

Stability of Oxidized Hemicellulose Films

Investigating the effect of storage conditions on mechanical and chemical stability

Master's thesis in Innovative and Sustainable Chemical Engineering

LINUS KRON

MASTER'S THESIS 2020

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chemical stability

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CHALMERS
UNIVERSITY OF TECHNOLOGY

Department of Chemistry and Chemical Engineering
Division of Forest Products and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2020

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Cover: Photograph of commercially available untreated xylan (left), periodate oxidized xylan (middle) and a piece of film casted from xylan, PVA and sorbitol (right).

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Abstract

Reducing the global dependence on fossil products is one of today's greatest environmental challenges. In order to overcome this, it is necessary to utilize the full range of bio-based materials that exists. One step in this process is improving packaging by replacing conventionally fossil-based gas barriers, such as ethylene vinyl alcohol, with bio-based alternatives.

In this thesis, the viability of making films from the bio-based hemicellulose xylan, envisioned as oxygen barriers, was investigated. First, xylan was functionalized by periodate oxidation to introduce aldehyde groups improving its film-forming properties. Secondly, the oxidized xylan was casted into films via solution casting. The stability of said films were studied by analyzing the change in chemical and mechanical properties after storage at different temperatures and levels of humidity. Methods used for characterization were high-performance anionic exchange chromatography, thermogravimetric analysis, and measurements of tensile properties and oxygen transfer rate.

While brittle on its own, the oxidized xylan formed flexible and transparent films when blended with poly(vinyl alcohol) and plasticized with sorbitol. These films showed initial values of 25 MPa and 70% for the tensile strength and strain at break respectively, which are comparable to conventional barriers, while also achieving acceptable oxygen permeabilities below $10 \text{ cm}^3 \mu\text{m}/(\text{m}^2 \text{day kPa})$. Furthermore, no apparent instability was found with respect to temperature nor humidity. However, the results indicated that films might experience a structural change following exposure to high humidity, affecting tensile and barrier properties. Moreover, two methods were identified that could potentially stabilize oxidized polysaccharides: further oxidation of the aldehyde groups or reduction using sodium borohydride.

It was concluded that periodate oxidized xylan shows promising properties as a potential replacement of current oxygen barriers, and is not apparently unstable in conditions of modestly high temperature and humidity. Thus, this work opens up for continued research on the oxidation of polysaccharide films.

Keywords: periodate oxidation, hemicellulose film, stability, aging, xylan, barrier.

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Contents

1	Introduction	1
1.1	Aim	2
1.2	Delimitations	2
2	Theory	3
2.1	Wood	3
2.1.1	Cellulose	5
2.1.2	Hemicelluloses	5
2.1.3	Lignin	7
2.2	Packaging	8
2.2.1	Conventional Barriers	8
2.2.2	Stability of Conventional barriers	11
2.3	Polysaccharide barriers	12
2.3.1	Earlier work	12
2.3.2	Oxidation of polysaccharides	14
2.3.2.1	Effect of oxidation on physicochemical properties	16
2.3.3	Stability of polysaccharides	17
2.4	Analytical methods	20
2.4.1	Thermogravimetric analysis	20
2.4.2	Liquid chromatography	20
2.4.2.1	High-performance anion exchange chromatography	20
2.4.3	Ultraviolet-visible spectroscopy	21
2.4.4	Tensile test	21
2.4.5	Oxygen Transfer Rate	21
3	Experimental method	23
3.1	Preparations prior to stability tests	23
3.1.1	Materials	23
3.1.2	Oxidation of Xylan	23
3.1.3	TGA	24
3.1.4	Film casting	24
3.1.5	Storage conditions	25
3.2	Characterization of film stability	26
3.2.1	Carbohydrate analysis	26
3.2.2	Oxygen permeability	26
3.2.3	Mechanical strength	27

3.3	Labeling of specimen and conditions	27
4	Results & Discussion	29
4.1	Characterization of oxidized xylan	29
4.1.1	Thermal stability	31
4.2	Film formation	32
4.3	Chemical stability	34
4.3.1	Carbohydrate analysis	34
4.3.2	Permeability	36
4.4	Mechanical stability	37
4.4.1	Thickness	37
4.4.2	Tensile properties	37
4.5	Stabilization of oxidized xylan	39
5	Conclusion	41
6	Future work	43
	Bibliography	45

List of Abbreviations

AX	Arabinoxylan	M_w	Weight average molecular weight
CMF/MF	Cellulose microfibrils	OP	Oxygen permeability
CNC	Cellulose nanocrystals	OX	Oxidized xylan
CNF	Cellulose nanofibrils	PDI	Polydispersity index
DAC	Dialdehyde cellulose	PVA	Poly(vinyl alcohol)
DO	Degree of oxidation	RH	Relative humidity
DP	Degree of polymerisation	SEOX	Simultaneously extracted and oxidized xylan
EVOH	Ethylene vinyl alcohol	TEMPO	2,2,6,6-tetramethylpiperidine-1- oxyl
GGM	Galactoglucomannan	TGA	Thermogravimetric analysis
HPAEC-PAD	High-Performance Anion Exchange Chromatography with Pulsed Amperometric Detector	UV-Vis	Ultra-violet and visible spectroscopy

1

Introduction

The rising awareness of the environmental impacts of our consumption and raw material use has led to an increasing demand for more sustainable materials [1]. Among these, bio-based materials have a potential to replace fossil-based materials and are of relatively high availability. However, bioplastics are today produced mainly from food-based feedstock, which is problematic with regard to the increasing demand on food production. Moreover, use of first generation feedstock also raises concern regarding land use. Lignocellulosics stemming from forestry resources are therefore a prospective group of materials that are renewable and are not competing for land-use with food crops. There are also large underutilized material streams of lignocellulosics from e.g forestry and paper making processes, providing further benefit in terms of sustainability [2]. Lignocellulosic biomass is composed of three different polymers: cellulose, hemicelluloses and lignin. Today, mostly cellulose is extracted and used in material applications. Further use and extraction of hemicelluloses shows potential and is a paramount step in the transition towards material efficient biorefineries [3].

One sector where demand for bio-based materials is high is within the packaging industry, which currently uses around 44% of all produced plastics [4]. In specific, in the food packaging industry, fossil-based coatings are commonly used, and using biopolymers is a key point in the transition away from petrochemical polymers [5]. However, common among biogenic films is that their properties depend strongly on the surrounding environment, especially temperature and humidity [6]. For example, biocomposites based on cellulose have shown poor moisture resistance in high humidity conditions [7].

There has been several studies on the use of xylans proving the possibility of using them for films. However, in many cases an inability to form self-standing films without modification or addition of plasticizers has been reported [8–11]. Periodate oxidation has been suggested as a potential mean to improve film-forming abilities of xylan [12, 13]. While there are some studies that have investigated the film-forming abilities of periodate oxidized xylan [14, 15], the research is still scarce regarding the stability of such films over time. These oxidative measures may reduce the stability of the molecules, leading to degradation. However, there are potential treatments that have been suggested to have stabilizing effects [16–18].

1.1 Aim

The aim of this thesis is to investigate the viability of making films out of oxidized xylan based on the stability and ageing properties of the casted films. This can be summarized in three main objectives:

- Oxidizing and casting xylan-based raw material into self-standing films.
- Analyzing key properties of the films and how they are affected when stored under different conditions.
- Identifying possible approaches to stabilize the films.

Ultimately, the aim of this work is to generate knowledge that can be used to further improve and create more sustainable packaging materials.

1.2 Delimitations

Due to the limitations in time and resources inherent to a Master's thesis, some limitations were made and are listed below:

- All films were casted in the same manner and under the same condition. The effect of the conditions during film formation was thus not investigated.
- The effect of the degree of oxidization (DO) of the xylan was not investigated.
- Only one type and concentration of plasticizer was used.
- All stability tests were run separately and only once (with replicate samples for the analyses). There was thus no way of determining the correlation between temperature and humidity effects.
- The films were only stored for a maximum of 4 weeks and the trial might thus not have been able to catch the full aging behaviour of the films, which may take months [19].
- Since the oxygen permeability (OP) and tensile tests were conducted on films supported by poly(vinyl alcohol) (PVA), they do not represent the pure xylan films, but were instead compared to values of pure PVA and PVA/xylan blends found in literature.
- All tests were performed at one occasion at the end of the trial run. The intermediate samples (e.g. 72h, 1 week etc.) were in the meantime stored at non-disruptive conditions, see Section 3.1.5

2

Theory

This section will first present the basics of wood structure, whereafter an introduction to food packaging is presented, together with requirements and properties of common packaging polymers. Then, a review on the current prospects of biopolymers in food packaging is given, followed by an overview of the current knowledge on using oxidation as a modification of polysaccharides. Finally, a basic theoretical background to the analytical tools used in this work is given.

2.1 Wood

Wood is one of the most important raw materials to society, with almost a third of the total land area covered in forests [20]. It consists of macromolecular polymers, extractives and mineral substances, but the polymers make up over 90% of the total weight. There are three main types of macromolecules in trees: cellulose, hemicelluloses and lignin. The general distribution of the three main components are 40-50% cellulose and 20-30% each of hemicelluloses and lignin. In the walls of tree cells, cellulose chains are bundled together via strong intermolecular bonds to semi-crystalline bunches called cellulose microfibrils (CMF). These fibrils are in turn ordered into larger macrofibrils, which are distributed inside the different sections of the wall of the cell, as is depicted in Figure 2.1. Within the macrofibrils, the microfibrils are surrounded by less orderly distributed hemicelluloses, which are in turn connected to lignin, see the upper right corner of Figure 2.2. The lignin-carbohydrate complexes contain covalent bonds that mainly occur between lignin and hemicelluloses [21].

Trees are often divided into two main groups: softwoods and hardwoods. Softwoods, or conifers, are in general evergreens with exposed seeds and needle-leaves, while hardwoods are deciduous with enclosed seeds and flat leaves. They also differ in their molecular composition, with softwoods in general having a larger portion of lignin and different types of hemicelluloses compared to hardwoods [22].

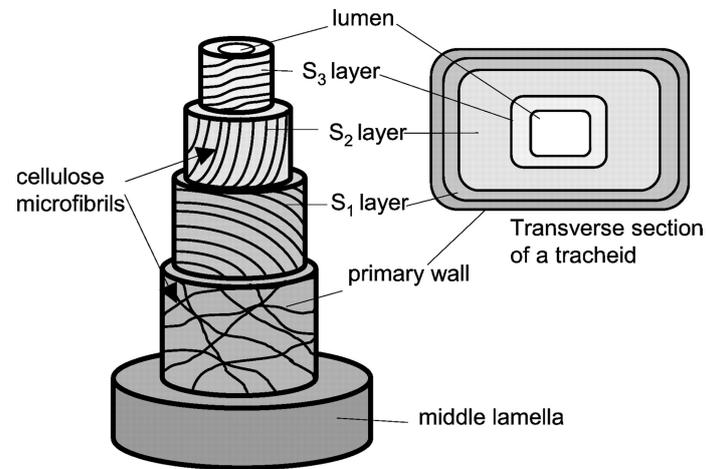


Figure 2.1: Three-dimensional structure of the secondary cell wall of a tracheid (xylem cell). The cell wall is divided into different layers, each layer having its own particular arrangement of cellulose MFs, which determine the mechanical and physical properties of the wood in that cell. These MFs may be aligned irregularly (as in the primary cell wall), or at a particular angle to the cell axis (as in layer S1, S2, and S3). The middle lamella ensures the adhesion between cells. *From [23]. Printed with permission.*

