JOURNAL OF Applied Polymer SCIENCE

Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

EDITORIAL

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REVIEW

Enzymatic-assisted extraction and modification of lignocellulosic plant polysaccharides for packaging applications

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ABSTRACT: Plant polysaccharides comprise the main renewable resource available in the biosphere for biomaterial production. However, the recalcitrant and heterogeneous structure of lignocellulosic biomass hinders the effective fractionation and exploitation of the polysaccharide components for the design of carbohydrate-based materials. Carbohydrate-active enzymes constitute a selective and versatile biotechnological tool that can assist during the biomass pretreatment steps to extract and fractionate the polysaccharide macromolecular components. Moreover, this enzymatic toolbox can be as well exploited for the tailored modification of the molecular structure of relatively pure polysaccharide components to achieve customized macroscopic properties. This review critically discusses the potential and challenges of the use of plant lignocellulosic polysaccharides and enzymatic modifications to design and prepare suitable materials for packaging applications in terms of their structure–property relations. Structural factors such as the molar mass and crystallinity of the polysaccharide fractions and functional factors such as water sensitivity and processability of the derived films are critical for the material performance. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42523.

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LIGNOCELLULOSIC BIOMASS AS SUSTAINABLE FEEDSTOCK FOR THE DESIGN OF CARBOHYDRATE-BASED PACKAGING MATERIALS

The global net primary production of carbon in the biosphere is estimated around 10^{11} tonnes per year,[1] from which polysaccharides account for approximately 75% of all biomass. In this context, plant biomass represents the main renewable resource for biofuel and materials production, as a future replacement of fossil-based energy and goods. New schemes for the sustainable exploitation of biomass have emerged in the last decades (the "biorefinery" concept), which integrate chemical, mechanical, thermal, and biotechnological conversion processes for the generation of energy, platform chemicals, and bio-based polymeric materials. Different generations of biorefineries have been implemented, depending on the biomass source (e.g., agriculture-derived crops and food waste, lignocellulosic biomass, marine feedstock, designer crops) and on the diversity of products that are converted (e.g., bioethanol after fermentation, syngas after thermochemical conversion, fine chemicals, materials). The main driving force in the implementation of biorefineries has been primarily toward the deconstruction of biomass feedstock into amenable sugars for bioenergy production or the synthesis of specialty chemicals. However, due to the instability and the high competence in the energy sector, other versatile and integrated alternatives toward high-value chemicals and materials should be considered. The focus of this review is on the so-called *materials biorefinery*, where the goal is to fractionate lignocellulosic biomass into valuable streams in polymeric form and the design of functional materials with high added value for advanced applications.

Lignocellulosic biomass constitutes a hierarchical polymeric network with cellulose microfibrils as the main structural component, embedded within a matrix of hemicelluloses, pectins, and polyphenolic lignins (Figure 1).[2,3] Cellulose consists of β-D-glucopyranosyl (Glc*p*) (1→4)-linked units that form long linear polymeric chains, which aggregate in partially crystalline microfibrils of few nanometers in diameter. Hemicelluloses comprise different families of structurally-complex sugar copolymers [xylans, mannans, xyloglucans (XyG), and mixed-linkage β-glucans] that share with cellulose a β-(1→4)-linked backbone of neutral sugars with equatorial conformation. However, unlike cellulose, hemicelluloses are decorated with a wide pattern of neutral sugar and uronic acid substitutions, and can be further

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chemically modified by acetylation and methylation.[4,5] Pectins constitute a heterogeneous family of heavily branched polysaccharides with high uronic acid content present mostly in the primary cell wall and the middle lamellae, contributing to cell adhesion and growth.[6,7] Lignin is an extremely complex polyaromatic compound formed by the nonrepetitive polymerization of substituted phenyl propylene units.[8] Due to its hydrophobic nature, lignin provides structural stability to secondary cell walls and it also makes them less permeable to water. The supramolecular organization of lignocellulosic biomass is still not fully understood, although strong covalent, intramolecular and intermolecular interactions exist among all the different polymeric components and contribute to their overall function, recalcitrance, and macroscopic properties. Cellulose microfibrils are interlocked by hemicelluloses by noncovalent intermolecular interactions. The nature of these interactions may be modulated by the complex and heterogeneous molecular structure of the different hemicelluloses in the different plant organisms, tissues, and developmental stages. Lignin, on the other hand, is believed to be covalently bound to hemicelluloses and pectins through different types of lignin–carbohydrate complexes.[9] These supramolecular interactions contribute to the highly crosslinked and tight network architecture of lignocellulosic biomass.

The structural heterogeneity of lignocellulosic biomass at the molecular level and its complex hierarchical organization from the nanoscopic to the macroscopic scale is fundamental for its specific functionality and adaptability in biological tissues.[10] This introduces, however, great variability on the composition and structure of the lignocellulosic feedstock, depending not only on the biomass source, but also on the seasonal and geographical parameters. Galactoglucomannan (GGM) and glucuronoarabinoxylan constitute the main hemicellulosic component in softwoods, whereas hardwoods include preferably glucuronoxylans and glucomannans in their structure. Finally, arabinoxylans and β-glucans are the main hemicellulosic components in cereal (herbaceous) lignocellulosic feedstocks. Pectins are normally minor components in lignocellulosic feedstocks, and they are mainly present in the primary cell wall and in the middle lamellae. The complexity and variability of the feedstock imposes major difficulties for the implementation of large-scale biorefinery platforms for the biotechnological exploitation of biomass into biofuels and biomaterials. Several families of plant polysaccharides are present in the different lignocellulosic biomass feedstocks, with clear structural heterogeneity in terms of the constituent sugars and pattern of intramolecular substitutions (Figure 2). Our main challenge as engineers is therefore to design technological processes that are able to extract and fractionate the different macromolecular components in lignocellulosic biomass and to modify the structure at the molecular level to target for specific properties exploited in the design of new materials with advanced applications. In this context, the use of carbohydrate-active enzymes (CAZymes) constitutes a versatile and extremely selective tool to assist on the extraction and modification of carbohydrate-rich fractions. CAZymes comprise all the different enzymes involved in the synthesis and degradation of complex carbohydrates in nature and they include a wide range of families that are constantly being expanded and categorized.[11,12] These enzyme families include (i)

