilization method to be followed (YEDRO et al., 2017). Annual plants contain less amounts of lignin. Thus, it is easier to isolate hemicelluloses from annual plants than from wood (EBRINGEROVÁ; HROMÁDKOVÁ, 1999). The solubilization processes can cause significant modifications in the carbohydrate structure. Thus, the choice of the solubilization method depends on the potential use of the final product (SJÖSTRÖM, 1993; YEDRO et al., 2017). In some cases, hemicelluloses can be directly extracted from wood. In most cases, wood is first delignified to holocellulose, and hemicelluloses are then extracted over one or several steps. Direct solubilization results in minimal chemical modifications.

The choice of the solubilization method influences the degree of polymerization and the process of monomer release. The solubilization method also dictates the nature of the degradation products and the type of substituents introduced into the hemicelluloses scaffold. Methods like acid hydrolysis and steam explosion can be efficiently used to obtain hemicelluloses in the form of monomers. The alkaline treatment and organic solvent solubilization methods result in the isolation of hemicelluloses in the form of macromolecules that exhibit a high degree of polymerization. Pretreatment methods involving the use of hot water, steam, and acid result in the partial hydrolysis of hemicelluloses, which results in the formation of oligomers.

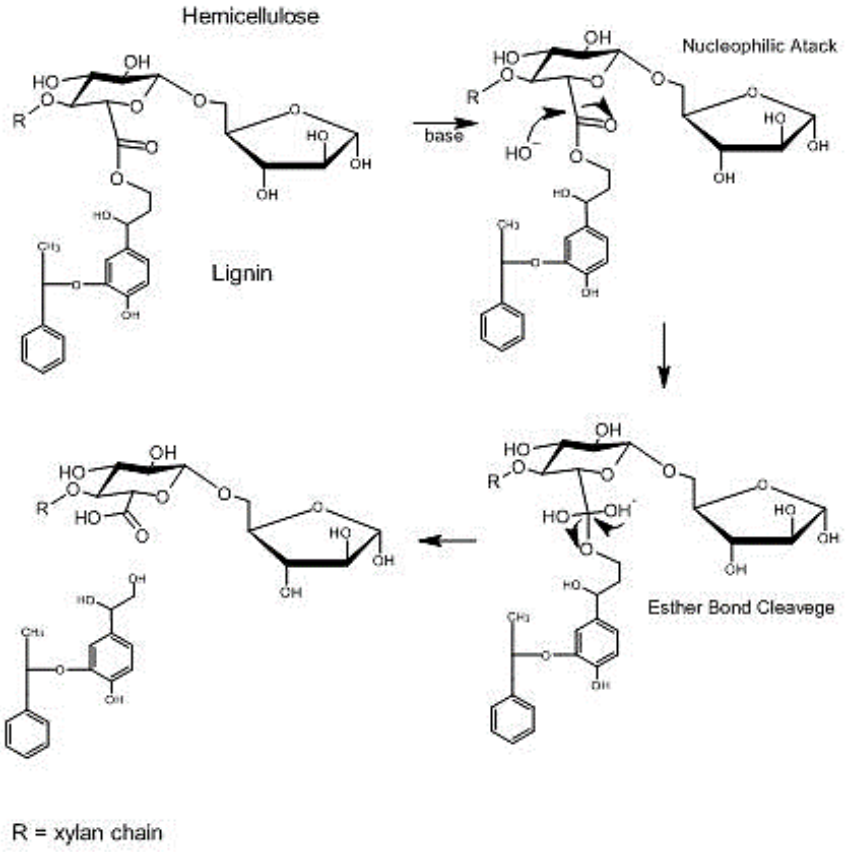
2.1. Solubilization of hemicelluloses in the form of high and low DP

2.1.1. Alkaline treatment method

The linkages between hemicelluloses and lignin are cleaved when the alkaline treatment method is used to treat lignocellulosic materials. The cleavage of the bonds results in the solubilization of hemicelluloses (BRIENZO et al., 2016) (Figure 3). The alkaline treatment method is used to effectively solubilize lignin present in lignocellulosic biomass. The solubilization of lignin helps reduce enzyme impediment and increases the availability of polysaccharides for reactions (SHIMIZU et al., 2020). The process results in the hydrolysis of uronic and acetic esters and swelling of cellulose. The cellulose crystallinity can decrease due to the alkaline treatment (BRIENZO et al., 2016; MELATI et al., 2019; SHIMIZU et al., 2018). The O-acetyl groups are cleaved and acetic acid is released. Experimental conditions of high pH are responsible for the deacetylation (PENG et al., 2012). The glycosidic bonds cannot be

broken under moderate reaction conditions to hydrolyze hemicelluloses molecules to form monomers. Therefore, the alkaline treatment method (NaOH or KOH is used) can be used to obtain hemicelluloses with a high degree of polymerization (ALVES et al., 2021; BRIENZO et al., 2016).

Figure 3 - Linkages between hemicelluloses and lignin are broken under alkaline conditions



Source: author

The use of hydrogen peroxide in the alkaline treatment method promotes delignification and solubilization of hemicelluloses (BRIENZO; SIQUEIRA; MILAGRES, 2009) present in lignocellulosic materials. Hydrogen peroxide is highly reactive and exhibits strong oxidizing ability (DUTRA et al., 2018). Hydrogen peroxide dissociates to produce hydroperoxide anions (HOO^-) which react with hydrogen peroxide in an alkaline medium to form hydroxyl radicals (OH^-) and superoxide anion (O_2^-) that oxidize lignin. Hydrophilic (carboxyl) groups are introduced into the scaffold and interunit bonds are cleaved resulting in the dissolution of lignin and hemicelluloses (DUTRA et al., 2018).

The alkaline treatment method can be used to solubilize hemicelluloses present in poplar. The sample is treated for 3 h at a temperature of 50 ℃. The liquid to solid ratio was 20:1. NaOH solution (10 %, (w/w)) was used to solubilize hemicelluloses (solubilization yield of xylan: 71.8 %; solubilization yield of galactan: 6.3 %; solubilization yield of arabinan and mannan sum: 11.9 %). The degree of polymerization was 167 (GENG et al., 2019). The efficiency of solubilization can be increased by delignifying poplar prior to subjecting it to the alkaline treatment method as NaOH solution cannot effectively react with hemicelluloses in the presence of lignin. The alkaline solubilization method resulted in the solubilization of xylan (solubilization yield: 90.1 %), galactan (solubilization yield: 18.8 %), arabinan (solubilization yield: 25.4 %), and mannan (solubilization yield: 25.4 %). The degree of polymerization was 89 (GENG et al., 2019). NaOH solution (10 %; reaction condition temperature: 50 °C; reaction time: 3 h) was used to extract hemicelluloses (degree of polymerization: 392) from partially delignified switchgrass. The solubilization yield was calculated to be 22 % (FARHAT et al., 2017).

An alkaline solubilization method that involves the use of peroxide was proposed for solubilizing xylan. The pH was adjusted using sodium hydroxide and xylan was extracted from sugarcane bagasse with varying mesh sizes. The amount of residual lignin was the least (4.40 %) in the xylan solubilized from 50 mesh-sugarcane bagasse (0.297 mm). The xylan solubilization yield was found to be 64.67 %. The minimum xylan solubilization (31.18 %) was recorded with 16 mesh-sugarcane bagasse (1.19 mm) (i.e., with sugarcane bagasse exhibiting high granulometry). The amount of residual lignin in the xylan was the maximum (6.19 %) in this case (ALVES et al., 2021). Highly soluble xylan was obtained (>96 % solubility) that is positive for further polysaccharide application such as could be enzymatically hydrolyzed to produce xylooligosaccharides (ALVES et al., 2021).

2.1.2. Liquid hot water treatment method

The liquid hot water treatment method hydrolysis of the acetyl group present in hemicelluloses, resulting in the formation of acetic acid (in solution) that is the catalyst in the treatment. The deacetylation of the xylan side chain during the pretreatment process results in the production of acetic acid. Consequently, H_3O^+ ions are produced, resulting in a decrease in the pH of the system. Under these conditions, self-hydrolysis of xylan occurs. This method can be effectively used to selectively obtain hemicelluloses oligomers over monomers. Degradation

of monosaccharides can be avoided as moderate reaction conditions are used (GALLINA et al., 2018).

The method involves cooking raw materials, using water as the solvent, in the temperature range of 130–180 ℃ to obtain an aqueous solution of hydrolyzed xylan (LIU; LUAN; LI, 2019). The use of water makes the process environmentally friendly and economically viable. At high temperatures as extreme reaction conditions can potentially lead to the hydrolysis of polysaccharides, resulting in the formation of monomers. Therefore, it is important to regulate the reaction temperature to predict the degree of polymerization. The solubilization yield increases and the degree of polymerization decreases with an increase in the reaction temperature (GALLINA et al., 2018).

With a flow-through reactor operated at 160 ℃ for 90 min (pressurized at 11 bar) under conditions of liquid hot water treatment method, 33.9 % of hemicelluloses (molecular weight: 1922 Da; degree of polymerization: 14.54) present in catalpa wood was solubilized (GALLINA et al., 2018). The solubilization yield was recorded to be 41.7 % when the temperature was increased to 170 ºC. The molecular weight was 1417 Da and the degree of polymerization was 10.72 (GALLINA et al., 2018). The number of hemicelluloses hydrolyzed increased with increasing temperature. This resulted in the detachment of the oligomers from the matrix and a decrease in the oligomer size. Thus, the molecular weight decreased with increasing temperature (GALLINA et al., 2018).

The liquid hot water treatment method has been used to solubilize arabinoxylan (degree of polymerization: 68.11) present in wheat bran. The process was catalyzed by ruthenium (III) chloride/aluminum-mobil composition of matter nº 48 ($RuCl_3$/Al-MCM-48) (reaction condition: 180 ℃/10 min). The pretreatment method involved destarching the wheat bran, with the solubilization yield recorded of 78 % (monosaccharide yield: 15 %). When the temperature was decreased to 160 ℃ and MCM-48 was used as the catalyst, compounds of higher molecular weight (65.2 kDa) were obtained. The degree of polymerization was 493.45. The solubilization yield decreased (24 %) and the monosaccharides yield was <10 % (SÁNCHEZ-BASTARDO; ROMERO; ALONSO, 2017). Therefore, the degree of polymerization of hemicelluloses (obtained following the liquid hot water treatment) may be partially controlled in regards to treatment conditions, such as temperature and presence of a catalyst.

The effect of the treatment conditions on the solubilization yield was studied when the liquid hot water treatment method was used to treat holm oak sapwood. The maximum yield of 59.47 % was obtained when the solubilization process was carried out at a temperature of 170 ℃ for 20 min. The highest degree of polymerization was recorded when the reaction time was

the shortest. The degree of polymerization decreased as the reaction time increased. The maximum average molar mass was 12.9 kDa when the treatment was conducted at 170 ºC for 5 min (degree of polymerization: 97.6). The lowest average molar mass of 1.8 kDa was obtained when the sample was treated at a temperature of 170 ºC for 60 min (degree of polymerization: 13.62) (YEDRO et al., 2017).

2.1.3. Organic solvent treatment method

The organic solvent treatment method can be used to isolate hemicelluloses. The scarcity of knowledge on the dynamic solvent effects limits the practical application of the method (BAIG; WU; TURCOTTE, 2019). The organic solvent treatment method involves the use of low-boiling organic solvents such as ethanol, methanol, butanol, and acetone. The process can be carried out at low temperatures in the presence of alkaline catalysts such as sodium hydroxide and potassium hydroxide for biomass fractionation (GURAGAIN et al., 2016; MESA et al., 2011).

The alkali-catalyzed organosolv process can be used to selectively cleave covalent bonds (α ester linkages) between hemicelluloses and lignin present in the cell wall matrix. The polymeric form of hemicelluloses is maintained. The process of fractionation of biomass also results in the cleavage of uronic acid and arabinose side chains (GENG et al., 2019; LIU et al., 2016; PENG et al., 2012). The solvents used in the organic solvent treatment method can be recovered by distillation. The process probably does not significantly impact the environment as it is a low energy consumption process (extremely high temperatures are not required) (PAN et al., 2006; VILA; SANTOS; PARAJÓ, 2003). However, a large volume of wastewater is needed to wash the resulting material. This limits the economic viability of the process (BAIG; WU; TURCOTTE, 2019; LAURE et al., 2014). Precautions need to be taken during the process as some organic solvents are inflammable, combustible, toxic, and/or hazardous. This increases the operational cost of the method (BAIG; WU; TURCOTTE, 2019). However, this process has been already used for biomass delignification.

Hemicelluloses obtained from flax shives were solubilized using pressurized aqueous ethanol (solubilization yield: 81 %; reaction temperature: 180 ºC; reaction time: 117 min; pressure: 5.2 Mpa). A high degree of polymerization was observed in 47 % of the solubilized hemicelluloses (BURANOV; MAZZA, 2010). An ethanol/water solution (50 %, v/v) was used during the organosolv pretreatment method to solubilize hemicelluloses present in sugarcane bagasse. The treatment was carried out at a temperature of 190 ºC. The reaction time was varied

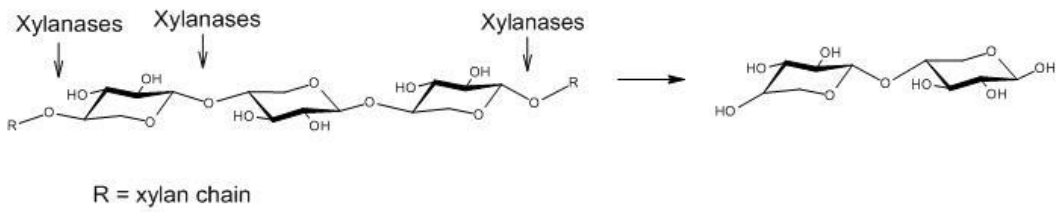
and the maximum number of hemicelluloses was solubilized when the solubilization reaction was carried out for 100 min. The sample was pretreated following the hydrothermal method prior to conducting the organosolv pretreatment process. It was observed that the maximum hemicelluloses solubilization could be achieved if only the organosolv pretreatment method was followed to treat the samples (ESPIRITO SANTO et al., 2018).

2.1.4. Enzymatic solubilization process

Numerous bacteria and fungi have the natural ability to enzymatically hydrolyze lignocellulosic biomass to obtain nutrients (JANUSZ et al., 2017). Large biopolymers cannot efficiently penetrate the cells of such microorganisms. The microorganisms secrete a mixture of enzymes that break polymers into smaller soluble oligomers. These smaller oligomers can be efficiently transported into the cells where they get metabolized (Figure 4) (LUO; BRINK; BLANCH, 2002).

The enzymatic hydrolysis processes involve the use of specific hemicelluloses enzymes that hydrolyze hemicelluloses to produce hemicelluloses derivatives. The enzymatic hydrolysis process is slower than the previously discussed processes of hydrolysis. The degree of polymerization can be controlled by the reaction time and enzyme activity. Monomers or degradation products are not released or formed in the enzymatic process (DE FREITAS; CARMONA; BRIENZO, 2019). The original structure and activity of hemicelluloses are retained. The enzymatic hydrolysis processes are more environmentally friendly than the chemical hydrolysis processes (ESCARNOT; AGUEDO; PAQUOT, 2012).

Figure 4 - Enzyme-based solubilization of hemicelluloses



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The enzymes need to penetrate the cell wall to efficiently react with hemicelluloses. Lignin, present in the cell wall, hinders the reaction between enzymes and hemicelluloses. Thus,

the efficiency of the enzymatic process depends on the composition of the biomass used (SHIMIZU et al., 2020). A pretreatment method that does not affect the hemicelluloses structure is followed to remove lignin. Chemicals (such as sodium chlorite and peracetic acid, at lab scale) are used to achieve delignification and bleaching (GENG et al., 2019; HAKALA; LIITIÄ; SUURNÄKKI, 2013).

Xylanase, obtained from *Thermomyces lanuginosus*, was used to hydrolyze xylans. The use of bulk aqueous, organic, or inorganic solvents was avoided and hemicelluloses present in chemically untreated biomass were directly hydrolyzed. Soluble xylooligosaccharides (with a low degree of polymerization) were obtained (sugarcane bagasse: 73 % yield; wheat straw: 84 % yield) when hydrolysis reactions were carried out for 72 h at a temperature of 55 ℃ in the presence of xylanase. The samples were ball milled for 30 min prior to conducting the hydrolysis reactions (OSTADJOO et al., 2019).

Approximately 22 % of xylan present in wheat straw was solubilized following the xylanase pretreatment process (treatment conditions: 60 ℃/6 h) conducted using 350 IU/g of straw. An increase in the xylanase load did not result in improved xylan solubilization. However, when the xylanase pretreatment process was conducted for 24 h (after soaking the biomass in aqueous ammonia (30 %, v/v) for 3 days), 56 % of the xylans could be hydrolyzed into xylose, xylobiose, and xylotriose (RÉMOND et al., 2010). Longer reaction times did not result in an increased extent of solubilization. The process could be used to successfully cleave the ester linkages in phenolic acids (present in the xylan chains), and 60 % and 76 % of *p*-coumaric and ferulic acids were removed, respectively.

Biomass was pretreated following an alkaline-sulfite chemithermomechanical process to facilitate the solubilization of xylan (using the enzymatic or alkaline treatment procedures). The enzymatic solubilization process was carried out in the presence of commercial xylanase (dosage: 8 IU/g of pretreated bagasse). A yield of 22 % (w/w; xylan solubilization yield) was observed (molecular weight: <6 kDa; degree of polymerization: <45.41). The process could be used to obtain xylan contaminated with less amounts of lignin and glucan (lignin: <4 %; glucan: <2.2 % in the final solid biomass) (SPORCK et al., 2017). The enzymatically extracted xylan exhibited a high substitution degree (primarily substituted by uronic acid groups), resulting in high water solubility. This material can be deposited onto cellulosic pulps to increase the xylan content. Thus, the importance of xylan from bagasse can be potentially increased (SPORCK et al., 2017).

A combination of xylanase and cellulase can result in improved hemicelluloses hydrolysis. Destarchment and deproteinization processes were conducted prior to conducting

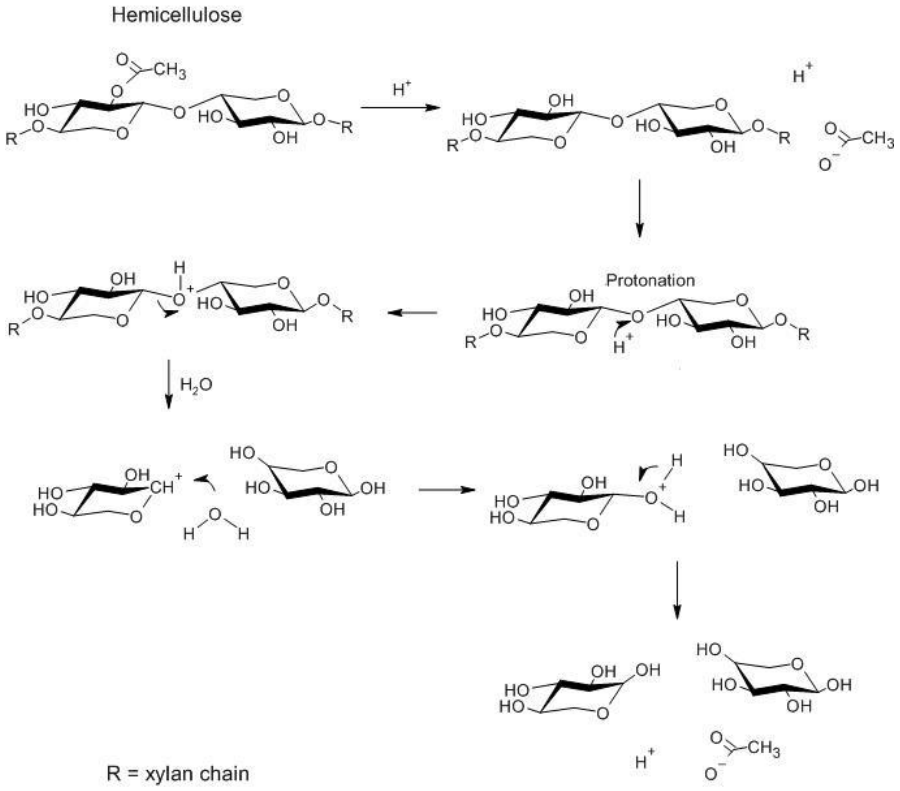
the solubilization processes used to solubilize hemicelluloses (present in oat bran) in the presence of enzymes. The biomass components were not separated prior to the solubilization processes. Various combinations of enzymes were tested and the reaction times were varied. The maximum solubilization yield of 69.7 % (for arabinoxylan) was obtained when a commercial cellulolytic preparation treatment method was followed (treatment conditions: 55 °C/24 h) and endoxylanase was used. The degree of polymerization was in the range of 1–1151. Approximately 50.3 % of the molecules were extracted in the form of monomers (ESCARNOT; AGUEDO; PAQUOT, 2012).

2.2. Solubilization of hemicelluloses in the form of monosaccharides

2.2.1. Acid hydrolysis method

The acid hydrolysis process of solubilizing hemicelluloses involves the use of a concentrated or dilute acid that can help break the linkages present between biomass components. The process results in the fragmentation/hydrolysis of hemicelluloses into their constitutional pyranose and furanose sugar units. During the hydrolysis process, the added acid dissociates, releasing protons, and diffuses through the biomass pore spaces to reach the reactive sites. The released protons subsequently catalyze the cleavage of the acetyl groups present in the hemicelluloses chains. The acidity of the medium increases during the process (Figure 5) (KAPU; TRAJANO, 2014). The monosaccharides are obtained in high yields. The yields depend on the reaction conditions used. Oligomers and monosaccharides are obtained as the products (BRIENZO et al., 2016; FORSAN et al., 2021).

Figure 5 - Acid-catalyzed hydrolysis of hemicelluloses



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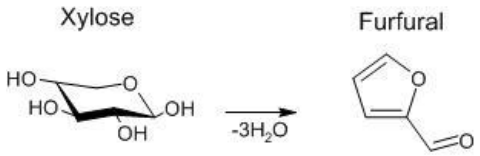
During this process, the acid penetrates the cell wall and causes the degradation of lignin, which physically hinders access to the polysaccharides. The rate of hemicelluloses hydrolysis is the fastest when the acid hydrolysis method is used to hydrolyze hemicelluloses. The rate is slower when the enzyme solubilization and liquid hot water treatment method are used for hydrolysis (GOLDMANN et al., 2017; MELATI et al., 2019).

The acid hydrolysis method can potentially lead to the degradation of sugar molecules. Furfural is produced when xylose is dehydrated under harsh reaction conditions (Figure 6). Acid insoluble pseudo-lignin is formed when aromatic compounds are formed from the structural rearrangement of furfural and lignin fragments repolymerize (HU; JUNG; RAGAUSKAS, 2012; SCHMATZ; TYHODA; BRIENZO, 2020). Furfural and acetyl compounds function as microorganism inhibitors when hemicelluloses hydrolysate is fermented. This results in reduced fermentation process efficiency (CANDIDO et al., 2020). The yields of the inhibitors increase when hydrolysis is conducted under conditions of high temperatures and acid concentrations (harsh solubilization conditions) (CANDIDO et al., 2020). When the reactions are conducted in the presence of concentrated acid, corrosion-

resistant equipment should be used. The acid can be recovered following the completion of the hydrolysis process.

Figure 6 - Xylose dehydration to form furfural



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Hemicelluloses present in poplar wood were solubilized using a binary solvent composed of formic acid and water (formic acid fraction: <77.5 % (w/w) of azeotrope). The reaction times and reaction temperatures were varied. The maximum hemicelluloses yield was obtained when the reaction was carried out at a temperature of 120 ℃ and the reaction time was 1 h (arabinose: 93.5 %; xylose: 77.8 %; mannose: 94.5 %, and galactose: 97.9 %) (XU et al., 2018). The yields of all the hemicelluloses-derived saccharides increased when the solubilization time was increased. The reactions (especially with mannose and galactose) were carried out in the temperature range of 90 ℃–100 ℃. The yields decreased as the solubilization times increased when the temperature was 120 °C. This can be attributed to the fast rate of degradation of the saccharides, the rate of degradation was the maximum when the temperature was 140 °C (XU et al., 2018). As the solubilization time increased, the mass loss of xylan increased. The maximum mass loss was recorded to be 18.57 % after 10 h. This indicated that substantial amounts of intermediates were formed during the conversion of hemicelluloses-derived saccharides to furanic compounds. The results also indicated that side condensation reactions occurred between the intermediates and the furfural or lignin-derived compounds (XU et al., 2018).

Hemicelluloses were extracted from birch (*Betula pendula*) sawdust using formic acid and hot water. Solubilization experiments were carried out under various reaction conditions. The maximum xylose yield (47.53 % xylose (w/w); reaction condition: 140 °C/2 h) was obtained using 7.24 % (w/w) of formic acid (GOLDMANN et al., 2017). The experimental results revealed that the maximum rate of hemicelluloses degradation, leading to the formation of furfural, was recorded when the rate of degradation of hemicelluloses increased as the reaction temperature and reaction time increased. The yield of xylose decreased with increasing

reaction time when the reaction temperature was 170 °C. The concentration of formic acid did not influence the yield as xylose was dehydrated to form furfural (GOLDMANN et al., 2017).

The reaction was conducted over a short period of time under conditions of low temperature in the presence of sulfuric acid. The process resulted in the recovery of 83.5 % of xylose when the samples were pretreated with sulfuric acid (35 mmol/L; treatment conditions: 170.05 °C/12 min). The degradation of xylose to form furfural and hydroxymethylfurfural under such moderate reaction conditions could be avoided (DIEDERICKS; VAN RENSBURG; GÖRGENS, 2013).

2.2.2. Steam explosion method

The method of steam explosion is used for biomass conversion, with effect in partial hemicelluloses solubilization. The auto-hydrolysis reaction results in the physical rupture of the biomass cell wall. The penetration of high-pressure steam into the plant cell walls leads to abrupt decompression, resulting in the physical rupture of the cell walls (BAIG; WU; TURCOTTE, 2019). As the pressure increases, steam starts to penetrate the biomass material. The vapor condenses, leading to the moistening of the biomass. At high temperatures, the condensed water (present inside the material) reacts with hemicelluloses and induces the hydrolysis of the acetyl and methylglucuronic groups. Acetic acid and uronic acid are produced, resulting in a decrease in the pH of the medium. The acids catalyze the depolymerization reaction. In the next step, a sudden drop in the pressure is observed. A fraction of the water present in the material condenses and promotes the rupture of the plant cell wall of the raw materials (GROUS; CONVERSE; GRETHLEIN, 1986). Centrifugation or filtration methods can be used to remove insoluble matter (such as cellulose) from the system. The hydrolysate containing the hydrolyzed hemicelluloses and lignin fragments is obtained (GROUS; CONVERSE; GRETHLEIN, 1986).

Water is the only reagent utilized in this simple process. Acid catalysts such as SO_2 or H_2SO_4 should be used to pretreat softwood materials such as pine. It is more difficult to autohydrolyze softwood materials (compared to agricultural residues and hardwoods) (NEGRO et al., 2003). The use of acid catalysts makes the reaction conditions harsh. Under these conditions, hemicelluloses can be extracted in the form of monomers and degradation products such as furfural and hydroxymethylfurfural (glucose degradation) are formed. The solubilization yield decreases when xylose is degraded. The results reveal that the steam

explosion method is unsuitable for the extraction of polymeric hemicelluloses (MIHIRETU; CHIMPHANGO; GÖRGENS, 2019).

The steam explosion method is regarded as one of the most cost-effective pretreatment processes that can be used to treat hardwoods and agricultural residues (GE et al., 2018). The installation cost is high. However, it was found to be the most efficient pretreatment method with an internal rate of return of 28.04 % (NIEDER-HEITMANN et al., 2020). The steam explosion method is an environmentally friendly and easy-operate method. It is one of the most efficient pretreatment methods that can be used for fractionating lignocellulosic materials (MELATI et al., 2019). However, the operation conditions lead to the hydrolysis of hemicelluloses present in biomass. Thus, the steam explosion method should be used to obtain hemicelluloses in the form of oligomers or monosaccharides.

Sulfuric acid was used as a catalyst in the steam explosion method to solubilize hemicelluloses present in slash pine sawdust. The maximum efficiency was recorded when the process was carried out at a temperature of 200 °C and the reaction time was 5 min (sulfuric acid: 3 % (w/w); solubilization yield: 90 %). The steam explosion method carried out under mild conditions results in low solubilization yield and high degrees of polymerization. Hemicelluloses are extracted as oligomers. However, under harsh reaction conditions, hemicelluloses were isolated predominantly in the form of monosaccharides and they were present in the corresponding pretreatment liquors (STOFFEL et al., 2017). A lower solubilization yield of 51 % was recorded under similar steam explosion conditions (204 ºC/10 min). In this method, used to solubilize hemicelluloses present in sugarcane, sodium hydroxide was used as the catalyst (MIHIRETU; CHIMPHANGO; GÖRGENS, 2019).

Under severe conditions, the maximum solubilization yield was recorded to be 19.4 % when hemicelluloses present in spruce sawdust was hydrolyzed in the presence of sodium hydroxide (catalyst). Low molecular weight products with low degrees of polymerization were obtained. High molecular weight compounds were obtained when the hydrolysis was carried out under milder reaction severity conditions (CHADNI et al., 2019).

Xylan was depolymerized to form xylose that was subsequently dehydrated to form furfural when the steam explosion biomass treatment method was used for solubilization. Structural rearrangement in furfural with lignin derivatives resulted in the formation of pseudo-lignin. Harsh treatment conditions can potentially lead to the accumulation of pseudo-lignin and degradation products (SANNIGRAHI et al., 2011).

3. Chemical modifications of hemicelluloses

Hemicelluloses can be chemically modified to produce compounds with novel properties. The structurally modified hemicelluloses molecules can find their applications in specific fields. The solubility and thermal stability of the compound can be improved by tuning the structural characteristics. The biodegradability, biocompatibility, and core structural features remain unaltered (KONG et al., 2018). The hydroxyl groups present in the backbones of the hemicelluloses molecules can be chemically modified. Thus, the ease of modification depends on the number of hydroxyl groups present. Various carbohydrates (such as cellulose and starch) that are available in the form of residues have been chemically modified. These polysaccharides contain three hydroxyl groups in each monomer, while hemicelluloses contain only one or two hydroxyl groups that can be chemically modified. Thus, it is more difficult to chemically modify hemicelluloses and easier to modify cellulose and starch (FANG et al., 1999).