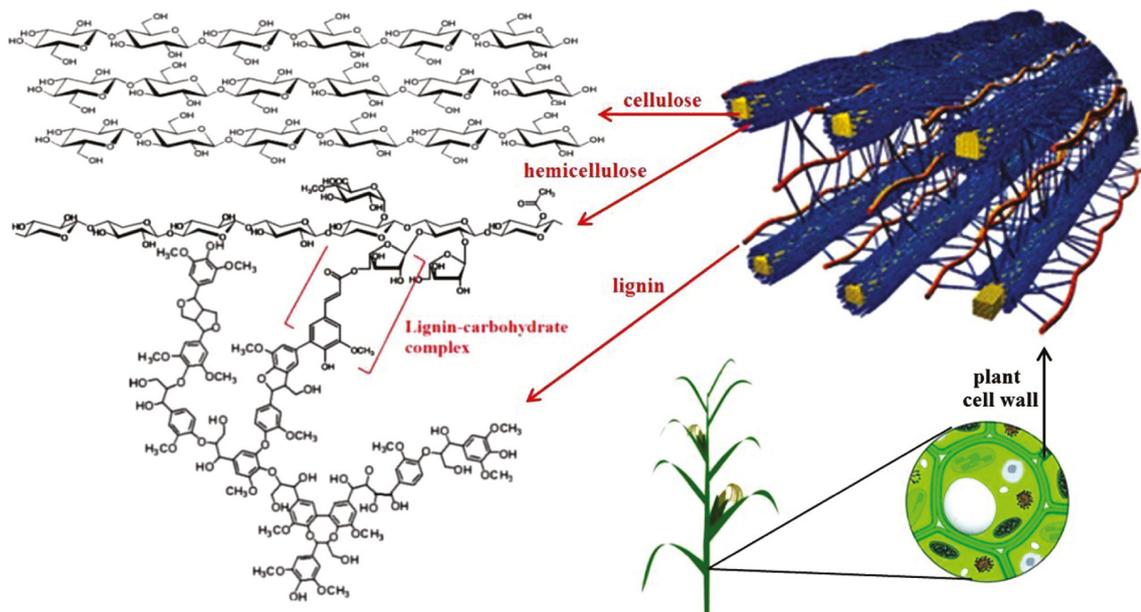


Figure 2.2: Structure of lignocellulose. *From [24], CC-BY.*

2.1.1 Cellulose

Cellulose is the world's most abundant organic polymer and consists of β -1,4-linked *D*-glucopyranose units, i.e. linearly arranged six-carbon monosaccharide units, see Figure 2.3. The bundles of cellulose chains (microfibrils) in which cellulose is naturally arranged in contains ordered (crystalline) and unordered (amorphous) regions. In the crystalline region, strong intermolecular bonds are formed resulting in a high resistance to chemical degradation [25].

Cellulose, in the form of wood or pulp, is most commonly used as building material, energy resource or in paper making. It has, however, some more uses such as viscose production or production of cellulose derivatives such as cellulose acetate, used as alternatives to petroleum-based products [26]. Cellulose also shows promising use in the future as microfibrillated cellulose and nanocrystalline cellulose, which are obtained by disintegrating cellulose into individual fibrils or nanocrystals. These materials show an array of properties such as large surface area to volume, biodegradability, and promising mechanical properties compared to fossil-based alternatives, and can be used as, for example, dispersion agents, reinforcing material for polymers or drug delivery components [27].

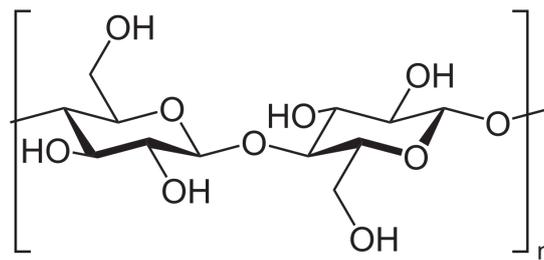


Figure 2.3: The molecular structure of cellulose.

2.1.2 Hemicelluloses

Hemicelluloses are polysaccharides, like cellulose, but exhibit far more variations in the form of different monosaccharides making up the backbone, while also containing branches and side groups. There are two main groups of hemicelluloses: xylans and glucomannans.

Xylans

Xylans are the main hemicelluloses in hardwoods, commonly in the form of 4-O-methylglucuronoxylans: a homopolymer of β -1,4-linked xyloses with 4-O-methylglucuronic acid side groups (4-O-Me-GlcA). It is also common for the OH-groups of the xyloses to be substituted by O-acetyl groups, as is seen in Figure 2.4. On average for hardwoods, every other xylose unit contains a O-acetyl group and every tenth unit contains a 4-O-Me-GlcA group. Hardwood xylan usually has a degree of polymerization (D)P of 100-200 [21].

In softwood, xylans only account for 5-10% of the total weight and the main polymer is arabinoglucuronoxylan: a xylose backbone like 4-O-methylglucuronoxylans, but with twice the amount of 4-O-Me-GlcA units and no acetyl groups. Instead, α -L-arabinofuranose side groups occur at every 8-9 xylose unit and the DP is slightly higher than for hardwood xylans [28].

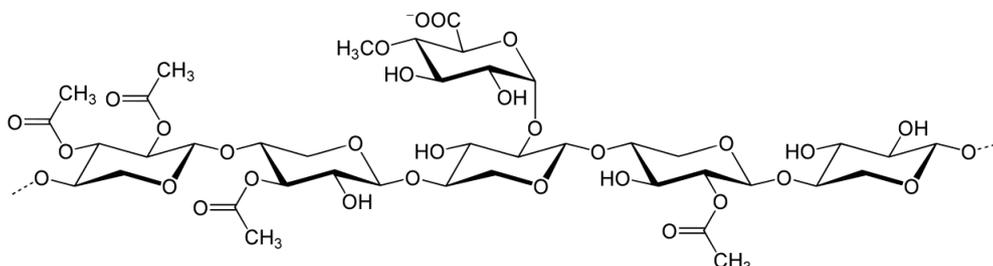


Figure 2.4: The molecular structure of 4-O-methylglucuronoxylan with four acetylated hydroxyl groups.

Glucomannans

Glucomannans consist of a mannose and glucose unit backbone. In hardwoods they are slightly branched and also acetylated, with a 1.5-2:1 ratio of mannose and glucose, and has a relatively low DP of 60-70. However, they only make up 3-5% of the total weight. In contrast, in softwoods the glucomannans account for 20-25% of the total mass, where the backbone together with acetyl groups and galactose units forms O-acetyl-galactoglucomannans, see Figure 2.5. The ratio is roughly 3:1:0.2 of Man:Glu:Gal, with a degree of acetylation of around 0.17-0.36 [28].

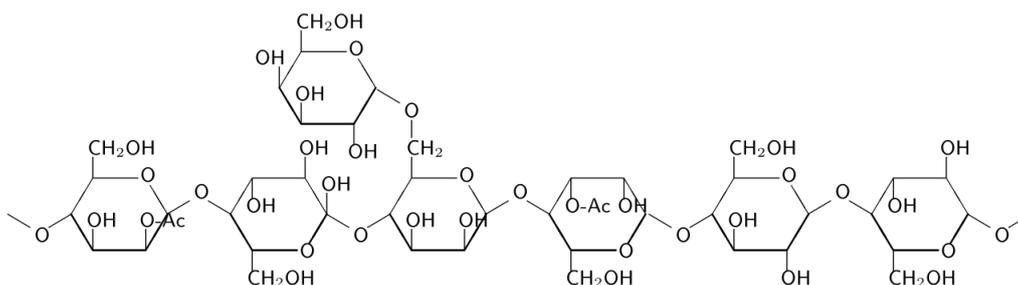


Figure 2.5: The molecular structure of galactoglucomanan.

Contrary to cellulose, wood hemicelluloses are seldom extracted or used industrially in their polymeric form, the only real exception being hemicelluloses left in pulp and paper which improves fibre-fibre interactions. The reason for this is the extensive degradation of hemicelluloses that takes place in most pulping processes, as a result of hemicelluloses being more amorphous and thus more susceptible to degrading reactions [21]. Instead, the main use of wood hemicelluloses today, apart from using solid wood itself and monomers recovered and fermented in sulfite mills, is for energy recovery and steam production in pulp plants, where the dissolved and degraded polymers are burned [29].

One important use of wood hemicelluloses are fermentation of the individual saccharides into alcohols. Bioethanol is seen as the most important fermentation product of hexoses, but because of the pentoses of hemicelluloses, yeast and other microorganisms conventionally used for fermenting glucose from starch and cellulose cannot be efficiently used [30]. Instead, other enzymes or yeasts are needed, and although there are several that show great potential, the fermentation is still problematic and much research is still needed [31]. Another potential value-added product of wood hemicelluloses is furfural, which can in subsequent steps be used as a chemical intermediates or as a fuel component [32].

2.1.3 Lignin

Lignin differs from cellulose and hemicelluloses in that it is not a polysaccharide, but is the world's largest source of aromatic organic polymers. The complete native structure of lignin is yet to be understood, but a leading model suggests that the lignin macromolecule mainly consists of three building units, as is seen in the box of Figure 2.6. These units, all phenylpropanes, are distributed randomly and with several types of linkages. In some models, the macromolecule consists of over 90 units with a total molecular weight of over 17 000 [21].

Lignin, like hemicelluloses, shows potential to be used as a green alternative to produce a wide array of organic compounds due to its aromatic structure. It also sees potential uses such as dispersants and adsorbents, but is currently mainly used as an energy resource [33–35]. The reasons stem from technical lignin having large varieties in molecular structure, inter unit linkages and molecular weights. Consequently, the properties cannot be well defined and the market is developing slowly [26].

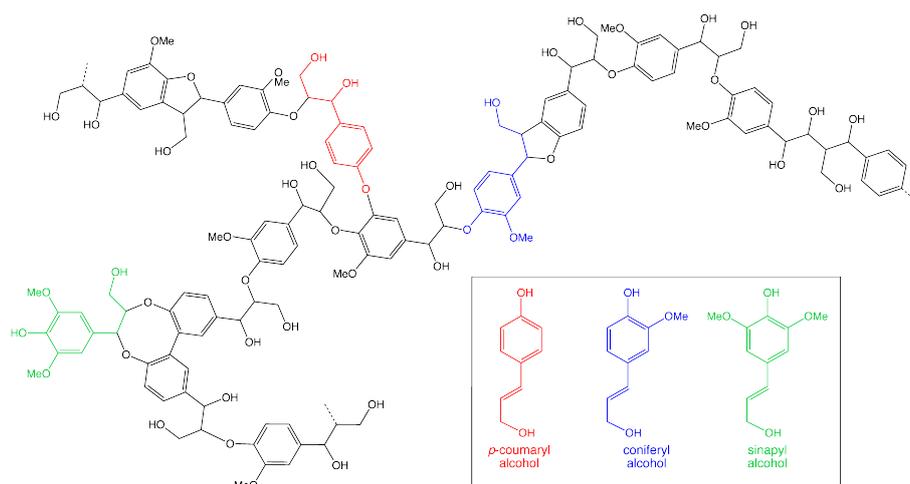


Figure 2.6: A representation of the different linkages found in lignin. The three molecules in the box showcase the main monomers of lignin. *From [36] CC-BY-SA.*

2.2 Packaging

Packaging is a cornerstone in today's consumer society, accounting for roughly 2% of the gross national product, half of which comes from the food packaging sector [37]. Packages have several key functions throughout the supply chain, which can be summarized in four categories:

- Containment - Keeping the products of the package in one place for easy handling and prevention of containment and pollution.
- Protection - Providing a barrier to the surrounding environment, protecting the goods from water, gases, microorganisms and external forces.
- Convenience - Allowing the production of goods at large scale while distributing them in size-appropriate packages for ease of handling with regards to size, shape and mobility.
- Communication - Acting as a means of communication through marketing and branding, information about the contents and nutritional value, and identification, e.g. through barcodes.

One of the main aspects in packaging is the choice of material for the packaging, which affects all of the above mentioned functions, especially the protective barrier. Fossil-based plastics stand for a substantial part of the packaging market. For example, in the flexible packaging market, plastics accounted for over 75% in 2009 [38]. Roughly 40%, or 100 million tonnes, of the annually produced petrochemical-based plastics are used for packaging. Meanwhile, the corresponding number for bio-based plastic packaging is 125 000 tonnes [37].

2.2.1 Conventional Barriers

The protective environment is crucial in food packaging to preserve adequate quality of the product. There are several factors affecting the quality, but the most important ones are gas and moisture levels. However, the specific required levels depend on the products. For example, products that need to retain low moisture content, such as instant coffee or dry crackers, require good moisture barriers while fresh bakery goods need some level of moisture transport to not go stale. Likewise, fresh fruit require oxygen to ripen and therefore need the packaging to allow some oxygen to enter, while meat should be kept at low oxygen levels [39].

A common approach to regulate these factors is to include one or more levels of polymer-based barrier in the packaging [39]. Figure 2.7 shows the molecular formula of some of the most commonly used polymers in packaging applications. Table 2.1 and 2.2 show values from literature of key properties for barrier films. There are no defined levels of permeability that constitutes a 'good oxygen barrier', but values below 4, 0.75 and $10\text{cm}^3\mu\text{m}/(\text{m}^2\text{day kPa})$ have previously been defined as thresholds for this [40, 41].