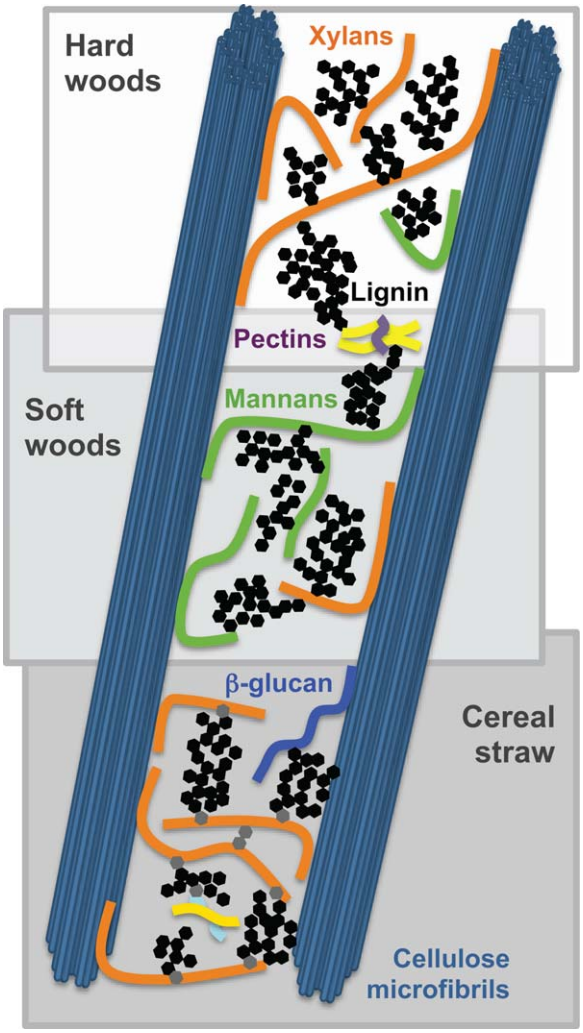

Figure 1. Schematic presentation of the supramolecular organization of lignocellulosic biomass from different sources (hardwoods, softwoods, and cereal straw). The main macromolecular constituents are cellulose microfibrils, hemicelluloses, and lignins, which are tightly interlinked by covalent and noncovalent bonds to create a highly dense polymeric network. The molecular composition and structure of the polysaccharide fractions differ depending on the biomass source. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

glycoside hydrolases (GH) responsible for the hydrolysis of the glycosidic bonds in carbohydrates; (ii) polysaccharide lyases (PLs) responsible for the nonhydrolytic cleavage of glycosidic bonds among acidic (uronic acid) carbohydrates; (iii) carbohydrate esterases (CEs) that catalyze the desterification of carbohydrate esters; (iv) glycosyltransferases (GTs) responsible for the formation of new glycoside units; and (v) auxiliary active (AA) enzymes including lytic polysaccharide monooxygenases (LPMOs) and lignin-degrading enzymes that act through redox mechanisms. The mode of action of some of the CAZymes discussed in this review for the extraction and structural modification of lignocellulosic plant polysaccharide substrates is presented in Figure 2.

This review focuses on the application of CAZymes as biotechnological tools in the fractionation and modification of plant polysaccharides from lignocellulosic biomass, in order to produce carbohydrate-based materials potentially applicable in the packaging sector. We will critically discuss the effects of the different enzyme combinations in the extraction and fractionation pretreatments. The possibilities for enzymatic modification of the different plant polysaccharide families will be presented, establishing important correlations between changes in molecular structure and macroscopic properties. Finally, the potential for the utilization of plant polysaccharide materials in packaging applications will be addressed, together with the current technological challenges to achieve a successful replacement of current oil-based packaging materials.

ENZYMATIC-ASSISTED EXTRACTION OF PLANT POLYSACCHARIDES IN A MATERIALS BIOREFINERY CONTEXT

Conversion of lignocellulosic biomass into valuable products, either through the targeted deconstruction into a sugar and phenolic platform for further fermentation and chemical synthesis or through the fractionation of their macromolecular components (polysaccharides and lignin), requires an efficient pretreatment stage. This stage is crucial as it has a strong influence in the subsequent enzymatic stages of bioconversion. The pretreatments should break the lignin seal, decrease cellulose crystallinity, and increase the surface area available for the enzymes to effectively penetrate into the biomass network and access the cellulose and hemicellulose substrates.[13] An efficient pretreatment involves fractionation of most part of the lignin from the polysaccharide components while minimizing carbohydrate loss or depolymerization. Ideally, the pretreatment step should also avoid excessive formation of enzyme inhibiting substances, such as furfural or other phenolic compounds, as well as the use of toxic or hazardous chemicals. Additionally, the equipment and waste management costs should also be taken into consideration if the process is conceived to be scaled-up. Many reviews can be found that directly or indirectly deal with the different physical, chemical, and biological pretreatment procedures, summarizing specific advantages and drawbacks.[13–15] It must be noted, however, that traditionally implemented procedures involving aggressive oxidative, acidic, or alkaline conditions mostly lead to structural changes of the native polysaccharide components, including depolymerization and deacetylation. Physical preprocessing, such as fine mechanical grinding, and more recently, steam explosion, microwave, or ultrasound-assisted extractions are also additional or alternative tools to assist in the isolation of hemicelluloses from different plant sources.[13,16] For the efficient extraction of high molecular weight polysaccharide fractions, organic solvents, organic acids, ionic liquids, or hot water (150°C–180°C) extraction with mild pH conditions (between pH 4 and 7) can be combined.[17–19]

In contrast with chemical treatments, enzymatic treatments are very specific and take place at much milder conditions. Therefore, enzymatic treatments are usually implemented after or even in-between pretreatment stages to assist in the extraction and fractionation of polymeric components or in the pursuit of complete conversion of plant biomass into energy or other fine