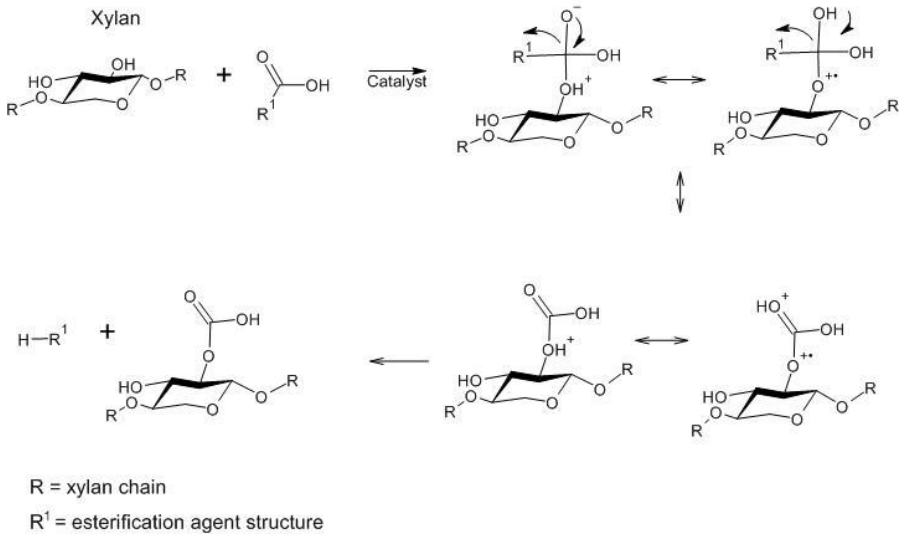
Numerous methods have been developed over the years for the production of hemicelluloses derivatives. The esterification and etherification reactions help introduce functional groups into the polysaccharide chains.

3.1.Hemicelluloses esterification

Alcohols and carboxylic acid (or derivatives of carboxylic acids such as acid chlorides and acid anhydrides) groups react to form esters. Esterification reactions have been conducted to produce modified hemicelluloses molecules. The hydrophobicity, solubility, and thermal processability of the modified hemicelluloses derivatives are different than those of the parent hemicelluloses. Hemicelluloses-based biodegradable films, paper coatings, medical implants, and hydrogels have been reported (BELMOKADDEM et al., 2011; FANG et al., 1999; FUNDADOR et al., 2012).

The first step of the esterification reaction involves a nucleophilic attack on the carbonyl carbon atom of the carboxylic acid molecule. The OH group of the sugar molecule acts as the nucleophile. The lone pair of electrons on the OH group attacks the carbonyl carbon. The leaving group departs, resulting in the formation of esterified hemicelluloses. This is often an acid- or base-catalyzed reaction (Figure 7). Researchers have used different solvents and catalysts to produce hemicelluloses esters (GRÖNDAHL; TELEMAN; GATENHOLM, 2003; MUGWAGWA; CHIMPHANGO, 2020b; RENARD; JARVIS, 1999; STEPAN et al., 2013).

Figure 7 - Esterification pathway of hemicelluloses



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Recently, ionic liquids (ILs) have gained immense attention and have been used as reactive solvents for esterification as they are eco-friendly, recyclable, and highly reactive. They also exhibit enhanced thermal stability and low viscosity. Negligible vapor pressure is produced at room temperature when ILs are used (BARTHEL; HEINZE, 2006; HEINZE; SCHWIKAL; BARTHEL, 2005; WU et al., 2004). ILs are commonly defined as salts that are in their molten states at temperatures below 100 °C. They can dissolve complex macromolecules and polymeric materials. Carbohydrates can be efficiently dissolved in ILs with high efficiency and are regarded as clean solvents that can be used in chemical reactions. Such solvents help break the extensive hydrogen-bonding network and promote the dissolution of polysaccharides (SWATLOSKI et al., 2002).

The esterification reaction is one of the most versatile reactions that can be used to achieve structural modifications in hemicelluloses molecules to make them suitable for industrial applications. For example, polysaccharides are modified to produce films that can replace plastic. Hemicelluloses containing one or two hydroxyl groups are hydrophilic in nature and synthetic polymers are hydrophobic in nature (FANG et al., 1999).

Esterified polysaccharides (acetylated cellulose, acetylated xylan, acetylated starch, starch propionate, starch butyrate, starch valerate, and starch hexanoate) can be used to reduce the anaerobic biodegradation of bioplastic. When the degrees of substitution of starch, cellulose, and acetylated xylan were >1.5, 1.5, and 1.2, respectively, the biodegradation of bioplastic was hindered (RIVARD et al., 1995).

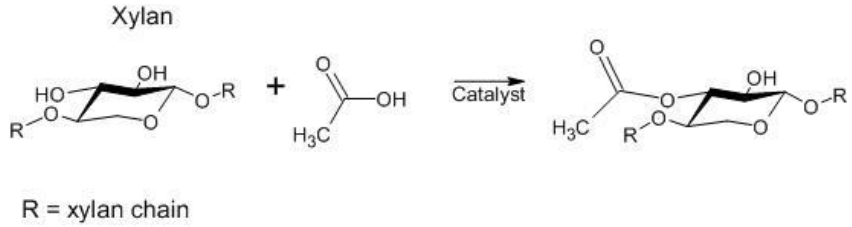
The lignocellulosic fibers (hemicelluloses and lignin) of different vegetables were chemically modified (esterified) to yield materials exhibiting enhanced surface adhesion properties (TSERKI et al., 2005). The thermal stability, crystallinity, and hydrophilicity of the modified fibers decreased. The modified fiber/polyester composites exhibited decreased fiber hydrophilicity and water absorption properties (TSERKI et al., 2005) that could potentially affect the biodegradation processes (TSERKI; MATZINOS; PANAYIOTOU, 2006). These modified fibers could be used to reduce the rate of biodegradation of esterified lignocellulosic fibers (TSERKI; MATZINOS; PANAYIOTOU, 2006). The rate of biodegradation decreased as the bioplastics could not efficiently interact with water as the OH groups present in the fibers were replaced by ester groups. Therefore, the extent of diffusion of water through the composite and the rate of biodegradation were affected.

3.1.1. Acetylation

Hemicelluloses contain acetyl groups in their chains. The nature of the acetylated polymer and the extent of acetylation differ between plant species, plant tissues, and types of plant cell walls (PAWAR et al., 2013). The xylans from graminaceous plants, for example, contain 1 – 2 % acetyl pending groups. Deacetylation occurs when the hemicelluloses molecules are solubilized in an alkaline medium. The resulting products are highly hydrophilic as they bear a large number of hydroxyl groups.

The acetylation reaction (an esterification reaction) helps introduce acetyl groups into the hemicelluloses backbone (Figure 8). Schuetzenberger was the first to synthesize carbohydrate acetates (in 1865) using acetic anhydride (DAVIS, 1929).

Figure 8 - Reaction representing the acetylation of hemicelluloses



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The increase in hydrophobicity of the compounds can be attributed to the acetylation of the hydroxyl groups present in hemicelluloses. Acetylation hinders the formation of hydrogen

bonds (between hydroxyl groups and water molecules), resulting in increased water resistance. These properties make the hemicelluloses derivatives suitable for application in various fields (MUGWAGWA; CHIMPHANGO, 2020b). The formation of intermolecular hydrogen bonds in hemicelluloses is hindered.

The degree of acetylation dictates the hydrophobicity of the acetylated hemicelluloses. The non-acetylated xylan (degree of acetylation: 0) is partially soluble in hot water. The partial solubility can be attributed to the spontaneous intra-molecular hydrogen bonding, possibly resulting in the formation of a crystalline network. The partially acetylated xylan (degree of acetylation: ~0.5) is fully soluble in water. The high solubility can be attributed to the presence of the free hydroxyl groups in the hemicelluloses chain. Xylan molecules in which all the hydroxyl groups have been acetylated (degree of acetylation: 2) dissolve in non-polar solvents like chloroform and polar aprotic solvents like dimethyl sulfoxide (STEPAN et al., 2013). The solubilities of the acetylated hemicelluloses in organic solvents such as chloroform, dimethylsulfoxide, and tetrahydrofuran increase with the increase in the degree of substitution (degree of acetylation) (SUN et al., 1999b).

Numerous acetylation methods have been reported that can be used to achieve varying degrees of substitution. These methods can also be used to produce different patterns of properties. However, the most common reaction used to acetylate hemicelluloses involves the use of acetic anhydride as the reagent. The gas-phase surface esterification and plasma treatment-assisted surface esterification reactions can be conducted to acetylate hemicelluloses. The samples can be pretreated with glacial acetic acid to achieve different levels of acetylation (BERLIOZ et al., 2009). The use of ionic liquids as the medium has shown great potential for the direct dissolution of hemicelluloses. These hemicelluloses can be completely acetylated in a short period of time a high molecular weight can be retained (STEPAN et al., 2013).

Acetylated hemicelluloses are often the primary polymer component of films. However, hemicelluloses can be used as a copolymer (with polycaprolactone) for the preparation of active packaging units. The film solubility reduced to 82 % when acetylation of hemicelluloses was carried out using acetic acid as the acetyl donor and sulfuric acid as the catalyst (MUGWAGWA; CHIMPHANGO, 2020b). The solubilities (in the fatty food simulants) of the acetylated hemicelluloses films were lower (solubility as low as 12.57 %) than the solubility of the polycaprolactone films and low-density polyethylene films (MUGWAGWA; CHIMPHANGO, 2020b). The degree of substitution was in the range of 0.59–1.25 and enhanced thermal stability could be achieved when acetylation of wheat straw hemicelluloses was carried out in a homogeneous organic solvent system consisting of *N*,*N*-

dimethylformamide and lithium chloride. Acetic anhydride was used as the esterification agent and 4-dimethylaminopyridine was used as the catalyst (FANG et al., 1999). A similar method was followed for the acetylation of arabinoxylan, where formamide was used as the solvent (single solvent) and pyridine was used as the catalyst. The resulting material was used for film production (EGÜÉS et al., 2014). The film formed with acetylated arabinoxylan exhibited increased thermal stability. The maximum weight loss was achieved at a temperature of 375 ℃, indicating a decrease in the number of hydroxyl groups. The hydroxyl groups get oxidized during heating (EGÜÉS et al., 2014; FUNDADOR et al., 2012). Acetylation resulted in increased tensile strength (elongation at break: 13.4 %; Young's modulus: 2241 MPa). Internal plasticization of the acetyl groups resulted in improved elongation (EGÜÉS et al., 2014).

Hemicelluloses present in softwood biomass could be directly acetylated. The sample was not impregnated with acetic anhydride at 120 ℃ prior to solubilization (SUN et al., 2019). The percent of weight gain, which varied from 13.6 % (reaction time: 30 min) to 22.3 % (reaction time: 8 h), helped determine the acetylation efficiency.

A maximum weight gain of 22.7 % was recorded when the acetylation reaction was carried out using acetic anhydride in the absence of catalysts and solvents. The reaction temperature was 120 ºC and the reaction time was 4 h. The reaction was carried out in the presence of potassium acetate that was produced during the alkaline solubilization method. The water solubility decreased from 46 % to 2.4 % and the moisture content decreased from 63 % to 12 % upon acetylation. The results revealed that this easy-to-operate, efficient, cost-effective, and environmentally-friendly method can be used to acetylate xylans in the absence of toxic catalysts (AKKUS; OZKAN; BAKIR, 2018).

The alkali-based organosolv treatment method can be used (prior to hemicelluloses solubilization) to optimize the acetylation reaction conditions (acetylation of hemicelluloses present in wheat straw). Acetic acid was used as the acetylation agent and sulfuric acid was used as the catalyst. To obtain the optimum yield, the reaction was carried out for 1 h at a temperature of 50 ºC (MUGWAGWA; CHIMPHANGO, 2020a). The organosolv treatment conditions were varied to determine the degree of acetylation of hemicelluloses. The acetylated hemicelluloses were used to produce films. The value of the water contact angle indicated the extent of hydrophobicity. When the organosolv treatment method (reagents: 80 % ethanol and 1 % NaOH; treatment time: 4 h) was used to treat the sample, the degree of substitution was recorded to be 1.7. The treated sample did not produce the most hydrophobic hemicelluloses-based film (contact angle: 31.34 °). The most hydrophobic hemicelluloses-based film (water contact angle: 64.22 °) was produced when the organosolv treatment method (reagents: 65 %

ethanol and 13 % NaOH; treatment time: 2 h) was used to acetylate hemicelluloses (degree of substitution: 0.45). The results confirmed that the hydrophobicity of hemicelluloses did not solely depend on the degree of acetylation (MUGWAGWA; CHIMPHANGO, 2020a).

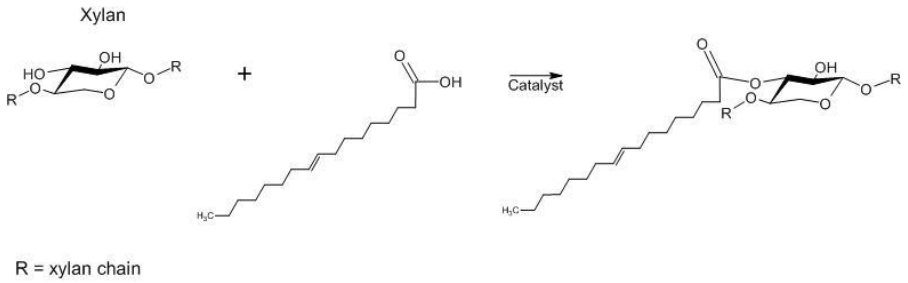
Numerous types of ILs can be used during acetylation. The acetylation reactions in ILs can be conducted in the presence or absence of catalysts. Hemicelluloses present in switchgrass were acetylated using acetic anhydride in 1-allyl-3-methylimidazolium chloride in the absence of a catalyst. This method of acetylation was environmentally friendly and was used to produce hemicelluloses acetate with a high degree of polymerization. The produced hemicelluloses can be used in various industrial applications (AYOUB et al., 2013).

The hydrophilicity of the acetylated polysaccharides (starch, cellulose, and xylan) decreased as the degree of substitution increased. The enzymatic degradability also decreased with increasing degrees of substitution (GLASSER et al., 1995). It is worth mentioning that in addition to the modifying polysaccharides and solubilization methods process, other factors such as type of enzyme, pH, and microorganisms must be considered in the enzymatic and microbiological degradation of bioplastics composed of modified polymers. It was reported that acetylated xylan did not hinder the process of degradation when the degree of substitution was in the range of 0–0.8 (MITCHELL et al., 1990).

3.1.2. Oleoylation

Oleoylation is a type of esterification reaction. The oleoylation reaction is conducted to convert the hydroxyl groups to oleoyl esters. Hydrophobic oleoyl groups are introduced into the scaffold (Figure 9). The hemicelluloses molecules are modified using a catalyst such as *N*-bromosuccinimide (or 4-dimethylaminopyridine). The *N*,*N*-dimethylformamide/lithium chloride system is used as the solvent system to conduct the reaction under mild conditions (SUN et al., 1999b; SUN; SUN; SUN, 2004).

Figure 9 - Reaction representing oleoylation of hemicelluloses



Source: author

Oleoylation alters the water solubility of hemicelluloses. The solubility of the compound in different organic solvents such as pyridine, tetrahydrofuran, toluene, and chloroform (SUN et al., 1999b) increases, indicating increased hydrophobicity. The decrease in the thermal stability of hemicelluloses (post oleoylation) can be attributed to the absence of intermolecular hydrogen bonds between the polymeric chains of hemicelluloses in the unmodified polymer matrix (SUN; SUN; SUN, 2004).

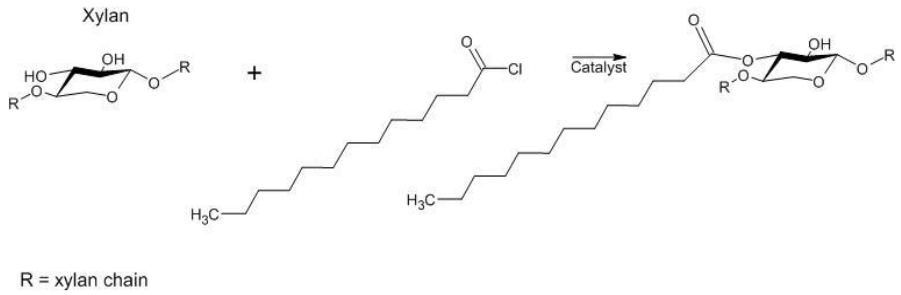
Sugarcane bagasse hemicelluloses were oleoylated, the degree of substitution was found to be 0.04. The thermal stability increased and the thermal degradation of the material was initiated at 187 ℃. The unmodified hemicelluloses started to decompose at 200 ℃ (SUN; SUN; SUN, 2004). When 4-dimethylaminopyridine was used as the catalyst and triethylamine was used as the neutralizer in a homogeneous solvent system composed of *N*,*N*-dimethylformamide and lithium chloride, >90 % oleoylation of the free hydroxyl groups present in native hemicelluloses could be achieved (SUN et al., 1999b). The minimum amount of degradation of the hemicelluloses chains was observed when this process was conducted.

Hemicelluloses esterified with fatty acids can find their applications in industries for coating paper/board. They exhibit unique hydrophobic and high moisture barrier properties. Oleoylation increases the hydrophobicity. Hence, the water-resistance of the esterified hemicelluloses is significantly higher than the water-resistance of the acetylated hemicelluloses when the degrees of substitution are the same. The use of esterified hemicelluloses is preferred over the use of acetylated hemicelluloses to develop barrier films used for the production of packaging materials in the food industry.

3.1.3. Lauroylation

The lauroylation reaction is used to introduce lauroyl groups into the hemicelluloses chains (Figure 10). This reaction is generally carried out in the presence of a base and a catalyst (FANG et al., 1999). Lauroyl chloride is a common lauroylation agent. It can be efficiently used to esterify hemicelluloses (REN et al., 2008; WANG et al., 2012; XU et al., 2008).

Figure 10 - Reaction representing lauroylation of hemicelluloses



Source: author

Lauroylation resulted in increased hydrophobicity and decreased thermal stability (WANG et al., 2012; XU et al., 2008). Lauroylated hemicelluloses exhibit a regular and homogenous morphology. The homogeneity increases as the amount of the lauroylating agent increases (WANG et al., 2012).

The degrees of substitution were in the range of 0.43–1.82 when ILs were used as the reaction (lauroylation) solvents. A significant amount of the hemicelluloses polymers could be degraded in the IL media under harsh reaction condition. The extent of degradation increased as the reaction time and reaction temperature increased (temperature: increased till 100 ºC, reaction time increased till 90 min) (WANG et al., 2012). The thermal stability of the lauroylated hemicelluloses (with a low degree of substitution) was lower than that of the native hemicelluloses. The thermal stability of the lauroylated polymer (with high degrees of substitution) was higher than that of the unmodified hemicelluloses (REN et al., 2008; WANG et al., 2012; XU et al., 2008).

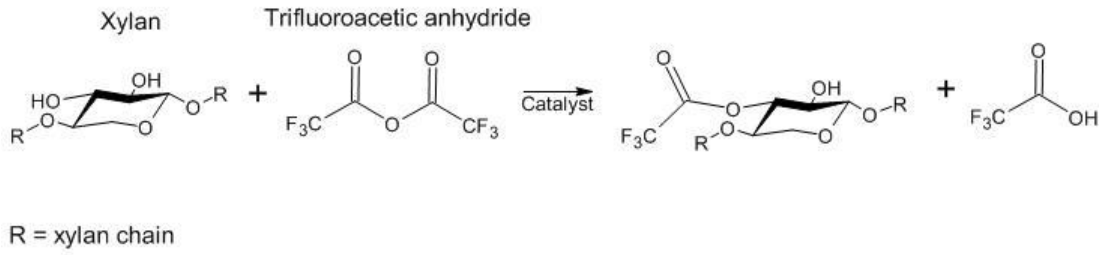
The lauroylation conditions were investigated. The effects of using various catalysts such as 4-dimethylaminopyridine, *N*-bromosuccinimide, *N*-methylpyrrolidine, *N*-methylpyrrolidone, and pyridine were tested (PENG et al., 2008). The reaction rate was accelerated when the catalyst concentration was 5 % (w/w, dried hemicelluloses). This resulted in increased product yield (from 56.2 % (control sample) to 83.2 %) and degree of substitution

(from 0.82 (control sample) to 1.54) in the absence of a catalyst. The maximum reaction rate was obtained when the concentration of 4-dimethylaminopyridine was 5 % (w/w, dried hemicelluloses). The lauroylation yield was 83.2 % and the degree of substitution was 1.54. An increase in the concentration of 4-dimethylaminopyridine resulted in a decrease in the efficiency. However, the cost-inefficiency of the method limits the industrial use of such catalysts. The recovery of the catalyst is economically unviable.

3.1.4. Fluorination

Fluorine molecules are introduced into the hemicelluloses chains following the process of fluorination (Figure 11). Polymers with unique chemical and surface properties are produced post fluorination. Super-hydrophobic fluorinated polymeric materials have been reported. These materials exhibit good chemical resistance and stability. A strong barrier toward gases and liquids is formed and a low coefficient of friction is recorded (TRESSAUD et al., 2007; WOODWARD et al., 2003). These characteristics make the fluorinated polymers suitable candidates for the preparation of marine coatings, medical implants, plasticized films, and protective clothing (WOODWARD et al., 2003).

Figure 11 - Fluorination of hemicelluloses with trifluoroacetic anhydride



Source: author

A common method of fluorinating hemicelluloses is to carry out the fluorination reaction in a fluorine containing atmosphere. This method can be used to synthesize a wide variety of fluorine-based compounds with altered surface properties (TRESSAUD et al., 2007). The various fluorinated gases used for fluorination are CF_4, CHF_3, C_3F_8, C_4F_8, NF_3, SF_6, F_2, NF_3, ClF_3, and $C_4F_6O_3$ (CARDINAUD; TRESSAUD, 2000; GRÖNDAHL; GUSTAFSSON; GATENHOLM, 2006; TRESSAUD et al., 2007). The elementary stages are highly exothermic

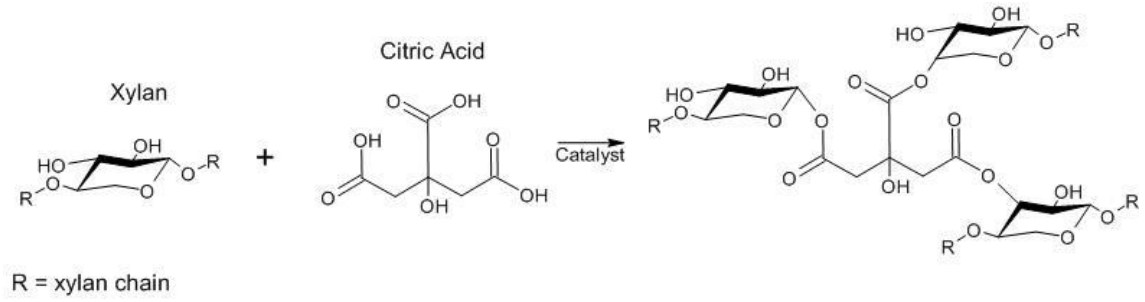
and fluorination proceeds spontaneously at room temperature. This process can find its utility in industries (TRESSAUD et al., 2007).

The process of fluorination can be potentially used to modify the surface of arabinoxylan films. This results in reduced hydrophilicity. The contact angle increased from 30 ° (indicating hydrophilicity) to 70 ° for an arabinoxylan film containing 7 % fluorine. The moisture content decreased from 18 % to 12 % (GRÖNDAHL; GUSTAFSSON; GATENHOLM, 2006).

3.1.5. Crosslinking/graft copolymerization

Crosslinking reactions can be used to esterify polymers (Figure 12). The modified polymers resist thermal degradation and exhibit decreased solubility. This results in improved water resistance properties (SHAO et al., 2019). The polymers are also resistant to creep and cold flow (DOTAN, 2014). Copolymerization applied to hemicelluloses used in film formation improves the resistance to cracking by liquids and other harsh environments (ZHAO et al., 2020).

Figure 12 - Crosslinking reaction with hemicelluloses and citric acid



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Crosslinked hemicelluloses are primarily used to produce hydrogels that exhibit limited water solubility and the ability to swell in water (PENG et al., 2011). Hydrogels are three-dimensional, hydrophilic, polymeric networks capable of imbibing large amounts of water or biological fluid into them. Different functional groups can be easily incorporated into the physically or chemically crosslinked networks to produce novel hydrogels. An increase in the degree of crosslinking results in a decrease in the distance between the crosslinking points. The volume of the available space for water absorption decreased. The hydrophobicity is increased as less amounts of free water are retained in the network.

At elevated temperatures and in the presence of catalysts such as sodium hypophosphite, carboxylic acid groups form five-membered cyclic anhydrides in the first stage. These further react with the hydroxyl groups present in the carbohydrate to form ester linkages (GU; YANG, 2000; MAO; YANG, 2001). The abstraction of the hydrogen atom from the hydroxyl groups in the hemicelluloses backbone results in the generation of active centers on the hemicelluloses backbone that initiate the radical polymerization reaction. A cross-linking reagent can be used to produce a copolymer network exhibiting a crosslinked structure (PENG et al., 2011).

The popular crosslinking agents used to crosslink different polysaccharide-based materials are formaldehyde-based reagents, *N*,*N*-methylenebisacrylamide, vinylethylbenzene, and ethyldiol methacrylate (HERNADI, 2000). However, the formaldehyde-based crosslinking agents can negatively affect human health and the environment. The less toxic polycarboxylic acids such as oxalic acid, citric acid, maleic acid, succinic acid, itaconic acid, and butane tetracarboxylic acid, which can be used as crosslinking agents, have attracted immense attention.

The incorporation of citric acid into the hemicelluloses scaffold resulted in a significant increase in the oxygen barrier and hydrophobicity of the films formed from such polymers. The maximum tensile strength was recorded when the citric acid content was 20 %. A further increase in the citric acid content resulted in a decrease in the tensile strength (SHAO et al., 2019).

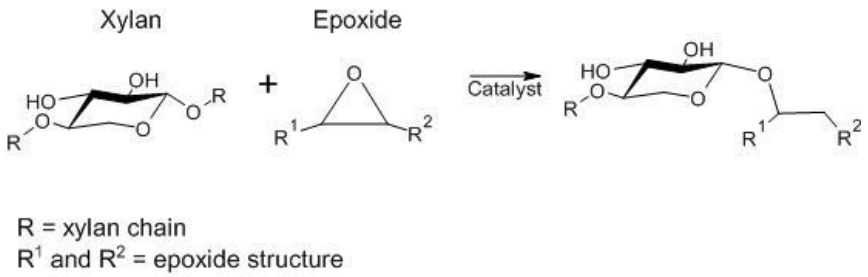
Crosslinking reactions in the presence of dihydroxymethyl (propionic acid) resulted in the formation of hyperbranched hemicelluloses. The number of carboxyl and hydroxyl groups increased and a polymer with an increased number of active end groups was produced, which can effectively adsorb different kinds of dye. The maximum degree of substitution recorded was 0.83, which increased the viscosity to an appropriate dye adsorbing value. The produced polymers can efficiently adsorb dyes. The adsorption yields were recorded to be 825 mg/g for methyl red, 675 mg/g for bromomethyl green, and 912 mg/g for bromophenol blue (ZHANG; XUE; GU, 2019).

3.2.Etherification of hemicelluloses

Alcohol reacts with an alkylating agent in the presence of a base to form an ether bond (etherification reaction; Figure 13). The alkylating agents that can be used in the reactions are alkyl halides (chlorides, bromides, and iodides), alkyl sulfonates, vinyl monomers, and epoxides. An epoxide is an unstable 3-member ring compound containing an oxygen atom in

the ring that induces electron withdrawal from the adjacent carbon atoms (SHAO et al., 2020). This increases the reactivity of the epoxide and they can efficiently react with alcohol-containing molecules such as hemicelluloses.

Figure 13 - Etherification of hemicelluloses in the presence of epoxide



Source: author

The hemicelluloses can potentially degrade in the presence of a base. A decrease in the degree of polymerization was recorded when the reaction was carried out in the presence of a base. The use of a base also resulted in the formation of compounds exhibiting poor mechanical properties (IBN YAICH; EDLUND; ALBERTSSON, 2017). Therefore, it is possible to obtain etherified hemicelluloses by directly precipitating alcohols (SHAO et al., 2020).

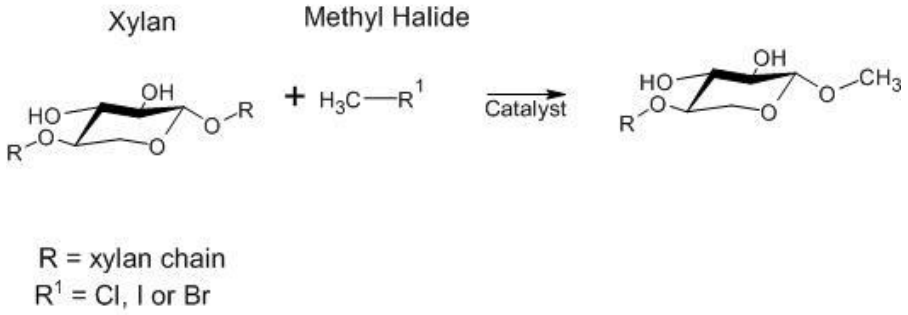
Etherification of polysaccharides can help tune the solubilities of the compounds. Etherification imparts stability to the molecules against microorganisms (biodegradability). These compounds exhibit film-forming abilities and increased viscosities (SHAO et al., 2020). Etherified hemicelluloses can be used to form films with enhanced mechanical properties such as hydrophobicity, thickness, tensile strength, and thermal stability (SHAO et al., 2020).