Polyethylene

The largest part of the plastic film packaging market is composed of two alkene polymers: polyethylene (PE) and polypropylene. PE is formed via polymerization of ethene units and is classified by the density, e.g low-density polyethylene (LDPE) [38]. The use of PE depends on the density. LDPE is commonly used in plastic films in food application, often together with other polymer types to enhance specific properties such as tensile strength, heat resistance or oxygen permeability. LDPE is also used as a coating on paperboards liquid packaging of milk and fruit juices, where it is acting as a barrier to water [42].

Poly(vinyl alcohol)

Poly(vinyl alcohol) is commercially produced via hydrolysis of poly(vinyl acetate), and is usually petroleum-based. It is water soluble with good gas barrier properties, as well as high chemical resistance and toughness [43]. Common application include warp sizing, paper coating and films.

Ethylene vinyl alcohol

Ethylene vinyl alcohol copolymer (EVOH) is composed of monomers of ethylene and vinyl alcohol, forming a semi-crystalline structure. It is produced by, similar to PVA production, first forming copolymers between ethylene and poly(vinyl acetate). These are then hydrolysed into EVOH. EVOH posses excellent gas barrier properties and has therefore been very prominent in food packaging as a gas barrier in multilayer films [44].

Poly(lactic acid)

Poly(lactic acid) (PLA) is the bio-based polymer that has proved to be the most commercially viable. PLA is produced from lactic acid, which in turn can be produced through fermentation of mono- and oligosaccharides such as glucose, lactose or sucrose. It has similar mechanical properties as LDPE [37]. PLA is traditionally used in food packaging applications, such as food containers, coated paper and boards, and candy wrap.

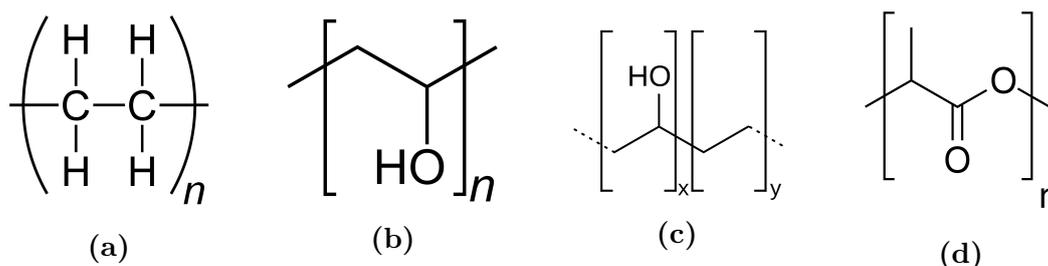


Figure 2.7: Structural formula of (a) PE, (b) PVA, (c) EVOH and (d) PLA.

Table 2.1: Tensile properties for different commercially available plastics.

Polymer	Stress ¹	Strain ²	Comment ³	Source
LDPE	8-20	500-1000		[37]
	10	700		[43]
PVA	15-86	-	20% glycerol	[45]
	48	350		[46]
	41	550	15% sorbitol	[46]
	72	200		[47]
EVOH	15	12		[48]
	35	4	at 43% RH ⁴	[49]
PLA	40-63	9		[37]
	21-60	3-6		[43]
	50	6		[50]
	40-70	-		[43]

1: [MPa] 2: [%] 3: Plasticizers added as w/w% on dry matter. 4: Relative humidity

Table 2.2: Oxygen permeabilities for films of commercially available plastics.

Polymer	Permeability ¹	Condition ²	Source
LDPE	490-1270		[51]
	1870		[9]
	1940-4300	0%	[37]
PVA	0.20	0%	[51]
	0.12-0.23	0%	[38]
	0.052	65%	[39]
	0.015	0%	[44]
	0.19	-	[52]
EVOH	0.060-0.28	20°C, 65%	[44]
	0.045		[49]
	0.078	0%	[37]
	0.044	65%	[39]
PLA	71	0%	[37]
	120	0%	[39]
	140		[43]

1: [$cm^3/(m^2 day kPa)$] 2: Testing conditions, 23-25°C and 50% RH if nothing else stated.

2.2.2 Stability of Conventional barriers

In a study of LDPE films, artificial aging was investigated by exposing the films to UV radiation. The results showed a decrease in tensile strain of 83% after 1000 h of exposure. The tensile strength was also significantly reduced during artificial aging and the films turned brittle. The effects are attributed to changes in chain length and cross-linking, which inhibits the flexibility of the polymers [53].

The use of EVOH in multilayer films has shown to lead to decreased stability against accelerated aging due to photo degradation under UV-light, mainly in the form of reduced strain at break [54]. EVOH films' barrier properties are known to heavily depend on both temperature and humidity [55], but they were also showed to experience a substantial permanent increase in oxygen permeability when stored in high humidity for periods of up to 60 days [48]. Similar results have showed that oxygen permeability of EVOH films continue to increase for up to 200 days when stored at high humidity [56].

The effect of storage time on PVA/starch films stored at 25°C and 53% RH has been investigated [57]. For the pure PVA films, the results showed difference in neither oxygen permeability nor tensile properties after 5 weeks of storage. The pure starch films exhibited an almost doubled tensile strength but halved strain at break, while the oxygen permeability slightly decreased. The changes of the starch films were attributed to water loss. The 1:2 blends of PVA:starch showed a slight increase in permeability and tensile strength, but no change in strain at break, mirroring the trends that the pure PVA films indicated. This is in contrast to an earlier study, which found a 0.3:1 blend of PVA:starch to experience a change in strain at break, but not tensile strength, when stored at 25°C and 42% RH [58].

A similar study used films with a 1:4 ratio of PVA:starch, stored under 3 different conditions: room condition for 15 days, room condition for 30 days followed by 24h of 60°C, and finally 30 days at room condition followed by 15 days at 25C, 75% RH. High temperature treatment significantly reduced both tensile strength and strain compared to samples only stored at room temperature. High humidity had less noticeable effect, but indicated a slight increase in both tensile strength and strain. However, both treatments (high temperature and humidity) led to stiffer films overall [59].

2.3 Polysaccharide barriers

Several studies have found films made of lignocellulosics material to exhibit comparable, or sometimes even improved, properties relative to petroleum-based alternatives. This section summarizes some recent research findings regarding the mechanical and chemical properties of, mainly, hemicellulose films. After that, a summary of one approach to modify the film properties, polysaccharide oxidation, is presented together with its effects on stability.

2.3.1 Earlier work

Reddy et al. reviewed the current status on biobased plastics and composites [7]. They concluded that although there is extensive research on and great potential in bioplastics, they are still not commercially viable at a large scale except for some starch-based plastics and PLA. Some of the mentioned drawbacks are extreme moisture sensitivity of starch-based products, while PLA has low thermal stability and is brittle on its own. For new materials, there is especially much focus on producing traditional plastics via biochemical means, such as PE, PP, and PET.

Unmodified hemicelluloses have in general poor film-forming capabilities and various studies report requiring plasticizers in order to form films from them. The reason has mainly been attributed to poor solubility and chain length [11, 60, 61]. However, some studies found that xylan could form self standing films [62, 63]. In agreement with the theory that solubility affects the film-forming capabilities, it has been suggested that increased arabinose content benefits film formation [19]. Sousa et al. succeeded in forming films without plasticizers [9], although brittle, through carboxymethylation and hydroxypropylation of beechwood xylan, whereas Mikkonen et al. found that for lower degrees of substitution, hydroxypropylated xylan was unable to form films [64]. Furthermore, Börjesson et al. found that etherification of both oxidized and un-oxidized arabinoxylan generated flexible films [15].

Numerous studies have shown promising results regarding the mechanical properties of hemicellulose-based films. Most films are rather stiff, transparent and show plastic behaviour during stress. They are successfully plasticized with sorbitol, glycerol and xylitol [60, 65], albeit there are studies where the effect of plasticizers only lowered the tensile strength, while maintaining a similar or sometimes even lower strain at break [9, 64]. In general, the reported values of tensile strengths reach above 40 MPa, while the strain rates rarely are above 10%, even when plasticized. However, as reviewed by Mikkonen et al., there are reported values of tensile strengths over 90 MPa, while some heavily plasticized films have reached strain rates of over 40% [41]. Table 2.3 shows some reported values for the mechanical properties of different hemicellulose films. Compared to conventional plastics used in packaging, the tensile properties are often comparable to those of EVOH and PLA, while PVA and LDPE have considerably higher strain rates. From this perspective, and as reported by many studies, hemicellulose films might find the greatest usage in applications as coatings and barriers, rather than individual food packaging films.

Table 2.3: Tensile properties of hemicellulose and cellulose nanocrystals (CNC) films. When ranges are given they represent the values from lowest to highest amount of additives.

Polymer	Stress ¹	Strain ²	Additive ³	Source
Arabinoxylan	41	8		[15]
	50.3	2.5		[65]
	27-4	4-11	10-40% Glycerol & Sorbitol	[19]
Arabinoxylan blend	>50	2.5		[63]
Arabinoglucuronoxylan	55-26	2.7-4.3	0-25% Sorbitol	[62]
Glucuronoxylan	39.4-3	2.1-10.4	20-50% Xylitol & Sorbitol	[65]
	>40	2	20% Xylitol	[11]
Glucomannan	57	11		[41]
	43	31	29% Glycerol	[41]
Galactomannan	12	43	29% Glycerol	[41]
	24	49	29% Glycerol	[41]
Glucomannan/CNC	46-82	6.3-9.4	0-4% CNC	[66]
PVA/cellulose nanofibrils (CNF)	40-50	125-85	0-5% CNF	[67]

1: [MPa] 2: [%] 3: Values given as w/w% on dry matter.

For hemicelluloses, both pure films and blends have shown potential in the form of oxygen barriers. Mikkonen and Tenkanen reviewed several studies on oxygen permeabilities of various hemicellulose films [41]. All reviewed studies showed levels below the previously stated $10 \text{ cm}^3\mu\text{m}/(\text{m}^2\text{day kPa})$, several of them even below $0.3 \text{ cm}^3\mu\text{m}/(\text{m}^2\text{day kPa})$. The films were all from unmodified hemicelluloses, but containing different additives such as plasticizers or CNC. The permeabilities' dependence on plasticizers showed no clear trend. Some studies suggest water vapor permeability decreases with increasing amount of plasticizers [9, 64], while others point out the opposite [19]. Likewise, studies suggest OP increases with plasticizers content [19, 68–70], while some suggest it depends on the type of plasticizer used [40]. Table 2.4 presents some values of OP for different hemicellulose films.

One way of improving the properties of polymer films is by reinforcing them with other materials to create composites. This generates barriers of increasingly bio based content that are less susceptible to moisture, while still possessing better gas barrier properties compared to commercial equivalents [73]. Two materials that have shown some of the greatest potential as oxygen barriers are CNC and CNF composites, which often possess very low permeabilities in comparison to other biopolymers [74], and have further shown to increase the mechanical properties in films [70]. Some reported values for tensile properties and permeability of CNC and CNF containing films are shown in Table 2.3 and 2.4.

Table 2.4: Oxygen permeability for films of unmodified, modified and plasticized hemicelluloses. Testing conditions: 23-25 °C at 50% RH.

Polymer	Permeability ¹	Additive ²	Source
Arabinoxylan	8.3		[41]
	0.15-0.22		[41]
	2	25% Sorbitol	[41]
	3.2	29% Sorbitol	[41]
	0.16		[65]
Arabinoglucuronoxylan	0.12-0.17	0-25% Sorbitol	[62]
Glucuronoxylan	0.21	35% Sorbitol	[11]
Galactoglucomannan	2-4.4	54% Sorbitol & Glycerol	[69]
Hydroxypropyl xylan	23.6-37.1	0-10% Glycerol	[9]
Carboxymethyl xylan	0.5		[9]
CNC	0.25		[71]
CNF	0.036-7		[72]
Xylan/CNF	0.23-0.19	25-100% CNF	[70]

1: [$\text{cm}^3\mu\text{m}/(\text{m}^2\text{day kPa})$] 2: Values given as w/w%.