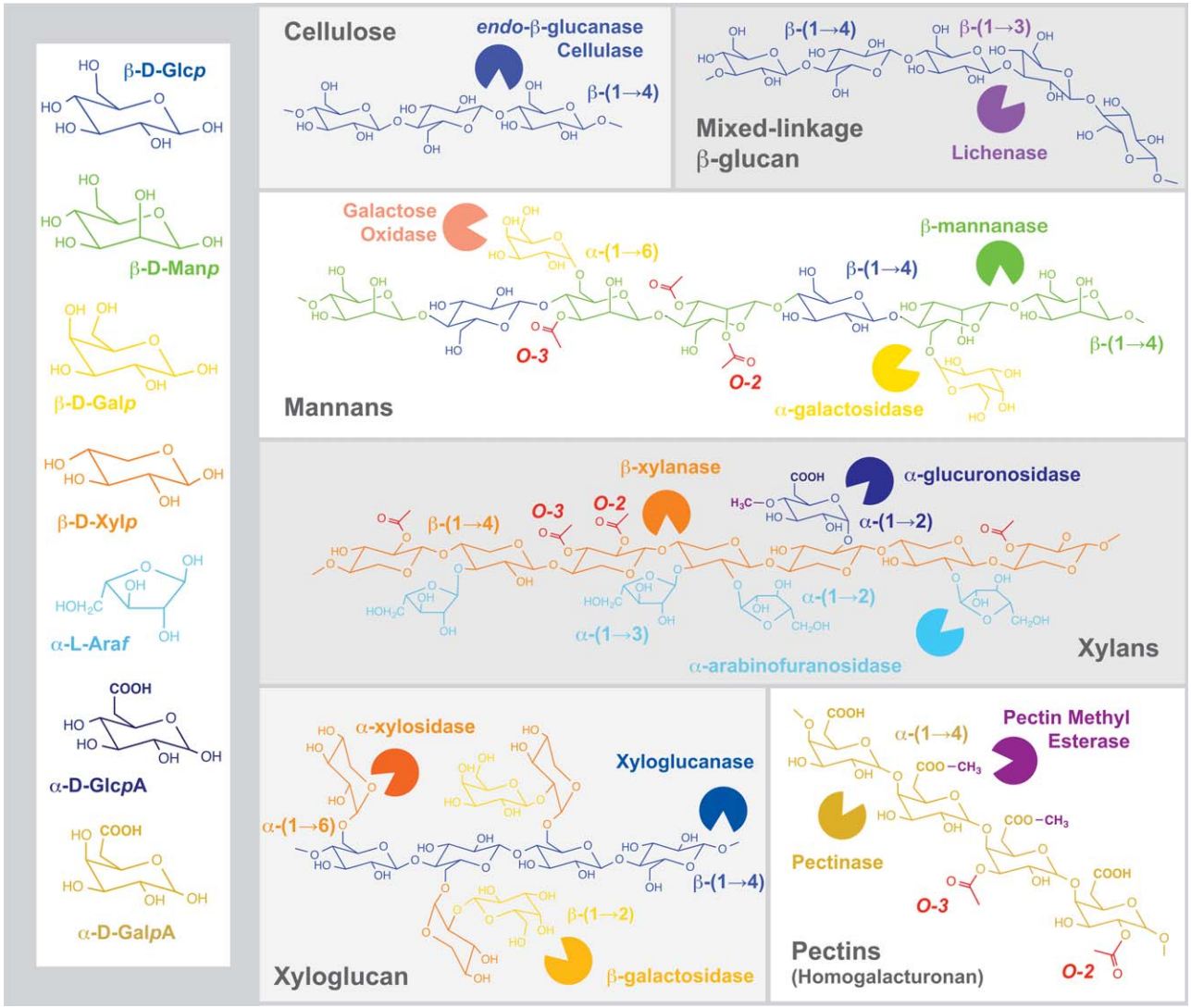

Figure 2. Polysaccharide constituents in lignocellulosic biomass and the action of selected carbohydrate-active enzymes (CAZymes) on the carbohydrate structures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemicals. The latter approach relies on the combination of multiple enzymes (enzyme cocktails), which would theoretically cleave all the existing linkages to systematically depolymerize plant polysaccharides. The extensive pool of GH, lyases, and esterases, their isolation sources, and their cleavage activities have been previously reported and are constantly being updated.[11,20] There are also several commercial grade enzymes and enzyme cocktails that have been used in this context, mostly incorporating polysaccharide backbone-cleaving enzymes, such as *endo*glucanases (UltraFlo®, FiberCare R®, Accellerase BG®), cellulases (Celluclast 1.5L®, Accellerase 1500®), xylanases (Pentopan Mono BG®, Accellerase XY®, NS50030®, NS50014®), mannanases (Mannaway®), and pectinases (Pectawash®, XPect®). Accessory enzymes, including hemicellulose debranching enzymes such as arabinofuranosidases, glucuronidases, galactosidases, and feruloyl esterases can be as well added to assist in saccharification. Nevertheless, even when a high number of hydrolases of different origin are synergistically combined, complete saccharification is not achieved,[21,22] which points out the complexity of enzyme synergism and biomass recalcitrance. On the other hand, many commercial grade enzymes have been observed to exert side activities.[23,24] As the enzymatic treatment results in most cases in a material that is partially depolymerized, the currently existing literature is mostly focused on applications for oligosaccharides or hemicellulosic materials with a low degree of polymerization. These applications range from dietary supplements[25,26] to hydrogels for the food or medical industry.[27–31]

Enzyme-assisted extraction of specific plant polysaccharide fractions in polymeric form has been mostly based on the action of glycosyl hydrolases to disrupt the lignocellulosic network by specifically cleaving one or more of its components. The most common example is the use of xylanases within the pulping industry. The addition of xylanases prior to alkaline treatment enhances pulp extraction yields and reduces the concomitant use of hazardous chemicals.[32,33] Additionally, the use of

xylanases could promote the transformation of kraft pulp into dissolving pulp, as xylanases increase the efficiency of subsequent *endo*glucanase treatments.[34,35] In this direction, the incorporation of a xylanase and a cellulase treatment before and in-between alkaline treatments increased the yield of cellulose and xylans extracted from hardwood pulp, and allowed the isolation of different fractions of polymeric xylan and/or xylo-oligosaccharides, depending on the desired application.[24] The effect of hemicellulases renders different behavior depending on the nature of the substrate. Enzymatic treatment with either a xylanase or a mannanase after mild alkali treatment at high temperature (150°C) and defibrillation was used to extract polymeric xylan and mannan from spruce wood. Surprisingly, the yield and the degree of polymerization of the extracted xylan increased with the xylanase treatment, whereas the degree of polymerization of mannan was significantly decreased, as mannan was found to be very sensitive to peeling at its reducing end.[36] This drawback was overcome recently by chemically modifying the reducing end of mannan, either by using a reducing agent or by oxidizing the reducing end to a carboxylate to prevent sequential depolymerization reactions during alkaline treatment.[37]

Similar studies have been performed in annual plant biomass feedstock, which possess the advantage of having hemicellulose fractions with higher molecular weight than their wood counterparts. A combination of xylanases and cellulases was applied to extract polymeric and oligomeric arabinoxylan (AX) hydrolysates from spelt bran and hull, with degrees of polymerization between 1 (xylose) and 1164 (polymeric xylan).[23] This generated a versatile palette of xylan materials with diverse applications, since polymerized AXs can form gels and consequently can be used in the food industry for texturization and stabilization,[38] arabino-xylo-oligosaccharides (AXOS) present interesting properties as prebiotics,[39] and monomeric xylose can be transformed into ethanol [40] and xylitol.[41] Another example is the use of cellulases to enable the extraction of pectins from fruit peels at high yield, releasing pectic polysaccharides with similar gelling and stabilizing properties to acid-extracted pectin.[42,43] This evidences that enzymatic-assisted extraction is a favorable alternative to traditional acidic extraction in terms of selectivity, energy consumption, and waste management.

Additionally, other auxiliary enzymes and proteins such as LPMOs, expansins, swollenin, and carbohydrate-binding modules (CBMs) can assist in opening up the lignocellulosic structure to enhance ulterior action of GHs. Some of these proteins do not only disrupt crystalline arrangements in biomass, but they can also assist in the extraction of hemicelluloses. The action of LPMOs onto lignocellulosic biomass has been ascribed to oxidative processes of the crystalline structures.[44] In addition to this, LPMOs can also degrade decorated XyG and therefore assist in their extraction.[45] However, the disruption mechanisms caused by the other proteins are not fully understood yet. Certain CBMs can induce amorphogenesis of the fibrillar structures in biomass without hydrolytic action, thus assisting in opening up crystalline structures.[46] On the other hand, swollenin, a non-hydrolytic disruptive protein, was observed to act synergistically with xylanases, enhancing xylan extraction, while no such synergy was found with cellulose degrading enzymes.[47]

Although extensive research has been dedicated recently for the optimized accessibility, release and fractionation of the different components in lignocellulosic biomass, comprehensive technologies for the selective isolation of the different polysaccharide fractions without extensive degradation during the isolation process still need to be implemented. The integrated and rational combination of physicochemical pretreatments with the synergistic action of specific proteins and hydrolytic enzymes will definitely contribute to the selective and efficient extraction, fractionation, and targeted modification of plant polysaccharides for the production of added-value materials in a number of applications.