The ether bond is more stable than the ester bond. The ester bond can be easily hydrolyzed (especially under alkaline conditions) (POURCHEZ et al., 2006). Methylation (FANG et al., 2002; PETZOLD et al., 2008), alkylation (SHAO et al., 2020), carboxymethylation (ALEKHINA et al., 2014; PETZOLD; SCHWIKAL; HEINZE, 2006; REN; SUN; PENG, 2008), and benzylation (HARTMAN et al., 2006; JUNLI et al., 2012) are a few types of etherification reactions.

3.2.1. Methylation

Methylation reactions are used to introduce methyl groups into the hemicelluloses chain. Etherification reactions can be carried out for methylating compounds. Methyl halides such as methyl chloride and methyl iodide are used as the reagents (Figure 14). The accessibility of the functional groups and the probability of the reaction between the functional groups of the reagents are increased when the hemicelluloses are activated. Heterogeneous activation of the material can be achieved. The dissolved polymer can be used as the starting material (PETZOLD et al., 2008) and sodium hydride (or sodium hydroxide) is used as the activator (FANG et al., 2002; PETZOLD et al., 2008).

Figure 14 - Reaction representing the methylation of hemicelluloses



Source: author

Factors such as the degree and uniformity of substitution, degree of polymerization, and molecular weight distribution influence the chemical and physical properties of the derivatives. Water-soluble products that exhibit a certain degree of amphiphilicity can be produced by methylating the compounds (PETZOLD et al., 2008).

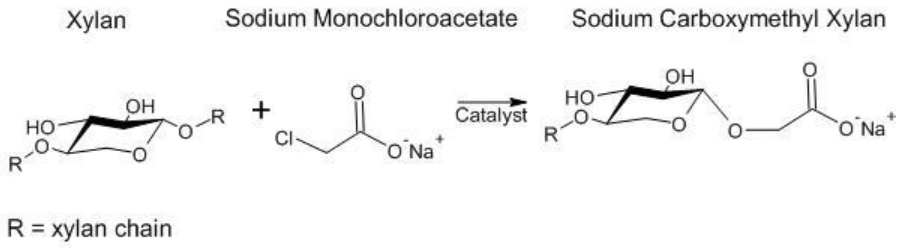
Methyl xylan was synthesized using methyl chloride (or methyl iodide) as the etherifying agent. Xylan was reacted with an excess of methyl chloride (under pressurized conditions) in the presence of aqueous NaOH (40 %) to yield methyl xylan (degree of substitution: 0.94) (PETZOLD et al., 2008). The strongly basic methylsulfinyl carbanion was used to generate the methylated hemicelluloses ether. Hemicelluloses obtained from wheat straw was used as the substrate. Methyl iodide and sodium hydride were used as the etherification agent and catalyst, respectively. The degree of substitution was 1.7. The thermal stability of the product increased upon methylation. The process can potentially lead to the degradation of hemicelluloses (FANG et al., 2002).

Methylation reactions resulted in the derivatization and fractionation of the sawdust. The methylation reaction was carried out in dimethyl sulfoxide/tetrabutylammonium to yield methylated cellulose, hemicelluloses, and lignin. Methylated hemicelluloses exhibited amphiphilic properties and could be used as a surfactant. These compounds possessed a flexible backbone. The hydrophilicity of the compound can be attributed to the presence of a relatively short molecular chain (MIKI et al., 2020).

3.2.2. Carboxymethylation

Carboxymethylation is a process following which carboxymethyl groups are introduced into the hemicelluloses chain. Etherification reactions can be conducted to introduce the carboxymethyl groups. Etherification agents (such as sodium monochloroacetate; Figure 15) (PETZOLD; SCHWIKAL; HEINZE, 2006) are used during the process. It is a versatile functionalization process that provides access to bio-based materials that exhibit interesting properties. These materials can be used for inspissation, filming, emulsification, producing suspensions, maintaining water quality, and binding target molecules (GENG et al., 2020; HEINZE, 1998).

Figure 15 - Carboxymethylation of hemicelluloses using sodium monochloroacetate



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The carboxymethylation reaction can proceed in a suspension containing hemicelluloses and ethanol/water. The reactions can be carried out under alkaline conditions. Under these conditions, the hemicelluloses are activated. However, a substantial amount of the hemicelluloses polymers can degrade during the carboxymethylation reaction carried out under alkaline conditions.

The hemicelluloses isolated from sugarcane bagasse were effectively converted into carboxymethylated hemicelluloses compounds in the presence of sodium monochloroacetate

and sodium hydroxide. A solution containing ethanol and water was used as the reaction medium. The maximum degree of substitution was 0.56. A significant amount of the polymers degraded during the process. The thermal stability of the compounds increased (REN; SUN; PENG, 2008). Reaction conditions used to carboxymethylate xylan were followed. Sodium monochloroacetate and sodium hydroxide were used as the reagents and 2-propanol was used as the reaction medium. Under these conditions, the degree of substitution was found to be 1.22 (PETZOLD; SCHWIKAL; HEINZE, 2006).

An increase in the water absorption ability (at high relative humidity) was observed during the xylan carboxymethylation process that resulted in the production of bioplastic. This indicated that the carboxymethyl groups were hydrophilic in nature. The hydrophilicity promotes biological and abiotic degradation (ALEKHINA et al., 2014). Carboxymethylation of hemicelluloses (obtained from poplar) was conducted using sodium chloroacetate and sodium hydroxide as catalysts. A solvent system consisting of ethanol and water (ethanol/water; 80 % (v/v)) was used as the reaction solvent. The degree of substitution was found to be 0.61 when the reaction was carried out for 60 min at a temperature of 85 ℃. Peeling occurred at high temperatures in the presence of sodium hydroxide, resulting in the slight degradation of hemicelluloses. Films formed from carboxymethylated hemicelluloses exhibited increased hydrophilicity, water vapor permeability, and elongation at break values. The tensile strength and oxygen permeability decreased (GENG et al., 2020).

The degree of substitution was recorded to be 0.45 when hemicelluloses were carboxymethylated at 70 ºC. The reaction was allowed to proceed for 2 h in a solvent system consisting of isopropanol and water (isopropanol: water = 25:75, v/v). Potassium hydroxide (KOH) supported on natural zeolite clinoptilolite (CP) was used as the catalyst. The reaction was carried out under varying KOH:CP ratios and the optimum ratio was found to be 1:2. The efficiency of the reaction, when the optimized catalyst concentration was used for the reaction, was approximate twice the efficiency of the reaction carried out using standard KOH solution (even under conditions of shorter reaction time and lower temperature). Under the optimized conditions, less amounts of hemicelluloses were degraded (KHALILZADEH; SADEGHIFAR; VENDITTI, 2019).

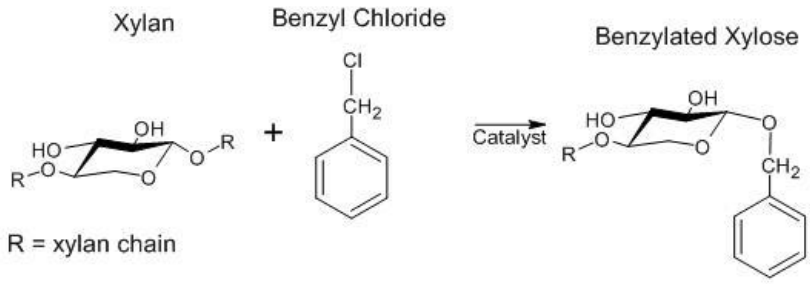
Carboxymethylated beechwood xylan was produced under alkaline conditions when sodium chloroacetate was used. The influence of the process parameters on the degree of substitution of xylan was explored. Carboxymethylated xylan with degree of substitution of 0.21 was produced under the optimized conditions (NaOH 0.75 M; reaction time: 2 h; 70 ℃).

The process of carboxymethylation resulted in increased molecular weight and enhanced thermal stability (KONDURI; FATEHI, 2016).

3.2.3. Benzylation

Benzylation of hemicelluloses involves the introduction of benzyl groups into the hemicelluloses scaffold. The hydrogen atoms present in the hydroxyl groups in hemicelluloses chains are replaced by the benzyl groups present in benzylating agents such as benzyl chloride (Figure 16) (SERESHTI; MOHAMMADI-ROUSHANDEH, 2003). During the process, the natural fibers are pre-swelled for 1 h using concentrated sodium hydroxide. Following this, they are reacted with benzyl chloride in the presence of a phase transfer catalyst. The reported reaction was carried out at 120 ℃ and the reaction time was varied between 5 h and 10 h. Subsequently, the benzylated fibers were washed with water and ethanol and dried under vacuum at 80 ℃ (PATEL; PARSANIA, 2017).

Figure 16 - Reaction representing the benzylation of hemicelluloses in the presence of benzyl chloride



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Etherification (benzylation) resulted in increased thermal stability and hydrophobicity as benzene ring was introduced into the hemicelluloses chain. The benzylated hemicelluloses can be potentially used for the production of hydrophobic films that can be used for packaging food items. These films can also be used to coat surfaces (TALIA et al., 2010).

Hydrophobic hemicelluloses with increased thermal stability were formed when hemicelluloses obtained from wheat straw were benzylated using benzyl chloride in the presence of sodium hydroxide as the catalyst. The reaction was carried out in an ethanol/water system (JUNLI et al., 2012). The process of benzylation helped develop oxygen barrier films. Hemicelluloses present in wheat straw were used as the substrate. The films exhibited high hydrophobicity and were moisture-resistant (HARTMAN et al., 2006).

4. Concluding remarks

Hemicelluloses can find their applications in various industrial fields. Hence, polysaccharides have been structurally modified to improve various properties such as hydrophobicity, thermal stability, viscosity, solubility (in different solvents), biocompatibility, and water resistance. The ability of the polysaccharides to resist degradability (in the presence of microorganisms) can also be improved. In the first step, hemicelluloses are isolated from biomass. The choice of the solubilization/isolation method depends on the use of the obtained carbohydrates. The degree of polymerization varies as the solubilization method is varied. The type of substituents introduced into the hemicelluloses chains, monomer released, and degradation products formed depend on the solubilization method. Hemicelluloses for film formation can be produced following the method of alkaline solubilization. In this method, the bonds between hemicelluloses and lignin units are broken, but the degree of polymerization is retained. The dilute acid pretreatment method can be used to yield products that can be used to produce bioenergy. The lignin structure is modified and sugar molecules are released as oligosaccharides or monosaccharides. These are subsequently fermented. The alkaline solubilization method can be potentially used to obtain fermentable sugars but it requires followed step of acid or enzymatic hydrolysis.

Hemicelluloses can be chemically modified and used to produce bioplastic, paper coatings, medical implants, and hydrogels. Acetylation of hemicelluloses is carried out to produce films/bioplastics. Acetylation results in increased hydrophobicity and enhanced thermal stability. The ability of hemicelluloses to form strong hydrogen-bonded networks decreases post acetylation. Hemicelluloses are crosslinked to produce hydrogels. Crosslinking results in increased resistance toward thermal degradation and decreased solubility. Carboxymethylation and benzylation (etherification methods) of hemicelluloses are conducted to produce biodegradable hydrophobic materials. This method is also followed to produce amphiphilic hemicelluloses derivatives (such as surfactants) that can be produced by methylating hemicelluloses.

There is a worldwide demand to identify renewable energy sources. Hemicelluloses can be potentially used to generate energy and can find applications in various industries. They are environmentally friendly and will be predominantly used in various fields in the near future. The solubilization process is cost-ineffective, and corrosive or hazardous substances need to be used. Moreover, hemicelluloses need to be chemically modified to improve the properties of the final products. Research is being conducted with hemicelluloses as they are a readily

available material (found in agricultural residues) and can be used to address the problem of shortage of energy. The results can be used to expand the application prospects of hemicelluloses.

CHAPTER III: NATURAL OCCURING AND CHEMICALLY INDUCED HEMICELLULOSES ACETYLATION: EFFECT ON PLANT FUNCTIONS AND INDUSTRIAL APLICATIONS – A REVIEW

ABSTRACT

The United Nations Organization predicts plastic pollution to double by 2030. Facing the increasing social, environmental, and economic pressure to substitute non-renewable fossil resources with renewable ones, hemicelluloses receive attention as a substrate for the production of high-value products such as packaging materials, due to their non-toxicity, abundance, and biodegradability. Hemicelluloses in the cell wall are naturally substituted with acetyl groups, and the degree and pattern of acetylation vary between plant species, tissue and cell types, and plant maturity. Hemicelluloses acetylation influences features such as flexural properties of wood, polysaccharide interaction, plant growth, and stress resistance. This paper reviews plant polysaccharide acetylation process, including the acetylation mechanism in the plant cell wall, as well as the influence of such esterification on plant properties and wood industrial application. However, hemicelluloses are deacetylated during separation from other biomass polymers by alkaline solubilization, which is a highly applied method. Therefore, when it would be more advantage for the industrial application that hemicelluloses present a certain acetylation degree, such as for packaging, chemical acetylation is necessary, which occurs through an esterification reaction that links acetyl groups to hemicelluloses, catalyzed or not. Acetylation is known to enhance some of the features of hemicelluloses-based packaging material such as mechanical strength, processability, thermal stability, hydrophobicity, and oxygen and water vapor permeability. Such properties are essential when it comes to replacing fossil fuels-based plastics on commercial scale. Therefore, we summarize the recent development and progress in hemicelluloses chemical acetylation strategies, disclosing the advantages and disadvantages of different solvents and catalysts applied, and acetylation evaluation methods. Finally, the influence of the degree of acetylation on bioplastics properties is brought up, indicating its role when it comes to product applicability.

Keywords: hemicelluloses; acetylation, chemical modification, bioplastic, biomass

1. Introduction

Lignocellulosic plant cell walls are composed of a tangled network of multiple structurally complex biomacromolecules, consisting mainly of polysaccharides, which comprise cellulose, hemicelluloses, and pectin, - besides lignin. Such polysaccharides vary in structure and may be constituted by different sugars organized linearly through strong linkages among them, with or without substituents in their backbones (ROJAS, 2016; ZHANG et al., 2019).

1.1 Natural occurring acetylation

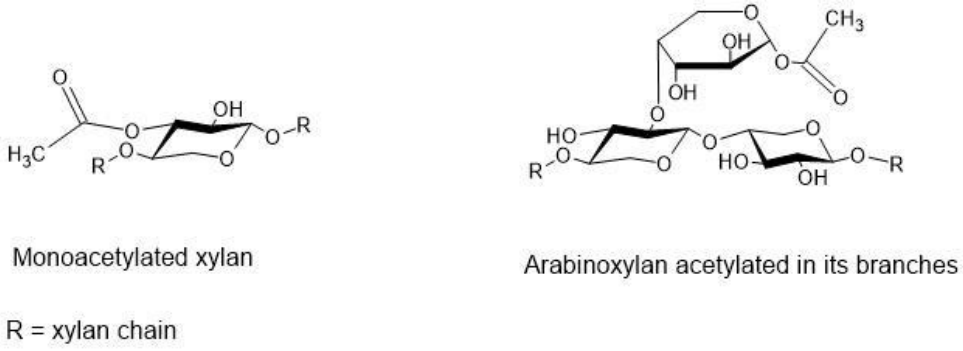
Acetyl group is a common substituent found on many of these polymers, usually connected to the sugar backbone through O-linkages, although not present in all polysaccharides (GILLE; PAULY, 2012). Whereas pectin and hemicelluloses can be highly acetylated, cellulose, callose, and mixed-linkage glucans do not present acetyl substituents (GILLE; PAULY, 2012). Overall, the biomass of plants contains considerable amounts of esterified acetate polysaccharides, even influencing the plant properties (hereafter addressed).

Hemicelluloses are a group of renewable and widely available polysaccharides present in lignocellulosic biomass. They account for 20~35 % of plant biomass such as corn stalk (30.3 %) (DONG et al., 2018), empty fruit bunch (27 %) (NASIR et al., 2018), meadow grass (20.2 %) (TSAPEKOS; KOUGIAS; ANGELIDAKI, 2015), sorghum straw (32.57 %) (HERNÁNDEZ-BELTRÁN; HERNÁNDEZ-ESCOTO, 2018), sugarcane bagasse (23.27 %) (FERNANDES et al., 2020), elephant grass (23.93 %) (SANTOS et al., 2018), spent coffee ground (28.12 %) (CHIYANZY et al., 2015), and wheat straw (26.9 %) (SHAH; ULLAH, 2019). Due to such heterogeneity of hemicelluloses chemical constituents, they may present amorphous or semi-crystalline organization in their natural state, with a degree of polymerization varying from 80 to 200, and diverse substituents and side chains in its backbone (LOUIS; VENKATACHALAM, 2020; SUN; LAWTHER; BANKS, 1996).

Cell wall hemicelluloses backbones can be either mono- or di- acetylated, sometimes also presenting acetyl groups in their branches, and such substitution may occur in different patterns, varying for instance the degree of substitution and the distribution of acetyl groups in the polysaccharide structure (Figure 17) (GILLE; PAULY, 2012). Presumably, when O-acetylation is located in the polymer backbone, it provides a greater influence on the polysaccharide properties, such as its morphology and hydrophobicity, as it prevents the

polymer from stacking and occupies hydroxyl groups that would be available for hydrogen bonding. Meanwhile, when found on the polysaccharide branches, acetyl groups might be seen as just an alternative substituent. This difference in acetylation pattern depends on hemicelluloses type, varying according to plant species, tissue types, cell types, and the plant maturity (GILLE; PAULY, 2012; JOHNSON et al., 2017; LOURENÇO et al., 2016; PAULY; KEEGSTRA, 2010; YUAN et al., 2016).

Figure 17 - Hemicelluloses acetylation pattern



Source: author

In grasses, xylopyranoyl residues commonly present one acetyl group attached at position O-2, while arabinose is attached at position three (PAWAR et al., 2013; PUCHART et al., 2020). Arabidopsis was found to present an average of 0.60 acetyl groups for each monosaccharide, in which 40 % (mol/mol) xylans were found to be non-acetylated, 18 % of xylans were found to be 2-O-acetylated, 25 % (mol/mol) xylans were found to be 3-O-acetylated and 17 % were found to be 2,3-di-O-acetylated (YUAN et al., 2016). Aspen wood also reaches a degree of substitution of 0.60, and acetyl groups represented 35 % (mol/mol) of xylan, of which 33 % are 2-O-acetylated and 67 % are 3-O-acetylated (TELEMAN et al., 2000). Wood samples from *Populus trichocarpa* presented an average of 5.2 % acetyl content (w/w, in relation to the biomass dry weight), ranging from 3.5 % to 6.7 % (w/w), including acetylation of all the plant polysaccharides (JOHNSON et al., 2017). In monocots, the acetylation occurs at the glucosyl residue on the xyloglucan backbone, more specifically in the C(O)6 position (GIBEAUT et al., 2005; JIA et al., 2005). Such variability in features found in nature is an evolved regulatory mechanism in response to internal and environmental stimuli (ZHANG et al., 2019).

The machinery of the formation of polysaccharides found in a modern-day typical plant wall can be drawn back to the Charophyte green algae, which is evidenced by the activity of a specific protein, Kf XYS1, the mechanism of acetylation of plant polysaccharides is thought to be similar to that proposed for the acetylation of peptidoglycan in Gram-negative bacteria (JENSEN et al., 2018; URBANOWICZ et al., 2014). However, only in more recent researches, the elemental mechanism for the control of cell wall acetylation has been studied, and scarce characterization of the enzymes involved makes it is still uncertain how plants establish and actively control the acetylation pattern in response to growth and environmental requirements (ZHANG et al., 2019). Multiple data sources suggest that acetylation of wall polysaccharides occurs during their biosynthesis in the Golgi complex (MOORE et al., 1986; SCHEIBLE; PAULY, 2004), and experiments demonstrate that the acetyl-CoA molecule present in the cytosol acts as the acetyl-donor for this process (GILLE; PAULY, 2012; RAYAMAJHI; DHAKAL; SOHNG, 2020; XING; POIRIER, 2012; ZHONG; CUI; YE, 2018b).

Biochemical studies and mutant screens have indicated three groups of proteins that act in acetylation of cell wall polymers, which are Trichrome Birefringence-Like (TBL) (XIONG; CHENG; PAULY, 2013; YUAN et al., 2016), Reduced Wall Acetylation (RWA) (MANABE et al., 2013; PAWAR et al., 2017), and Altered Xyloglucan 9 (AX9) (GILLE et al., 2011; SCHULTINK et al., 2015). Also, the degree of xylan acetylation has shown to be regulated by the group of protein Brittle Leaf Sheath1 (BS1), localized in the Golgi apparatus, and the BS1 mutant presented altered xylan acetylation patterns (ZHANG et al., 2017). The first protein family, TBL, comprises polysaccharide O-acetyltransferases, which are well known for their ability to catalyze the acetylation of cell-wall polymers (STRANNE et al., 2018; ZHONG; CUI; YE, 2017). They act with regiospecificity for 2-O and/or 3-O-acetylation of xylose, which was recently reaffirmed in Arabidopsis, rice, and poplar, in which different members of TBL protein family catalyzed the transfer of acetyl groups onto xylooligomer with different acetylation patterns (ZHONG; CUI; YE, 2018a, 2017, 2018b, 2018c). The second protein family, AXY9, was also demonstrated as influencing polysaccharide O-acetylation when Arabidopsis mutants with affected AXY9 expression presented a substantial reduction of up to 70 % and 35 % in total wall O-acetylation in stems tissues and leaf materials, respectively (SCHULTINK et al., 2015). AXY9 is evolved especially as O-acetyltransferases of xyloglucan (ZHONG; CUI; YE, 2018a). The third group of proteins directly involved in plant polysaccharide O-acetylation is RWA (MANABE et al., 2011; PAWAR et al., 2017). As acetyl donors used for polysaccharide acetylation, the acetyl-CoA molecules, lack an acetyltransferase domain and the Golgi lipid membrane is impermeable to acetyl-CoA, RWAs are proposed to be a transporter of such

molecules from the cytoplasm to the Golgi lumen (GILLE et al., 2011; MANABE et al., 2013; PAWAR et al., 2017; XING; POIRIER, 2012). Therefore, RWAs facilitate the transport of acetyl CoA through the membranes in order to provide the base material for the two O-acetyltransferases families to complete the acetylation process (AXY9 and TBLs) (XING; POIRIER, 2012). There are four RWA proteins found in the Arabidopsis genome used for O-acetylation of polysaccharides, and mutants with loss-of-function of all four members of the RWA exhibited a 63% reduction in total wall O-acetylation (MANABE et al., 2013).

Both acetylation and deacetylation mechanisms are essential, as many important plant functions and biological processes depend on highly regulated hemicelluloses substitution patterns by acetyl groups, and excess acetylation may be as detrimental as low acetylation (ZHANG et al., 2017). The main enzymes involved in xylan deacetylation are xylan esterases, which have the ability to hydrolyze the ester linkages between acetyl groups and the xylan backbone. The deacetylation of arabinosyl branches in arabinoxylan from grasses was studied to show this protein family activity (CHRISTOV; ALEXANDER, 1993; DIALLO et al., 2019; ZHANG et al., 2017) and different acetyl xylan esterases act on different acetyl positions (BIELY, 2012; DEWHIRST; MORTIMER; JARDINE, 2020; NEUMÜLLER et al., 2015; PAWAR et al., 2013). If acetylation of monomers was performed previously to the polymerization, this can give rise to deacetylation (hydrolysis) during the process.

1.2 Acetylation influence in the biological functions

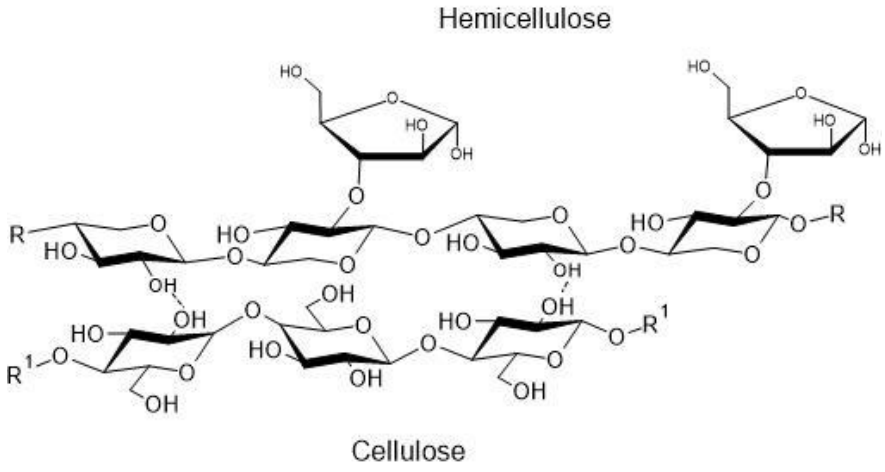
The biological significance of hemicelluloses O-acetylation pattern in plants is wide and, in many cases, not fully evident. Some studies indicate that controlling the cell wall acetylation pattern may be a meticulous mechanism to manipulate the cell wall properties and structure, thereby adjusting the plant's biological functions, such as flexural properties of wood, polysaccharide interaction, plant growth, and stress resistance, aiming, for instance, wood industrial application: wood processing, pulping and bioconversion (GAO et al., 2017; GRANTHAM et al., 2017; JOHNSON et al., 2017; PAULY; RAMÍREZ, 2018; VOGEL et al., 2004; YAN et al., 2018; ZHANG et al., 2017; ZHU et al., 2014).

Xylan acetylation influences directly the interaction between polymers present in the cell wall, which affects the rigidity of the cell wall and different physiological plant functions (GRANTHAM et al., 2017; PAULY et al., 2001). The bonding between hemicelluloses and cellulose fibrils is likely to influence the strength, flexibility, and elasticity of walls, and contribute to the resistance of the walls to enzymatic degradation, whereas separation of xylan

from cellulose is essential in many industrial processes (GRANTHAM et al., 2017). Therefore, knowledge of cellulose and hemicelluloses interactions and the molecular organization in cell walls is vital for industrial sectors such as food, construction, paper, and bioenergy, in which hemicelluloses are mostly applied.

The linkage of hemicelluloses to cellulose hydrophilic surfaces occurs through several hydrogen bonds, which prevents cellulose crystals from aggregating (Figure 18). Less substituted hemicelluloses form aggregate with low solubility, which adsorbs efficiently on the cellulosic surface (ANDREWARTHA; PHILLIPS; STONE, 1979; KABEL et al., 2007). The presence of acetyl groups on the hemicelluloses backbone decreases hemicelluloses placing on the cellulose surface, which is modulated by the acetylation pattern and degree of substitution (KABEL et al., 2007; KANG et al., 2019; KÖHNKE; ÖSTLUND; BRELID, 2011; MAZEAU; CHARLIER, 2012).

Figure 18 - Non-acetylated hemicelluloses interaction with cellulose

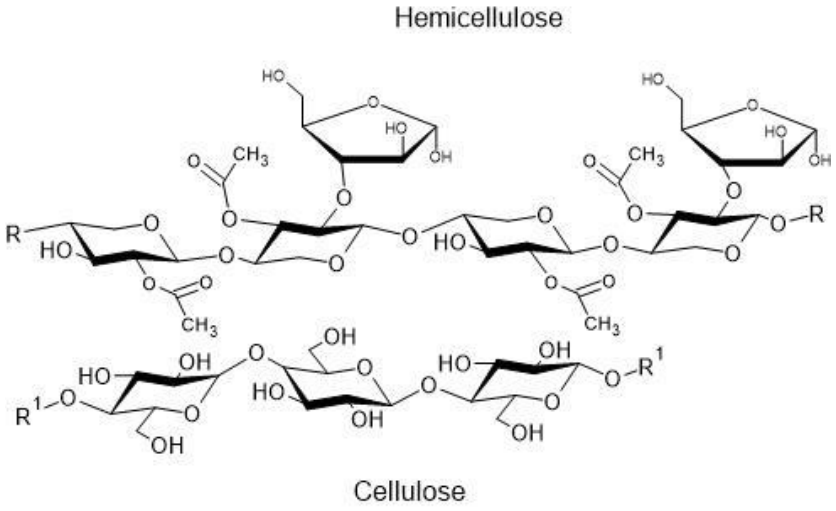


Source: author

Relatively hydrophobic acetyl substituents linked to hydroxyl groups on both sides of the hemicelluloses backbone hinder xylan interactions with cellulose hydrophilic surface (

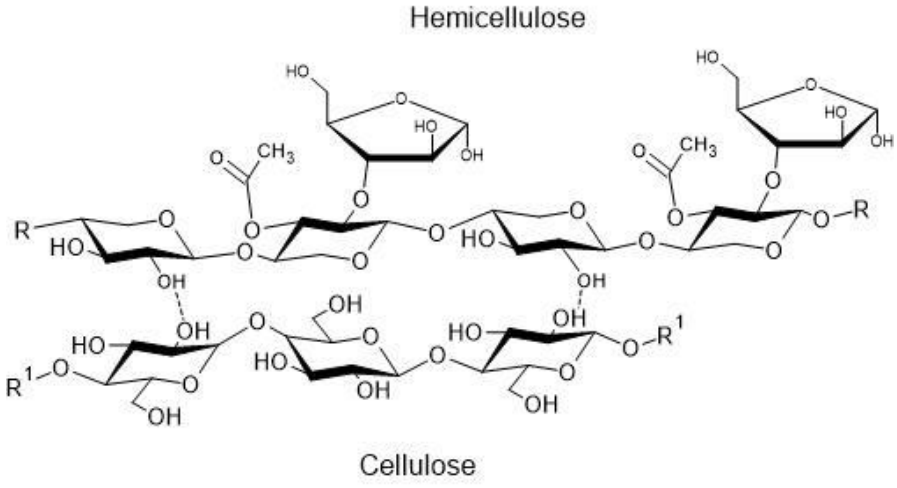
Figure **19**). If these acetyl groups are present on only one side of the hemicelluloses chain, it is possible for the other side to link to cellulose, avoiding the hindrance usually caused by hemicelluloses acetylation (Figure 20) (BUSSE-WICHER et al., 2014).