In summary, there is potential in the use of polysaccharides in packaging. While the tensile properties in some cases have been shown to be able to compete with commercial plastics, especially regarding composites of nanomaterials such as CNF, they are often rather stiff in comparison. Instead, the greatest potential seems to be found in gas barrier applications, where they show excellent permeabilities and sufficient mechanical properties. Some of the challenges for this to happen are the moisture sensitivity of hemicelluloses and their insolubility in water, which yield reduced properties and complicates film formation. The former can be solved by incorporating the polysaccharide films in multi-layer packaging with a designated separate moisture barrier, while increasing the solubility may require various chemical modifications.

2.3.2 Oxidation of polysaccharides

In order to utilize polysaccharides in more applications, chemical modification of the polymers is an important step. One such thing is oxidation of the hydroxyl groups of the monosaccharides to introduce e.g carbonyl groups or to partly cleave the monomers. Periodate is a common oxidizing agent, although not commonly commercially applied to hemicelluloses. However, it has found emerging use in the oxidation of secondary alcohols of primarily cellulose, and recently some studies demonstrate its ability to oxidize hemicelluloses as well [75].

Periodate oxidation was initially used as a step in the structural analysis of carbohydrates. Measuring the periodate uptake and various reaction products was then used to determine molecular sizes or the sequence of monomers in polysaccharides [76]. Today, it has been replaced by modern and improved methods, but periodate oxidation still remains as a promising method to modify polysaccharides [77]. When

periodate oxidizes 1,2-diols, e.g. saccharides, it forms a cyclic intermediate between the two hydroxygroups, as is seen in Figure 2.8. When the iodate detaches two aldehyde groups are formed and the carbon-carbon bond is cleaved, resulting in a ring opening [78]. These aldehyde groups can serve as anchor points for further modification to achieve the required properties, for example to attach amine groups [79]. Another benefit of the periodate-oxidation is the ring opening which creates "hinges", resulting in more flexible polymers with altered properties and improved solubility [14, 80].

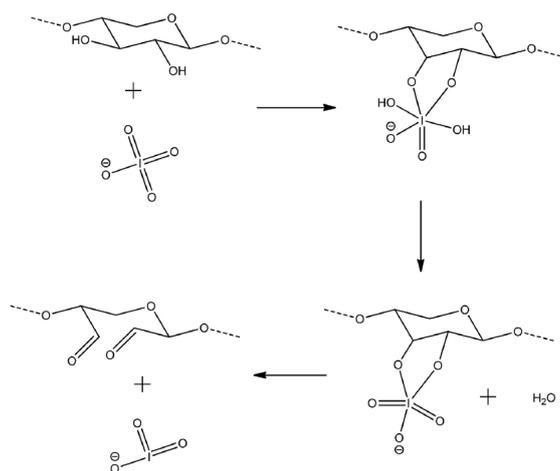


Figure 2.8: Mechanism of periodate oxidation on xylan. *From [13], printed with permission.*

While periodate targets secondary alcohols, the primary alcohols of hexapyranoses, such as glucose, require different methods. One promising method uses 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), which exhibits advantages such as high yield, selectivity and reaction rate [75]. TEMPO-oxidation only targets primary alcohols and, as is seen in Figure 2.9, does not cleave any carbon-carbon bonds. Likewise, TEMPO oxidation cannot be used on pentopyranoses, e.g. xylan, as they contain no primary alcohols.

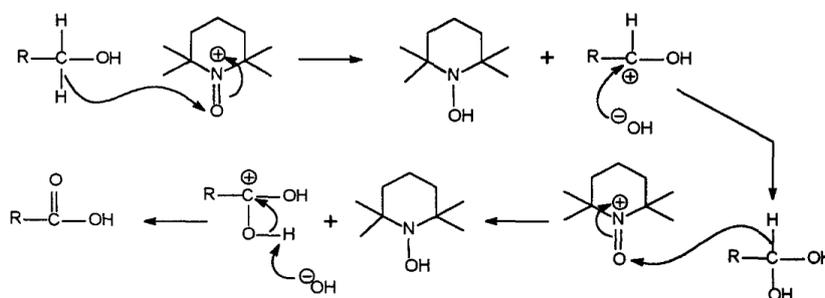


Figure 2.9: Mechanism for the oxidation of primary alcohol groups of carbohydrates to carboxylic acids by 2,2,6,6-tetramethyl-1-piperidino oxoammonium ion. *From [81], printed with permission.*

2.3.2.1 Effect of oxidation on physicochemical properties

There are several studies on the effect of periodate oxidation on molecular weight. The results differ between different polysaccharides, where many experience a decreased molecular weight [82], while for cellulose it may instead increase, probably due to cross-linking [79, 82]. For xylan, it seems to decrease when oxidized, due to polymer degradation and absence of severe cross-linking [12, 14]

One reason for the difficulty of utilizing xylans is their limited solubility in water, which also depends on the extraction method [83]. Similarly, other hemicelluloses [80], and cellulose [77] are also known to have poor solubility in water. It is mainly the substituents and side chains, but also possibly the molecular weight and DP, that is the reason for the insolubility [84, 85]. The solubility of polysaccharides may be improved by oxidation. For example, the solubility of cellulose increased by converting the primary hydroxyls into carboxylic groups via TEMPO-oxidation [75, 81]. However, oxidizing cellulose with periodate may render the product insoluble at high degrees of oxidation due to cross-linking [82].

Although not abundant, there are studies on mechanical properties of oxidized polysaccharides. However, among the studies there are no clear trend between the DO and the tensile properties. While most studies find a drop in the tensile strength and an increase in the strain at break when compared to unoxidized samples, the effect of increased DO differs between different studies. One study found the tensile strength to significantly decrease, while the strain at break somewhat increased upon oxidation of the xylan based films. At higher DO the maximum stress remained unchanged, while the strain experienced a considerable increase [15]. The same trends have been seen in another study, where films of oxidized xylan showed a significantly decreased tensile strength and increased strain at yield upon oxidation [86]. This was theorized to stem from internal plasticization due to the ring opening of the xylose units. Further oxidation led to even lower stress and higher strain values, although this change was less pronounced. A third study found the tensile strength to decrease with increased DO, while the strain remained stable [87].

When xyloglucan films were oxidized, their oxygen permeabilities have been found to increase when measured in a dry environment, while the opposite happened at 50% RH. This suggests that oxidation is initially detrimental to the permeability at low humidities while decreasing the moisture sensitivity, and is thus more beneficial as the humidity increases. The reason for this was thought to be the decreased absorption of moisture for the oxidized grades, which reduced the otherwise detrimental effect humidity has on gas permeability [86]. Regardless of humidity, the study also reported the permeability to decrease with increased oxidation time, a trend which was later reproduced [88].

Moreover, the effect of periodate oxidation on nanofibrillated cellulose (CNF) has been studied [17]. Similar to earlier studies, the tensile strength dropped upon oxidation, but so did the strain. The oxygen permeability decreased as well and, interestingly, remained unchanged even at high humidities. This supports the theory that periodate oxidation stabilizes against moisture related effects, which was further

showed as the oxidized films also showed a significantly lowered change in elastic properties at increased humidity.

2.3.3 Stability of polysaccharides

While the chemical and mechanical properties of polysaccharide films is an area that has recently gained increasing interest, the stability over time of said properties is an area that has yet to see much research. Much of the research regarding stability over time has been focused on polysaccharides in solutions and thus the focus has laid on chemical stability. Further research on the mechanical stability of polysaccharide films would therefore be valuable, especially so in combination with chemical stability. This could grant insights into what effects previously studied phenomena of polymers, such as molecular weight loss or aldehyde content, has on the mechanical stability of the films.

Chemical stability

Münster et al. investigated the stability and aging of periodate-oxidized cellulose (dialdehyde cellulose, DAC) in solution [89]. Over the span of 28 days the results showed no significant change in solubility or thermal stability, and only a small decrease in aldehyde content. However, changes in molecular weight (M_W) were discovered, which were attributed to cross-linking of hemiacetals (see Figure 2.10) and cleavage of the polymers. There may also be some changes between the ratio of different side groups, but no degradation products could be detected. In a later study, Münster et al. yet again found that the aldehyde content decreased over the span of 28 days [90]. There are studies that suggest that severe degradation of DAC occurs shortly after solubilization [82, 91], while others have proven the opposite [92].

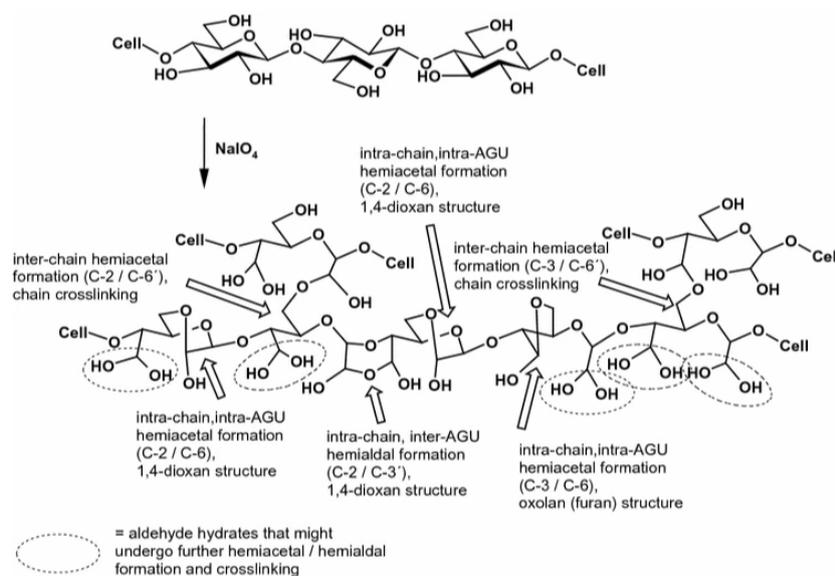


Figure 2.10: Overview on cross-links (inter- and intra-hemiacetals and hemialdals) in aqueous solutions of dialdehyde cellulose. *From [82], printed with permission.*

In a similar study, Yan et al. also studied the stability of DAC in solution [93]. They found that, contrary to Münster et al., M_W decreased with time independent of degree of oxidation, although their study covered a 6 months time span and the molecular weight reached a stable value after 3 months. Interestingly, they also found that the stable molecular weight was the same for all samples, independent of degree of oxidation and, thus, initial molecular weight. Furthermore, the study showed that prolonged oxidation or oxidation at elevated temperatures decreased the molecular weight. In accordance with Münster et al, the resulting polydispersity index¹ (PDI) increased in general over the span of 6 months. However, for high degrees of oxidation it experienced a slight decrease, and for all cases the PDI reached its peak value after 1 month of storage. This behaviour was explained, in accordance with Münster et al., to stem from two processes: hydrolytic chain scission and recombination of molecules. Finally, Yan et al. found the aldehyde content to decrease with time and, similarly to molecular weight, reach a stable value after 3 months.

Since periodate targets the 2,3 hydroxy groups and TEMPO targets the primary alcohol, the resulting oxidized products will have different properties and aging characteristics. For example, the β -alkoxy-elimination related to aging degradation has significantly higher rate constants for the 2,3 aldehydes than for the primary aldehydes of cellulose [94]. However, it might still be of some use to compare periodate oxidized and TEMPO oxidized cellulose given the larger amount of research that has been done on TEMPO oxidation. Milanovic et al investigated the effect of natural aging on TEMPO-oxidized cotton fibers [95]. After 5 years, mildly oxidized fibers experienced a decrease in molecular weight. On the contrary, for highly oxidized fibers no such deterioration was measured, although this was attributed to the fact that the fibers molecular weight severely decreased during oxidation and had thus already reached a stable stage prior to aging. Similar to Münster et al, Milanovic et al. also detected a broadening of the molecular weight distribution and likewise attributed this to the combination of depolymerization and cross-linking. Furthermore, aging resulted in a lower carbonyl content, which was partly explained by a conversion of aldehydes to carboxylic acids. Other factors that influenced the loss of carbonyls were thought to be masking of aldehydes via hemiacetal and hemialdald bonds. Lastly, a severe loss of tenacity, and thus tensile strength, could be seen upon aging. This was partly attributed to the decrease in molecular weight.

¹Poly dispersity index (PDI) is defined as $\frac{M_W}{M_n}$, i.e a measure over the spread or width of the range of detected molecular weights

Mechanical stability

Mikkonen et al. studied the effect of storage time on the tensile properties of plasticized arabinoxylan [19]. Films were stored in 23°C and at 50% RH for up to 5 months. The results showed the films plasticized with glycerol experienced a significant increase in tensile strength while strain at break decreased. This behaviour was explained as the migration of glycerol, leading to de-plasticization. For plasticization with sorbitol the differences were less pronounced, and the tensile strength even decreased slightly over time.