TAILORING THE STRUCTURE AND PROPERTIES OF POLYSACCHARIDE-BASED MATERIALS USING ENZYMATIC MODIFICATIONS

Once isolated from the initial lignocellulosic feedstock in the biorefinery pretreatment, extraction, and fractionation stages, the relatively pure polysaccharide fractions can be used in a wide variety of functional products and applications. Indeed, in addition to being a major nutritional source, polysaccharides are extensively used due to their functional properties, such as thickeners, gelling agents, stabilizers, interfacial agents, flocculants, and encapsulants. Typical applications include food modifiers, adhesives, coatings, construction, paper, pharmaceuticals, and personal care.[48–51] For many of these applications, polysaccharides need structural modifications in order to improve or customize their properties. These structural modifications can be achieved by chemical reactions and by enzymatic treatments (e.g., [49,52,53]). The major advantages of enzymes in polymer modification compared with chemical methods involve the high specificity and regioselectivity of the reactions onto the polysaccharide substrates, and the milder and environmentally benign reaction conditions with minimal side reactions and degradation.[54] In this section, we will thoroughly review the enzymatic modification of the different families of lignocellulosic-derived polysaccharides, focusing on the selective structural changes and the tailored macroscopic properties achieved by such modifications (Table I).

Pectins

Pectins are highly complex macromolecules with high uronic acid content that involve different interconnected linear and heavily branched domains, including homogalacturonan (HG), rhamnogalacturonan I and II, arabinan, and arabinogalactan.[6,7] In particular, HG consists of a linear chain of α-D-galacturonic acid (GalA) (1→4)-linked residues, being partly methylesterified at O-6 [55] and sometimes acetyl-esterified at O-2 or O-3.[56] Pectins are used in the food industry since they provide viscosity and enable gelling, they stabilize proteins and act as a fat mimetic.[56–58] The functional properties of pectins (e.g., the gelling properties) and their reactivity toward calcium and other cations is largely dependent on the amount of methylated GalA units (degree of methylation, DM) and their distribution pattern within the galacturonan stretches (Figure 2). Two general patterns of methyl ester distribution are recognized, random, or ordered. These patterns are normally measured by the size of the demethylesterified blocks (DMBs).[59] Since the DM and the size

Table I. Summary of the Enzymatic Modification of Specific Plant Polysaccharides: Structural Modifications, Tailored Macroscopic Properties, and Potential Applications.

Polysaccharide	Enzymes involved	Structural modification	Tailored properties	Application
Pectins	Pectin methylesterase (PME) (EC 3.1.1.11) Pectin acetyl esterases *Exo*-α-L-arabinofuranosidases (EC 3.2.1.55) Rhamnogalacturonase (RGase) (EC 3.2.1.171) Polygalacturonase (PGase) (EC 3.2.1.15) *Endo*-arabinanase (EC 3.2.1.99)	Demethylesterification Deacetylation Side group cleavage Backbone cleavage (M_w reduction)	Solubility Rheology Gel formation	Gelling agent
Xylans	*Exo*-α-L-arabinofuranosidases (EC 3.2.1.55) *Exo*-α-glucuronidase (EC 3.2.1.131) *Endo*-β-xylanase (EC 3.2.1.8)	Side-group cleavage Backbone cleavage (M_w reduction)	Solubility Tensile and barrier properties	Encapsulant Binder Films/coatings
Mannans	*Exo*-α-galactosidase (EC 3.2.1.22) *Endo*-β-mannanase (EC 3.2.1.78) Galactose oxidase (GalOx) (EC 1.1.3.9)	Side-group cleavage Backbone cleavage (M_w reduction) Introduction of carbonyl groups	Gel/film formation Rheology	Gelling agent Thickener/emulsifier Stabilizer Hydrogels/aerogels
Xyloglucan	*Exo*-β-galactosidase (EC 3.2.1.23) Xyloglucanase (XEG) (EC 3.2.1.151) Xyloglucan endo-transglycosylase (XET) (EC 2.4.1.207)	Side-group cleavage Backbone cleavage (M_w reduction) Transfer of XG oligosaccharides onto a XG polymer	Solubility Gel formation Introduction of chemical functional groups	Gelling agent Packaging Textile Papermaking Surface functionalization Generation of biocomposites
Cellulose	*Endo*-glucanases (EC 3.2.1.4)	Hydrolysis	Solubility	Generation of cellulose nanostructures

of DMBs are related to pectin functionality, detailed knowledge of pectin fine structure, block sizes, and their numbers could aid in understanding the functional properties obtained from rheological measurements. Demethylation of pectin can be accomplished by enzymatic or chemical (alkaline demethylation) methods, which influence firmness via calcium-pectin interactions.[60] For enzymatic demethylation, three different modes of action have been hypothesized,[61] two of which lead to blockwise (ordered) removal of esters. Some studies have demonstrated the feasibility of modifying HG enzymatically and characterizing the introduced nanostructure, correlating functionality with structure and modeling the enzyme mode of action under different reaction conditions.[60,62–65] Demethylesterification of a model HG with a salt-independent pectin methyl esterase (PME) isolated from *Citrus sinensis* generated sample series with tailored DM, between 50% and 90%, showing different rheological properties and calcium sensitivity. However, the size and the number of DMBs per molecule, which can be manipulated, need to be considered as well to account for the pectin functionality.[63] In a parallel study, the gelling properties were correlated with the methyl ester distributions using the concept of degree of blockiness (DB), which is related to the length of the methylated GalA accessible for enzymatic degradation by an *endo*polygalacturonase (from family GH28) and thus related to the length of the methylated blocks. The ability to form calcium-induced pectin networks seems to depend more on the DB than on the DM, with increasing gel strength for pectins with a higher DB.[64]

Other routes for the enzymatic modification of pectins involve the removal of acetyl groups by pectin acetyl esterases (family CE12). These deacetylation treatments result in an improvement of the gelling properties.[43,66–69] Finally, other studies have focused on the enzymatic modification of the hairy segments of pectin, that is, the rhamnogalacturonan, arabinan, and the arabinogalactan domains. Arabinans extracted from sugar beet pulp could be used as fat replacer after debranching with α-arabinofuranosidase.[70] On the other hand, synergistic enzymatic combinations of *exo* arabinofuranosidase B (AF) plus *endo*-α-arabinase (EA), rhamnogalacturonase (RGase) plus rhamnogalacturonan acetyl esterase (RGAE), and finally polygalacturonase (PG) plus PME were used to modify the physicochemical properties of rhamnogalacturonans and arabinans and commercial acid extracted beet pectin.[43] In general, the intrinsic viscosity of the polysaccharides decreased only when the backbone-degrading enzymes were used.[43] On the other hand, enzymatic modifications for the removal of side chains, including the simultaneous release of methoxyl, acetyl, arabinose, and xylose

residues, yielded pectins with significantly improved gelling properties only in the presence of calcium without a significant loss of viscosity.[67,71] However, these enzymatic alterations in the absence of calcium caused a considerable decrease in viscosity.[71] This increase in functionality was attributed to the decrease of neutral sugar content and increase of the acidic nature of the modified pectins.[71]