Figure 19 - Both sided acetylated hemicelluloses interaction with cellulose



Source: author

Figure 20 - One-sided acetylated hemicelluloses interaction with cellulose

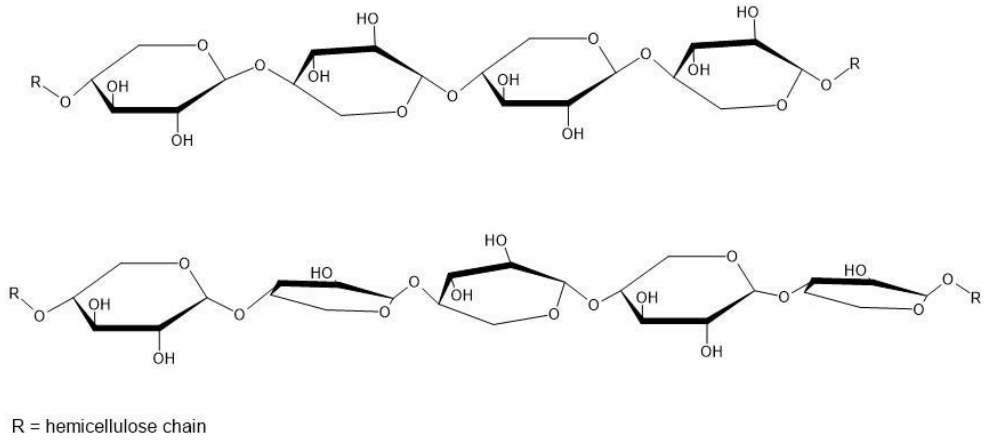


Source: author

There are two possible conformations for xylan backbones: minor domains with three xylose residues per turn, known as threefold screws, and major domains with two xylose residues per turn, known as twofold screws, which is similar to the cellulose two-screw fold structure (Figure 21) (SIMMONS et al., 2016). The major domain xylan, with a twofold screw, does not form aggregates with each other, instead, it enters as a rigid, less hydrated layer on the grooves of hydrophilic cellulose microfibrils, with which it forms hydrogen bonds, whereas xylan with three residues per turn, forms more viscous and swollen layers (JAAFAR et al.,

2019; PEREIRA et al., 2017; SIMMONS et al., 2016). O-acetylation is vital in such conformation, as acetyl groups present in O-2 position of the xylan backbone favor the twofold screw structure, and acetyl groups present in O-3 position stabilize the complex formed between xylan and cellulose, whereas deacetylated xylan is mostly found in the threefold conformation (PEREIRA et al., 2017).

Figure 21 - Xylan backbone twofold screw and threefold screw conformations



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Therefore, hemicelluloses interaction with cellulose depends directly on acetyl distribution, and precise hemicelluloses acetylation is necessary for its binding with cellulose and other wall polymers in plant cell walls. Any change in acetylation pattern will not only affect its interaction with these polymers but will also cause misfolding of the hemicelluloses backbone (GRANTHAM et al., 2017; PAULY et al., 2001). It is worth mentioning that, in addition to acetyl, hemicelluloses can also present other substitution groups, such as (methyl)glucuronic acid, which also impacts its binding to cellulose (BUSSE-WICHER et al., 2014).

A patterned secondary cell wall is found surrounding xylem vessels responsible for facilitating the translocation of water and nutrient through the plant. Therefore, hemicelluloses acetylation influences its functionalization, and both lowered and excess acetylation may alter xylem vessel properties, influencing their biological functions (SCHULTINK et al., 2015; ZHANG et al., 2017). For that reason, changed hemicelluloses acetylation may cause plant dwarfism, the low mechanical strength of the stem, and collapsed vessels (BISCHOFF et al., 2010; LEE et al., 2011; SCHULTINK et al., 2015; XIONG; CHENG; PAULY, 2013).

Suppressing an enzyme responsible for hemicelluloses deacetylation, therefore, creates a mutant with a changed acetylation pattern, resulting in a plant with general retarded growth, which included reduced plant height, small panicle size, and reduced tiller number, therefore reflecting in substantially decreased biomass yield and grain weight (ZHANG et al., 2017). Such dwarfism may be explained by a reduction in polysaccharide content in the plant, as a changed substitution pattern alters hemicelluloses solubility and hinders its secretion from the Golgi apparatus to the cytoplasm, which results in the accumulation of intracellular aggregates containing xyloglucan (GENDRE et al., 2013; KONG et al., 2015). However, such influence is relative and depends on the degree of substitution and pattern of distribution of acetyl groups in hemicelluloses, as well as plant growth conditions. Xyloglucan completely lacking sidechain O-acetyl substitution presented no apparent alteration on plant development and growth of *Arabidopsis* originated from Taynuilt, Scotlan (GILLE et al., 2011). In aspen, when testing a moderate decrease in xylan acetylation, there was no sign of decreased plant growth, and biomass saccharification was improved (PAWAR et al., 2016). Many structural abnormalities and increased saccharification were observed as a result of excess acetylation in rice (ZHANG et al., 2017), while low acetylation affected plant development and secondary cell wall patterning, as a 55 % reduction in xylan substitution by acetyl groups caused reduced growth, resulting in specimens with varying degrees of dwarfism (GAO et al., 2017). A mutant with an 80 % decrease in xylan O-acetylation exhibited a severe growth defect, much smaller and darker green leaves, and alterations in xylem structure, with collapsed xylem vessels (SCHULTINK et al., 2015).

Acetylation of plant cell wall polymers was obtained through an evolutionary process, also, as a mechanism of protection of plant tissues from possible physical and biochemical attacks, as the presence of acetyl groups reduces the efficiency of polysaccharides hydrolases released by pathogens. The protection of the plant against environmental and biotic stresses depends on the cell wall rigidity and stiffness, which is influenced, among other factors, by hemicelluloses acetylation (BACETE et al., 2018; GILLE; PAULY, 2012).

Resistance to external stresses such as pathogens attacks and freezing conditions have been proved to be influenced by members of the TBL protein family. As TBLs are known to be directly related to polysaccharide O-acetylation patterns, it is possible to connect such characteristics to the biological influence of wall polysaccharides O-acetylation (GILLE; PAULY, 2012; LIU et al., 2016). It was indicated by in vitro polysaccharides experiments that O-acetylation inhibits the action of enzymes, presumably through conformational changes of the polymer or steric hindrance (GILLE; PAULY, 2012). In order to overcome such

evolutionary gain and be able to consume plant cell walls, some pathogens evolved to secrete a variety of acetyl esterases proteins, which deacetylate polymeric hemicellulosic molecules (PAWAR et al., 2016). Mutant with reduced o-acetylation presented low resistance to leaf blight, as the lesion length in its leaves caused by the pathogen were threefold longer than those of wild-type plants (GAO et al., 2017).

When facing environmental stress, plant cell wall modification is the first line of defense, and plant esters, such as methyl and acetyl, are responsible for sensing and signaling routes that stimulate such modifications (AMSBURY et al., 2016; DEWHIRST; MORTIMER; JARDINE, 2020; LEE et al., 2011). The acetate from the cell wall, present in polysaccharides acetyl groups, is released and subsequently transported into the environment, as volatile organic compounds. The plant immune response is activated by such signaling, as it results in damage-associated molecular patterns, indicating the role of cell wall-derived acetate in signaling immune responses (BACETE et al., 2018).

Acetylation showed an influence on heat stress tolerance in plants, as it reduced the decarboxylation of many important cell polymers by providing an alternative carbon source, from cell wall-derived acetate (DEWHIRST; MORTIMER; JARDINE, 2020). On the other hand, an increased survival rate was seen when exposing Arabidopsis plants with reduced acetylation to severe drought stress, due to low water loss, resulting in more drought tolerance than wild types (YAN et al., 2018).

1.3 Acetylation influence on industrial applications

Plant biomass has been widely used in many industrial segments, such as paper, bioethanol, packaging, and other consumer goods. However, O-acetylation may be problematic for some applications, and deacetylation may facilitate processes such as pulping, saccharification, and fermentation. For bioethanol production, an important step is the hydrolysis of polysaccharides into monosaccharides, which are then fermented to ethanol. The tighter associations with cellulose from deacetylated hemicelluloses or hemicelluloses with a low degree of acetylation make isolation of entire wall materials difficult, resulting in the need for more extreme treatments for the separation of biomass components. Also, during enzymatic hydrolysis, hemicelluloses acetylation causes steric hindrance in the binding of many enzymes applied, which reduces the enzymatic yield and increases the process costs, as a larger number of enzymes is required (PAWAR et al., 2016). An improve in saccharification sugar yields were found due to a reduction of 30 % in arabidopsis xylan acetylation, as hemicelluloses were more

easily extracted when applying hot water and alkali pretreatments, showing increases in the amounts of reducing sugars of up to 20 % after enzymatic hydrolysis by β-1,4-endoxylanases and significantly increasing fermentation yields up to 70 % in ethanol production (PAWAR et al., 2016).

Hemicelluloses O-acetylation may be advantageous in other industrial applications, such as bioplastic production, due to its influence on gelling properties, viscosity, hydrophobicity, interactions with other polymers, solubility, and thermal stability (BUSSE-WICHER et al., 2014, 2016; HUANG et al., 2002).

Acetylation of the hydroxyl groups of hemicelluloses increases its hydrophobicity, as acetyl groups occupy hydroxyl groups, hindering hydrogen bonding to water molecules, creating resistance to water and thus increasing possible applications of hemicelluloses derivatives (MUGWAGWA; CHIMPHANGO, 2020b). Acetylated hemicelluloses hydrophobicity depends on the degree of acetylation achieved, and decreases in water solubility from 46 % to 2.4 % and in moisture content from 63 % to 12 % were observed upon acetylation (AKKUS; OZKAN; BAKIR, 2018). Hemicelluloses with a degree of substitution of 1.7 were less hydrophobic than that with a degree of substitution of 0.45, showing that, although hemicelluloses acetylation influences its interaction with water, there are other factors involved, and hydrophobicity is not a direct function of the degree of acetylation only (BUSSE-WICHER et al., 2014; MUGWAGWA; CHIMPHANGO, 2020a). Due to their relative hydrophobicity, acetylated hemicelluloses are often used as the main polymer in bioplastic formation; however, they may be applied as a co-polymer with polycaprolactone as active packaging. In such a case, the hemicelluloses acetylation reduced bioplastic solubility by 82.8 % (MUGWAGWA; CHIMPHANGO, 2020b). In addition, bioplastic formed with acetylated hemicelluloses presented reduced solubility of 12.57 % in the fatty food simulant, when compared to bioplastics formed with polycaprolactone and low-density polyethylene (MUGWAGWA; CHIMPHANGO, 2020b).

Acetylation may also lead to conformational changes, by occupying hydroxyl groups, making them less available for hydrogen bonding between hemicelluloses chains and therefore reducing the formation of hemicellulosic networks. This process also contributes to the gelling properties and viscosity of the isolated hemicelluloses, as an increased degree of acetylation leads to more elastic gels, which is an important matter for food applications (HUANG et al., 2002; ROMBOUTS; THIBAULT, 1986).

Wheat straw hemicelluloses chemically acetylated to a degree of substitution between 0.59 and 1.25 presented enhanced thermal stability due to the reduction in the amount of free

hydroxyl groups, which go through oxidation when heated (EGÜÉS et al., 2014; FANG et al., 1999; FUNDADOR et al., 2012). The bioplastic formed with acetylated arabinoxylan also showed an increase in thermal stability, with maximum weight loss with high heating at 375 ºC (EGÜÉS et al., 2014; FUNDADOR et al., 2012).

2. Chemical hemicelluloses acetylation

For hemicelluloses industrial application, a method widely applied for its solubilization from biomass is the alkaline treatment of lignocellulosic materials, which cleaves the linkages between hemicelluloses and lignin and swells cellulose, decreasing its crystallinity (BRIENZO et al., 2016). During this process, as the high pH of the solution causes a split-off of acetyl groups from hemicelluloses chains, deacetylation occurs, consequently forming acetic acid (PENG et al., 2012) (Figure 22). Therefore, when hemicelluloses application is other than obtaining sugars by hydrolysis, extracted hemicelluloses are used often after modifications. When the industrial application intended requires hemicelluloses with a certain acetylation degree of substitution, chemical acetylation is necessary. Chemical acetylation leads to esterified acetyl groups on free hydroxyl groups in the polysaccharides (Figure 23).

Figure 22 - Cleavage of hemicelluloses acetyl groups in alkaline media

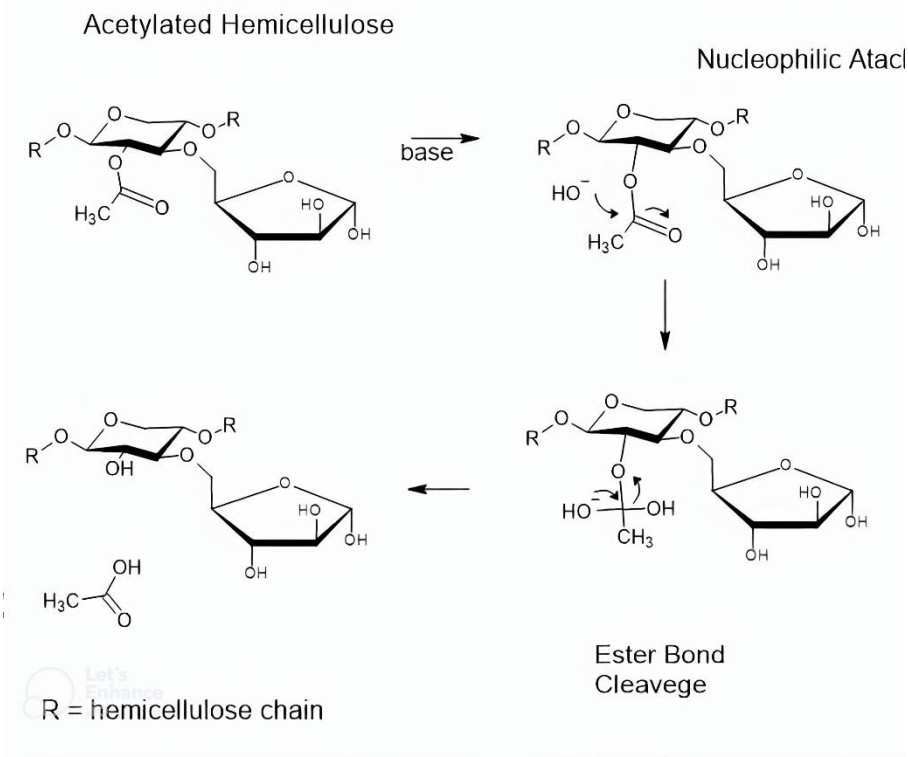

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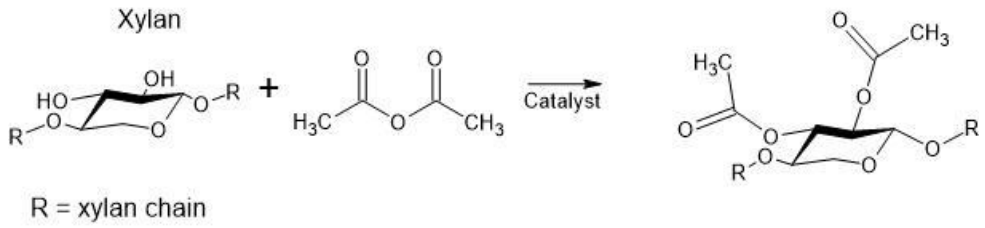
Figure 23 - Hemicelluloses chemical acetylation reaction



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A variety of acetylation methods have been studied, resulting in different substitution degrees and patterns, in which the most common reaction of hemicelluloses acetylation is based on acetic anhydride as acetyl donor and esterification agent. Hemicelluloses may be acetylated with their previous separation from other biomass components, or directly from biomass, varying reaction conditions such as the solvents and catalysts applied, and the methods of analyzing and quantifying the acetylation achieved. Some reaction conditions that may influence resulted acetylation are reaction temperature and time, acetic anhydride ratio to hemicelluloses hydroxyl groups, the presence of salt in the biomass (AKKUS; OZKAN; BAKIR, 2018), previous hemicelluloses organosolv treatment (MUGWAGWA; CHIMPHANGO, 2020a), among others. The following topics addressed the role of reaction solvents and catalysts, and tables 1 and 2 summarize results found in the literature by hemicelluloses acetylation with different solvents and catalysts.

Table 1 – Results of acetylation reaction applying different solvents

Biomass component	Solvent	Time (h)	Temp (ºC)	Result	Reference
Corncob hemicelluloses	No solvent	0.25 - 8	60 - 120	Weight gain due to acetylation varying from 0.1 to 23.5 %	AKKUS; OZKAN; BAKIR, 2018
Softwood	No solvent	0.5 - 8	120	Weight gain due to acetylation varying from 12 to 22.3 %	SUN et al., 2019
Cornstalk	No solvent	0.5 - 8	90	Acetyl content varying from 3.65 to 11.20 % (w/w)	JIANG et al., 2014
Soy sauce hemicelluloses	AmimCl	0.5	100	Acetylation DS of 1.65	CHEN et al., 2015
Soy sauce hemicelluloses	BmimCl	0.5	100	Acetylation DS of 1.57	CHEN et al., 2015
Soy sauce hemicelluloses	BmimOH	0.5	100	Acetylation DS of 1.53	CHEN et al., 2015
Switchgrass hemicelluloses	AmimCl	1 – 20	24 - 95	Acetylation DS varying from 0.03 to 1.25	AYOUB et al., 2013
Rye arabinoxylan	(Emim)(OAc)	20	50	Substitution varying from non-acetylated to fully acetylated	STEPAN et al., 2013
Rye arabinoxylan	(Amim)(Cl)	20	50	Substitution varying from partially acetylated to fully acetylated	STEPAN et al., 2013
Poplar hemicelluloses	(EmimAc)	2 - 8	75	Acetylation DS varying from 0.17 to 0.37	ZHU et al., 2020
Wheat straw hemicelluloses	Dmac/LiCl	12 - 72	60 - 85	Acetylation DS varying from 0.74 to 1.49	SUN et al., 1999a
Hardwood kraft pulp xylan	Dmac/LiCl	0.5 - 6	50	Acetylation DS varying from 0.6 to 2.0	FUNDADOR et al., 2012
Eucalyptus xylan	DMSO	24	25	Acetylation DS varying from 0.09 to 1.48	MORAIS DE CARVALHO et al., 2019
Wheat straw hemicelluloses	N,N-DMF-LiCl	2 - 72	60 - 90	Acetylation DS varying from 0.59 to 1.25	FANG et al., 2000

Table 2 - Results of acetylation reaction applying different catalysts

Biomass component	Catalyst	Time (h)	Temperature (ºC)	Result	Reference
Extracted wheat bran arabinoxylan	No catalyst	24	25	Acetylation DS of 1.2	YILMAZ-TURAN et al., 2020
Commercial wheat bran arabinoxylan	No catalyst	24	25	Acetylation DS of 1.7	YILMAZ-TURAN et al., 2020
Hemicelluloses from soy sauce residue	No catalyst	0.3 – 1	80 – 120	Acetylation DS varying from 0.76 to 1.68	CHEN et al., 2015
Hemp fibers	No catalyst	3	25	Acetylation confirmed by FTIR analysis	KABIR et al., 2013
Wheat straw hemicelluloses	Iodine	1	85 – 100	Acetylation DS varying from 0.49 to 1.53	REN et al., 2007
Wheat straw hemicelluloses	Sulfuric acid	1	50	Acetylation DS of 1.7	MUGWAGWA; CHIMPHANGO, 2020a
Oat Spelts Xylan	Sulfuric acid	8 - 24	25	Acetylation DS of 0.85	HETTRICH et al., 2005
Corn fiber arabinoxylan	Methanesulfonic acid	1 - 14.5	35 – 60	Acetylation DS varying from 1.58 to 2.33	BUCHANAN et al., 2003
Wheat straw hemicelluloses	4-dimethylamino pyridine	12 – 72	60 – 85	Acetylation DS varying from 0.74 to 1.49	SUN et al., 1999a
Rye arabinoxylan	Pyridine	30	25	Full acetylation	STEPAN et al., 2012
Locust bean gum galactomannan	Pyridine	17 – 30	25	Acetylation DS varying from 0.2 to 2.5	(BI et al., 2016
Corncob arabinoxylan	Pyridine	30	25	Acetylation DS of 1.9	EGÜÉS et al., 2014)
Corncob hemicelluloses	Pyridine	30	25	Acetylation DS of 1.8	GORDOBIL et al., 2014
Poplar wood	Pyridine	1	80	Decrease in wood accessibility by 45 %	YANG et al., 2020

2.1.Reaction solvents

2.1.1. No solvent

Hemicelluloses acetylation has been studied without the presence of any solvent in the reaction, either after hemicelluloses solubilization from biomass (AKKUS; OZKAN; BAKIR, 2018), or through the reaction of the whole biomass such as softwood (SUN et al., 2019), and corn stalk (JIANG et al., 2014). The absence of a solvent in acetylation may reduce the reaction costs and create a more environmentally friendly process, as it reduces the amount of waste generated. However, the yield of acetylation may be compromised, as solvents are usually applied in order to dissolve hemicelluloses, breaking hydrogen bonding between their molecules and making hydroxyl groups available for the esterification reaction.

2.1.2. Ionic Liquids

Lignocellulosic biomass polymers such as cellulose and hemicelluloses usually form tight inter and intramolecular networks of hydrogen bonds, which makes them insoluble in most of the commonly applied industrial solvents (ABUSHAMMALA; MAO, 2020; HIMMEL et al., 2007; PARTHASARATHI et al., 2011), and the solvents currently available are either toxic for humans or detrimental for the environment. Therefore, more environmentally friendly solvents for wood processing are being searched for (ABUSHAMMALA; MAO, 2020).

In this sense, ionic liquids (ILs) have emerged and are known as “green solvents” for biomass polysaccharides solubilization. They are salts, consisting of ion pairs of cations and anions, that are found liquefied at temperatures below 100 ºC (ABUSHAMMALA; MAO, 2020; HU et al., 2020; SINGH; SAVOY, 2020). They possess unique properties that make them attractive for use, such as high thermal and chemical stability, low vapor pressure, non-flammability, a broad electrochemical window, low melting point, recyclability, and environment-friendliness (ABUSHAMMALA; MAO, 2020; HU et al., 2020; HUDDLESTON et al., 2001; WANG; GURAU; ROGERS, 2012). ILs are known to present strong interaction forces between their constituting ions, which results in low vapor pressure and low volatilization. This prevents the release of potentially harmful compounds during use, handling, and transportation, which is one of the reasons why they are considered green solvents in general (ROGERS; SEDDON, 2003). ILs are, therefore, excellent substitutes for the currently applied corrosive and toxic solvents in chemical processes using wood (ABUSHAMMALA;

MAO, 2020; KRINGSTAD; LINDSTROM, 1984; THOMPSON et al., 2001). For that reason, together with the degree of success in wood dissolution, ionic liquids are a rapidly developing technology, attracting great interest in research for their application as chemical compounds (BARTLEWICZ et al., 2020).

A disadvantage that ILs carry is their very high prices. In 2021, the dissolution of the same amount of hemicelluloses would cost up to 20 times more when using ILs instead of regularly applied organic solvents such as dimethylformamide and dimethylsulfoxide (MORAIS DE CARVALHO et al., 2019; SIGMA-ALDRICH, 2021; STEPAN et al., 2013; YILMAZ-TURAN et al., 2020). However, these prices have already been decreasing and are predicted to continue to drop due to the development of the ionic liquids market. Nevertheless, the recovery and reuse of the IL is a required step after biomass processes to be successful on an industrial scale, compensating for the high prices invested.

The recovery of ionic liquids may be hindered due to possible losses through its degradation in high temperatures applied in polysaccharides dissolution (LI et al., 2011). Through side reactions and polysaccharides depolymerization, oligomers or sugar degradation products, which are difficult to be recovered from the ionic liquid, may be generated (ABUSHAMMALA; KROSSING; LABORIE, 2015; ABUSHAMMALA; MAO, 2020; KÖHLER et al., 2007; SINGH; SAVOY, 2020). To remove such oligomers, one possible technique is to evaporate the ionic liquids. However, such a process would demand a high-energy input in order to reach ionic liquids boiling point, which would increase the process costs (BRENNAN et al., 2010; LIPSCOMB et al., 2012). When recovering EmimAc ionic liquid from a mixture of hemicelluloses, minor impurities were found, such as hemicelluloses contaminants and their degradation products, and further effort would be needed to recover the IL with high purity (HU et al., 2020). AmimCl applied for hemicelluloses acetylation was recovered by evaporating the filtrate, and reused for the same process at least four times, resulting in a similar degree of substitution values (CHEN et al., 2015). Some possible solutions for ionic liquid recovery would be the use of nanofiltration membranes (AVRAM et al., 2017; WANG et al., 2016), electrodialysis (ENDO et al., 2017; SATRIA et al., 2017), and the addition of moderately polar acetonitrile (DA COSTA LOPES; ŁUKASIK, 2018).

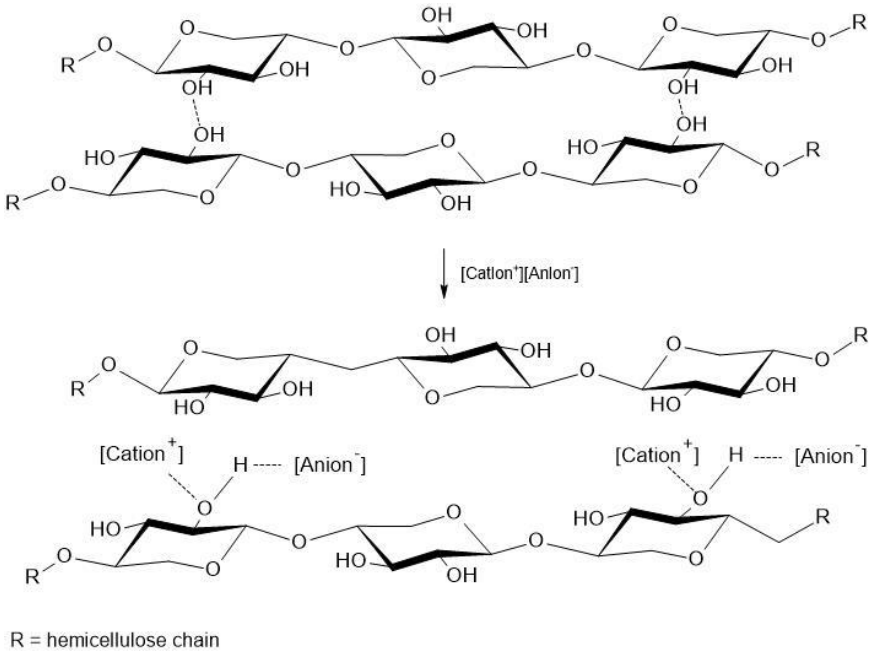
ILs are widely known as “green solvents”, and assessments of their life cycle show that the majority of ILs are non-toxic and biodegradable (HOSPIDO; RODRÍGUEZ, 2019). However, in some cases, large amounts of chemicals are needed for the synthesis of ILs, which results in the generation of side products as waste (FRADE; AFONSO, 2010). Also, ILs may

leash to water and soil (STEPNOWSKI; MROZIK; NICHTHAUSER, 2007; THUY PHAM; CHO; YUN, 2010), and some studies have shown that there could be a toxic effect of ionic liquids in humans, animals (DOCHERTY; HEBBELER; KULPA, 2006; PRETTI et al., 2006; WELLS; COOMBE, 2006), and microorganisms (DOCHERTY; KULPA, 2005; PERNAK; GOC; MIRSKA, 2004; PERNAK; SOBASZKIEWICZ; MIRSKA, 2003).

There is a large structural diversity of cations and anions that may compose an ionic liquid, comprehending a wide range of applications and promoting the opportunity of selecting the most suitable ions for each case (ABUSHAMMALA; MAO, 2020; SEDDON, 1997; SHAMSHINA; ZAVGORODNYA; ROGERS, 2019). It is also possible to control the properties of the ionic liquids to be applied, such as density, melting point, electrical conductivity, viscosity, and hydrophobicity, in accordance with each case (ABUSHAMMALA; MAO, 2020; JOHNSON, 2003; PLECHKOVA; SEDDON, 2008).

The mechanism of action of ionic liquids to dissolve biomass polymers is believed to be mainly by the disruption of the inter and intramolecular hydrogen bonds, and the stronger the interaction between IL and biopolymers, the higher the solubilization (MOYER et al., 2018) (Figure 24). However, other reactions may be involved depending on the conditions applied, such as the hydrolysis of polymers molecules and their chemical derivatization (ABUSHAMMALA; MAO, 2020). For the processing of lignocellulosic biomass, ionic liquids based on 1-alkyl-3-alkyl imidazolium $[Amim]^+$ as cation has been the most commonly applied, as $[Amim]^+$ cation is small and presents a double bond, which facilitates its attack on the oxygen atom in the hydroxyl groups (ABUSHAMMALA; MAO, 2020; ZHANG et al., 2005). When it comes to the choice of anion for the synthesis of ionic liquids, the small size of chloride and its ability to accept hydrogen bonds results in the most effective anion to dissolve cellulose and hemicelluloses, in comparison to large anions, with weak interaction with cations. Therefore, the most commonly used ionic liquids for the dissolution of wood polymers are 1-Ethyl-3-methylimidazolium acetate ([EMIM][OAc]), 1-Allyl-3-methylimidazolium chloride ([AMIM][Cl]), and 1-Butyl-3-methylimidazolium chloride ([BMIM][Cl]) (XIE et al., 2015).

Figure 24 - Hemicelluloses solubilization in ionic liquid



Source: author

The use of ILs to dissolve hemicelluloses has been shown to keep its core structure almost unchanged, with no apparent degradation, with only a slight decrease in its thermal stability (HU et al., 2020). When applying various imidazolium-based ionic liquids to dissolve guar gums under mild conditions, the integrity of the chain with high molecular weight was maintained after modification (LACROIX et al., 2012). The recovery of the biomass material from ionic liquids after dissolution occurs commonly by the re-precipitation of the polysaccharides by adding an anti-solvent solution such as water or ethanol (AMARASEKARA, 2019).