Heikkinen et al. also investigated the effect of storing hemicellulose films at room condition for up to 4 months [96]. They used films of arabinoxylan (AX) and galactoglucomannan (GGM) plasticized to 40% with different blends of glycerol and sorbitol. AX films plasticized with only glycerol showed an increase in tensile strength over time, while the sorbitol films slightly decreased. However, for the GGM films the tensile strength increased independent of plasticizer. For the AX films, the strain at break decreased with glycerol, but increased with sorbitol. GGM films also showed a decreased strain with glycerol, while the values were statistically unchanged when sorbitol was used. This would suggest that glycerol is more prone to migrate out of the films, leading to de-plasticization and thus explaining the behaviours of stress and strain over time. The same behaviour was not seen with sorbitol, which was theorized to be due to accumulation of sorbitol clusters over time, leading to decreased strength. Additionally, the mechanical properties seem to stabilize over time, with much less apparent changes after 2 months. Furthermore, the effect of aging on oxygen permeability was also studied. Independent of plasticizers, the films experienced an increased permeability after 4 months compared to after 1 week, although all values were still below $10 \text{ cm}^3 \mu\text{m}/(\text{m}^2 \text{day kPa})$ and thus considered good barriers. The results combined with the change in mechanical properties indicated that a structural change takes place over time.

In the previously cited study of Münster et al., the Young's modulus² was measured for xerogel films of PVA/DAC blends. These results showed no significant difference in neither Young's modulus nor strain at break after 28 days of aging [90].

²Youngs modulus is defined as the tensile strength divided by the strain at the initial linear (elastic) region of the stress-strain curve

2.4 Analytical methods

The following paragraphs present short summaries of the different analytical tools used in this work. Thermogravimetric analysis and anionic exchange chromatography were used for characterization of solutions, while tensile tests and oxygen transfer rate testing were used to determine the stability of the films.

2.4.1 Thermogravimetric analysis

In a thermogravimetric analysis (TGA), the mass changes of a samples are measured over time and varying temperature. The change of mass stems mainly from the evaporation and decomposition of the samples. The temperature is often linearly increased to temperatures up to 1200°C, and the results are plotted as percentage of initial mass against temperature. A purge gas, commonly N₂, can be used to create an inert environment. The derivative of the signal, termed DTG, can be used to measure the kinetics of the different degradation steps [97].

For beechwood xylan, the degradation starts at 200°C, with a maximum value around 250-300°C [9]. For other hemicelluloses, the degradation begins at 250-200°C. There may also be a decrease of mass around 100-150°C due to the removal of water in the samples [98, 99].

2.4.2 Liquid chromatography

Liquid chromatography uses a set of packed columns through which the samples is driven by an eluent, pumped at a fixed volumetric rate. The columns contain a stationary phase, e.g a packed bed of porous material, which will have different interactions with the different molecules of the sample. The molecules with the least interaction will have the shortest residence time and thus be the first to exit the columns. After separation the molecules are detected by typically measuring one of three properties: The concentration via spectroscopic methods like UV, the intrinsic viscosity, or the light scattering [100].

2.4.2.1 High-performance anion exchange chromatography

In basic solutions, saccharides show weak anionic properties, stemming from the many hydroxyl groups. The distribution of hydroxyl groups within the different monomers results in differences in pK_a and thus in their anionic-exchange interactions with the stationary phase which typically contains cationic sites (based on quaternary ammonium structures). A very popular tool for separating saccharides are therefore high-performance anion exchange chromatography (HPAEC), where the different anionic-exchange interactions results in different eluation times [101].

Saccharides contain no chromophoric groups and therefore cannot be detected using spectrometric methods. Instead, HPAEC with aqueous alkaline eluent is most commonly paired with a pulsed amperometric detector (PAD). PAD uses a noble metal

electrode that oxidizes the carbohydrates. This generates a current which can be measured, allowing detection with high sensitivity [102].

2.4.3 Ultraviolet-visible spectroscopy

In ultraviolet-visible spectroscopy (UV-vis), molecules of the samples is irradiated with light in the ultraviolet and visible range (200-400 nm & 400-800 nm respectively), causing the excitation of electrons when the light is absorbed. The measured absorption at a certain wavelength depends on the functional groups of the molecules, and can thus be used to characterize the sample. Moreover, UV-vis is commonly more suitable for qualitative measurements, but may be employed in quantitative analyses if a proper calibration curve is used [103].

2.4.4 Tensile test

One important mechanical property of films is their deformation under load, which can be measured in a tensile test. An oblong piece is fastened between two clamps which are moving away from each other at a constant rate. The resulting load required and distance elongated are recorded up until the point where the sample breaks. Dividing with the cross-sectional area of the sample, the stress at break is calculated from the load at which the piece breaks, while the strain at break is given as a percentage of the original length the sample piece has been stretched for when it breaks [104].

2.4.5 Oxygen Transfer Rate

The oxygen transfer rate (OTR) of films is determined by clamping the films between two chambers. The chambers are purged of any ambient air, whereafter a test gas of, usually, pure O₂ is flowed through the diffusion cell chamber. On the opposite side, oxygen that permeates through the barrier is transported with a carrier gas of mainly N₂ that flows through the chamber and into the oxygen sensor. The temperature and humidity of both sides of the test chamber are strictly controlled. The OTR is then calculated as the flux of oxygen (volume per surface area) that is transferred across the film during a set amount of time. The oxygen permeability of the film can then be calculated by multiplying the OTR with the thickness of the film and dividing by the relative difference in partial pressure of oxygen at either side in the diffusion cell chamber [105].

3

Experimental method

This chapter presents the preparatory steps taken to modify the material, the experimental setup of the stability tests followed by the methodology used to analyze the final films.

3.1 Preparations prior to stability tests

In summary, xylan was oxidized with sodium periodate and casted into films via solution casting. The films were stored in either an oven or in desiccators maintaining a set humidity for a period of up to 4 weeks. The different raw materials were also analyzed for thermal stability with TGA.

3.1.1 Materials

Two different grades of raw material were studied. The first was commercial grade birch-wood xylan with a molar weight of 132.1 g/mole. The second grade was a solution of polysaccharides composed mainly of xyloses and glucoses, from eucalyptus wood meal. Some films were also supported by PVA in the form of *Mowiol*[®] 28-99 with a molecular weight of ~145000 g/mol. Furthermore 99% D-Sorbitol was used as plasticizer. All chemicals were bought from Sigma-Aldrich.

3.1.2 Oxidation of Xylan

Xylan was oxidized with sodium periodate according to the method adapted from Amer et al. [12]: first, 4 g of xylan was dissolved in 165 ml of deionized water and stirred overnight at room temperature using a magnetic stirrer. To prevent the xylan from reacting with radicals that may be formed during decomposition of IO_4^- , 10 ml of iso-propanol was added under stirring. After 30 minutes of stirring a solution of 25 ml deionized water and 4 g NaIO_4 (corresponding to 61.8% mole per mole of the added xylan) was added. The flask was covered with aluminum foil and left to be stirred at room temperature. The progress of the reaction was monitored by measuring the IO_4^- -concentration with UV-vis, using the absorption at 290 nm [106].

After approximately 48 hours the reaction was terminated and the solution of the oxidized xylan (OX) was dialyzed in continuously changed deionized water for 4 days using a dialysis membrane with a weight average molecular weight (M_w) cutoff of 2 kDa. It was then spread out on a tray and freeze-dried at $-20\text{ }^\circ\text{C}$ and 0.1 Bar for 7 days, after which it was collected and stored in an air-tight container in a freezer until further used.

The second grade, the simultaneously extracted and oxidized xylan (SEOX), was produced in previous experiments. An amount of 2.5 g eucalyptus wood meal was suspended in an acetate buffer (0.1M, pH set to 5.6 with acetic acid). Then, 3.3 g NaIO_4 and 7.25 g NaCl was added, and the suspension was stirred in a dark environment at $60\pm 5\text{ }^\circ\text{C}$ for 3 h. Afterwards, around 5 ml ethylene glycol was added and stirred for 15 min to quench the remaining periodate. The solution was then filtered through a Büchner funnel, after which the filtrate was dialyzed against deionized water for 48 h and then freeze-dried. The solid fraction was suspended in 50 ml deionized water, stirred for 12 h and then frozen. Finally, it was freeze-dried at the same conditions as the OX solution, but required 10 days due to a higher water content and the container having a smaller surface area.

3.1.3 TGA

Thermal stability of the different oxidized grades was analyzed and compared to that of un-oxidized xylan. A *TGA/DSC 3+ STARe system (Mettler Toledo)* was used to linearly increase the temperature from $25\text{--}500\text{ }^\circ\text{C}$ with a rate of $10\text{ }^\circ\text{C}/\text{min}$ and in an N_2 -environment with a flow of $50\text{ ml}/\text{min}$. The sample sizes were roughly 5 mg and the onset of degradation temperature T_O and temperature of maximum degradation rate T_M was calculated using the *STARe Excellence Software*.

3.1.4 Film casting

Three different kinds of films were prepared: One of each oxidized grade (OX and SEOX) plus a third type that consisted of OX supported by PVA and plasticized by sorbitol. PVA was used to ensure the films stayed stable enough for mechanical testing and without need of excessive amount of material, chosen because previous research had shown that unmodified xylan formed films in PVA blends. In each case, the corresponding amounts of hemicellulose and sorbitol was dissolved in deionized water overnight under continuous stirring. PVA was dissolved in deionized water heated to $90\text{ }^\circ\text{C}$ using a condenser to prevent evaporation. The room temperature PVA solution was added to the hemicellulose/sorbitol mixture and stirred for another 30 minutes, after which it was poured into moulds. All three solutions had a dry content of 2% w/v, and the ratio of the third solution was 1:3:1.2 xylan:PVA:sorbitol. The volume casted into each mould was chosen such that the dry content of each film would be $5.1\text{ mg}/\text{cm}^2$. The films were kept in a fume hood in room conditions ($\sim 22\text{ }^\circ\text{C}$, $\sim 30\%$ RH) for 24 h until the solvent had evaporated and the films could be manually removed and placed in the designated storage condition.

3.1.5 Storage conditions

The aging stability of the films was analyzed with respect to two parameters: at elevated temperature and at two different levels of relative humidity (RH). The values for the three different storage conditions are presented in Table 3.1, and only one parameter at a time was controlled for. The films were aged for a duration of minimum 72 hours and up to 4 weeks. After each film had been aged for the appointed amount of time, they were stored in a desiccator at room temperature with an approximate relative humidity of 9% for 3 days, whereupon they were placed in an airtight container in the freezer until further analyzed.

Table 3.1: Temperature and relative humidity for the three storage conditions.

Condition	T	RH
High T	60°C	~4 % ¹
Low RH	~22°C ¹	36±2 %
High RH	~22°C ¹	92±2 %

1: The value represents an average over time and was not controlled.

Relative humidity

The RH was controlled for by storing the samples in desiccators containing approximately 20 ml of saturated salt solutions. Different salts results in a different values of the RH according to Wexler & Haswgawa [107]. Saturated MgCl₂ and K₂SO₄ was used for the low and high-humidity condition respectively. The desiccators were stored in room condition with a surrounding RH of around 30%.

Temperature

Assigned samples were stored in an oven at 60°C. The oven used an extractor to circulate the air flow, but all samples were covered either in the form of Petri dishes with lids or wrapped in aluminum foil.

3.2 Characterization of film stability

Table 3.2 summarizes all the analyses that were performed to analyze the stability of the films. All analyzed properties were measured prior to storage, and after 2 and after 4 weeks of storage. Furthermore, tensile tests were also performed after 72 h and after 1 week of storage.

Table 3.2: A list of all analytical methods used to characterize the films and follow the aging progression.

Film Properties	Analytical method
Carbohydrate analysis	HPLC
Oxygen barrier ¹	OTR test
Film thickness ¹	Micrometer
Mechanical strength ¹	Tensile test

1: Methods using films supported with PVA.

3.2.1 Carbohydrate analysis

In preparation for the carbohydrate analysis, the methodology of Klason lignin analysis was followed in order to convert the polysaccharides into monomers [108]. An amount of 30 mg of each film sample was dissolved in 0.45 ml of 72% H₂SO₄ and kept under vacuum for 15 minutes. The samples were then kept in a water bath of 30°C for 60 minutes with occasional stirring. 12.6 g of deionized water was added to the samples which were then covered in aluminum foil and placed in an autoclave of 125°C for 60 minutes. Lastly, the insoluble residue, termed Klason lignin, was filtered off using glass microfiber filters. The filtrate was kept for carbohydrate analysis while the residue was dried at 105°C overnight and measured gravimetrically.