Xylans

Xylans are one of the most abundant biopolymers in biomass, since they are the main hemicellulose in annual plants and hardwoods, and can also be found in softwoods.[4,72] Xylans are heteropolysaccharides with varying degrees and types of substitution, depending on plant species, but also between different parts of the plant. Xylan consists of a backbone of (1→4)-linked *β*-D-xylopyranose (Xyl*p*), which may be substituted by acetyl groups (especially in hardwoods), arabinofuranosyl (Ara*f*) in the α-(1→2) and/or α-(1→3) positions, and 2-*O*-substituted by α-D-glucuronic acid (either unsubstituted –GlcA- or methylated in the C4 position 4-*O*-Me-GlcA) (Figure 2).[73,74] *Endo*-*β*-xylanases cleave the *β*-Xyl*p*-(1→4)-linked units of the backbone, whereas *exo*-α-arabinofuranosidases and *exo*-α-glucuronosidases remove the Ara*f* and GlcA substitutions, respectively. Different studies have focused on tailoring the substitution pattern in xylans by chemical or enzymatic means, in order to modify the macroscopic properties and to assist on the preparation of xylan-based films with barrier applications.[75–80] The variation in arabinose substitution has a great impact on the solubility and material properties of the xylans. The arabinose substituents can be partially removed using mild acid in combination with heat, but this causes the concomitant reduction of chain length. The use of specific α-L-arabinofuranosidases that cleave terminal arabinofuranosyl residues from different arabinose containing polysaccharides or oligosaccharides constitutes a more controlled method for tailoring the AX structure.[73,81] Different α-L-arabinofuranosidases acting on polymeric xylans (arabinoxylan arabinofuranohydrolases, AXH) can be exploited depending on their substrate specificities. Some AXHs act on (1→2)-linked and (1→3)-linked α-L-arabinofuranosyl units on monosubstituted xylopyranosyl residues (AXH-m, family GH51), whereas others release solely (1→3)-linked α-L-arabinofuranosyl units from disubstituted xylopyranosyl residues (AXH-d3, family GH43).[82] AXH-m was used to prepare a gradient of rye AX materials with controlled Ara*f*/Xyl*p* ratio, so as to investigate the effect of arabinose substitution on the material properties.[75] Progressive debranching of AX caused not only agglomeration of the polysaccharide in water, but also a higher degree of crystallinity and increased oxygen barrier properties of the prepared films. The water sorption of debranched rye AX decreased at high RH, but increased at low RH, as compared to untreated AX. These effects were further confirmed in following works.[76–79] While elongation at break was significantly decreased with debranching, in most cases the tensile strength of the films was generally not improved. Further studies combined an α-L-arabinofuranosidase (AXH-m) with an *endo*-*β*-xylanase onto a high molecular weight rye AX, to mimic different naturally occurring xylans.[76] This allowed a systematic control of the degree of substitution (DS) and the molecular weight. The enzymatic modification enabled the formation of self-ordered structures with higher crystallinity and also influenced the interactions with microfibrillated cellulose and their reinforcing effect on the mechanical properties. Finally, a comprehensive study on the effect of both mono-substitution and di-substitution of Xyl*p* units on the film properties of water-soluble wheat AXs was performed, covering the tensile and barrier properties, as well as morphology and sorption studies.[80] The degree and pattern of Ara*f* substitution were systematically tailored using both a single-substitution and double-substitution selective α-arabinofuranosidases (AXH-m and AXH-d3, respectively), producing modified AX samples with similar Ara*f*/Xyl*p* ratios, but they differed in the number of unsubstituted Xyl*p* units. An increase in the number of unsubstituted Xyl*p* units decreased the temperature of relaxation of small-scale molecular motions of AX (*β*-relaxation) and increased the degree of crystallinity of the films. Thus, the increase in crystallinity, elongation at break, oxygen barrier properties, and the decrease of the tensile strength and water solubility were attributed to the DS (e.g., presence of substituted Xyl*p* units) rather than to the overall Ara*f*/Xyl*p* ratios.

There is still lack in evaluating the effects of such enzymatic modifications in xylans derived from other sources than cereals. An attempt to tailor the structure of xylans from sugarcane bagasse and eucalyptus wood using selective removal of arabinose and 4-*O*-methyl glucuronic acid (4-*O*-MeGlcA) side chains by treatment with α-L-arabinofuranosidase and α-glucuronidase, respectively, is reported by Chimphango *et al.*[83] As a result, the α-L-arabinofuranosidase removed about 14% of the available arabinose in the xylans extracted from bagasse, which led to precipitation in water. However, the α-glucuronosidase removed only 2% of the available 4-*O*-MeGlcA from bagasse and eucalyptus xylans, and no visible precipitation of the xylan in water was observed.[83] These studies prove the complex and sometimes conflicting effect of the molecular structures of xylans, namely the substitution pattern and the molecular weight, on the macroscopic properties of the derived carbohydrate-based materials.

Mannans

Mannans constitute the main hemicelluloses in softwoods and are also present in great abundance in seeds as nonstarch energy-reserve polysaccharides.[4,84,85] Mannans consist of a backbone of *β*-D-mannopyranosyl (Man*p*) (1→4)-linked solely or in combination with D-glucopyranose (Glc*p*), which may be substituted by single D-galactopyranosyl (Gal*p*) groups in the O−6 positions and also acetylated (especially in softwoods) in the C-2 or C-3 positions.[86,87] *Endo*-*β*-mannanases cleave the *β*-Man*p*-(1→4)-linked backbone, whereas exo-α-galactosidases remove the α-(1→6)-Gal*p* substitutions. Galactose oxidase (GalOx) selective oxidizes the hydroxyl group in the C-6 position of Gal*p* (Figure 2). Depending on the backbone and substitution pattern, mannans can be further classified into linear mannans, glucomannans, galactomannans (GM), and GGM. GM such as guar and locust bean gum are widely used in food products to improve mouth feel and chewiness, elongate shelf-life through moisture retention, and prevent syneresis.[88] Many of these functions are achieved by mixing GM with other polysaccharides, such as xanthan and carrageenans. GM have the ability to affect gelation in polysaccharide systems that are otherwise nongelling,

rendering stability, texture, and controlled rheological characteristics to food.[89] GM can be selectively modified by enzymatic hydrolysis at two sites, namely, the β-(1→4) linkages between the Man*p* sugar units on the backbone and the α-(1→6) linkage between the mannose unit on the backbone and the Gal*p* side chain. Enzymatic degradation of native guar gum by *endo*-β-mannanase drastically reduces the viscosity of the solutions, due to the molecular weight reduction caused by the backbone-cleaving enzyme.[89] Furthermore, enzymatic modification by *endo*-β-mannanase and *exo*-α-galactosidase was applied to native guar gum and locust bean gum to systematically examine the effect of the degree of polymerization and the DS on the properties of GM-based films.[90] GM with lower galactose content (locust bean gum, modified guar gum) produced films with higher elongation at break and tensile strength. Moreover, the mechanical properties of guar gum GM-based films with higher Gal*p* content could be improved by decreasing the degree of polymerization with controlled β-mannanase hydrolysis to be comparable to those of locust bean gum.[90]