2.1.3. Dipolar aprotic solvents

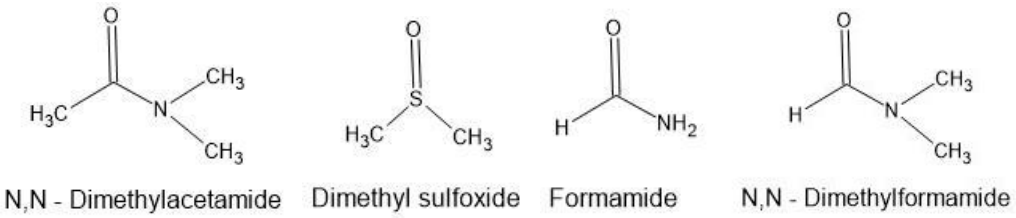
Dipolar aprotic solvents have been applied in hemicelluloses dissolution, with the aim of its isolation from the biomass or to manipulate such polysaccharide after its isolation. They are powerful bases with high hydrogen-bond acceptation, resulting in strong interactions with substances that are strong hydrogen-bond donors (PARKER, 1969; REICHARDT; WELTON, 2011). The dissolution of the polysaccharide occurs by the substitution of one molecule of the aprotic solvent by the hydroxyl group of hemicelluloses (DUPONT, 2003). The most common

dipolar aprotic solvents applied for hemicelluloses dissolution are formamide or N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO) (Figure 25).

Formamide ($HCONH_2$) is an aprotic substance, and its molecules may present hydrogen bonds between the C=O and N–H groups, with, on average, two hydrogen bonds per molecule (BELLISSENT-FUNEL; NASR; BOSIO, 1997). Liquid formamide exhibits mainly a three-dimensional N–H–O hydrogen bond network (PUHOVSKI; RODE, 1995), which results in relatively high viscosity and a low self-diffusion coefficient. Liquid formamide also presents a small number of small clusters and cyclic dimers participating in the H-bond network (PUHOVSKI; RODE, 1995). Successful hemicelluloses dissolution in formamide occurs through strong hydrogen bonding with –NH and =O groups (ANTONIOU et al., 2010).

Dimethyl sulfoxide (DMSO) ($(CH_3)_2SO$) is a highly dipolar aprotic solvent, important for industrial and biological applications as a drug carrier and cryoprotection (LUZAR; CHANDLER, 1993). As its oxygen atom from the S=O group presents two lone electron pairs, a single DMSO molecule may form simultaneously four strong O–H··O hydrogen bonds with hemicelluloses molecules, resulting in high dissolution (ANTONIOU et al., 2010; BORDALLO et al., 2004). Such substances are usually applied with a co-solvent, and the most common is lithium chloride (LiCl). The polar aprotic nature of such chemicals allows ionic compounds such as LiCl to dissolve in them readily, extensively solvating their cations (STRIEGEL, 1997). This solvent system may be described as a complex between lithium and the aprotic substance, with a free chloride anion, i.e. $[Li + DMAc]^+ Cl^-$., $[Li + DMSO]^+ Cl^-$ and $[Li + DMF]^+ Cl^-$.

Figure 25 - Molecular structure of dipolar aprotic solvents



Source: author

An ion-dipole complex is formed, in the form of [DMAc + Li]+ macrocation, in which the lithium cations reside adjacent to the oxygen of the carbonyl group of DMAc, while the

chloride anions are free in the solution. This conformation is the base of the generally accepted mechanisms for hemicelluloses dissolution by this solvent system (DUPONT, 2003). Due to its basicity, the chloride anion interacts with the hydroxyl hydrogens of hemicelluloses, by strong bonding similar to their bonding to hydroxyl oxygen atoms, which weakens the hydrogen bonds of the polysaccharide. Hemicelluloses molecules are then pushed afar due to the intra-chain electrostatic repulsion known as a polyelectrolyte effect, which results in its chain extension. Then, further disruption of hemicelluloses hydrogen bonding occurs due to a continuous influx of solvent, caused by the high osmotic pressure, until hemicelluloses are dissolved (MEDRONHO; LINDMAN, 2014). Through such a process, LiCl also prevents hemicelluloses reaggregation, by forming hydrogen bonds with the polysaccharide (PETRUŠ; GRAY; BEMILLER, 1995). The process occurs more readily with chloride than when other anions are applied, such as the bromide anion, which is more tightly bound to the solvent (MEDRONHO; LINDMAN, 2014; STRIEGEL, 1997). When it comes to the cations' solvation by DMAc and DMF, lithium has shown to be more easily solvated, when compared to sodium, potassium, and cesium (STRIEGEL, 1997).

Lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) is a promising solvent system for polysaccharides dissolution as it doesn't cause derivatization of cellulose and hemicelluloses (QI et al., 2017). Hemicelluloses were shown to dissolve in LiCl/DMAc with no degradation and without the formation of chemical bonds between the solvent system and the polysaccharide molecule (EL-KAFRAWY, 1982; STRIEGEL, 1997). However, it was seen to cause a slight decrease in the intrinsic viscosity of polysaccharide solutions (MCCORMICK; CALLAIS; HUTCHINSON, 1985)

Experiments showed that DMF and DMSO were less effective in dissolution, or caused more degradation of the polysaccharide molecule than DMAc (STRIEGEL, 1997). A possible reason is the highest electron density, and, therefore, electrostatic potential, at the carbonyl oxygen, which is where the lithium cation is supposed to be bounded (STRIEGEL, 1997). Therefore, DMAc/LiCl is proposed to be a fine solvent for a great variety of polysaccharides (STRIEGEL, 1997).

2.2.Catalysts

2.2.1. No catalyst

Although catalysts have been shown to increase acetylation rates, many studies have successfully acetylated hemicelluloses without the use of any catalyst, only applying acetic anhydride as the esterifying agent. Such process has been applied both for the acetylation of hemicelluloses previously solubilized from biomass (AKKUS; OZKAN; BAKIR, 2018; AYOUB et al., 2013; MORAIS DE CARVALHO et al., 2019; YILMAZ-TURAN et al., 2020; ZHU et al., 2020) and for the acetylation of the whole biomass (JIANG et al., 2014; KABIR et al., 2013; SUN et al., 2019).

2.2.2. Iodine

In carbohydrate acetylation reactions, in which acetic anhydride is applied as an esterifying agent, iodine transforms in iodide (KONIECZNY; LOOS, 2018) which is responsible for activating the carbonyl present in acetic anhydride, increasing its reactivity and an excellent acylating reagent, as the iodine-acetic anhydride system results in a favorable disposition of the electron density (KARTHA, 1986). This method was already used by several groups for carbohydrates modification, such as cellulose acetylation (GILLE et al., 2011; HO; CHIN; PANG, 2020; NEMR; RAGAB; SIKAILY, 2017; YADOLLAHI et al., 2019) and esterification of starches (BARTZ et al., 2015; CHANG; LV, 2017; KONIECZNY; LOOS, 2018), while reactions of hemicelluloses acetylation using iodine as a catalyst are still scarce in the literature.

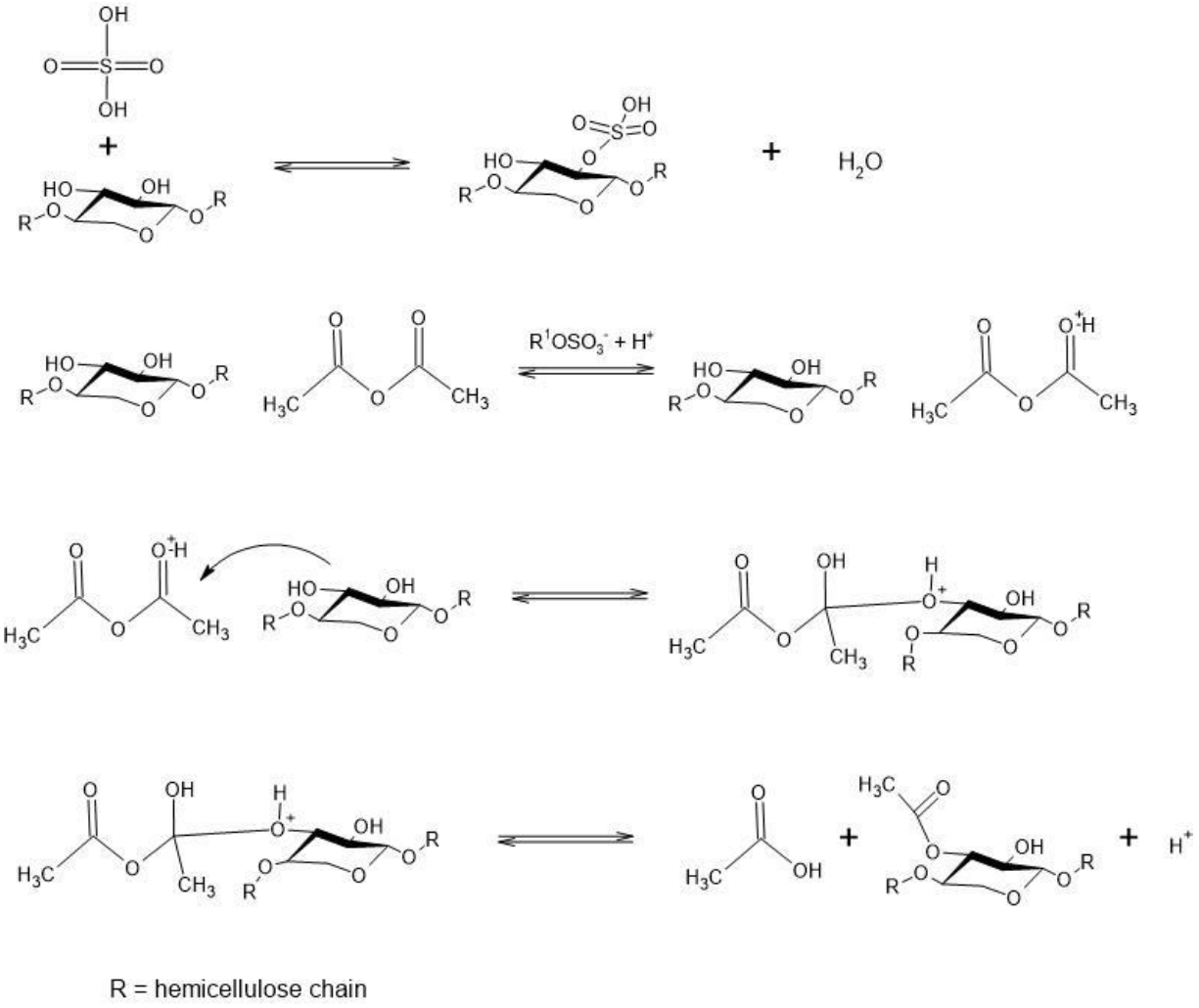
2.2.3. Strong sulfur-based acids

Homogeneous catalysts such as sulfuric and methane sulfonic acids are frequently used in organic synthesis (SANZ et al., 2007; VAN LEEUWEN, 2004). However, these acid catalysts bring some disadvantages such as their toxicity, corrosivity, harmfulness, and difficulty to handle, and their disposal may bring complications for the chemical industry (FARINA, 2004). Also, when used in polysaccharide derivatization reactions, these acids may lead to cleavage of acid-sensitive glycosidic linkages and loss in molecular weight. Sulfuric acid is one of the most promising homogenous acid catalysts for industrial organic synthesis,

because of its high activity and low cost (TING et al., 2008). Methanesulfonic acid has shown to be a very effective catalyst for the esterification reaction of polysaccharides, with low hydrolysis of polysaccharides molecules and little molecular weight loss at moderate temperatures (BUCHANAN et al., 2003).

The acid-catalyzed esterification reaction of polysaccharides can be considered to occur in two steps. In the first stage, the reaction between the acid and the hemicelluloses generates the catalyst R–O–SO3H, which catalyzes the esterification process in the following step (MURAD et al., 2018; ZENG et al., 2012). The second stage begins with the protonation of the carbonyl oxygen on the carboxylic group of acetic anhydride molecule, thereby activating the nucleophilic attack by the hydroxyl group from hemicelluloses to form a tetrahedral intermediate (LOTERO et al., 2005). Disproportionation of this intermediate complex ultimately yields the ester (LIU; LOTERO; GOODWIN, 2006) (Figure 26). Based on this process, the absence of water is required in acid-catalyzed esterification, in order to avoid the competitive formation of carboxylic acids and concomitant reduction in the yields of desired esters products (KAUSHIK; KUMAR; KUMAR, 2008; STOFFEL; CHU; AHRENS, 1958).

Figure 26 - Acid-catalyzed hemicelluloses acetylation



Source: author

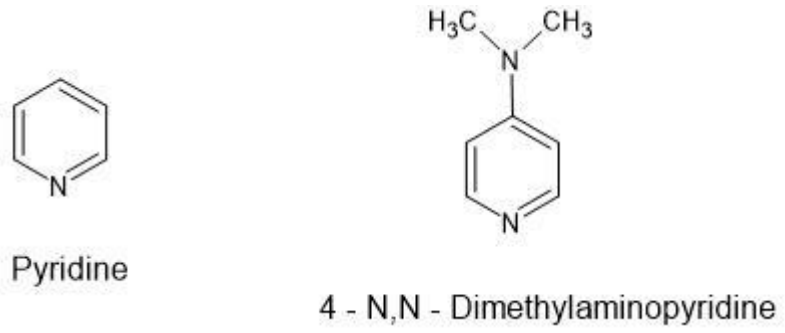
2.2.4. Pyridine and derivatives

Pyridine is a six-membered, one nitrogen containing heterocyclic ring compound (BHASKARUNI et al., 2020), and 4-dimethyl aminopyridine is a derivative of such molecule (Figure 27). Pyridine and 4-dimethyl aminopyridine are commonly applied catalysts in hemicelluloses acetylation reactions (BI et al., 2016; EGÜÉS et al., 2014; FANG et al., 2000; GORDOBIL et al., 2014; STEPAN et al., 2012, 2013; SUN et al., 1999a; YANG et al., 2020). They are usually applied when using formamide or N,N-dimethyl formamide as a reaction solvent (BI et al., 2016; EGÜÉS et al., 2014; FANG et al., 2000; GORDOBIL et al., 2014; STEPAN et al., 2012), which represents a nonaqueous swelling system, resulting in

homogeneous reaction conditions. However, such catalysts have also been applied in ionic liquids (STEPAN et al., 2013) and without the presence of any solvent (YANG et al., 2020). When they are applied as catalysts in esterification reactions, the use of nonpolar solvents boosts their performance, as solvent polarity greatly stabilizes reactants in specific steps of esterification, which impedes continuity of the reaction (DE RYCKE; COUTY; DAVID, 2011).

DMAP is the precursor of nitrogen-based nucleophilic catalysts, and its application brings a dramatic enhancement of kinetics, in which the reaction is accelerated by a factor of 6000 when compared to pyridine. This highlights the central role played by the strong donating ability of an amino moiety (DE RYCKE; COUTY; DAVID, 2011; LITVINENKO; AMANMURADOV; ABUBAKIROV, 1967). In many cases, it is necessary to use only 0.05-0.2 mol of catalyst per mol of substance (HOFLE; STEGLICH; VORBRUGGEN, 1978). However, DMAP brings the disadvantages of slight hemicelluloses hydrolysis and difficulty in handling, as it is a very toxic compound, and contact of DMAP with the skin should therefore be avoided because of the danger of local and systemic effects (Hofle et al., 1978; R. Sun et al., 1999).

Figure 27 - Pyridine and 4-N,N-Dimethyl aminopyridine molecular structure

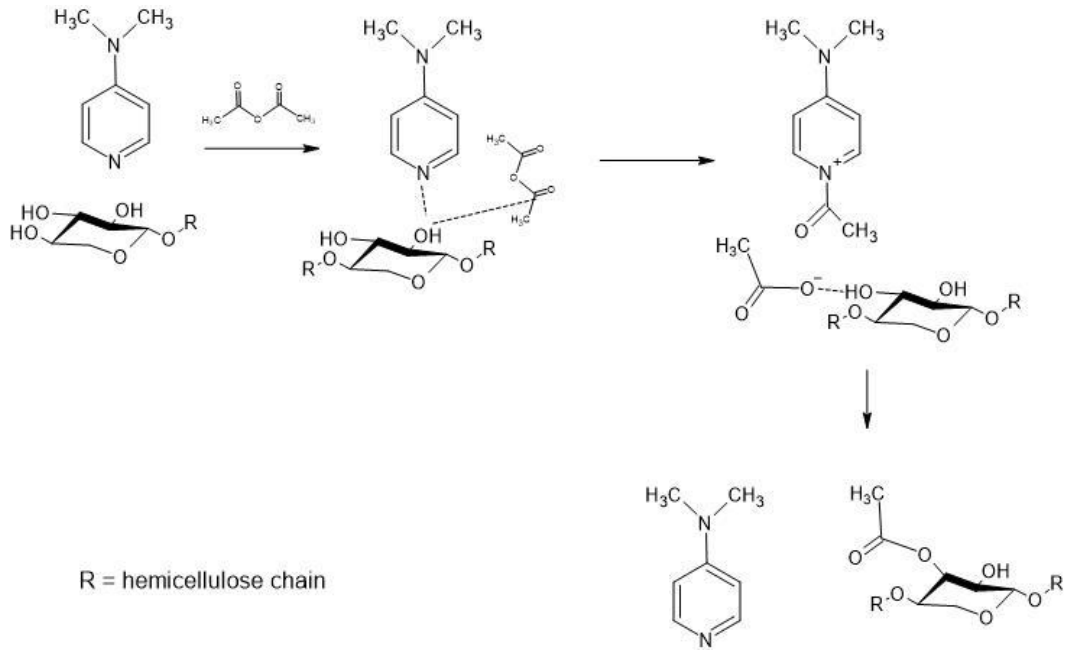


Source: author

The catalytic effect of DMAP in hemicelluloses acetylation begins with the formation of a stable complex between the hydroxyl group from hemicelluloses and DMAP through hydrogen bonding. Meanwhile, the oxygen atom in such a hydroxyl group also interacts with the carbonyl group present in the acetic anhydride. Then, the nitrogen atom from DMAP, with the assistance of hemicelluloses hydroxyl group hydrogen bonding, attacks the carbonyl group of the acetic anhydride. A loose ion pair of acyl pyridinium acetate is then obtained, in which the acetate anion is complexed with hemicelluloses. After conformational rearrangement, the

oxygen atom from the hydroxyl group now attacks the acyl group with basic assistance from the acetate anion. A very stable complex between DMAP and acetic acid is thus produced; the latter showing a secondary interaction hydroxyl group from hemicelluloses, liberating the ester, producing hemicelluloses acetate (Figure 28) (DE RYCKE; COUTY; DAVID, 2011).

Figure 28 - DMAP-catalyzed hemicelluloses acetylation



Source: author

3. Evaluation of the acetylation reaction

After acetylation of hemicelluloses, the determination of the degree of acetylation and analysis of structure modifications are essential to indicate the success of the reaction. The most common way by wet chemistry to quantify the degree of acetylation is by saponification of the samples, followed either by HPLC analysis or titration. Other common methods, with a qualitative approach, are FTIR and NMR analysis, which have been widely applied. Gas-chromatography analysis, scanning electron microscope, and weight percentage gain can also be used to observe the modifications generated by the acetylation reaction.

3.1. Titration and HPLC

Classical determination of the degree of substitution of acetylated hemicelluloses by titration involves complete basic hydrolysis of the ester linkages and titration of the excess alkali (CHI et al., 2008). Frequently, the basic hydrolysis is conducted by a solution of NaOH, and the excess alkali is then titrated with a solution of HCl to the phenolphthalein endpoint (GORDOBIL et al., 2014; MUGWAGWA; CHIMPHANGO, 2020a, 2020b). The difference between the volume of HCl used to titrate the native and the acetylated sample will indicate how much NaOH solution was needed to hydrolyze the ester linkages. This value is used to calculate the percentage of acetyl content and the degree of substitution. Another similar method applied is by hydrolyzing ester linkages with NaOH, and then adding HCl solution to react and neutralize the excess alkali, followed by titration of the excess acid with NaOH solution, to the phenolphthalein endpoint (CHEN et al., 2015). In this case, the total volume of NaOH and HCl added are taken into consideration in order to calculate the percentage of acetyl content and the degree of substitution.

NaOH is also applied to hydrolyze ester linkages the following quantification by HPLC. In this case, NaOH is added to the acetylated hemicelluloses, and neutralization with 37 % HCl is applied previously to HPLC analysis in order to quantify released acetic acid (BI et al., 2016; DE CARVALHO et al., 2017; MORAIS DE CARVALHO et al., 2019; YILMAZ-TURAN et al., 2020).

3.2. Zemplén method

The methods described above for the quantification of acetyl groups in polysaccharides are based on the cleavage of the ester bounds of such acetyl groups and subsequent quantification of the released acetic acid, by titration or chromatographic techniques. However, such approaches bring one general problematic deficiency, as they end up quantifying both bound and free acetate, not being able to distinguish between them (ZWECKMAIR et al., 2014). Thereby, analytical results may be widely misleading, as those methods just observe the total acetate present, and acetate released from the bounded ester groups cannot be differentiated from free acetic acid present in the samples (ZWECKMAIR et al., 2014).

To overcome such issue, the Zemplén reaction may be applied, which is the reaction between sodium methanolate and acetyl groups, resulting in the formation of methyl acetate,

which is quantified by gas-chromatography (ZEMPLÉN; GERECS; HADÁCSY, 1936; ZWECKMAIR et al., 2014). As only the covalently bound acetyl groups are transesterified in this reaction and free acetic acid is converted into sodium acetate in the highly alkaline sodium methanolate solution, this method is able to differentiate between them (ZWECKMAIR et al., 2014).

3.3. Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) may also be applied to evaluate the success of the acetylation reaction, in a semi-quantitative approach. It is based on the magnetic properties that nuclei of atoms carry, which can be utilized to yield chemical information in a strong constant magnetic field, in which nuclei are perturbed and respond with an electromagnetic signal with a frequency characteristic of the nucleus analyzed. This process allows identifying the composition of the desired samples.

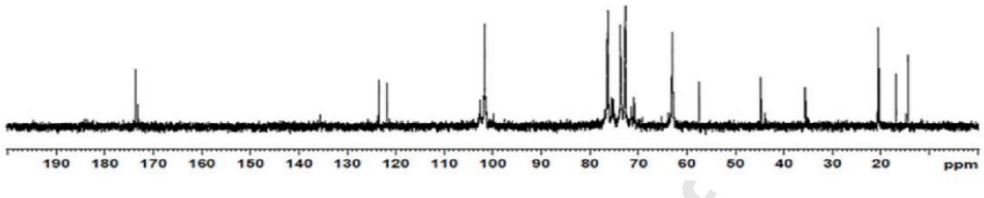
For hemicelluloses acetylation, the observed features and respective ^{13}C NMR signals are displayed in Table 3. In ^{1}H NMR spectroscopy, the main signal that confirms hemicelluloses acetylation is at around 2 ppm, which indicates the methyl protons of acetyl groups (ZHU et al., 2020). The appearance of acetylated hemicelluloses ^{13}C NMR and ^{1}H NMR spectroscopy are provided in Figure 29 and Figure 30, respectively.

Table 3 - Acetylated hemicelluloses features and respective 13C NMR signals

Signals regions (ppm)	Features
20 - 21	Methyl group of an aliphatic acetyl group
99 - 100	Anomeric carbon peaks of 2-O-Ac-β-D-Xylp
~102	Anomeric carbon peaks of 3-O-Ac-β-D-Xylp
169 - 170	Carbonyl group in an esterified acetyl group
173 - 174	Acetyl group at positions C2 and C3 of xylose

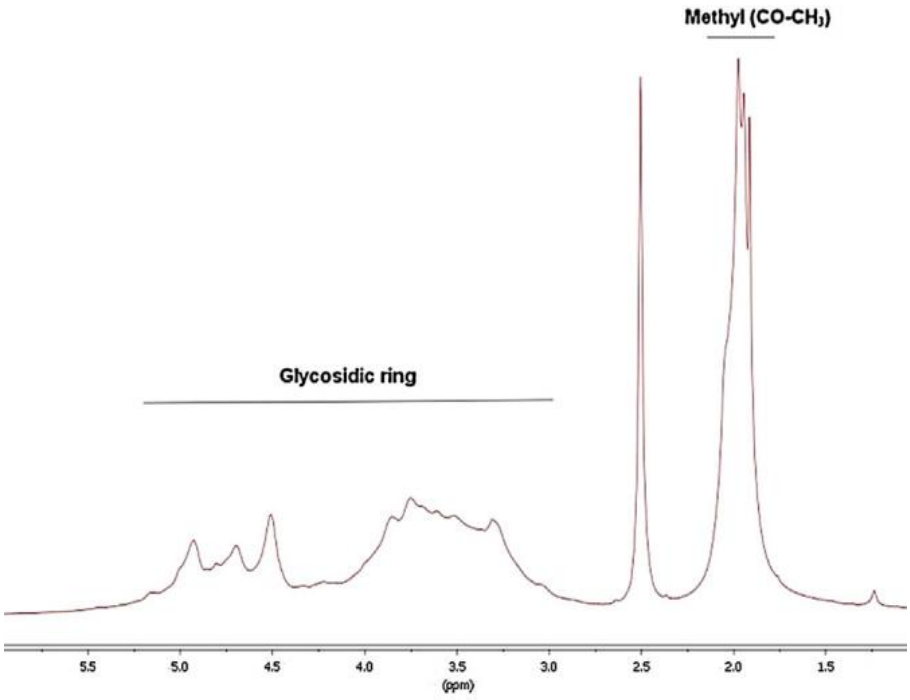
Source: HETTRICH et al., 2005; REN et al., 2007; ZHU et al., 2020

Figure 29 - Acetylated hemicelluloses 13C NMR spectrum (in DMSO-d6)



Reference: ZHU et al., 2020

Figure 30 - Bleached acetylated hemicelluloses 1H NMR spectrum (dissolved in DMSO-d6).



Reference: GORDOBIL et al., 2014

^{1}H NMR spectroscopy has been used to indicate the success of acetylation reaction, and also to determine the degree of acetylation obtained. A possible method is to compare the area of peaks of methyl protons of ester chains, present in acetyl groups, indicated around 2.0 ppm, with the area of peaks of anomeric proton of xylans, indicated around 4.5 ppm, or with the area of peaks that indicates all carbohydrate signals, between 3.2 and 5.3 ppm (AYOUB et al., 2013; BELMOKADDEM et al., 2011; BUCHANAN et al., 2003; EGÜÉS et al., 2014; GORDOBIL et al., 2014)

3.4.Weight percentage gain

The weight percentage gain of the samples has also been applied in order to demonstrate the success of the acetylation reaction, as the addition of acetyl groups would increase hemicelluloses mass (AKKUS; OZKAN; BAKIR, 2018; SUN et al., 2019; YANG et al., 2020). In xylan, for instance, the maximum weight gain would be 65 % when an acetylation DS of 2 is obtained. However, there may be possible interference in the results by moisture contamination and hemicelluloses degradation during the reaction.

3.5.Fourier Transform Infrared Spectroscopy – FTIR

Fourier Transform Infrared is an analytical technique widely applied in order to evaluate hemicelluloses acetylation, by observing the changes in sample chemical linkages (AKKUS; OZKAN; BAKIR, 2018; AYOUB et al., 2013; BERTOTI; LUPORINI; ESPERIDIÃO, 2009; BI et al., 2016; CHEN et al., 2015; GORDOBIL et al., 2014; JIANG et al., 2014; KABIR et al., 2013; REN et al., 2007; STEPAN et al., 2013; SUN et al., 2019; SUN; HUGHES, 1999; ZHU et al., 2020). Such a method is based on infrared radiation of about 10,000 to 100 cm^{-1} passed through the sample, in which part of such radiation is absorbed, while the rest passes through, depending on the sample structure. The sample molecules convert the absorbed radiation into rotational and/or vibrational energy, which generates a signal that is detected as a spectrum, typically from 4000 cm^{-1} to 400 cm^{-1}, representing a molecular fingerprint of the sample (POURYA; ABDOLNABI; SOLTANI, 2021).

Table 4 shows the absorption spectra bands that are taken into consideration in FTIR analysis in order to analyze hemicelluloses acetylation. It is understood that an increase in linkages found in acetyl groups, such as C-O, C-CH_3, and C=O indicates an increase in acetylation degree, likewise a reduction in O-H stretching vibration, indicates a decrease in the amount of hydroxyl groups available.

Table 4 - Assignments of absorption IR spectra bands that indicate hemicelluloses acetylation

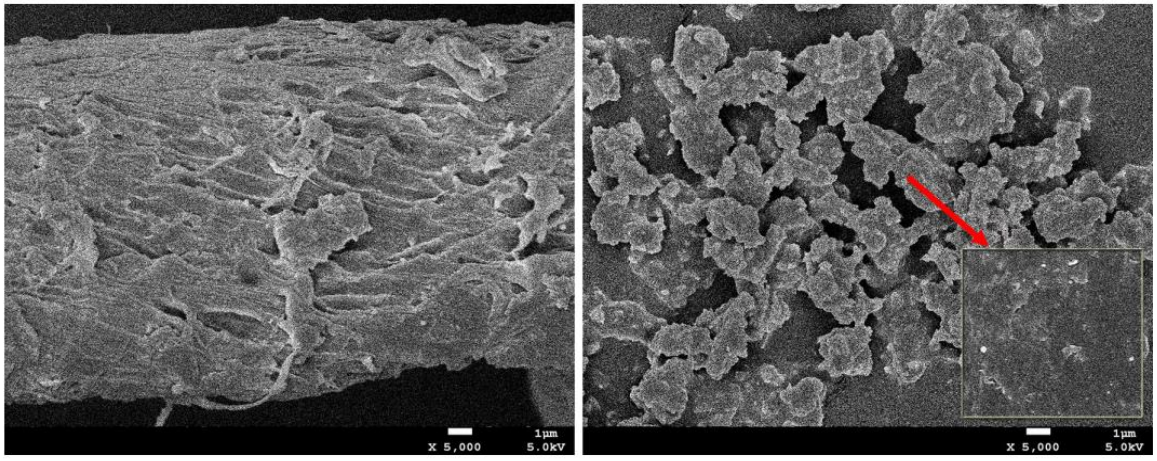
Wavenumber (cm-1)	Assignments and remarks
1233-1248	C-O stretching
1372-1376	C-H deformation
1738-1752	C=O stretching
3349-3420	O-H stretching

Source: PANDEY, 1999; SAIKIA et al., 1995; SUN; HUGHES, 1999; ZHAO; WANG; LIU, 2008

3.6.Scanning Electron Microscope

Also, for qualitative analysis, a scanning electron microscope (SEM) may be used in order to detect visual alterations on the acetylated hemicelluloses surface, as well as to analyze its morphology (CHEN et al., 2015; KABIR et al., 2013). Native hemicelluloses can be seen in the form of fibers, whereas acetylated hemicelluloses have been shown to present a small, broken, and irregular structure, which have a smooth surface, which can be assumed to result from the acetyl groups (CHEN et al., 2015). Figure 31 shows SEM electron microscopy micrograph of native and acetylated hemicelluloses.