The filtrate was then diluted 20 times with deionized water mixed with fucose (used as a standard), such that the final concentration of fucose was 8 mg/L. The final solutions were then filtered using a 0.45 μ m syringe filter before analyzed using *Dionex ICS-5000 HPIC* system, *Carbopac PA1* columns and a gold electrode. Eluents used were a NaOAc-NaOH mixture, NaOH, and pure MilliQ water, all stored under helium. The system detected arabinose, galactose, glucose, mannose, and xylose. Measured values were corrected for with respect to hydrolysis yield of the different monomers [109], and for the weight added by water molecules to the anhydrous saccharides compared to their polymeric form [110]. The data were analyzed with *Chromeleon*[®] 7, *Chromatography Data System software*, *Dionex Chromeleon*, *Vers. 7.1.3.2425*.

3.2.2 Oxygen permeability

The oxygen permeabilities of the films were tested at BillerudKorsnäs facilities in Skärblacka. An *OX-TRAN OTR Analyzer (AMETEK MOCON)* was used at 23°C, 50% RH and 1 atm, with oxygen partial pressures of 21% and 100% at either side

of the film. Films were cut into pieces of at least 10 cm², of which 5 cm² were used for each analysis. The time of testing ranged from 30h to 90h.

3.2.3 Mechanical strength

Mechanical strength was measured by analyzing the tensile properties with an *Instron 5565A Mechanical tester (INSTRON)* using a 100 N load cell, a 30 mm test span and a separation rate of 10mm/min. Each measurement was repeated at least 4 times. Prior to testing, the samples were conditioned as described in Section 3.1.5, this time with a salt solution of Mg(NO₃)₂, averaging at 22°C and 52% RH for at least 48 hours to ensure all samples held the same humidity. The sample dimensions were 15x50 mm and the mean thickness varied between 32.2-46 μm. Testing was done in uncontrolled temperature and humidity, which averaged at 28% RH at 22°C during the time of testing. However, all samples specimens were kept in the desiccator until right before testing to minimize the effect of the surrounding humidity, and they were analyzed at once.

3.3 Labeling of specimen and conditions

In the following chapter the results are presented. The abbreviations used are explained in Table 3.3. For example, L72 refers to a film of OX (with or without PVA/sorbitol) that has been stored at 36% RH for 72h. When denoting SEOX films that have been stored in various conditions, the subscript *S* is used, i.e L2_S. When statistical differences are discussed they refer to a two-way t-testing using an α of 0.05.

Table 3.3: Abbreviations used for samples when presented in Section 3.1.5

Abbreviation	Description
OX	Xylan oxidized by periodate as described in Section 3.
SEOX	Simultaneously extracted and oxidized xylan from the eucalyptus wood meal.
0	OX/PVA/Sorbitol films that were not stored at any of the three storage conditions described in Section 3.1.5, but instead immediately dried and stored in a freezer.
T/L/H	Refers to samples stored at elevated temperature/low humidity/high humidity.
72/1/2/4	Refers to samples stored for a period of 72 hours, 1 week etc.

4

Results & Discussion

This chapter presents and discusses the results from the oxidation of xylan, film casting and finally the characterization of the films. Lastly, a short review is presented of literature findings on stabilization of oxidized polysaccharides.

4.1 Characterization of oxidized xylan

The final degree of oxidation was 30.0%, corresponding to a 48.5% consumption of periodate, see Figure 4.1. When Börjesson et al. investigated the effect of isopropanol on periodate oxidation of xylans they saw a significant increase in experimental DO compared to samples without isopropanol. Their final consumption of periodate was 80% at a 50% theoretical DO [14]. Since isopropanol was used in the present study the results should therefore be closer to that of Börjesson et al. This is further supported by Chemin et al., who found periodate consumptions of 90 and 80% respectively for 0.2 and 1.0 ratios of periodate to xylan [13]. They also found that the periodate consumption at a given ratio depended on the total concentration of xylan, although even for their most dilute samples the final consumption was higher compared to the present study.

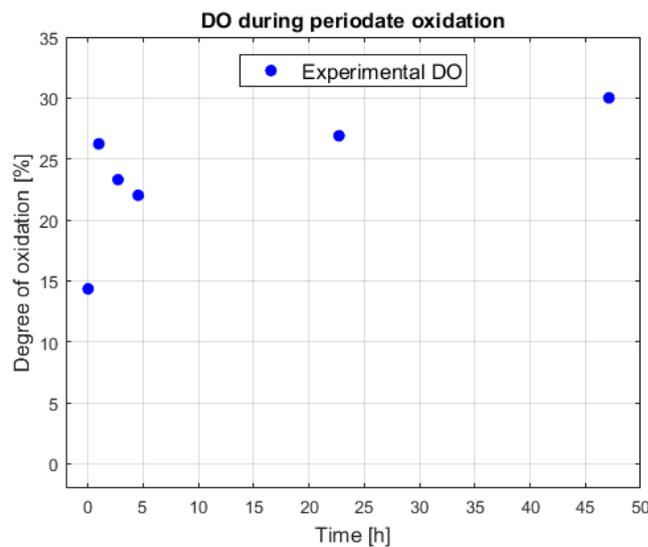


Figure 4.1: The measured DO over time during the oxidation of xylan.

The progress of the oxidation indicates that the consumption rate is initially fast over the first 10h but then decreases, although not fully steady after 48h, which is slower than that of Chemin et al. The results of Börjesson et al. also indicate a faster reaction, but for a theoretical DO of 42.5% and higher, the consumption were not stable after 24h when they terminated the experiment.

The overall lack of full consumption of periodate has previously been explained by the formation of hemiacetals, leading to inter- and intramolecular bonds that shield OH groups from the oxidant [12–14]. As the present work used similar temperatures and concentrations as previous studies it is still unclear why the consumption rate was slower. Different amount of substituents and DP may affect the yield, although this was not investigated further. Moreover, the measurements within the first 5 hours show either contradictory trends or a rather large margin of error. One factor that could have affected these results is the photo sensitivity of periodate. Exposure to light results in reactions consuming periodate, which would then increase the measured degree of oxidation. Different handling times between sampling and detection with the UV-Vis equipment (at which the samples were exposed to light) may thus have affected the results.

Another estimate of the DO can be made by comparing the decrease in detected amount of unmodified xylose from the carbohydrate analysis. The resulting ring-opening of the xylose units during periodate oxidation will yield monomers that will not be detected using HPAEC-PAD. As is seen in Table 4.1, the amount of xylose detected decreased by 32.0%, thus indicating a DO of equal size. This is in line with the final measured DO using the UV-Vis, opposing the idea that a severe photo degradation of the periodate ions had occurred. However, it should be noted that even this measurement only gives indications, and several factors affect the results such as degradation during the acid hydrolysis prior to the analysis.

Table 4.1: Xylose content as determined by HPAEC-PAD. Values are averages of 2 measurements.

Sample	Detected mass [mg/L]
Xylan	25.9
OX	17.6

From the initial 4 g of xylan roughly 2.8 g of OX was synthesized, leading to an approximate yield of 70%. This is lower than previously reported values of 80% and 90%, at 91.5% and 50% DO respectively [12, 79]. Some losses are expected, as periodate oxidation has been reported to induce chain scissoring, which will lead to smaller fractions of polymers that will be removed during dialysis. In contrast to this reasoning the yield should then have been larger than for Amer et al., since they reached a DO of over 90% yet still achieved a higher yield. The molecular weight, M_W , was neither measured on the pure nor the oxidized xylan, but a value of 17.7 kDa has been reported for birch xylan from the same supplier [60]. This is higher than the 7.7kDa reported by Amer et al., speaking against the theory that the low yield of this study stemmed from a lower average molecular weight.

4.1.1 Thermal stability

To investigate the thermal degradation stability TGA was performed on 3 samples: unmodified xylan, OX and SEOX. The resulting mass loss curves are shown in Figure 4.2, with corresponding values for onset and maximum degradation temperatures presented in Table 4.2. The most prominent difference is SEOX, which experienced an earlier and protracted degradation, but which had a significantly lower loss of mass at the end of measurements. This also might indicate a larger amount of thermally stable residues in this sample, such as metal ions or other inorganics. For the two other grades, the differences are much less pronounced, especially when compared to the results of Amer et al [12]. However, this is to be expected as the degree of oxidation is higher in that study.

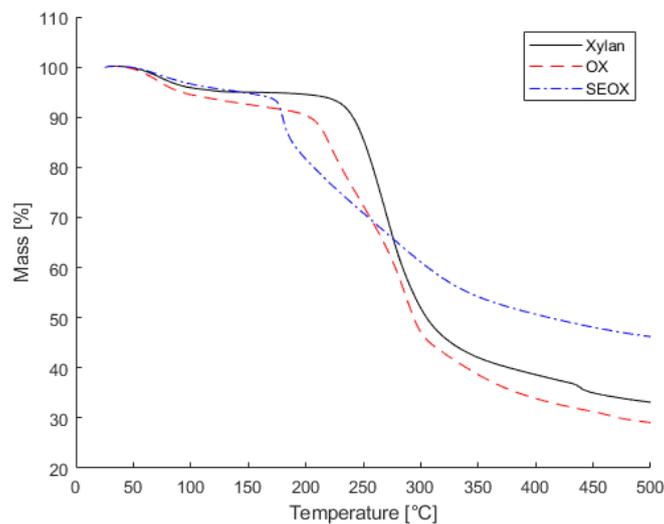


Figure 4.2: TGA results for unmodified xylan and the two oxidized grades.

Table 4.2: Temperatures at the onset of degradation (T_O) and maximum degradation rate (T_M), as measured during the TGA.

Sample	T_O [°C]	T_M [°C]
Xylan	227	266
OX	174	219 & 283
SEOX	118	175

What can be seen is that the oxidized grades seem to start degrading at a lower temperature. In agreement with Amer et al., the onset temperature was significantly reduced via oxidation. However, although there is a local maximum in degradation rate that occurs at lower temperatures for OX, the global maximum is delayed after oxidation. This is similar to the results of Börjesson et al, which showed only a slight change in the temperature at the start of degradation, while no clear trend was found regarding the point of maximum degradation rate [14]. Furthermore, unoxidized xylan showed the same behaviour as other hemicelluloses, both with regard to the start of degradation as well as the point of maximum degradation rate.

4.2 Film formation

The results from the casting showed that plasticized films with the support of PVA were transparent, pliable and easily removed from the moulds, see Figure 4.3. This is in agreement with previous studies that used similar ratios between PVA and (unmodified) xylan [111, 112]. On the contrary, films without support of PVA and plasticized by sorbitol exhibits poor film-forming properties. All species of these films were brittle and the majority cracked upon solvent evaporation or adhered too strongly to the mould to be removed. Examples are shown in Figure 4.4. One possible improvement would be to increase the humidity at which the moulds were kept during solvent evaporation. It was noted during the stability studies that there was an apparent visual difference between the samples kept at low and high humidity, see Figure 4.5. Therefore, by keeping the films at higher humidity during casting they would hold a higher moisture level and would thus be more flexible and easier to remove from the mould. Yet, it is unclear whether the films would refrain from cracking upon drying outside of the mould or if they would still have to be kept at a high humidity.

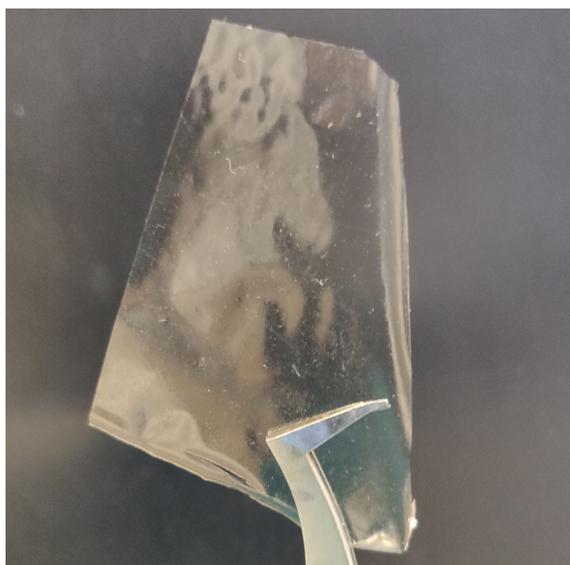


Figure 4.3: Image of OX/PVA/sorbitol film immediately after casting and before any treatment. The films were transparent and flexible.