Another route to tailor the structure, chemistry, and properties of galactose containing polysaccharides consists of using GalOx. Plant polysaccharides as GM, GGM, arabinogalactan, and XyG include terminal galactose in their molecular structures, with contents varying from 6% to 40%. GalOx is capable of selectively oxidizing the C-6 hydroxyl groups of such terminal galactose moieties to carbonyl groups, thus opening new routes for further chemical derivatization.[91] Catalase and horseradish peroxidase were used to enhance the action of GalOx and the best oxidation degrees of terminal Gal*p* groups were obtained with XyG (85% Gal*p*) and spruce GGM (65% Gal*p*).[91] The oxidation resulted in changes in the hydrodynamic properties of the polysaccharide solutions. Tamarind XyG formed a gel after oxidation; on the other hand, spruce GGM exhibited larger particles in solution after oxidation, but changes in its rheological properties were not observed.[91] Partially oxidized high molecular weight GM by GalOx were used to prepare hydrogels[27] and aerogels.[92] The resulting hydrogels showed improved solution properties when forming highly viscous gels and a significantly increased thermal stability. On the other hand, the freeze-dried aerogels exhibited enhanced mechanical and thermal performance.

Xyloglucan

XyG is a major hemicellulose constituent of the primary cell walls of plants and can also be found as storage polysaccharides in certain seeds and fruits.[93,94] XyG has a very distinct molecular structure, consisting on a (1→4)-linked β-Glc*p* backbone, heavily substituted in O-6 with α-xylopyranosyl residues that can themselves be occasionally further substituted in O-2 with β-galactopyranosyl units.[95] Xyloglucanases (XEG) specifically cleave the unsubstituted Glc*p* units in XyG, whereas β-galactosidases and α-xylosidases progressively trim the Gal*p* and Xyl*p* decorations, respectively (Figure 2). The available enzymatic palette for the modification of XG is quite versatile, involving not only glycosyl hydrolases but also transferases (XET, xyloglucan endotransglucosidase) capable of attaching two XyG polysaccharides together. The removal of Gal*p* decorations by β-galactosidase can influence the gelling behavior of tamarind seed XyG. Indeed, gelation was observed when approximately 35% of the galactose residues had been removed. The enzymatically tailored XyG showed to have two sol–gel transition temperatures, which is a rather uncommon phenomenon only observed in pectin and carrageenan.[95] On the other hand, XyG films possess high strength, stiffness, and oxygen barrier properties, but are sensitive under high humidity conditions. The hydrothermal stability was improved by the removal of side-chain galactose residues by β-galactosidase.[96] The modified XyG samples showed significantly reduced solubility in water, which could be predicted by the estimation of Hansen solubility parameters. The elastic modulus and the oxygen barrier properties increased markedly at high relative humidity (50–80%), due to the lower sensitivity toward moisture absorption of XyG after side-chain removal. This enhanced preservation of mechanical and barrier properties of modified XyG at large humidity conditions may be significant in applications such as food packaging.

The potential of XyG to bind to cellulose surfaces without disrupting cellulose fiber integrity was exploited to selectively perform surface modification with a chemoenzymatic procedure using xyloglucan endotransglycosylases (XET). XET enzymes regulated the flexibility of plant cell walls during growth by mediating the cleavage of the XyG backbone in an *endo*-manner and the transfer of the cleaved XyG chain onto the 4-*O* position at the nonreducing end of another XyG molecule.[97] This enzymatic selectivity was here exploited to transfer a wide range of chemically-modified XyG oligosaccharides (XGOs) with well defined structures onto polymeric XyG.[98] These chemoenzymatically modified XyGs can be afterwards adsorbed onto cellulose surfaces, introducing a broad variety of chemical moieties without disrupting the mechanical integrity and properties of the cellulosic fibers.[99] This XET technology has been consequently expanded to provide a new route for the generation of biocomposite materials, by the controlled graft polymerization of methyl methacrylate (MMA) on cellulose fibers through a combination of the XET and atom transfer radical polymerization (ATRP) techniques.[100] This method can thus be used to functionalize cellulose surfaces to develop novel, high-performance paper and packaging materials, or in the design and manufacture of advanced biocomposite materials with defined structures and properties.[100]

Cellulose

Cellulose in plant cell walls is arranged in partially crystalline microfibrils oriented by interchain and intrachain hydrogen bonding, due to the rigid conformation of the linear β-(1→4) linkage, embedded in less-oriented amorphous regions.[101–103] The presence of three reactive hydroxyl groups on each β-D-Glc*p*-(1→4)-linked unit enables chemoenzymatic modification and functionalization of cellulose, in order to improve dispersibility or to give higher added-value for some specific applications. Different reviews focus on the chemical modification of celluloses either in the bulk or specifically on the cellulose surfaces.[104–111] However, literature on the enzyme-assisted functionalization of celluloses is still scarce. Additional functionalities can be achieved by transforming the hydroxyl groups into their oxidized form as either carbonyl (aldehydes and ketones) or

carboxyl groups, which then determine the macroscopic properties and chemical behavior of such cellulosic derivatives.[107,112] In this way, enzymes such as esterases and cutinases can be used as biocatalysts in the modification of cellulose structure, introducing long chain fatty acid esters by enzymatic acylation.[113] Lipases were used to catalyze the acetylation of water-soluble carboxymethyl cellulose. However, when tested on solid cellulose substrates in aqueous solution, lipases proved limited acetylation extent.[114] On another route, laccases were exploited to assist on the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation of cellulose surfaces to generate aldehyde and carboxylic acid derivatives.[107] Hydrolytic enzymes such as *endo*glucanases can be used to facilitate the disintegration of cellulose microfibrils and assist on the preparation of cellulose nanocrystals and nanofibers from different sources,[115–117] instead of promoting a functionalization of the structure. These enzymatic treatments are beneficial in comparison to more aggressive chemical hydrolysis, in terms of sustainability and control of the morphology of the derived nanostructures.

APPLICATIONS OF PLANT POLYSACCHARIDE MATERIALS IN THE PACKAGING SECTOR: CHALLENGES AND FUTURE PROSPECTS

Although plant polysaccharides constitute an immense source of potential packaging materials, related literature is still relatively scarce. The inherent recalcitrance of plant biomass feedstock has been traditionally confronted with aggressive physicochemical and thermomechanical treatments, which cause depolymerization and drastic changes in the native structure of the different polysaccharides. Milder alternative pretreatment stages are only starting to be explored and finding the suitable combination of physicochemical and enzymatic conditions is still a pending challenge. Additionally, there is a significant lack of knowledge as to the intricate supramolecular structure of the different constituents in plant biomass depending on the origin, geographical, and seasonal conditions, which makes it difficult to predict and design suitable extraction as well as enzymatic modification methods.