Figure 31 - Scanning electron microscopy (95000) micrograph of native hemicelluloses (left) and acetylated hemicelluloses (right)



Reference: CHEN et al., 2015

4. Acetylated hemicelluloses for bioplastic production

Traditional plastic used in industrial food packaging is mostly non-renewable petroleum-based synthetic materials. Hemicelluloses found in renewable biomass resources, as a naturally abundant biopolymer, share the advantages of being biodegradable in the environment, biocompatible, and presenting bioplastic-forming properties that can be therefore used as food packaging, in replacement of the petroleum-based synthetic polymers (HANSEN; PLACKETT, 2008; ZHAO et al., 2020). To cast hemicelluloses-based bioplastics, it is important to determine some features such as polysaccharides content, the application of a plasticizer, and the use of a convenient solvent.

Seeking an improvement to hemicelluloses bioplastic mechanical properties, such as its brittleness, the addition of plasticizers has been proved effective to a certain extent, as it breaks hydrogen bonds between hemicelluloses molecules, increasing free volume and chain fluidity (HARTMAN et al., 2006; MENDES et al., 2017; ZHAO et al., 2020). However, some disadvantages that have been seen when applying plasticizers are the decrease of tensile strength and the enhancement of bioplastic hydrophilicity, leading to slightly increased water absorption of the bioplastic (HARTMAN et al., 2006; XU et al., 2019).

In non-acetylated polysaccharide-based bioplastic, frequently added plasticizers are polyols, such as glycerol, sorbitol, xylitol, and polyethylene glycol, as their structure resemble those of the polysaccharides, and their hygroscopic nature allows them to attract water vapor and retain it in the system (FERNÁNDEZ-BOLANOS et al., 2001; MENDES et al., 2017; MIKKONEN et al., 2012).

The efficiency of each plasticizer depends on its molecular size, shape, number of oxygen atoms, spacing of oxygen atoms, and water binding ability (ANTONIOU et al., 2014; HAQ; HASNAIN; AZAM, 2014; MENDES et al., 2017; MIKKONEN et al., 2007). Glycerin presents a relatively small molecular size, which facilitates its insertion and fixation in the hemicelluloses matrix, resulting in the best plasticization effect, while the addition of sorbitol as plasticizes results in a higher tensile strength (XU et al., 2019). However, the mentioned plasticizers present a hydrophilic structure, which may hinder its application along with highly acetylated hemicelluloses, that have a hydrophobic feature. Recently, triacetin has been used as a nonpolar plasticizer (YILMAZ-TURAN et al., 2020). Still, as acetylation replaces the hydroxyl groups, therefore reducing the tendency of hydrogen bond network formation, acetylated hemicelluloses bioplastic itself shows increased flexibility, which might compensate

for the lack of utilization of a plasticizer, as acetyl groups perform an internal plasticization (PETZOLD-WELCKE et al., 2014).

For bioplastic casting, the use of water as a solvent is the most basic method for xylan applications in novel sustainable materials. However, such route sometimes must be reviewed as, depending on biomass characteristics such as plant source and separation methods, xylan is not always able to form cohesive bioplastics.

Xylan from barley husk, for instance, was able to form bioplastics only by water casting regardless of the isolation method, among acidic or enzymatic pretreatment, chlorite or organosolv delignification, and extraction with aqueous alkali (HÖIJE et al., 2005), while glucuronoxylan from hardwood required the addition of xylitol or sorbitol as plasticizers in order to form bioplastics (GRÖNDAHL; ERIKSSON; GATENHOLM, 2004). Xylan isolated from sugarcane bagasse through two different methods, either through a one-step alkaline peroxide solution method or through a two-step alkaline extraction-delignification method could both form bioplastics with the addition of sorbitol as a plasticizer, distinguishing only in the bioplastic final properties (JIN et al., 2019). Highly acetylated hemicelluloses hydrophobic structure may hinder the use of water for bioplastic casting, which has been substituted by other solvents, such as chloroform (EGÜÉS et al., 2014; FUNDADOR et al., 2012; GORDOBIL et al., 2014; STEPAN et al., 2012, 2013), tetrahydrofuran (AYOUB et al., 2013), DMSO (MUGWAGWA; CHIMPHANGO, 2020a, 2020b), dimethyl carbonate (STEPAN et al., 2013) and acetone (BUCHANAN et al., 2003).

4.1.Hemicelluloses acetylation influence on bioplastic features

Acetylated hemicelluloses have been applied for bioplastic formation especially due to the hydrophobicity such derivatization provides. However, the degree of acetylation has been found to influence other properties such as flexibility, elongation at break, tensile strength, stiffness, and oxygen and light barrier (HARTMAN et al., 2006; MENDES et al., 2017; ZHAO et al., 2020).

Tensile tests measure features such as the tensile strength and the elongation at break when pulling the bioplastic sample from opposite edges, which represent the force required to rip the sample, as well as the extent to which it elongates until reaching that breaking point, respectively. Young’s modulus is a mechanical property that measures the stiffness of solid material (CHADNI et al., 2020). Overall, the elongation is improved by acetylation due to the

internal plasticization caused by acetyl groups, and tensile strength and Youngs modulus are normally increased (EGÜÉS et al., 2014).

Hemicelluloses acetylation has shown to increase the tensile strength, the elongation at break, and the Young's modulus of the bioplastics formed from 33.4 MPa, 5.3 %, and 3 MPa in native hemicelluloses, to 44.1 MPa, 5.7 %, and 2300 MPa, respectively, in acetylated hemicelluloses with a DS of 1.8 (GORDOBIL et al., 2014). Acetylated arabinoxylans formed bioplastics with a tensile strength ranging from 55 MPa to 60 MPa, depending on the branching degree, as well as elongation at break ranging from 7 % to 22 % and Young's modulus ranging from 2000 MPa to 2500 MPa, which shows that the acetylation of arabinoxylan with a high arabinose content was able to produce flexible bioplastics without the need of an external plasticizer (STEPAN et al., 2012). Such enhancement of mechanical properties was also seen when bleached arabinoxylans presented tensile strength of 53.56 MPa, elongation of 8.17 %, and Young's modulus of 1432 MPa, while such values were increased to 67.30 MPa, 13.4 %, and 2241 MPa, respectively, for acetylated arabinoxylans with a DS of 1.9 (EGÜÉS et al., 2014).

However, it is important to bear in mind that such mechanical properties are not only influenced by hemicelluloses degree of acetylation, but also by the presence of other substituents in its chains and by hemicelluloses molar mass. Acetylation reaction conditions were responsible for hydrolyzing arabinoxylan molecule, which decreased its molar mass and resulted in inferior mechanical properties of tensile strength of 10.3 MPa, elongation at break of 7.2 %, and Young's modulus of 318.3 MPa, when compared to native arabinoxylan, which presented tensile strength of 26.7 MPa, elongation at break of 17 % and Young's modulus of 752.0 MPa (YILMAZ-TURAN et al., 2020). Also, when creating xylan derivatives with both acetyl and propionyl side groups, the increase in the DS from 0.6 to 1.1 resulted in a reduction in tensile strength and elongation at break from 48 MPa to 46 MPa and 10 to 8 %, respectively (FUNDADOR et al., 2012).

A common way of testing bioplastics hydrophilicity is by the water contact angle (WCA). When placing a drop of water on the bioplastic surface, it will spread based on the intermolecular interactions, and the contact angle between the water and the bioplastic surface indicates how wet the solid bioplastic is, in which the higher the measured angle, the more hydrophobic is the bioplastic.

Using bleached hemicelluloses with glycerol as a plasticizer, the resulting bioplastic showed a WCA around 57 º, while the bioplastic elaborated by acetylated hemicelluloses with

a DS of 1.8 without any plasticizer showed a WCA of 72 º (GORDOBIL et al., 2014). The same phenomenon was seen by acetylation of bleached corncob arabinoxylan to a DS of 1.9, which increased WCA from 77.6 º to 82.1 º (EGÜÉS et al., 2014). Also, when preparing bioplastics based on arabinoxylans, the nonacetylated bioplastics soak water rapidly, with a WCA of 0 º, while the acetylated bioplastics presented a WCA ranging from 61 º to 66 º, depending on the arabinoxylan debranching degree (STEPAN et al., 2012). However, other characteristics of hemicelluloses may influence bioplastic hydrophobicity, despite its degree of acetylation.

Residual lignin content and arabinose/xylose ratio in arabinoxylan, as produced by organosolv treatment previous to acetylation, had a more significant influence on the hydrophobicity of the resulting bioplastic than the arabinoxylan acetylation degree. Bioplastics made from hemicelluloses with a DS of 0.4 had higher a WCA of 68.1 º than those made from hemicelluloses with a DS of 1.7, with a WCA of 39.9 º (MUGWAGWA; CHIMPHANGO, 2020a).

Acetylation may also cause alteration of the solubility of the bioplastics in different media, which is a recognized method to assess the stability of packaging material, such as in aqueous, acidic, alcoholic, and fatty food simulants (SANCHES SILVA et al., 2007; THE EUROPEAN COMMISSION, 2011). The solubility of the biobased bioplastics in water is of special interest, as their disintegration when in contact with food containing humidity must be avoided, due to possible effects on the integrity of the bioplastic and the quality of the packaged food, as well as possibly being a health hazard to consumers (BHUNIA et al., 2013; GAVRIIL; KANAVOURAS; COUTELIERIS, 2018). The increase in the acetylation degree of polysaccharides reduced the solubility of a bioplastic based on acetylated hemicelluloses and acetylated nanocellulose, from 30.88 % to 16.30 %, in the food simulants (MUGWAGWA; CHIMPHANGO, 2020b). Furthermore, strong hydrophobic networks were formed between acetyl groups of both polysaccharides, which restricted water absorption and bioplastic swelling when in water-based simulants (FORTUNATI et al., 2012; MUGWAGWA; CHIMPHANGO, 2020b).

The hydrophobic character of acetylated hemicelluloses bioplastics also influences the water vapor sorption, which is calculated by the weight of water absorbed in an environment with controlled humidity, in ratio with the bioplastic initial weight (STEPAN et al., 2012). When testing the water sorption at a relative humidity of 97 %, it was seen that the acetylated bioplastic interacted with water to a low extent, since its water content was 8 %, when compared to non-acetylated samples, with water content ranging between 6 and 7 % (STEPAN et al.,

2012). A similar analysis of water vapor permeability is of great importance when applying biobased bioplastics for food packaging, as it influences the exposure of food to external humidity, and may prevent it from losing water content by evaporation. The bioplastics of acetylated arabinoxylan with a DS of 1.4 had a water vapor permeability value of 1.9 g mm /kPa m^2 d, which was significantly lower when compared to the permeability of 2.9 g mm /kPa m^2 d of the corresponding non-plasticized bioplastics of the native arabinoxylan, as acetylation reduced the water affinity of the bioplastics (KOCH et al., 2014; YILMAZ-TURAN et al., 2020). However, when plasticizer was applied to native non-acetylated arabinoxylan bioplastics, the water vapor permeability was even lower, reaching 0.7 g mm /kPa m2 d, which suggests that plasticization is also a suitable strategy to improve the water barrier properties of bioplastics (YILMAZ-TURAN et al., 2020).

Hemicelluloses-based bioplastics generally present a good oxygen barrier, as the hydrogen bonds between adjacent polysaccharide chains create a dense macromolecular network, which contributes to good packing of the molecules and thus low gas permeability (CHADNI et al., 2020; HEIKKINEN et al., 2013). For that reason, when acetylated arabinoxylan with a DS of 1.4 was applied to bioplastic formation, which reduces the formation of hydrogen bonding in polysaccharides, the oxygen permeability increased majorly from 0.8 to 154.9 cm^3 μm/m^2 d kPa (YILMAZ-TURAN et al., 2020).

One of the main influences of acetylation of biobased bioplastics is the increase in its thermal stability, by the reduction of the number of hydroxyl groups, which are oxidized during heating (EGÜÉS et al., 2014; FANG et al., 1999; FUNDADOR et al., 2012). The thermal stability is analyzed by the degree of degradation of the bioplastics in high temperatures, and high thermal resistant behavior after the acetylation process is desired for thermoplastic processing conditions. Another important thermal property when applying polysaccharides for bioplastic formation is the glass transition temperature. Such temperature marks the point of transition from which the physical properties of plastics behave similar to those of a glassy state, to which they behave like rubbery materials, with gaps between the molecular chains 2.5 times higher (MCKEEN, 2014).

Acetylated arabinoxylan bioplastics presented thermal decomposition at around 380 ºC and a temperature range for the glass transition region, at 130 – 220 ºC, when varying the ratio of debranching of arabinoxylan (STEPAN et al., 2012). The thermal decompositions of biobased bioplastics from acetylated hemicelluloses with a DS of 1.4 initiated at 322.4 ºC, with a maximum temperature of 351.3 ºC and mass loss of 50.8 %, which was an increase, when

compared to native hemicelluloses, whose thermal decomposition initiated at 243.7 ºC, with a maximum temperature of 284.2 ºC and mass loss of 65.6 % (YILMAZ-TURAN et al., 2020). Also, the glass transition temperature decreased from 44.7 ºC to 18.1 ºC by acetylation (YILMAZ-TURAN et al., 2020). A small mass loss was found at around 205 ºC, with a maximum weight loss rate observed at 299 ºC for biobased bioplastics with native hemicelluloses, with a solid residue above 20 % at 600 ºC, while acetylated bioplastics with a DS of 1.8 started to decompose at 302 ºC and had a maximum decomposition rate at 368 ºC, and an 18.5 % solid residue at 600 ºC (GORDOBIL et al., 2014).

5. Concluding remarks

Hemicelluloses properties improvement is essential to use all plant biomass components for the commercial success of future biorefineries, besides hydrolysis and further fermentation, as this would bring new application opportunities as energy and materials, reducing or compensating for processing costs. The development of green pathways that apply environmentally friendly solvents, catalysts, and reactants for hemicelluloses derivatization, mainly acetylation, must be considered in future studies, and once these novel acetylation methodologies become well understood, combining them into industrial-scale production could lead to a more sustainable future and decreased environmental impact. As one example in a short-term application, acetylated hemicelluloses have great potential in establishing relevance in the packaging industry. Therefore, materials properties can be improved by combining functionalized hemicelluloses with different biopolymers and polymers, giving rise to a new family of not-rigid and linear polymers.

CHAPTER IV: NOVEL RENEWABLE BIOPLASTICS FORMULATION BY XYLAN ACETYLATION AND STARCH, WITH OIL AND WATER VAPOR BARRIER

ABSTRACT

In 2015, greenhouse gas emissions caused by plastics were equivalent to 1.7 gigatons of CO_2. However, by 2050, emissions are projected to increase to 6.5 gigatons, which shows the urgency in replacing such materials by renewable ones. This process requires for the renewable materials to present competitive properties, when compared to traditional plastics. Hemicelluloses are a group of a plant cell wall polysaccharides that could have its applications expanded with acetylation. Acetylation may enhance xylan bioplastics properties, such as mechanical strength and water vapor barrier. However, xylan bioplastics may be brittle and acetylated xylan requires the application of costly or hard to handle solvents, such as chloroform or dimethylsulfoxide. By partially acetylating xylan in the present study, it was possible to apply water as solvent for the filmogenic solution, and starch as a second polysaccharide in bioplastics formation. Acetylated xylan blended with starch in bioplastics formation is here reported for the first time. Xylan was modified by partial chemical acetylation, by varying reaction time and solvent and catalyst content. Reaction time influenced final acetylation as well as mass recovery. Bioplastics were formed by non-acetylated xylan, and acetylated xylan with DS of 0.45 and 0.9, with starch in order to form blends, and glycerol as the plasticizer. Acetylation with DS 0.45 showed better results in increase bioplastics hydrophilicity but still soluble in aqueous allowing combination with starch. Acetylation influenced the thermal stability of the bioplastics, increasing the maximum degradation rate temperature from 302 to 329 and 315 ºC. It was also responsible for increasing the bioplastics crystallinity and Young's modulus from 2.99 to 290.61 and 274.67 MPa to the non-acetylated bioplastic and bioplastic with a DS of 0.45 and 0.90, respectively. The DS acetylation of 0.9 affected bioplastics disintegration, which was only attested by ecotoxicity analysis. The bioplastics presented oil barrier properties for up to 30 days, suggesting a potential for diverse applications, especially in packaging, which comprises for the largest plastic sector.

Keywords: Bioplastic, Sugarcane Bagasse, Xylan, Acetylation, Water-Soluble, Chemical Modification.

1. Introduction

The significant growth of the world population and its consumption habits has led to an increase in the plastic materials production. Approximately 360 million tons of plastic were produced worldwide in 2018, leading to several negative impacts on the environment (PLASTICSEUROPE, 2020). Drastic loads of plastic debris are being dispersed over long distances in the ocean. When they finally settle in sediments, plastics may persist for centuries (GOLDBERG, 1997; RYAN, 1987).

Synthetic polymers are not directly consumed by microorganisms. Their degradation is a very slow process that involves environmental factors, such as light, heat, moisture, and chemical conditions. These agents cause the rupture in the bonds of macromolecules resulting in radical sites, which are essential for the action of microorganisms (DEVI et al., 2015; WILKES et al., 2017). Bioplastic based on renewable and biodegradable polysaccharides could collaborate to partially replace fossil-origin plastic.

Currently, new technologies and bioproducts are under study as an alternative for the mitigation of such environmental problems. However, a total replacement of synthetic plastics can hardly be considered in the short or even long term, due to the higher production costs and concerns over functionality. In this scenario, much effort has been directed to the application of biopolymers in the production of bioplastics, such as cellulose, hemicelluloses, and pectin. Such polysaccharides vary in structure and may be constituted by different sugars organized linearly through strong linkages among them, with or without branches and/or substituents in their backbones (ROJAS, 2016; ZHANG et al., 2019) For the formation of polysaccharide-based bioplastics, intra and intermolecular interactions and cross-links are formed between such polymeric constituents. This process creates a semi-rigid three-dimensional network (GUILBERTT; GONTARDS; CUQS, 1995; THARANATHAN, 2003). Different biopolymers used can bring some disadvantages when compared to synthetic plastics, such as high water vapor and oxygen permeability, brittleness, low thermal resistance, low mechanical properties, vulnerability to degradation, and high production costs (ABE et al., 2021; COLUSSI et al., 2017; GORDOBIL et al., 2014; KOCH et al., 2014; XIANG et al., 2014).

Hemicelluloses are a group of polysaccharides with great potential for bioplastics formation (GORDOBIL et al., 2014; MUGWAGWA; CHIMPHANGO, 2020b; YILMAZ-TURAN et al., 2020). They are renewable and widely available polysaccharides close to cellulose in lignocellulosic biomass, which can be potentially used in various fields, both in their native and modified forms (LI; PAN, 2018). In order to overcome hemicelluloses

drawbacks for packaging application, acetylation reaction has been widely investigated as chemical hemicelluloses modification (MARTINS; ABE; BRIENZO, 2022; MORAIS DE CARVALHO et al., 2019; STEPAN et al., 2012; YILMAZ-TURAN et al., 2020; ZHU et al., 2020). Acetylation is an esterification reaction that introduces acetyl groups into the hemicelluloses backbone. This chemical modification results in altered hydrophobicity of the molecule, as well as influencing other properties, such as thermal degradation and mechanical resistance. The increase in hydrophobicity of the compounds can be attributed to the substitution of the hydrophilic hydroxyl groups present in hemicelluloses by relatively hydrophobic acetyl groups. The presence of acetyl groups hinders the formation of hydrogen bonds between hydroxyl groups and water molecules, resulting in reduced water susceptibility (MUGWAGWA; CHIMPHANGO, 2020b).

The degree of acetylation dictates the hydrophobicity of the acetylated hemicelluloses, such as xylan. The non-acetylated xylan has shown partial solubility in hot water, as hydroxyl groups in its backbone are available for hydrogen bonding with water molecules. However, hydroxyl groups can also cause spontaneous intra-molecular hydrogen bonding between hemicelluloses chains, resulting in the formation of a crystalline network. The partially acetylated xylan, with a degree of acetylation of around 0.5, presented complete solubility in water, due to the presence of the free hydroxyl groups in the hemicelluloses chain, while acetyl groups hinder molecule aggregation (ZHU et al., 2020). Xylan molecules in which all the hydroxyl groups were acetylated, that is, with a degree of acetylation of 2, can be dissolved in non-polar solvents like chloroform and polar aprotic solvents like dimethyl sulfoxide (STEPAN et al., 2013). The solubilities of the acetylated hemicelluloses in organic solvents such as chloroform, dimethylsulfoxide, and tetrahydrofuran increase with the increase in the degree of substitution (SUN et al., 1999a).

Numerous methods for hemicelluloses acetylation have been reported to achieve varying degrees of substitution (DS) and controlled hemicelluloses properties (AKKUS; OZKAN; BAKIR, 2018; MORAIS DE CARVALHO et al., 2019; REN et al., 2007; SUN et al., 1999a; YILMAZ-TURAN et al., 2020; ZHU et al., 2020). In the present study, partial xylan acetylation was obtained, which allowed for the application of water as solvent in bioplastics formation, instead of costly or hard to handle solvents, such as chloroform or dimethylsulfoxide. Free hydroxyl groups in xylan also allowed the application of starch as a second polysaccharide and glycerol as plasticizer, which was responsible for a more cohesive and flexible bioplastic. For xylan acetylation, acetic anhydride was applied as an acetylation reagent, and sulfuric acid

was used as a reaction catalyst. Different reaction conditions were evaluated, achieving various degrees of acetyl substitution. The different DS aimed to obtain a xylan soluble in an aqueous medium, avoiding the use of hazardous solvents. Xylan with different acetylation degrees was employed in starch/xylan-based bioplastics. Acetylated xylan blended with starch in bioplastics formation is here reported for the first time and were evaluated for mechanical resistance, thermal degradation, water-solubility, oil barrier, disintegration, and ecotoxicity.

2. Materials and methods

2.1.Xylan Solubilization from Sugarcane Bagasse

Sugarcane bagasse *in nature* (without the previous removal of extractives or resins) supplied by the company Sao Joao (Araras—SP) was dried at 60 ºC for 24 h and milled in a knife mill (Marconi, MA 580 - Piracibaba/Brazil) using a 20 mesh (0.841 mm) sieve, in order to increase the surface contact and optimize the reaction yields (FERNANDES et al., 2020). For oxidative delignification, 200 mL of 6 % (w/v) hydrogen peroxide solution with the pH adjusted to 11.6 using NaOH (6 M) solution was mixed with 10 g of ground bagasse, and the mixture was stirred in a shaker (Solab, SL - 222) for 4 h at 25 °C at 110 rpm (ALVES et al., 2021; BRIENZO; SIQUEIRA; MILAGRES, 2009). Then, the material was vacuum filtered on filter paper, and the pH of the liquid fraction (consisting of xylan and lignin) was adjusted to 6 using HCl (5 mol/L). The liquid fraction was concentrated by drying in an oven at 50 °C until it reached about one-third of its initial volume. Then, 3 volumes of 92.8 % ethanol were added for xylan precipitation, followed by the removal of the liquid fraction. The same procedure was repeated four times with 70 % ethanol. The excess of ethanol was removed, and isolated xylan was oven-dried at 40 ºC. Xylan isolation yield was calculated by the xylan mass obtained, compared to the total xylan content in the initial sugarcane bagasse.

The xylan molar mass was determined by Ultra Performance Liquid Chromatography equipment (Waters), using an ACQUITY UPLC BEH SEC column (4.6 x 150 mm), temperature of 40 ºC, eluent: water, flow of 0.5 mL/min, sample volume of 20 uL and refractive index detector at 35 ºC.

2.2.Xylan Acetylation

Xylan acetylation was carried out testing different reaction times and acetic acid and sulfuric acid contents (Table 5), used as polar aprotic solvent and catalyst, respectively. One gram of xylan was thoroughly mixed with the respective amount of acetic acid in a Schott bottle, and placed in a thermostated bath (Dubnoff model 145/ FANEM) at 50 °C for 5 min, and cooled to 25 °C in an ice bath. Then, 6.6 mL of acetic anhydride and the respective amount of sulfuric acid 98 % were pipetted, and the Schott bottle was once again placed in the thermostated bath at 50 ºC. Acetylation was carried out with agitation of 110 rpm at 50 °C, varying the reaction time from 0.5 to 48 h. After the reaction, the acetylated xylan was precipitated with 150 mL of 92.8 % ethanol. Residual acetylation reagents were removed by precipitating the acetylated xylan four times with 100 mL of 92.8 % ethanol, with subsequent removal of the liquid fraction. Acetylated xylan was then oven-dried for 24 h at 40 °C (MUGWAGWA; CHIMPHANGO, 2020b).

Table 5 - Xylan acetylation reaction conditions

Sample	Sulfuric Acid (mL)	Acetic Acid (mL)	Reaction time (h)
1	0.2	25	1
2	0.2	25	2
3	0.5	25	1
4	0.5	25	2
5	0.2	2.5	1
6	0.2	2.5	2
7	0.5	2.5	1
8	0.5	2.5	2
9	0.2	2.5	0.5
10	0.2	2.5	8
11	0.2	2.5	16
12	0.2	2.5	24
13	0.2	2.5	48

Source: author

2.3.Determination of xylan acetylation degree

The degree of acetylation was determined by titration, in triplicates. About 0.1 g acetylated xylans were added to 8 mL NaOH (0.25 mol/L) and 5 mL ethanol, which was used to dissolve the unreacted acetic anhydride, in a Schott glass bottle. This mixture was stirred at 110 rpm for 24 h at room temperature in a shaker (Solab, SL - 222), after which, 15 mL HCl (0.25 mol/L) was added to the system. After 30 minutes of rest, the mixture was titrated with 0.25 mol/L NaOH solution with phenolphthalein as the indicator (Fig 3) (CHEN et al., 2015). The percentage of acetyl groups and the DS of acetylated hemicelluloses were determined by equations 1 and 2, respectively:

Eq 1:

$$AG\ \% = \frac{([(V_{bi} + V_{bt}) \times\ C_b - V_a\ \times\ C_a] \times M_{acetyl}\ \times 100}{m_a}$$

where AG % is the percentage of acetyl groups;

Vbi, Vbt and Va are the volumes of NaOH added to the system and used in titration, and HCl added to the system in milliliter, respectively;

Cb and Ca are the concentration of NaOH and HCl in mol/L;

M acetyl is the acetyl molar mass (43 g/mol);

ma is the weight of the acetylated hemicelluloses sample in grams.

Eq 2:

$$Degree\ of\ substitution = \frac{\left[Acetyl\ content \times M_{xylan}\right]\ \times 100}{\left(M_{acetyl}\ \times 100\right) - [\left(M_{acetyl} - 1\right) \times Acetyl\ content]}$$

Where M_{xylan} is the molar weight of the hemicelluloses unit, which, for xylose residues, is 132 g/mol, and 2 is the theoretical maximum DS.

2.4.Fourier-transform infrared spectroscopy (FTIR)

A Fourier Transform Infrared Spectroscopy (Shimadzu IRAffinity-1S) was used to analyze sugarcane bagasse solubilized xylan and acetylated xylan. The sample was mounted on

a sample holder in contact with ZnSe crystal. The spectra were recorded using 32 scans at resolutions of 4 cm^{-1} with a spectral range between 400 – 4 000 cm^{-1}.

2.5.Bioplastic formation

Bioplastics were formed with only starch (commercial, from Exodo cientifica) as polysaccharide, and with a blend of starch and xylan as polysaccharides, applying non-acetylated xylan, and xylan with acetylation DS of 0.45 and 0.9. The filmogenic solution for both non-acetylated and acetylated xylan-based bioplastic formation was composed of 5 % (w/v) polysaccharides, which was comprised of 25 % (w/w) xylan and 75 % (w/w) commercial starch (MACEDO et al., 2022). For plasticization, 20 % of glycerol (w/w of polysaccharides) was added, and water was used as a solvent. About 0.375 g xylan was solubilized in 28.2 g distilled water in an Erlenmeyer flask by heating the solution in a microwave in several alternating cycles between a short heating time (e.g. 10 seconds) and manual agitation until the boiling point, and complete solubilization, which took about 2 minutes. After cooling, 1.125 g starch and 0.3 g (0.24 mL) glycerol were added, and the constituents were homogenized in a shaker (Solab, SL - 222), at room temperature, with constant agitation of 110 rpm for 1 h. After homogenization, the starch present in the solution was gelatinized in a thermostatic bath at 85 ºC for 3 min with manual agitation until the solution reached a viscous consistency and translucent appearance. Using the casting technique, 22.7 g of the solution were transferred to a polystyrene Petri dish with 56.71 cm^2 area (0.4 g/cm^2 of filmogenic solution), and the bioplastics were left to dry in an oven (Solab, SL-100) at 30 ºC for approximately 24 h. For comparison means, bioplastic consisting of only 1.5 g commercial starch as carbohydrate was prepared, also with 20 % glycerol (w/w of polysaccharides) as the plasticizer.

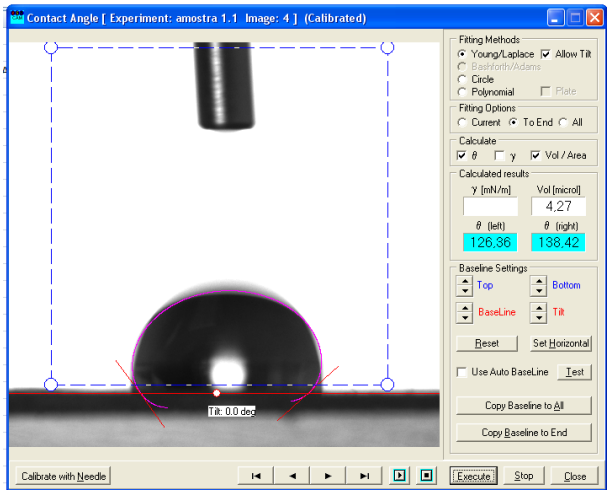
2.6.Crystallinity

The Ultima IV diffractometer model from Rigaku was used equipped with a Cu anode. The equipment operated with a voltage of 40 kV and 30 mA, through a normal scan going from 10º to 100º at a speed of 2º/min and X-ray diffractograms of samples were recorded for 2θ.