Moreover, it is clear from previous studies that unmodified xylan rarely forms self standing films, and that modified xylan needs a certain degree of modification to form films. Furthermore, it has been suggested that modifications or substituents that increase the solubility also are beneficial in film formation. Thus, one way to improve the film-forming properties would be to increase xylan solubility by letting the xylan achieve a higher DO than used in this work. This introduces characteristics facilitating solubility such as potentially increased chain flexibility and decreased molecular weight. However, while high solubility in itself enables a homogeneous distribution of the polymer favourable for casting of the films, the decreased chain length is detrimental to the mechanical properties of the films and

has been reported as one of the main reasons behind the inability of hemicelluloses to form films. Furthermore, high DO enables inter- and intra molecular cross-linking leading to a decrease in solubility, and leads to higher strain at break but lower tensile strength. Consequently, the influence of the oxidation of xylan with respect to film properties is complex. There is a balance to achieve the optimal DO for making films, and further research in the area is needed.

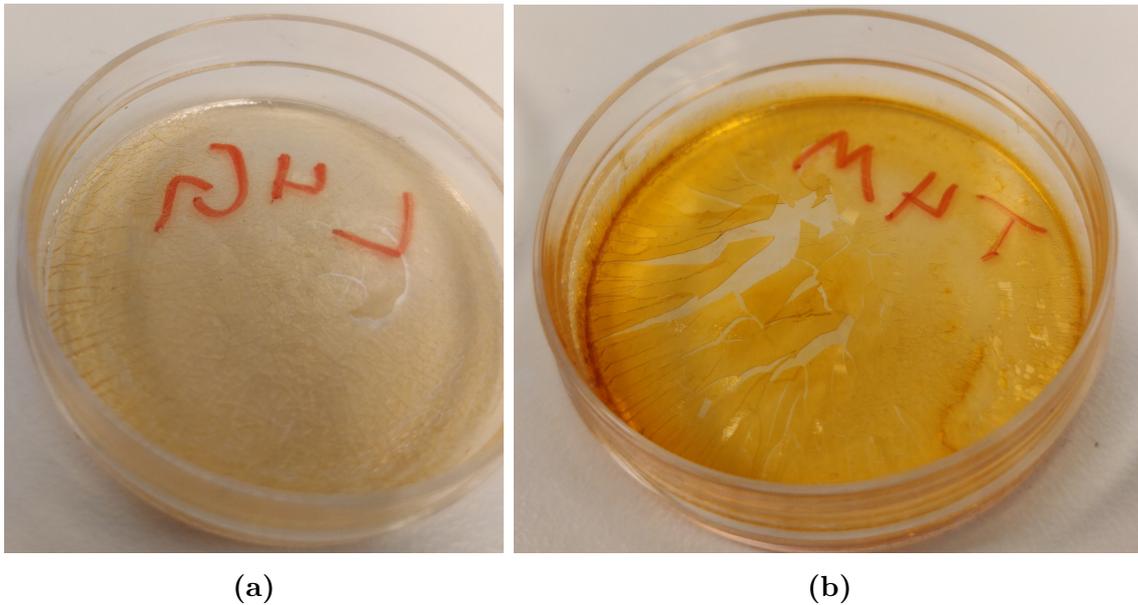


Figure 4.4: Images of films of pure (a) OX and (b) SEOX immediately after casting and before storage. Both films were brittle with varying amounts of cracks.



Figure 4.5: Comparison between OX/PVA/sorbitol films stored for 72h at (left) 30% and (right) 90% RH.

4.3 Chemical stability

In this section the results from the carbohydrate analysis and oxygen permeability measurements are presented.

4.3.1 Carbohydrate analysis

The total average yield from the carbohydrate analysis was 50.3% for the unmodified xylan and 35.3% for the OX samples. The average Klason lignin content was 1.9% and there were no statistical differences between neither different storage conditions, nor between unmodified xylan and OX regarding Klason lignin. The yield was significantly lower than that of a previous study with periodate oxidized xylan [14]. It is not clear whether this was due to severe degradation during the hydrolysis and storage prior to the analysis, or due to faulty measurements. However, since all samples were treated the same since storing and analysed under the same conditions, the differences in relative errors were assumed small and thus the results were still used to compare the different storage conditions.

The carbohydrate content of the OX films is presented in Figure 4.6 along that of unmodified xylan. Apart from trace amounts of other carbohydrates in the unmodified xylan, only xylose was detected for these samples. As previously discussed, there was a large drop in detected xylose content after oxidation corresponding to the DO. Once oxidized, all samples seemed to be stable. There were only two conditions, films stored at high humidity ($H1$ and $H4$), that yielded samples that were statistically different ($p < 0.05$) from the other. However, neither of these samples were statistically different from the OX sample, which indicates that the stability of all of them was similar.

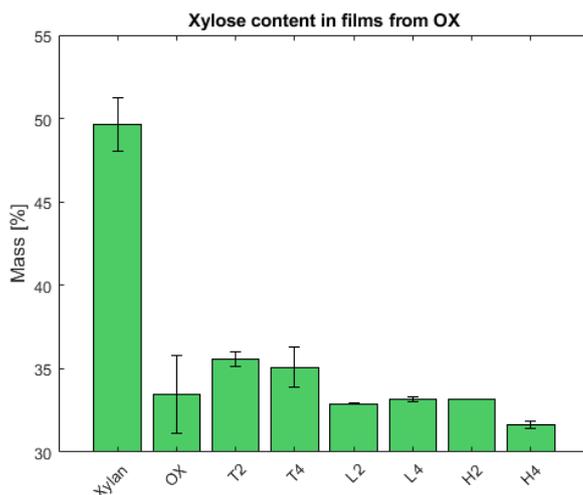


Figure 4.6: Results from the carbohydrate analysis showing xylose content of OX films after different treatments along that of unmodified xylan. The data presented is the mean of 2 measurements with the corresponding standard deviations.

Table 4.3: Average carbohydrate and Klason lignin content of SEOX-based films.

	Mass content [%]
Xylose	3.08
Glucose	7.60
Others	<0.1
Klason lignin	6.06
Total detected	16.83

Table 4.3 presents the average carbohydrate and Klason lignin content across all SEOX samples. The high glucose content is likely stemming from the extraction process used to generate the SEOX, which will co-extract glucomannan and affect cellulose polymers closely bonded to the targeted xylans in the cell wall of the wood meal. The resulting yield was even lower in this case, suggesting that this grade might have been even further oxidized or otherwise degraded during the extraction step, such that the affected monosaccharides were not detected. This would explain the earlier degradation during the TGA, consistent with higher DO. Other possible explanations could be a higher content of non carbohydrate residue such as lignin, or various inorganics as was suggested by the larger residue content shown in the TGA. Similarly to OX, neither did the SEOX samples show any statistically significant tendencies of instability under any of the tested conditions, see Figure 4.7.

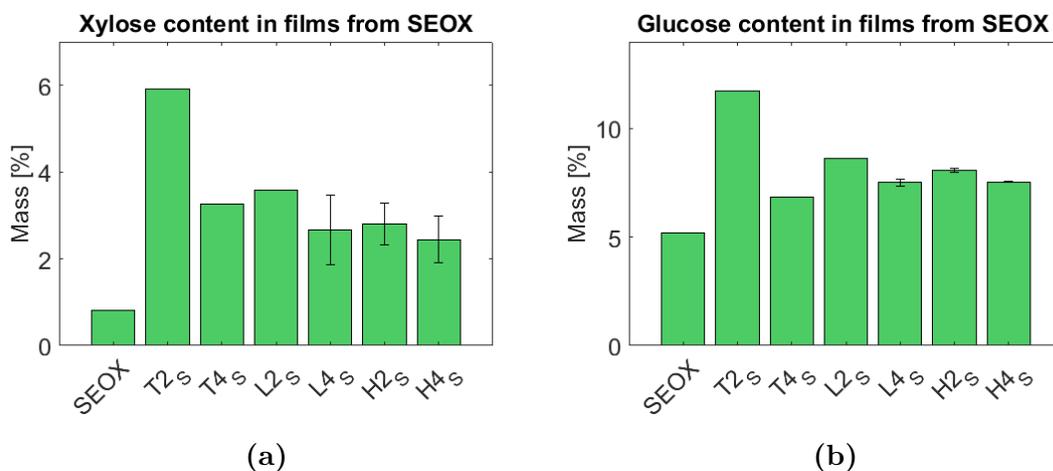


Figure 4.7: Results from the carbohydrate analysis using the HPAEC-PAD showing content of (a) xylose and (b) glucose in SEOX films after different treatments. The data presented is the mean of 2 measurements along the corresponding standard deviations. The data for SEOX, T1_s, T4_s and L2_s are each from a single sample. The sample weights of SEOX and T2_s were 8mg and 22mg respectively.

In summary, both SEOX and OX samples show some indications that carbohydrate monomers are unstable when stored over prolonged times, as the mean concentrations are lower after 4 weeks compared to after 2 weeks for all treatments. This was also seen for OX samples stored at high temperature or high humidity. Interestingly, the glucose content showed lower variations, both relative and absolute, suggesting that different saccharides are affected differently by storage.

4.3.2 Permeability

The resulting permeabilities are shown in Table 4.4. Interestingly, all samples had a lower mean permeability after storage compared to the control. While all films showed permeabilities significantly higher than reported values for pure PVA films, all values were still well below the "good barrier" level of $10 \text{ cm}^3 \mu\text{m}/(\text{m}^2 \text{ day kPa})$. Moreover, compared to plasticized hemicellulose films, the levels presented in Table 4.4 are comparable and in many cases even below the reported values [41, 69]. To what extent the low values can be attributed to OX in this study is unclear, as only one ratio of xylan/PVA was used, and it is probable that the inherently low OP of PVA contributes as well. One study even suggested the blending of PVA with starch yielded lower permeabilities than either material did alone [57].

Table 4.4: Permeability coefficients for films after different treatments. Values are means of 2 measurements with standard deviations given in parentheses.

Sample	Permeability ¹
0	3.8 (0.7)
T2	3.0 (- ²)
T4	3.7 (- ²)
L2	2.1 (0.9)
L4	- ²
H2	3.4 (0.4)
H4	1.7 (0.1)

1: [$\text{cm}^3 \mu\text{m}/(\text{m}^2 \text{ day kPa})$] 2: Values could not be determined due to lack of samples.

Previous research on polysaccharide films found the permeability to increase with time [96], which was not accounted for in the present work as all samples, including the control, were of equal age. Nonetheless, the results still indicate that even compared to the presumed non-disruptive condition of the freezer in which the control was stored, the films did not experience an increased instability with respect to permeability. This is especially noteworthy in the case of high humidity, as humid environment in general is detrimental to the permeability, and has showed to induce permanent increases in OP for EVOH films [48, 56]. Even so, in this respect the results correspond well with the previous studies of PVA/starch films that found the permeability to remain stable with respect to time [57]. The results can also be seen as further proof that oxidation stabilizes against moisture, similarly to previous findings [17, 86].

In conclusion, and in agreement with previous findings, oxidized xylan could be used as a biobased oxygen barrier based on its permeability. Depending on the requirements of the specific application it could be blended with common barriers such as PVA, thus yielding not only a higher bio-based content of the PVA films, but also possibly an improved stability against moisture. Finally, however, it should be noted that the experimental variation in this study are rather large, and more research is needed in the area, such as on the effect of DO on the permeability of xylan films and on film formation.

4.4 Mechanical stability

This section presents results from measurements of thickness and tensile strength.

4.4.1 Thickness

The average thickness of OX/PVA/sorbitol films were measured after storage and is presented in Table 4.5. The results show no significant difference in thickness over time for any of the three storage conditions. Furthermore, the standard deviations are rather large for almost all films, indicating an uneven thickness. This will affect the measurements of tensile properties and oxygen permeability, which calls for careful measurements of each individual test sample to ensure reliable results. It is also an indication that the casting conditions are suboptimal. Thus, the effect of casting mould surface morphology, casting inclination and variations in drying rate due to different placements in the fume hood should be minimized in future studies.

Table 4.5: Average thickness in μm of the films after the different treatments. Values are the mean of 5 measurements with corresponding standard deviations in parentheses. All films was dried in a desiccator and frozen according to Section 3.1.5 prior to measurements.