Table II summarizes the state-of-the-art literature on the generation of carbohydrate-based materials for potential use in packaging applications, together with the preparation methods employed and the resulting macroscopic properties. In the pursuit for new carbohydrate-based film materials, there are several crucial inherent structural and external parameters affecting the potential film forming properties and the mechanical, thermal, and barrier properties of the generated films. These include molecular weight, presence of salts, water content and water sensitivity, aging, and thermal stability.

Effect of Molecular Weight

Probably, one of the factors that most predominantly promote the potential film-forming capacities of polysaccharides, as well as the suitability of materials' properties for packaging applications, is the molecular weight. Successful extraction of a high molecular weight polysaccharide with film-forming capacity has been achieved from tamarind seed XyG.[96] The potential use of XyG in the production of films has been enzymatically improved by reducing galactose substitution, which increased the oxygen barrier properties and the toughness of the polymer matrices.[96,118] Although the high glass transition temperature (245°C) of the XyG films can limit their use for thermal processing, this drawback could be surmounted by chemical oxidation with periodate.[119] However, this chemical oxidation resulted in a concomitant decrease in oxygen barrier properties, which poses future challenges as to elucidate a possible milder chemical or even enzymatic treatment. As suitable methods for the extraction of high molecular weight hemicelluloses are being optimized, other ways of increasing molecular weight have been explored involving chemical or enzymatic modification. Chemical crosslinking of GGM has been accomplished with glyoxal or ammonium zirconium carbonate.[120,121] In both cases, the crosslinking allowed the production of continuous films without the addition of plasticizers. When ammonium zirconium carbonate was used, crosslinking also improved the mechanical and oxygen barrier properties.[121] However, crosslinking can also be enzymatically approached without the use of chemicals. This has been successfully implemented by the use of laccase (EC 1.10.3.2.). This enzyme crosslinks lignin associated aromatic residues, consequently increasing the molecular weight of the extracted polymer and improving the mechanical and barrier properties.[122–125] Blends of spruce GGM and carboxymethylcellulose exhibited improved mechanical properties due to crosslinking with laccase.[122] On another study, films were prepared from relatively low molecular weight xylans from pulp process water, after crosslinking with laccase and separating the high molecular fraction by membrane filtration.[123] Finally, laccase crosslinking could also add additional oxygen scavenging functionalities while improving mechanical properties, when starch films were mixed with lignosulfonates and subsequently crosslinked.[124,125]

Introduction of Plasticizers, Blends, and Reinforcing Agents

So far, the use of enzymatically extracted hemicelluloses with lower molecular weight such as AX or GGM has shown detrimental film-forming capacities. This can be overcome by the addition of plasticizers, such as sorbitol or glycerol (10–60 wt %) to promote film formation, as well as by blending the polysaccharides with other materials, which might reinforce or complement the mechanical and barrier performance. One interesting approach is the use of blends of hemicelluloses from different origin to create all-carbohydrate materials. Blends of purified water-extractable AX from rye bran and partially hydrolyzed β-glucan from oat showed both increased strength and elongation at break while maintaining the oxygen barrier properties of AX.[126] Mikkonen *et al.* produced blends of GGM from spruce pulp with AX and partially hydrolyzed GM extracted from konjac. While the addition of konjac GM exerted a positive effect on the mechanical properties of the materials, AX did not enhance the toughness of the material but resulted in a plasticizing effect similar to glycerol or sorbitol.[127] Enzymatically debranched AX was used in subsequent blends with other cellulose-based materials, such as microfibrillated cellulose,[76] cellulose nanowhiskers,[128] and bacterial cellulose.[77] The addition of these fillers to partially debranched rye AX did not affect the thermal behavior or the crystallinity of

the materials and enhanced the toughness of the blends as compared to commercial rye AX.[76,77] Although there were slight improvements in the blends due to debranching, the improvements in mechanical performance could mostly be attributed to the cellulose reinforcement rather than to the enzymatic treatment itself. The complementary positive effects of blending xylan and GGM hemicelluloses with cellulose in its different forms without any enzymatic treatment have been shown in several works.[129] Analogously, GGMs have been blended with carboxymethylcellulose,[122] microfibrillated [130] and nanofibrillated cellulose.[132] Other noncarbohydrate fillers have been added to extracted and modified hemicelluloses as reinforcing agents. In this sense, clays such as sepiolite have also been used to substantially enhance mechanical properties of rye AX at concentrations as low as 2.5 wt %.[132]

Presence of Salts and Water Sensitivity

Another factor that influences the ability of extracted polysaccharides to form films with suitable properties is the presence of salts. High salt concentrations are found in polysaccharides after most chemical extraction methods. These salts have been found to have serious detrimental effects on the film forming and mechanical properties of the produced materials,[133,134] which implies additional costs for salt removal. Interestingly, Bahcegul *et al.* investigated the influence of potassium acetate salt on the film properties of corn cob xylan films, and found that its addition without the presence of other salts actually enhanced the properties of the films.[134]

Water content and water sorption isotherms are very important features in hemicellulose-based films, due to the high hydrophilic nature and moisture susceptibility of such materials. Indeed, the water content has a huge impact on the plasticization of the carbohydrate-based materials, which in turn influences the mechanical and barrier properties. Although most studies evaluate these parameters at similar conditions (e.g., 50% RH and room temperature) easing comparison (Table II), the effect of water sensitivity after aging at different possible ambient conditions is sometimes neglected. This has deep implications for the potential application in a real changing environment. In this sense, enzymatic debranching of hemicelluloses has shown to decrease the influence of RH on the mechanical properties of XyG [118] and AX [77] films, with a concomitant enhanced thermal stability in debranched AX films.[27] In another study, the aging of GGM and AX films with 20–60% incorporated glycerol or sorbitol revealed interesting changes of the materials after 4 months. Elongation at break and water vapor permeability decreased and the strength and Young's modulus increased, while degree of crystallinity and oxygen barrier properties remained unaffected with time.[135] These changes were suggested to be associated with the water content in the films.