2.7.Superficial Hydrophilicity

The affinity of the bioplastics with water was measured in triplicates through contact angle tests, using CAM 101 equipment. The water drops were deposited through a syringe (Hamilton) in two specimens for each sample and about 40 images were captured by a DMK 21AF04 camera (The Imaging Source), in an interval of 16 ms (Figure 32). The images were analyzed using the CAM 2008 software version 4.04 (KSV Instruments).

Figure 32 - Water contact angle analysis



Source: author

2.8. Moisture content and water solubility

Bioplastic samples of 0.9 x 1.5 cm were weighed in triplicates at room temperature and oven-dried at 105 ºC. The samples were again weighed every 24 h until a constant mass was obtained, and its moisture percentage was then determined by the difference in mass before and after drying (MEDINA-JARAMILLO et al., 2017). The dried samples were inserted into a glass beaker with 50 mL distilled water, and stirred in a shaker at 110 rpm, at room temperature for 24 h. After this period, the samples were again oven-dried at 105 ºC and weighed every 24 h until constant mass, and the final dry mass was obtained. The solubilized content was calculated by the difference in mass before and after solubilization in water. To better understand the process of bioplastics solubilization, the liquid resulting from solubilization was submitted to acid hydrolysis with 4 % sulfuric acid, and analyzed by High performance liquid chromatography (Waters) BIO-RAD Aminex HPX-87C column (300 x 7.8 mm), temperature

of 50 ºC, eluent: water and 0.005 M sulfuric acid, flow of 0.6 mL/min, sample volume: 20 uL and refractive index detector (Waters 2414) (AZEREDO et al., 2015; FAKHOURI et al., 2007; MEDINA-JARAMILLO et al., 2017).

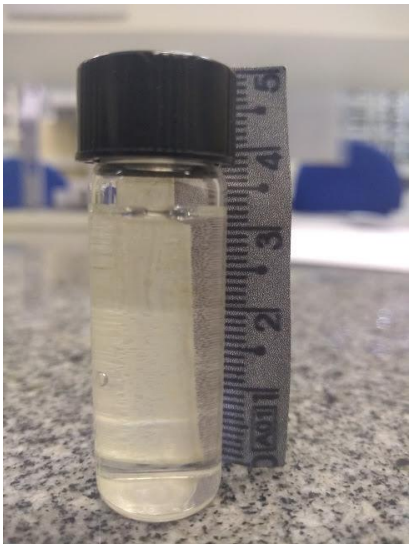
2.9.Opacity

A UV-Vis spectrophotometer was used to determine the opacity of the bioplastic, using a glass cuvette to hold samples with 3 x 0.9 cm. Different standard places of the bioplastic were read in triplicate, with a wavelength of 450 nm, in triplicates. The calculation was performed by dividing the absorbance by the thickness of the bioplastic, measured by a digital micrometer 0-25 mm with 0.001 mm resolution (Mitutoyo 293- 230) (GOUNGA; XU; WANG, 2007).

2.10. Water vapor and oil barrier

A glass flask with 1.2 cm base diameter and 3.5 cm height was filled with 4 mL of water, and the bioplastic was attached to an opening with 11.5 mm diameter in the lid. The lid was firmly closed so that the only passage of water vapor would be through the bioplastics. The flask was placed in a desiccator, and silica gel dried at 105 ºC for 24 hours was placed in the bottom of the desiccator. A printed ruler was vertically attached to the side of the flask in order to measure the reduction in water level over the days, in centimeters, which was used to calculate the volume and mass of water loss in the form of vapor (Figure 34). The desiccator with the whole set remained conditioned at 30 ºC for 10 days (ASTM E96/E96M, 2010).

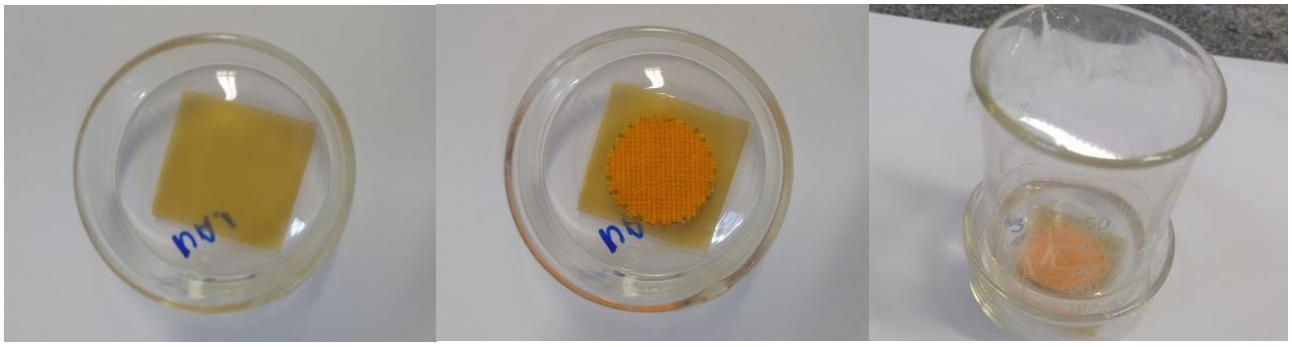
Figure 33 - Round flask with 4 mL water and a printed ruler attached, in order to measure water vapor transmission rate through bioplastic, which is attached to the lid opening



Source: author

For the oil barrier, samples of the bioplastics with 3 x 3 cm dimensions were placed on glass Petri dishes. Two overlapping flannel discs, with 2 cm in diameter, were placed over the center of the bioplastic. A 50 g weight was placed on the discs and the set was preheated to 40 ºC in an oven. With the set still in the oven, the weight was removed, and with the aid of a dropper, six drops of soy oil (brand Cocamar) were added to the flannel discs (Figure 34). The weight was placed back on the soaked discs. Afterward, the presence of signs of oil passing through the bioplastic was periodically verified every 15 min for the first hour; every 30 min for the next 4 hours, and at convenient intervals thereafter (ASTM F119-82, 2008).

Figure 34 - Assembly of oil barrier test



Source: author

2.11. Mechanical analysis

Tensile Stress at Maximum Load and Elongation at break of the bioplastics were measured in triplicates using a testing machine model TXT ENG 5K. Specimens with 1.5 cm in length and 1 cm in width had their thickness previously measured in three pre-established places by a digital micrometer 0-25 mm with 0.001 mm resolution (Mitutoyo 293- 230). The test was carried out with a displacement speed of 5 mm/min, with a 5 kg load cell, and the stress and elongation at break were calculated (Fig 9).

2.12. Thermogravimetric analysis (TGA)

Thermal analyzes of bioplastics were performed in the equipment of TGA brand SII Nanotechnology model TG/DTA 6200 in the range from 30 to 730 °C, 10 °C / min in N_2 at 100 mL/min, resulting in Tg curves.

2.13. Disintegration in Soil and Ecotoxicity

Samples with dimensions of 3.5 x 3.5 cm of the bioplastics were placed on the surface of 150 g of soil with 40 % moisture content inside hermetic containers with a sealing system and volume of 1 L (Yazi) (Fig 10). The test was conducted for 14 days, in which the moisture content was periodically adjusted when needed by adding water to the system. The rate of disintegration was assessed through visual alterations of the bioplastics, through color change, surface roughness, cracks, and holes (ABE; BRANCIFORTI; BRIENZO, 2021).

In order to better understand bioplastics disintegration in soil, ecotoxicity tests were conducted. Each soil sample used for disintegration tests was washed with deionized water and then analyzed regarding ecotoxicity. A volume of 300 mL of distilled water was added to 100 g of soil (dry weight) in a 500 mL Schott bottle. The samples were subjected to continuous stirring of 110 rpm for 24 h and allowed to settle. Then, around 5 mL of the liquid phase (water extract) was transferred to a Petri dish containing a filter paper disk. Fifteen cucumber seeds (*Cucumis sativus*) were then placed on top of each filter paper and the plates were covered with film paper, to avoid moisture loss, and dark paper, to avoid photo-induced processes. The Petri dishes remained at room temperature for 10 days, and the percentage of germination (%, G) and inhibition (%, I) were calculated according to (PAPADIMITRIOU et al., 2008). The ecotoxicity dataset for root and hypocotyl growth was obtained from the same plates used for

germination quantification. Root and hypocotyl measurements were calculated for each seedling, according to the recommendation of (PAPADIMITRIOU et al., 2008). Milli-Q water and soil washing (soil without any bioplastic) were used in the control assays.

2.14. Statistical analysis

Tukey-ANOVA ($p \leq 0.05$ significance level) assisted by version Minitab software was applied to compare the various treatment groups.

3. Results

3.1.Xylan Solubilization

A solubilization yield of 45 % of the sugarcane bagasse xylan content was obtained using an optimized methodology. Similar results were reported elsewhere (GENG et al., 2019), which were able to solubilize 50.7 % of the hemicelluloses content from poplar, using 10 % (w/w) NaOH at 50 °C for 3 h. However, higher xylan solubilization yield of 71.43 % was obtained when applying peroxide in an alkaline medium (6 % w/v, 25 ºC for 4 h) to sugarcane bagasse sieved to particle size lower than 50 mesh (0.297 mm) (ALVES et al., 2021). Such different results may be explained by the small particle size, which collaborates to expose the polysaccharide to the chemical action.

After solubilization, xylan presented a molecular weight of 164339 g/mol. Similar hemicelluloses isolation conditions from dewaxed sugarcane bagasse were applied, using 6 % H_2O_2 solution (adjusted to pH 11.5 with 5 mol/L NaOH) at 60 °C/3 h under continuous magnetic stirring at 350 rpm, which resulted in an extraction yield of 61 %. However, lower molecular weight of 28942 was reported, probably due to the higher temperature applied, which was successful in breaking hemicelluloses bonds to lignin, but also responsible for breaking the glycosidic bonds between hemicelluloses molecules (JIN et al., 2019).

3.2.Xylan Acetylation

The xylan acetylation and the degree of acetylation were monitored by FTIR and titration. Different acetylation degree results were found by varying reaction conditions (Table

6). It was observed that increasing the catalyst or the acetic acid content did not have a positive effect on the acetylation degree, as the lowest amounts applied of 0.2 mL and 2.5 mL, respectively, were sufficient for the reaction to take place. However, increasing the reaction time from 1 h to 24 h, while maintaining the lowest sulfuric and acetic acid contents, resulted in the increase of the acetylation degree from 0.70 to 0.91, in samples 5 and 12, respectively. Also, when increasing such time from 24 h to 48 h, in samples 12 and 13, respectively, the acetylation degree was reduced to 0.49, and the mass recovered also decreased, from 44.88 % to 22.41 %. This indicates a great amount of xylan hydrolysis due to the longer time xylan was in contact with the sulfuric acid applied, which comprised the acetylation reaction (BUCHANAN et al., 2003).

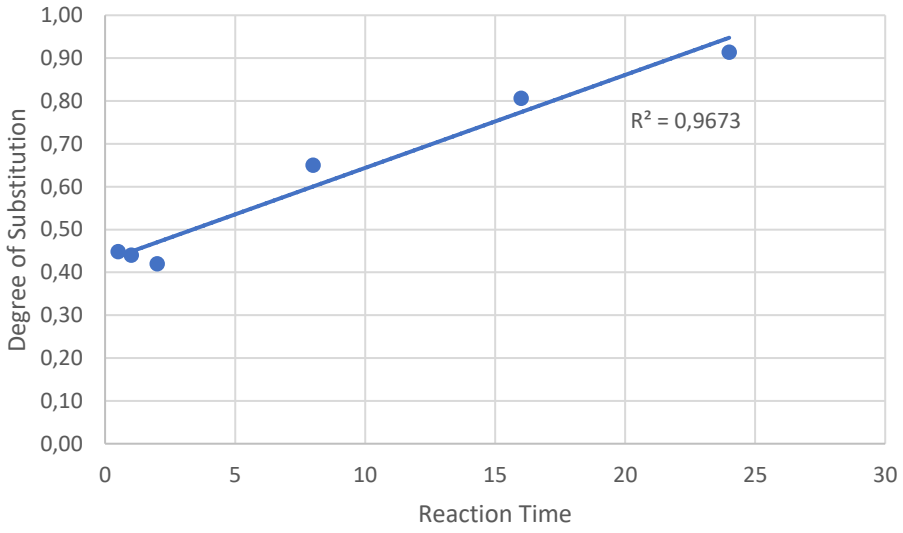
The same acetylation reaction method as in sample 5 of the present study was applied in arabinoxylan, however, with the previous alkali catalyzed organosolv pretreatment, which increases hemicelluloses accessibility to acetyl groups (MUGWAGWA; CHIMPHANGO, 2020a). The DS obtained varied from 0.11 to 1.7, which corroborates the fact that such a method will hardly achieve maximum substitution, as arabinoxylan presents three hydroxyl groups available for acetylation. It was possible to increase xylan acetylation DS from 0.85 to 1.17 when increasing the reaction time from 8 h to 24 h, at room temperature (HETTRICH et al., 2005). These reaction conditions are comparable to the ones applied in samples 10 and 12 of the present study, which resulted in DS of 0.61 and 0.91, respectively. In this case, the slightly lower DS obtained in the present study may be due to the higher temperature applied, which was responsible for accelerating xylan hydrolysis, which hindered acetylation (BUCHANAN et al., 2003). The influence of reaction time in the degree of acetylation obtained can be seen in Figure 35, which shows that their linear correlation resulted in a high coefficient of determination (R^2) of 0.9673.

Table 6 - Mass recovery and degree of substitution obtained after xylan acetylation

Sample	Conditions	Degree of Substitution	Mass Recovery (%)
1	$Sulf_{0.2}Acet_{25}T_1$	0.51 ± 0.02	58.15 ± 1.12
2	$Sulf_{0.2}Acet_{25}T_2$	0.61 ± 0.03	40.86 ± 2.34
3	$Sulf_{0.5}Acet_{25}T_1$	0.44 ± 0.01	27.97 ± 1.40
4	$Sulf_{0.5}Acet_{25}T_2$	0.42 ± 0.03	24.26 ± 3.20
5	$Sulf_{0.2}Acet_{2.5}T_1$	0.70 ± 0.05	40.33 ± 2.95
6	$Sulf_{0.2}Acet_{2.5}T_2$	0.71 ± 0.04	39.94 ± 3.10
7	$Sulf_{0.5}Acet_{2.5}T_1$	0.47 ± 0.02	25.6 ± 1.76
8	$Sulf_{0.5}Acet_{2.5}T_2$	0.56 ± 0.07	21.87 ± 2.05
9	$Sulf_{0.2}Acet_{2.5}T_{0.5}$	0.45 ± 0.03	44.63 ± 1.23
10	$Sulf_{0.2}Acet_{2.5}T_8$	0.61 ± 0.05	43.68 ± 3.20
11	$Sulf_{0.2}Acet_{2.5}T_{16}$	0.81 ± 0.08	53.13 ± 3.57
12	$Sulf_{0.2}Acet_{2.5}T_{24}$	0.91 ± 0.06	44.88 ± 2.69
13	$Sulf_{0.2}Acet_{2.5}T_{48}$	0.49 ± 0.03	22.41 ± 1.47

Source: author

Figure 35 - Correlation between reaction time and degree of substitution obtained



Source: author

Due to similar structural properties, comparable results may be found when applying the same acetylation method to other polysaccharides such as cellulose and starch, varying reaction conditions. An increase in the acetylation degree when increasing the reaction time, from 10 min to 240 min, was previously reported, and acetylated nanocellulose with DS ranging from 0 to 2.34, respectively, was obtained (MUGWAGWA; CHIMPHANGO, 2020b). The increasing reaction temperature from 20 ºC to 47 ºC was also responsible for increasing the DS

of cassava starch from 0.6 to 1.1 (SCHMIDT et al., 2019). However, scanning electron microscopy analysis showed that higher acetylation temperature caused a destruction degree on the surface of the starch granules. This can be attributed to a high reaction intensity, which damaged the hydrogen intermolecular bonds and promoted the disruption of some starch granules. Such damage to inter and intramolecular bonds was also observed in xylan chains in the present study.

Acetylation reaction was responsible for the loss of xylan mass, depending on the reaction conditions applied (Table 6). It is possible to observe that samples 3, 4, 7, and 8, with a higher sulfuric acid content of 0.5 mL, presented the lowest mass recovery after the acetylation reaction, as well as sample 13, with the highest reaction time of 48 h. Therefore, the application of sulfuric acid may have been responsible for xylan hydrolysis during the acetylation reaction, when applied in high amounts or for long periods of time. Hemicelluloses hydrolysis was also reported when applying sulfuric acid as a catalyst for hemicelluloses esterification, which resulted in a 71.6 % reduction in molecular weight after 10 h of reaction (BUCHANAN et al., 2003). Sulfuric acid is known to catalyze glycosidic linkages cleavage, as it dissociates and protonates the glycosidic oxygen to form a carbonium cation, and subsequently a water molecule is added to form monomeric sugars (BIERMANN, 1988; KAPU; TRAJANO, 2014).

Even though cellulose is known for its crystallinity organization and, therefore, higher resistance to degradation, a similar acetylation method as the one applied in the present study was responsible for fiber damage (FRISONI et al., 2001). Scanning electron microscope images showed a rather smooth surface in native cellulose fibers, and no significant morphological changes are observed after acetylation in the reaction of 1 h and 7 h. However, the sample with the highest reaction time of 28 h and acetylation degree showed fiber surface damage (FRISONI et al., 2001).

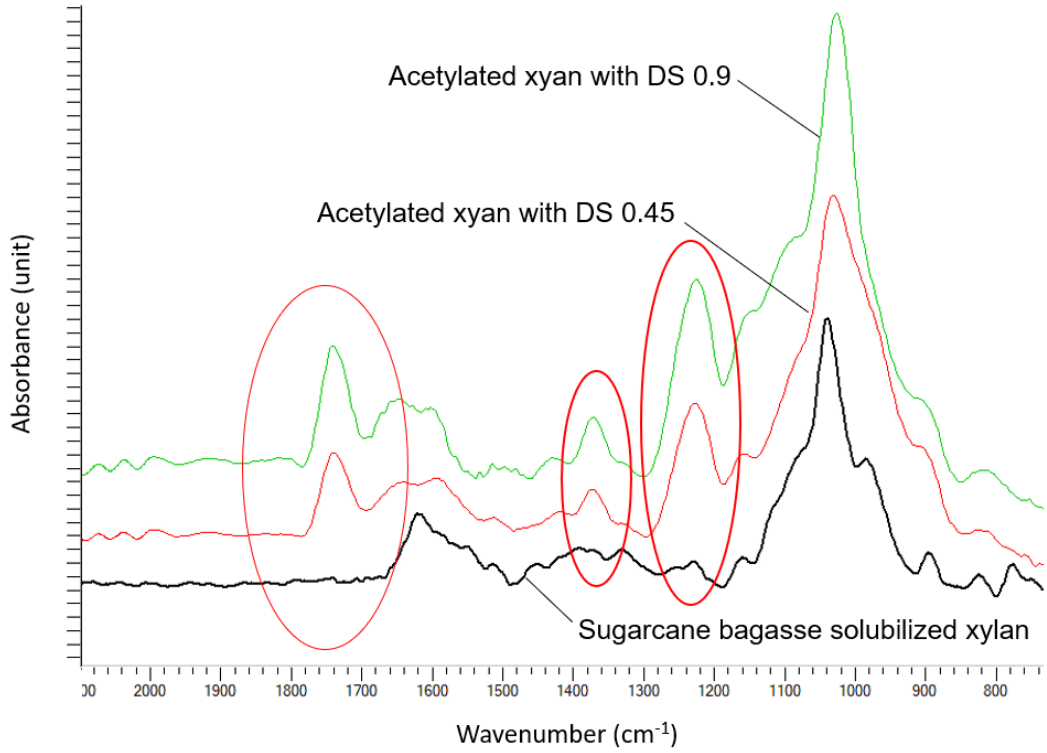
3.3.Fourier Transform Infrared Spectroscopy (FTIR)

Differences were observed in the infrared spectra between acetylated and non-acetylated samples, and also between acetylated ones with different acetylation reaction conditions (Figure 36). Characteristic patterns of xylan were observed in the FTIR analysis in all of the samples, such as peaks around 890 cm^{-1}, which indicate the presence of β-glycosidic bonds between the xylose monomers in the chain (AKKUS; OZKAN; BAKIR, 2018; ZHU et al., 2020), and peaks

around 1060 cm^{-1}, which are associated with CO bonds of glycosidic bonds (AKKUS; OZKAN; BAKIR, 2018; SUN et al., 2019; ZHU et al., 2020).

The presence of acetyl groups could be evaluated through three distinct peaks, around 1730, 1375, and 1220 cm^{-1}, which represent the three important ester bonds in acetylation, C=O, C–CH_3, and C–O, respectively (AKKUS; OZKAN; BAKIR, 2018; SUN et al., 2019; ZHU et al., 2020). This indicates a successful xylan acetylation reaction.

Figure 36 - FTIR analysis of solubilized xylan from sugarcane bagasse and acetylated xylan with DS of 0.45 and 0.9



Source: author

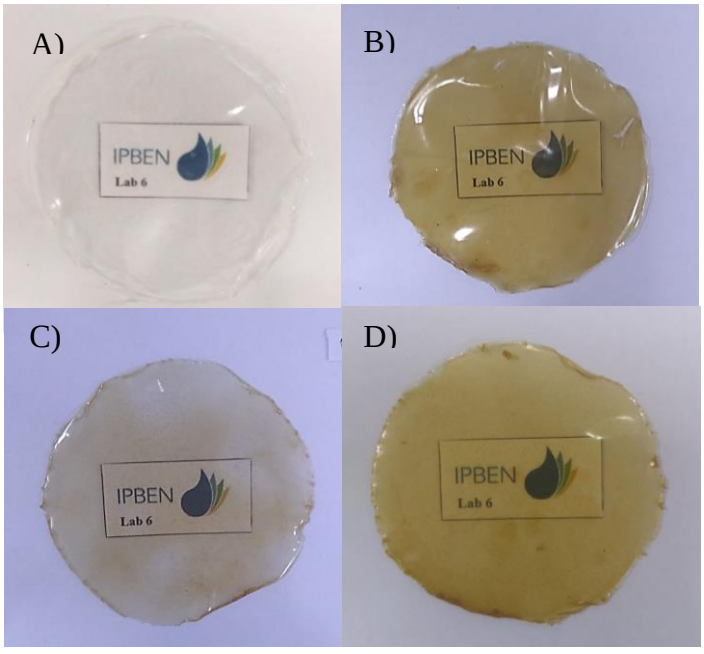
3.4.Acetylated xylan applied for bioplastic production

Xylan with DS of 0.45 (low acetylation degree) and 0.9 (medium acetylation degree) were chosen for bioplastic formation. As xylan present 2 free hydroxyl groups per xylose molecule, such DS indicates that there are still hydroxyl groups available for the xylan to be solubilized in water, as well as to bond with starch and glycerol molecules applied in the bioplastic formation (ZHU et al., 2020). It also possibly enhances some of the bioplastic properties, such as mechanical strength and thermal degradation.

Therefore, the present study was successful in developing a chemical modified material with potentially enhanced properties by acetylation, while still being able to use water as a solvent in bioplastic production. In many cases, due to xylan high acetylation degree and obtained hydrophobicity, solvents such as chloroform (EGÜÉS et al., 2014; FUNDADOR et al., 2012; GORDOBIL et al., 2014; STEPAN et al., 2012), acetone (BUCHANAN et al., 2003; YILMAZ-TURAN et al., 2020), dimethyl sulfoxide (MUGWAGWA; CHIMPHANGO, 2020a, 2020b), dimethyl carbonate (STEPAN et al., 2013), and tetrahydrofuran (AYOUB et al., 2013) needed to be applied for bioplastics formation. However, these solvents are either toxic for humans or detrimental to the environment and may be responsible for increasing the production costs, when compared to aqueous medium.

Using distilled water as a solvent, 4 types of bioplastics were produced and analyzed (Figure 37): bioplastic formed with starch as the only polysaccharide (SB), with starch and non-acetylated xylan as polysaccharides (NAB), with starch and xylan acetylated with a low DS of 0.45 as polysaccharides (LAB), and with starch and xylan acetylated with a medium DS of 0.9 as polysaccharides (MAB).

Figure 37 - The four types of bioplastics formed in the present study.



A) SB - starch as the only polysaccharide; B) NAB - starch and non-acetylated xylan as polymers; C) LAB - starch and xylan acetylated with a low DS of 0.45 as polymers; D) MAB - starch and xylan acetylated with a medium DS of 0.9 as polymers. Source: author

3.5. Crystallinity

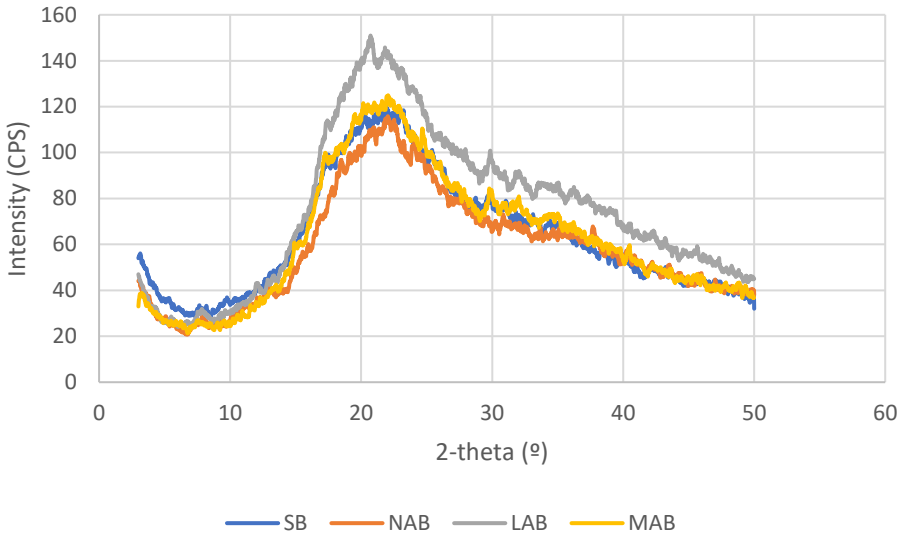
The bioplastic with the higher crystalline structure was the low acetylated one (LAB), followed by MAB, SB and then NAB samples, respectively (Figure 38). This means that the LAB sample presented the highest content of atoms arranged in a periodic pattern, which might be explained by the presence of the acetyl groups. As the acetyl groups prevent the xylan chains from aggregating, the hydroxyl groups from xylan can make hydrogen bonds with hydroxyl groups from starch, which increases the bioplastics overall crystallinity, as it is dependent upon the extent of hydrogen bonding on the film (BERTUZZI; ARMADA; GOTTIFREDI, 2007).

The same phenomenon might explain why the MAB sample is the second most crystalline, however, when compared to the LAB sample, the highest amount of acetyl groups was responsible for increasing the distance between polysaccharides chains, and the intra- and inter-molecular hydrogen bonds were reduced, leading to less crystalline materials (CHOI et al., 2022; JO et al., 2016; TEODORO et al., 2015). This was also seen when acetylating starch prior to the preparation of films, in which an increase in the acetylation DS, due to an increase from 1 mL to 9 mL in the acetic anhydride applied in the reaction, was responsible for decreasing film relative crystallinity from 4.27 % to zero (CHOI et al., 2022).

As for the SB sample, recrystallization of starch after gelatinization is known to occur in foods as well as in thermoplastic materials, which promotes high crystallinity in starch films (BERTUZZI; ARMADA; GOTTIFREDI, 2007). However, such property is also highly dependent on the drying time, as a lower drying rate gives the chains a longer time to arrange into more favorable conformations, i.e. in the form of crystals (RINDLAV; HULLEMAN; GATENHOLM, 1997; YANG et al., 2019).

For the NAB sample, xylan chains were found to aggregate or reorder during the precipitation process by ethanol, in the alkaline isolation process (YANG et al., 2019). Xylan aggregation may have prevented hydrogen bonding and a more organized arrangement with other film components, therefore decreasing the film crystallinity.

Figure 38 - X-Ray Difraction analysis of bioplastics



Source: author

3.6.Superficial Hydrophilicity

SB presented a fairly hydrophilic surface (Table 7), which is corroborated by results in the literature, which found WCA of 84.1 º for starch films (CHEN et al., 2020). It is possible to note that the low acetylation degree of 0.45 in the LAB sample was responsible for a decrease in the WCA from 90.07 º to 81.56 º, when compared to the NAB sample, representing a more hydrophilic surface, which was caused by the disaggregation of the polysaccharide's molecules due to the presence of acetyl groups, while still leaving free hydroxyl groups, which are able to bind to water. On the other hand, the medium acetylation degree of 0.9 was responsible for a WCA value of 95.51 ± 3.48, the highest of the present study. This result reveals the lowest hydrophilicity, which indicates that a great amount of hydroxyl groups was substituted by relatively hydrophobic acetyl groups. The same phenomenon was observed when acetylating xylan and cellulose used in film formation, as hemicelluloses with a DS of 1.9 was responsible for increasing the WCA from around 55 º to 70 º (GORDOBIL et al., 2014).

3.7.Moisture content and water solubility

SB and NAB samples presented similar moisture contents, of 23.72 and 23.14 %, respectively, indicating their hygroscopic features (Table 7). However, LAB showed the highest moisture content of 27.65 %. This suggests that the low degree of acetylation was responsible for keeping the xylan chains from aggregating and forming hydrogen bonds with each other, making them available for hydrogen bonds with water. Also, MAB presented the lowest moisture content of 21.26 %. This shows that the relatively hydrophobic acetyl groups were responsible for impeding the water molecules from linking to the hydroxyl groups of xylan chains. Similar results were reported for acetylated cassava starch bioplastics, in which acetylation with a DS of 1.1 was responsible for decreasing the moisture content from 12.45 g/g, in the non-acetylation starch bioplastic, to 8.51 g/g (SCHMIDT et al., 2019).