Thermal Processing

Although the vast majority of materials in the packaging industry are produced by thermal processing, research literature on hemicellulose-based films is exclusively focused on casting techniques with a few exceptions. Heat treatments usually increase crystallinity of cellulose and produce crosslinking of lignin,[136] which might improve the film forming and materials properties of carbohydrate-based films. On the other hand, relatively high temperature treatments during thermal processing might reduce the molecular weight of the hemicellulosic components. Recently, a study on the influence of different thermal treatments on corn cob extracted AX revealed interesting improvements in the materials properties of the films.[136] The AX was extruded at 90°C, thermally annealed for 1 h at different temperatures and then conditioned for 7 days at room temperature and controlled humidity. Extruded AX films showed tensile strength, elastic modulus, and elongation at break of 70 MPa, 1.2 GPa, and 45%, respectively, which are already higher compared to those films produced by solvent casting. The subsequent thermal annealing produced a significant increase in ultimate tensile strength (~120 MPa) and elastic modulus (~1.6 GPa), while maintaining certain ductility (~12% elongation at break). Moreover, the thermally annealed films showed less sensitivity to humidity. The differences were ascribed to the decrease in water content and its concomitant plasticizing effect.[136] Again, the use of enzymatic treatments could be a complementary tool of interest, as it has been reported that debranching of AX also increases thermal stability while decreasing water sensitivity.[27]

Preparation of Coatings, Hydrogels, and Aerogels

The potential utilization of enzymatically modified plant material is not restricted to the formation of films. The excellent oxygen barrier properties of AX can be exploited as to fabricate high barrier coatings, with enhanced oxygen and aroma barrier properties. These properties have been shown to be enhanced after enzymatic debranching and several treated and modified AX such as Xylophane® or Skalax® are already commercially available.[137] Surface modification can be a potential way of producing added-value materials from lignocellulosic materials in form of smart or high barrier coatings. Cationization or acetylation could be used to produce polyelectrolyte layers of interest in packaging or pharmaceutical applications,[138] while carboxymethylation and hydroxyalkylation provided increased barrier properties to xylans.[139,140] The specificity of enzymes could also be a useful tool in the targeted functionalization of these substrates. As an example, conductive biocomposites were produced by grafting polyaniline onto GGM or cellulose surface with laccase.[141] In another study, peroxidase was efficiently encapsulated into AX by debranching AX with arabinofuranosidase in a controlled in situ reaction.[28] This evidences an additional potential use of enzymatic treatment of plant polysaccharides in the encapsulation of bioactive substances, which may be of interest in a number of biomedical and food applications. Finally, the enzymatic oxidation of GM with GalOx has been shown to produce an increase in the mechanical strength, thermal stability and oxygen barrier properties of the hydrogels or aerogels produced in this manner. The possible applications for these aerogels range from adsorbents, bioactive compound carriers or mechanical support in medical or active packaging applications.[142] All these findings put forward the use of enzymatically treated plant hemicelluloses without addition of other reinforcing fillers, either as barrier and smart coatings, drug carriers or in other medical or packaging applications.

Table II. Macroscopic Properties of Carbohydrate-Based Materials from Lignocellulosic Biomass for Potential Packaging Applications. Comparison with Benchmark Bio-Based and Oil-Based Synthetic Polymers.

Material	Enzyme	Additives	Tensile strength (MPa)	Elastic modulus (GPa)	Strain at break (%)	Oxygen permeability $(m^3\ m)/(m^2\ s\ Pa) \times 10^{-20}$	Vapor permeability $(kg\ m)/(m^2\ s\ Pa) \times 10^{-14}$	M_w (kDa)	References
Rye AX	α-1,2-Arabinofuranosidase		36.8-57.7	0.63-1.75	4.7-10.4	1.3-2.3	-	-	75
Wheat AX	α-1,2 and α-1,3 Arabinofuranosidases		31-32	0.8-1	5.8-6.1	5	7.8	-	80
Guar gum GM	α-Galactosidase and β-mannanase	40% Glycerol	22	-	47	-	-	-	90
rye endosperm AX	Endo-β-xylanase and α-arabinofuranosidase (AXH-m)		60-37	1.6-1.8	7-12	-	-	49-152	76
Tamarind seed XG	β-Galactosidase		51.1-88.0	3.20-5.43	1.7-14.5	1-7.4	-	1500-2000[a]	96
Tamarind seed XG	β-Galactosidase	30% Glycerol	30-72	1.2-4.3	3.1-12.0			2500[a]	118
Rye AX	α-Arabinofuranosidase	15% BC	32-49	2.2-3.7	2.1-2.8				77
Rye AX	α-Arabinofuranosidase	15% MFC	60-82	1.7 −1.9	11-12			152	76
Rye AX	α-Arabinofuranosidase	15% MFC	37 - 41	1.7-1.9	4			59	76
Rye AX	Lichenase	20-80% β-Glucan	30-35	0.4-0.7	9-12	1-2.3	8.9-11.5	232	126
Spruce GGM	Laccase	20% CMC 10% Glycerol	15	0.43	6			59.5	122
Birchwood xylan	-	40% CMC	53	0.6	1.3	2.4	-	3.4	143
Rye AX	-	2.5% Sepiolite	42.5-73.6	2.3-3.9	10.4-11.9	0.2-0.6	2.5-2.6	-	132
Oat spelt AX	-	10% Glycerol	~27	1.1	~4.3	3.5	3.8	-	133
Corn starch	-	-	37	1.2	3	-	83	-	144
Polyhydroxybutyrate (PHB)	-	-	25.8	1.0	6.7	220	0.08	-	145
Polylactic acid (PLA)	-	-	54	1.85	4.9	261	1.31	150	146
Ethylene vinyl alcohol (EVOH32)	-	-	52	1.4	93	<0.1	2.1	-	147,148
Polypropylene (PP)	-	-	26-32	1.2-2.0	10-140	1700	16	1-5400	149
Polyethylene (LDPE)	-	-	22-32	0.1-0.3	130-270	220	68	69-411	150
Polyethylene terephthalate (PET; biaxially oriented)	-	-	24-41	2.0-2.7	100-250	40	113	19-66	151

[a] Molecular weight prior to enzymatic treatment; BC (bacterial cellulose); MFC (microfibrillated cellulose); CMC (carboxymethyl cellulose)

CONCLUSIONS

This review critically addresses the potential and challenges of exploiting lignocellulosic plant polysaccharides for the design of bio-based packaging materials. However, the recalcitrant nature of the biomass and the high variability in composition and structure of the polymeric components poses major challenges to the design of biotechnological processes for the extraction and isolation of homogeneous polysaccharide fractions. Plant polysaccharides can generate materials with comparable mechanical performance to other common synthetic biopolymers, as well as excellent barrier properties matching benchmark fossil-based packaging materials (Table II). However, the development of homogeneous carbohydrate-based continuous films with suitable properties is still standing, as current literature typically involves the addition of relatively high amounts of conventional plasticizers as well as other reinforcing fillers. Further emphasis should be placed on the modification of these materials to reduce their water sensitivity and enhance their heat stability for eventual thermal processing. In contrast to chemical treatments, the use of enzymes offers a wide range of possibilities for the selective and targeted modification of polysaccharides at milder conditions. Throughout this review, the use of enzymatic treatments has been put forward as a powerful tool both for the assisted extraction of high-quality polysaccharide fractions, as well as for the targeted structural modification of these substrates with enhanced thermomechanical and barrier properties. However, research in this field is still at early stages of development and much needs to be learned for the successful exploitation of plant hemicelluloses as packaging materials. A valuable route for the future could be the introduction of bioactive functionalities onto the lignocellulosic polysaccharide-based materials to be able to compete with other well-established synthetic polymeric systems.

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