However, acetylated bioplastics were the most soluble in water, with 56.36 and 75.48 % of the LAB and MAB masses solubilized in 24 h, respectively. This phenomenon might be explained by the increase in distance in the polymers network of the bioplastics, due to the incorporation of acetyl groups, which weakens intermolecular linkages making them more easily breakable during solubilization (ZHU et al., 2020). Another possible explanation is that xylan molecules in LAB and MAB sample presented lower degree of polymerization, due to degradation during acetylation reaction, which resulted in soluble chain fragments.

The bioplastics components released during solubilization were analyzed by High Performance Liquid Chromatography. It was observed glucose as the main molecule released from the acetylated bioplastics. This result suggests that starch was the most solubilized component. Therefore, it is possible to assume that the acetyl groups weakened the hydrogen bonding between xylan chains and starch molecules, and the latter was easily solubilized in water due to its hydrophilicity (ZHU et al., 2020). An increase in water solubility due to an increase in the acetylation DS was also reported for cassava starch bioplastic, in which the water solubility increased from 20.42 to 22.27 g/100 g when the DS increased from 0.6 to 1.1 (SCHMIDT et al., 2019).

3.8.Opacity

The opacity of the bioplastics was highly influenced by the acetylation degree, and such results are corroborated by the bioplastic crystallinity, as the increase in crystalline zone

decreases the absorbance and, therefore, decreases the film opacity (BERTUZZI; ARMADA; GOTTIFREDI, 2007).

The SB sample presented the highest opacity values, of 1.75, closely followed by the NAB sample, with 1.14. Also, among the xylan-based bioplastics, NAB presented the highest opacity. This can be explained by the presence of residual lignin in the extracted xylan. Lignin molecule has chromophores mainly represented by quinoids, catechols, aromatic ketones, stilbenes, conjugated carbonyls with phenolics, and metal complexes, and some chromophores derived from carbohydrates (DE LUCENA et al., 2017; RUIZ et al., 2013; ZHANG; FU; CHEN, 2020). As any residual lignin was isolated during acetylation reaction and subsequent ethanol washes, it is thought that acetylated bioplastics present lower contents of such structure in its composition. The lowest opacity values can also be explained by the decrease in acetylation brings in the refractive index. With an increase in the acetylation degree, the gap in the refractive index between the bioplastic components became wider, resulting in a decrease in opacity (IFUKU et al., 2007).

However, the LAB sample presented lower opacity than the MAB sample, of 0.53 and 0.79, respectively. Studies with bacterial cellulose nanofibers showed that an increase in acetylation DS may increase transmittance and, therefore, reduce the opacity. However, this phenomenon is observed on a DS up to 0.74, from which the increase in DS will be responsible for increasing the opacity of the material (IFUKU et al., 2007). The increase of the acetylation degree causing an increase in opacity was also reported, for bioplastics with acetylated rice starch with 20 % amylose (COLUSSI et al., 2017). The increase of acetylation degree from 0.99 to 2.96 in acetylated chitin nanofiber composites caused a decrease in the transparency of the nanocomposite from 77 % to 73 %, which indicates an increase in its opacity (IFUKU et al., 2010).

Table 7- WCA, moisture content, water solubility, and opacity of the bioplastics

Sample	WCA (º)	Moisture (%)	Water Solubility (%)	Opacity
SB	86.19 ± 3.21	23.72 ± 2.17	29.39 ± 1.83	1.75 ± 0.31
NAB	90.07 ± 2.85	23.14 ± 0.47	36.36 ± 1.07	1.14 ± 0.00
LAB	81.56 ± 3.50	27.65 ± 1.01	56.36 ± 2.73	0.53 ± 0.17
MAB	95.51 ± 3.48	21.26 ± 0.32	75.48 ± 5.03	0.78 ± 0.03

Source: author

3.9.Water and oil barrier

The water barrier property of bioplastic is an important factor to be studied. In many applications, especially food packaging, it is necessary to have greater control of the passage of water vapor through the material, thus preventing its exit or entry (MIKKONEN et al., 2012). The water vapor transmission of the bioplastics varied from 24.95 g/h m^2, in the MAB sample, to 40.83 g/h m^2, for the SB sample (Table 8). When compared to the test in which there was no barrier (control sample), they were much more efficient in controlling the amount of water vapor transferred.

Edible cassava starch bioplastics, using 1 % (w/w) glycerol as a plasticizer, presented a Water Vapor Transmission Rate of 6.89 x 10^{-7} g mm/h cm ² (PARRA et al., 2004), which is drastically lower than the SB sample in the present study. The higher glycerol content of 20 % (w/w) applied resulted in a water vapor transmission value of 7.35 x 10^{-04} g mm/h cm ². Also, potato starch bioplastics presented a water vapor transmission of around 875 g/ d m² at 25 ºC (ZHANG; WANG; CHENG, 2018). This result is slightly lower than the results found for the SB sample in the present study, which found a water vapor transmission of 979.96 g/dm². Although the bioplastic/films compositions are fairly similar, the present study applied a higher temperature of 30 ºC, which would explain the higher WVTR.

The NAB sample of the present study presented a water vapor transmission rate of 40.83 g/h m². This result is lower than the results found in xylan bioplastics, with a water vapor transmission rate of 304 g/hm² (SAXENA; RAGAUSKAS, 2009). These different results are probably due to the higher temperature of 37 ºC applied by such study, which increased the evaporation rate of water.

The low acetylation degree in the LAB bioplastic was sufficient to impede the xylan molecules from aggregating, creating more space between the polymeric chains in the bioplastic, which increased the water vapor transmission, when compared to the NAB sample. However, the MAB sample presented the lowest water vapor transmission rate. This result suggests that the medium acetylation degree was able to decrease the hydrophilicity of such bioplastic and hinder the passage of water vapor molecules. Chitosan bioplastic that went through deacetylation process for 20, 90, and 240 minutes presented water vapor permeability values of 1.96, 2.95, and 3.95 g mm/m² kPa d. This indicates that higher acetylation degree resulted in lower water vapor permeability (MOURA et al., 2011).

Table 8 - Bioplastics water vapor transmission values

Sample	Water Vapor Transmission		Water Vapor Transmission Rate	
	WVT (g/dm²)	**WVT (gmm/cm²)**	**WVTR (g/hm²)**	**WVTR (gmm/hcm²)**
Control	2517.96 ± 27.22	-	104.91 ± 1.13	-
SB	979.96 ± 32.66	0.176 ± 0.01	40.83 ± 1.36	7.35E-04 ± 2.45E-05
NAB	653.31 ± 21.77	0.121 ± 0.00	27.22 ± 0.9	5.04E-04 ± 1.68E-05
LAB	816.63 ± 32.66	0.179 ± 0.01	34.03 ± 1.36	7.45E-04 ± 2.98E-05
MAB	598.87 ± 10.89	0.106 ± 0.00	24.95 ± 0.45	4.42E-04 ± 8.03E-06

Source: author

In order to understand the possible coverage of applications of the bioplastics produced, the oil barrier test was applied. The passage of oil was analyzed daily in all of the samples. As a result, in the period of 30 days, there was no signal of oil passage through any of the samples. After this period, the moisture lost due to the temperature applied in the stove caused the bioplastics to crack, which caused the interruption of the tests. However, it was possible to confirm that all of the bioplastics are applicable for uses that require an efficient oil barrier.

Cassia-gum based bioplastic presented an increase in its oil barrier properties from 0.550 (g mm/ m² d) to 0.064 (g mm/ m² d) of oil permeability when comparing native cassia-gum based bioplastic to the one reinforced with carboxylated cellulose nanocrystal whisker (CAO et al., 2020). This indicates that the incorporation of carboxylated cellulose nanocrystal whisker forms a dense network with cassia-gum, which seals the numerous spaces between the chains at the molecular level (FERRER; PAL; HUBBE, 2017). The same phenomenon may explain the good oil barrier found in bioplastics in the present study, as the polysaccharides applied in bioplastic formation present good affinity, as the moderate acetylation degree applied still allows for intermolecular hydrogen bonding. This leads to a more compact packing and lower permeability.

3.10. Mechanical analysis

The tensile stress at break (Table 9) was higher for the SB sample than NAB sample, with 4.35 and 1.56 MPa, respectively. However, xylan acetylation was responsible for increasing the tensile stress needed for the rupture of the bioplastics. Acetylated bioplastics presented the highest tensile strength values, with 6.70 and 7.83 MPa, indicating an increase of

76.72 and 80.01 % when compared to NAB sample, respectively, for LAB and MAB, owed to the elimination of OH groups and reduced water sensitivity (EGÜÉS et al., 2014). Also, acetyl groups may have been responsible for preventing the starch chains from slipping, blocking their movement, which resulted in lower elongation and higher tensile stress values. The results found for the LAB samples are corroborated by bioplastics prepared with acetylated hemicelluloses with a DS of 0.4, with similar tensile stress of 4.5 MPa (MUGWAGWA; CHIMPHANGO, 2020a). The increase in the tensile stress due to acetylation was also found when an acetylated bioplastic with DS of 1.9 presented tensile stress 25.6 % higher than the non-acetylated one, owing to the elimination of OH groups (EGÜÉS et al., 2014). In this case, acetylation was also responsible for increasing Young's Modulus from 1432 MPa to 2241 MPa. This phenomenon was also seen in the present study, in which acetylation with DS of 0.45 and 0.9 was responsible for increasing the Young's Modulus from 2.99 MPa in the NAB, to 290.61 MPa and 274.67 MPa, respectively (EGÜÉS et al., 2014).

The presence of native xylan in the bioplastic was responsible for increasing the elongation at break. However, xylan acetylation caused a drastic decrease in the elongation of the bioplastic. The elongation of the SB and NAB bioplastics could have been owed to their hygroscopic nature in which water acts as a plasticizer (EGÜÉS et al., 2014). A similar phenomenon was found when testing the acetylation of polysaccharides in a hemicelluloses-based bioplastic reinforced with 1 % acetylated cellulose. In this case, acetylation with DS of 1.8 was responsible for a decrease in the tensile strain from 19.7 % to 3.5 % (GORDOBIL et al., 2014).

Table 9 - Bioplastics mechanical properties

Sample	Tensile Stress at Break (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
SB	4.35 ± 1.85	33.81 ± 1.35	12.88 ± 5.69
NAB	1.56 ± 0.25	52.01 ± 1.18	2.99 ± 0.42
LAB	6.70 ± 1.23	2.48 ± 0.66	290.61 ± 20.10
MAB	7.83 ± 1.96	2.90 ± 0.22	274.67 ± 16.53

Source: author

Overall, LAB and MAB presented the highest stiffness values of the present study, caused, among other factors, by their high crystallinity. The crystalline domain has a role in

reinforcing the resistance of films against external stress and increased stiffness, which is reflected in a high Young's modulus (CHOI et al., 2022; XIANG et al., 2020).

3.11. Thermogravimetric analysis

An initial drop in the TGA curve of all samples could be observed during the early stage of heating at around 100 ºC, derived from water loss, and a second decomposition stage is seen initiating at around 250 ºC, due to starch and hemicelluloses decomposition (Figure 39). Hemicelluloses are reported to decompose between 250 - 320 ºC, whereas starch is reported to decompose at around 350 ºC (LIU et al., 2013; POLETTO, 2016). For that reason, all of the samples in the present study showed a maximum rate of decomposition (T peak) between 250 and 350 ºC, which indicates the process of bioplastic depolymerization, with slight changes due to the presence of glycerol and acetyl groups. It was found that glycerol highest decomposition rate occurs at around 158 ºC (LEMOS et al., 2018; SURIYATEM; AURAS; RACHTANAPUN, 2018). Therefore, it is possible to assume that the glycerol content in the bioplastics is responsible for the slight decrease in their thermal stability, when compared to starch and xylan molecules.

The SB sample had 85 % of its weight loss before reaching the temperature of 350 ºC. Similar results were found for blend films from rice starch using glycerol as a plasticizer, where the maximum degradation rate occurred at around 325 ºC, and by 350 ºC up to 80 % of the bioplastic weight had been lost (SURIYATEM; AURAS; RACHTANAPUN, 2018).

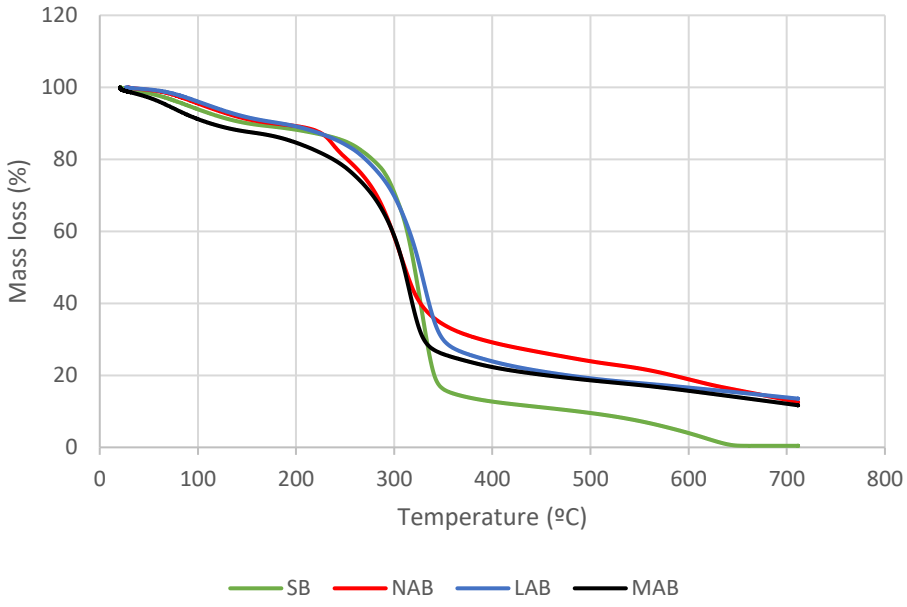
Meanwhile, all of the xylan-based bioplastics were only 75 % degraded at 350 ºC and still presented a residue of about 12 % of the original mass when reaching 700 ºC, whereas the SB sample was completely degraded. It was reported that hemicelluloses thermal degradation resulted in a high amount of residue at 700 ºC (LYU; WU; LOU, 2010), which indicates the formation of chars and explains the higher amount of residue in xylan-based bioplastics in the present study, when comparing to SB sample (KATAOKA; HIDALGO FALLA; LUZ, 2021). The complete decomposition of starch biocomposite was also reported elsewhere (SURYANTO et al., 2019).

The maximum decomposition rate for NAB occurred at 302 ºC. The T peak for sugarcane bagasse xylan was found to be at around 265 ºC (MORAIS DE CARVALHO et al., 2019). Therefore, it is possible to assume that the presence of starch in the bioplastic in the present work is responsible for increasing the T peak temperature. An increase in xylan

maximum decomposition rate temperature due to acetylation was found along with acetylation DS, to 289 ºC and 367 ºC for xylan with DS of 0.25 and 1.76, respectively (MORAIS DE CARVALHO et al., 2019). This phenomenon also occurs in xylan-based bioplastics in the present study, as acetylation was responsible for increasing the temperature of the maximum rate of decomposition (T peak), from 302 ºC to 329 ºC and 315 ºC for bioplastics NAB, LAB, and MAB samples, respectively (Figure 40). Such results were corroborated by the ones found in arabinoxylan acetylation, which was responsible for increasing the temperature of the maximum decomposition rate from 284 ºC to 351 ºC for non-acetylated and acetylated arabinoxylan from wheat bran with a DS of 1.4 (YILMAZ-TURAN et al., 2020). The enhanced thermal stability occurs due to the reduction in the amount of free hydroxyl groups, which go through oxidation when heated (EGÜÉS et al., 2014; FANG et al., 1999; FUNDADOR et al., 2012).

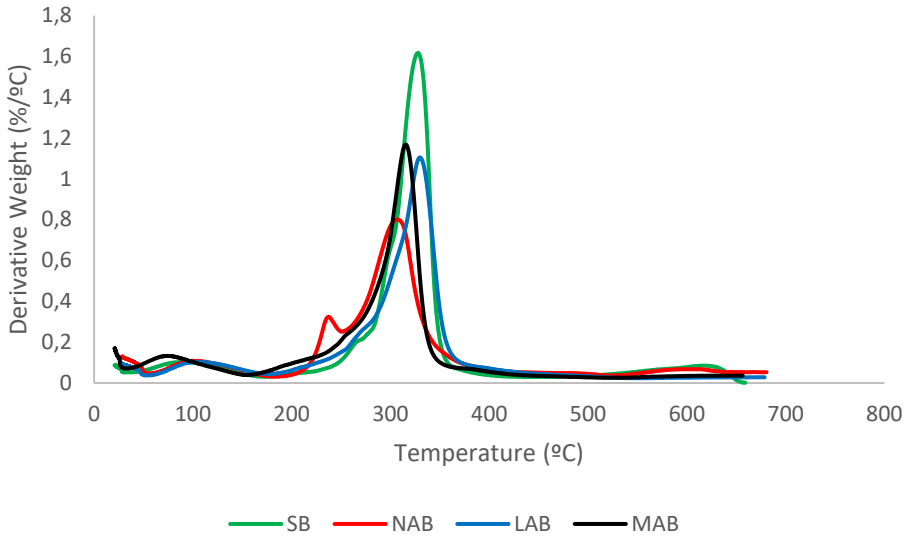
Testing hemicelluloses thermal decomposition, it was found that xylan presented a low decomposition rate of only up to 0.5 %/ºC mass loss (WERNER; POMMER; BROSTRÖM, 2014). This phenomenon explains why the derivative weight loss reached lower values for the xylan-based bioplastics in the present study.

Figure 39 - Bioplastics thermal degradation



Source: author

Figure 40 - Bioplastics degradation derivative weight

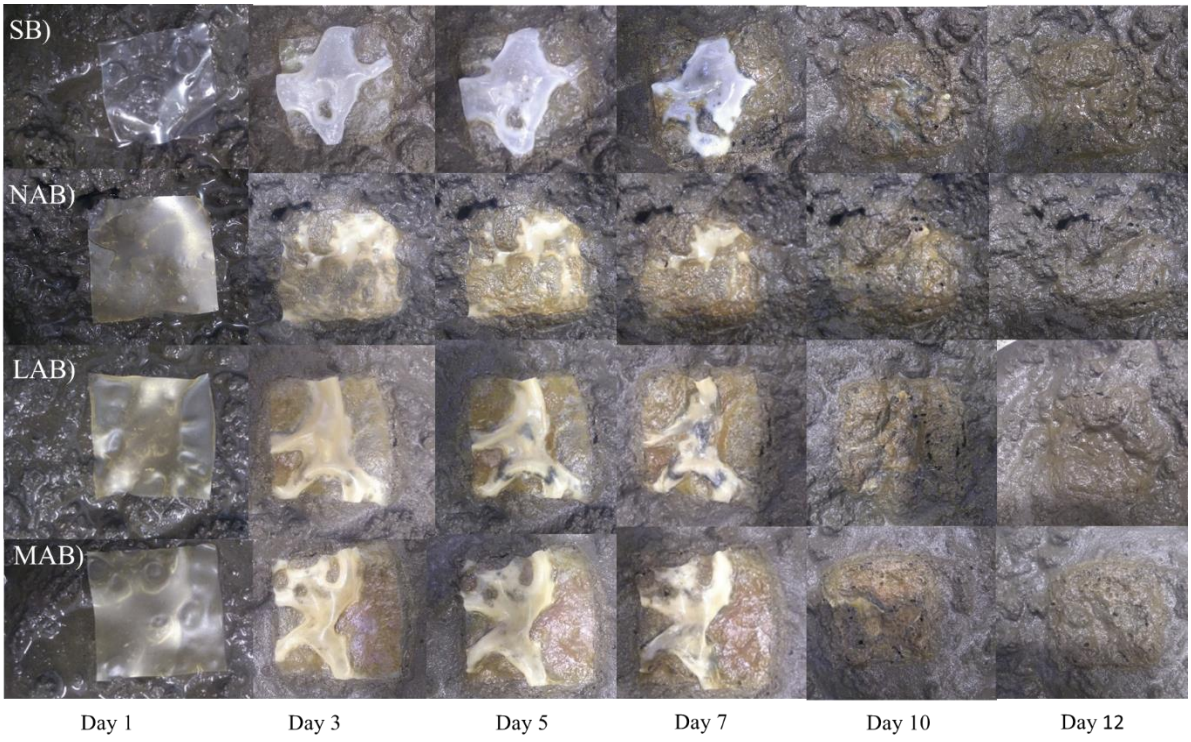


Source: author

3.12. Disintegration in Soil and Ecotoxicity

Bioplastics were deposited on the soil surface to evaluate by visual analysis the disintegration (Figure 41), which was later attested by ecotoxicity. The visual disintegration occurred in 12 days, with no apparent negative effect of the xylan acetylation. The effect of acetylation on the microbial degradation of mannans was reported, as acetylation was responsible for reducing the number of different colonies formed (BI et al., 2016). Such results indicate that fewer organisms have the ability to degrade acetylated polysaccharides than non-acetylated ones. Acetyl groups may hinder the enzymatic breakdown through steric hindrance to enzymatic access and new enzymes would be required for further hydrolysis (ABE; BRANCIFORTI; BRIENZO, 2021; BI et al., 2016). Moreover, the acetylation hindrance to xylan degradation was only observed in higher acetylation degrees (RIVARD et al., 1995). Therefore, the DS of 0.45 and 0.9 applied in the present study could not be sufficient to impede the bioplastics disintegration. Still, ecotoxicity analysis has shown to be detrimental to understanding such results.

Figure 41 - Visual bioplastics disintegration on soil surface at 30 °C, 40 % moisture



Source: author

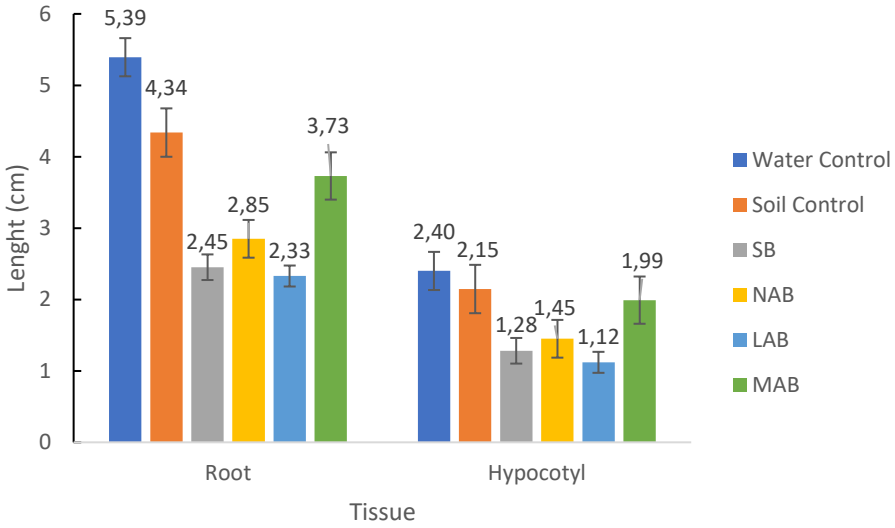
Rice straw cellulose-based bioplastic was completely degraded in the soil after 105 days. The biomaterial remained virtually unchanged during the first month in the soil, and significant mass variations were found after 70-80 days. An accelerated mass loss process after 90 days was seen, when the bioplastic started to become a fine powder (BILO et al., 2018). Evaluating cassava starch disintegration, it was reported a fast increase in the mineralization during the first 10 days of testing (CASTRO-AGUIRRE et al., 2017). A possible explanation is that the presence of starch for microbial assimilation caused a rapid large increase in the microbial population. In the course of 30 days, starch reached 68.3 % mineralization. In similar experiments, cellulose powder reached 100 % mineralization in the course of 60 days (CASTRO-AGUIRRE et al., 2017).

Seed germination, as well as root and hypocotyl sizes, were examined during the ecotoxicity testing with cucumber seeds. Control samples were germinated in both soil washing and Milli-Q water. In the tests, there was no evidence of germination inhibition ($p > 0.05$), and the germination rate was 100% in all samples.

The root and hypocotyl development, however, were both more responsive to the treatment (Figures 42 and 43). The length (cm) of the cucumber root and hypocotyl in comparison to the Milli-Q water control shows that soil washing hindered the tissue growth of

the seeds ($p < 0.05$) in 19.4 and 10.4 %, respectively, indicating the presence of harmful substances in the soil. (ABE et al., 2022). The process of plant tissues development is more vulnerable to toxins than germination, as the first stage of germination doesn't require substrate, which might explain why the tissue development was hindered, while there was no germination inhibition (BALESTRI et al., 2019; LAMONT, 1997).

Figure 42 - Cucumber root and hypocotyl length



Source: author

Figure 43 - Cucumber growth after 14 days in control soil

Source: author

An even higher inhibition was found when applying washing from soils that went through bioplastics disintegration, showing that disintegration exerted a negative effect on tissue development, with 43.47 %, 34.30 %, 46.31 % and 14.01 % inhibition for root development, and 40.29 %, 32.45 %, 47.83 % and 7.25 % inhibition for hypocotyl development, for SB, NAB, LAB and MAB samples, respectively, compared to the growth at soil washing ($p < 0.05$). This result may be related to the production of toxic microbial metabolites, as metabolites produced by microorganisms from both soil and aquatic environment, resulting from biodegradation of polymers, can exert ecotoxic effects (LUCAS et al., 2008).

Another factor that may have affected cucumber tissue development is soil alteration due to bioplastics disintegration, such as the increase in microbial biomass and soil pH change. This phenomenon was also seen when testing ecotoxicity of starch and xylan bioplastics, in which bioplastics disintegration was responsible for an increase in soil pH. Such phenomenon occurred due to the production of alkaline substances, related to the increase in the number of bacterial colonies, owing to the availability of organic matter in the soil, from bioplastics polysaccharides (ABE et al., 2022).

However, due to a higher acetylation degree, MAB presented the highest hydrophobicity, which may have been responsible for impeding microorganisms to utilize its organic matter as substrates. Therefore, a lower amount of microbial metabolite was present in the soil, and pH was not as altered, not affecting cucumber tissue development as much as the disintegration of other bioplastics in the present work.

4. Conclusion

Sugarcane bagasse xylan acetylation with DS ranging from 0.42 to 0.91 was achieved by varying acetylation reaction conditions such as catalyst and solvent contents and reaction time. Both low (0.45) and medium (0.9) DS were chosen in order to analyze the influence of acetyl groups on bioplastic properties as well as compare them to non-acetylated xylan and starch-based bioplastics. A low acetylation degree was responsible for increasing the bioplastics hydrophilicity, water content and solubility, while decreasing the water vapor barrier, due to the hindrance of aggregation among xylan chains.

However, medium acetylation degree caused a reduction in the bioplastic water content and an increase in the water vapor barrier, as acetyl groups reduced xylan affinity with water, which was indicated in the water contact angle analysis. Acetylation in both low and medium degrees caused an increase in the bioplastics rigidity. Due to an increase in their crystallinity,

the mechanical strength needed for its break increased, while its elongation decreased. This resulted in Young's Modulus up to 100 times higher when compared to non-acetylated xylan-based bioplastic. The acetylation degree used in this study showed low influence on the thermal degradation, but DS of 0.9 may have hindered disintegration in soils. The results indicated that the bioplastics show potential for application in food packaging (oil barrier), especially the one with medium acetylation degree due to its oil and water barrier properties, and low affinity with water.

CHAPTER V: GENERAL CONCLUSIONS

The present study aimed to evaluate the influence of reaction conditions on the acetylation degree obtained, as well as the influence of the acetylation degree in the bioplastic formation and properties. It was possible to control xylan degree of acetylation by varying the reaction parameters such as catalyst content and reaction time. Increasing reaction time was responsible for increasing the DS obtained, while the higher sulfuric acid content caused hemicelluloses hydrolysis. Sugarcane bagasse xylan acetylation with DS ranging from 0.42 to 0.91 was achieved and confirmed by FTIR analysis. Acetylated xylan with such DS was water-soluble, which allowed for the application of water as a solvent, and starch and glycerol as copolymer and plasticizer in the bioplastic formation. Both low (0.45) and medium (0.9) acetylation DS showed influence on xylan-based bioplastic properties when compared to non-acetylated xylan and starch-based bioplastics.

In general, the low DS of 0.45 caused an increase in the bioplastics water affinity, while the medium DS of 0.9 has the opposite effect. For instance, low DS bioplastic presented a higher moisture content and water permeability rate when compared to the non-acetylated bioplastic, whereas medium DS bioplastic presented a reduction in both of those properties. This indicates an increase in the hydrophilicity of the low DS bioplastic due to the hindrance of aggregation among xylan chains. However, the low DS applied was not enough to cause an increase in hydrophobicity, which was observed in the bioplastic with medium DS of 0.9, which was indicated by water contact angle analysis.

Acetylation in both low and medium degrees caused an increase in the bioplastics Young's modulus up to 100 times higher when compared to non-acetylated xylan bioplastic. All of the bioplastics studied present oil barrier property, an advantage for package application. Although acetylation is known to hinder polymer biodegradation, the low DS applied in the present study of 0.45 apparently was sufficient to impede the bioplastics disintegration in soil. However, the medium DS of 0.9 may have hindered microbial activity, which caused lower alterations in the soil and, therefore, presented reduced ecotoxicity when compared to other bioplastics in the present work.

The results indicated that acetylation shows potential for enhancing bioplastics properties for packaging material, especially by the increase in mechanical and thermal resistance, and water barrier properties. Polymers chemical modifications have shown to be a great tool in order to enhance biomaterials properties, while still applying renewable sources as

feedstocks. Such researches are detrimental to gradually reducing the application of traditional petroleum-based plastics in society. Therefore, reducing environmental damage, such as threatening wildlife, spreading toxins, and contributing to global warming. Some examples of renewable polymers developed through research and produced and distributed on an industrial scale are cellulose acetate, polylactic acid, starch thermoplastics, and, more recently, ethylene derived from sugarcane, among others. Therefore, the investigation of increasing the application of renewable materials in a wider variety of fields is one of the main tools for a more sustainable society.

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