Time of aging	72 hr	1 day	2 days	4 days
Low Humidity	32.6 (8.9)	35 (14.4)	36.4 (17.0)	32.2 (10.0)
High Humidity	46 (17.4)	37 (10.14)	43 (5.0)	34.6 (5.2)
High Temperature	33.8 (5.4)	33.4 (13.6)	34.4 (9.4)	44.6 (7.3)

4.4.2 Tensile properties

The results from the tensile tests are presented in Figure 4.8. The tensile strength of the pure PVA/sorbitol films are somewhat lower than the reported values in Section 2.2.1, although this is expected since the films in this work have a plasticizer content of 30%, which should then lower their tensile strength. However, they also seem to have a lower strain at break compared to reported values, which is contradicting in regards to plasticizer content. A possible explanation to this could be the moisture content of the films. Since the testing was done in unregulated environment, the humidity was lower than that specified by standards (50% RH at 23°C). High humidity is usually positively correlated with strain and negatively correlated with tensile strength [113, 114]. Thus, the drier-than-standard environment could have led to decreased strain at break in the samples.

The addition of OX to PVA films resulted in no detectable change in tensile strength, while the strain at break decreased heavily, as is seen in Figure 4.8a and 4.8d respectively. While a high xylan:PVA ratio led to films with severely lower strength and strain at break [111], several other have studied blends of unmodified xylan and PVA, using the same ratio as in this work, but plasticized with 10% glycerol [112, 115, 116]. The resulting tensile strengths reported are between 15-25 MPa, correlating well to the results presented here. However, the reported values for the strain

at break are all higher, between 200-420%. This, again, indicates that the films in this study are stiffer than comparable previously studied films, even though sorbitol has proved to be an effective plasticizers in both PVA and xylan films [62, 117]. Moreover, periodate oxidation of xylan has been reported to yield films with increased strain at break but substantially decreased tensile strength at increased DO [15]. On the contrary, the results here suggests the opposite: Addition of oxidized xylan to PVA leads to similar or increased tensile strength but lower strain at break compared to unmodified xylan/PVA blends.

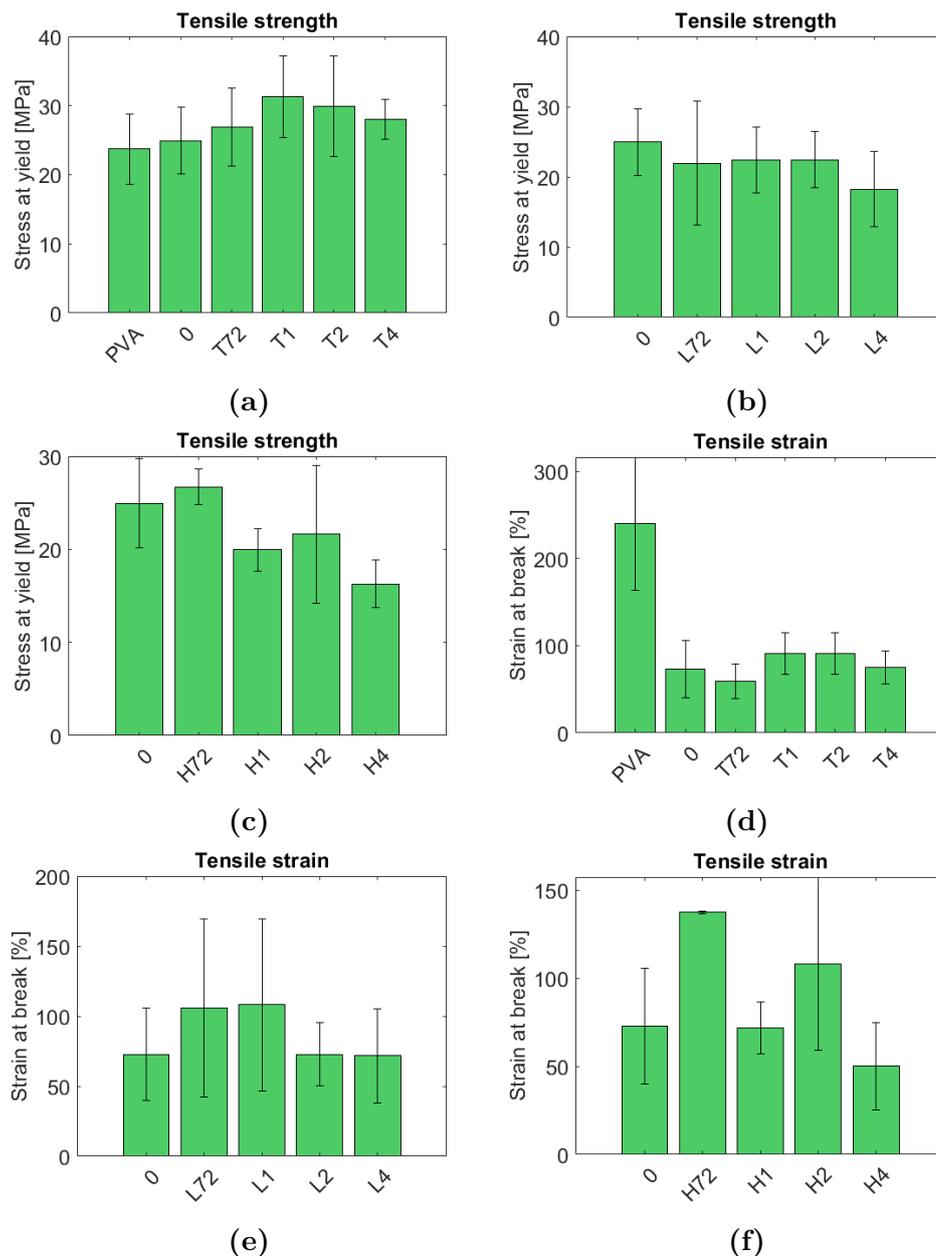


Figure 4.8: Tensile strength (a-c) and strain at break (d-f) of OX/PVA/sorbitol films stored at different conditions. Data represents means of at least 4 measurements with corresponding standard deviations. The data for H72 is from 2 samples.

Similarly to the carbohydrate content, neither did the mechanical properties appreciably change with time for either storage condition. There are no clear trends in the measured values, and even when the change in mean values are indicating a trend the deviations are too large for them to be statistically significant. The only exception is $H4$, which is lower than 0 and $H72$, indicating that prolonged exposure to high humidity environment is detrimental to the tensile strengths of the films. One possible reason for this could be that the films absorb such amount of moisture that they don't have time to fully equilibrate during the pre-conditioning prior to the tensile measurements. However, this should in that case also increase the strain at break, which in contrast shows no such indications. Another possible cause could be that irreversible changes in the morphology of the films occur when moisture is absorbed. This is further supported by the fact that the films that were stored at high humidity are visibly different from the rest, even after having been equilibrated at the same condition for a prolonged time. Figure 4.5 shows this difference immediately after storage but before equilibrium.

An additional trend is that for all the conditions, both the tensile strength and strain at break are lower after 4 weeks than after 1 or 2 weeks. This would suggest that some aging does in fact take place, deteriorating the mechanical properties of the films. Still, no such trend could be seen during the initial 2 weeks of aging, and the differences over all 4 weeks are still within the experimental variation.

Moreover, it is noted that the variations are especially large for many of the strain measurements. Although all measurements where the specimen broke within the clamps that held the film were discarded, the end points might still have influenced the results. Preferentially, in future measurements the test specimen should be dog bone-shaped, i.e wider at the ends, to ensure that end effect can be neglected. Further improvement to the tensile tests would be to ensure a more even thickness of the films, as uneven films will raise the average thickness without increasing the tensile strength which depends on the minimum thickness.

4.5 Stabilization of oxidized xylan

Although the films in this study seemed to be mostly stable with respect to time under different conditions, there might still be an instability over a longer period of time. This, coupled with the fact that the thermal stability of the films at high temperature is significantly reduced upon oxidation, motivates to look further into stabilizing measures.

One method that has been suggested is reduction of the dialdehyde groups with sodium borohydride, NaBH_4 . In a study on oxidized arabinoxylans, subsequent reduction with borohydride increased the degradation temperatures back to values close to that of the unmodified xylan [15]. It was also shown to stabilize against β -elimination [77], which is associated with the chain scissoring due to aging [89]. Additionally, the flexibility introduced by oxidation is retained after reduction [118], or might even be improved as the reduction cleaves hemiacetal crosslinks [77]. Thus

borohydride reduction, in combination with the increased alcohol content yielding higher solubility [79], grants further benefits in the context of film making. However, it is also known to cause the polymers to be more susceptible to acid hydrolysis, and the reducing process itself has been shown to decrease the molecular weight under alkaline conditions [119].

Another means of stabilization is via oxidation with sodium chlorite, NaClO_2 . Instead of generating hydroxyl groups, oxidizing the aldehydes creates carboxylic groups. Similar to reduction by borohydride, chlorite oxidation has been shown to lead to increased alkaline stability for both periodate- and tempo oxidized cellulose. There was also evidence that it led to increased stability towards yellowing. However, tensile properties were somewhat deteriorated [87]. For TEMPO-oxidized cellulose, chlorite oxidation has further been seen to somewhat increase thermal stability [120] and stability against temperature induced aging [121]. However, there is also risk of overoxidation, which leads to complete degradation into formic acid and carbon dioxide, although this can mostly be neglected for branched hemicelluloses such as xylan [122].

Durán et al. did an extensive comparison of the above mentioned post-treatments on periodate and TEMPO oxidized cellulose nanofibrills (CNF) [17]. Their findings confirmed that borohydride reduction led to an increased thermal stability and a slight increase in flexibility. It also led to a slight increase in oxygen permeability. However, the reduction did not stabilize against moisture, where an increased moisture level resulted in drastically changed Young's modulus, moisture uptake and oxygen permeability. In samples only treated with periodate, instead, the changes were small to none. Chlorite oxidation, on the other hand, lead to decreased thermal stability and stiffer films. This was attributed to the lack of covalent cross-links due to loss of aldehyde groups. Likewise, oxidation neither led to increased stability towards moisture, but followed the same trend as that of the reduced films.

There are several other methods that have been mentioned as potential means of stabilizing the aldehyde groups, often through oxidation. Ozone introduces carboxylic groups via oxidation while still leading to a possible increase in tensile strength [16], and treatment with diazomethane led to higher tensile strengths and stability against alkali solubilization [18]. All in all, however, research on the area is scarce, especially on hemicelluloses and even more so in regards to stabilization against aging over time.

5

Conclusion

The aim of this thesis was to oxidize and cast xylan into films, analyze their mechanical and chemical properties over time with respect to storage conditions, and finally identify some potential means of stabilizing the films. The initial literature review showed promising future for polysaccharides to be used as oxygen barriers, with the values of both oxygen permeability and mechanical strength comparable to conventional barrier materials.

The results further supported previous findings in that xylan was unable to form self standing films, even when oxidized to a DO of 30%. On the contrary, in PVA blends plasticized with sorbitol, OX was successfully casted into flexible self-standing transparent films. These films showed tensile properties and acceptable permeability levels comparable to conventional barriers. Moreover, the addition of OX lead to no change in tensile strength, while the strain at break decreased.

When stored at low humidity, irrespective of temperature, the films showed no signs of instability with respect to the analyzed properties. At high humidity, some indications showed a potential degradation of saccharide monomers and loss of tensile strength, while showing increased barrier properties. However, the changes were small and further research is needed to establish the findings.

Lastly, the literature review on stabilizing measures found mainly two ways: either reducing the aldehydes to hydroxyl groups, or oxidizing them into carboxylic groups. Both methods seem to stabilize against common degrading reactions, although neither stabilizes against high humidity effects. Reduction also seems to have less impact on the tensile strength of the films, although the differences were mostly minor.

To summarize, the findings of this study support the possibility of using oxidized xylan for the purpose of making oxygen barrier films, although extensive research is needed to fully establish this.

6

Future work

As a final concluding remark, the list below presents some suggestions for continued work on this subject:

- Further study the effect of DO on various properties of casted films. Presently, only a handful of studies have been carried out, many of which use different polymers yielding different properties. Especially interesting would be further research on the influence of DO of various xylans on their film-forming capabilities in conjunction with various degrees of plasticization.
- Investigate the effect of, and develop a strategy for controlling, the conditions during casting, thus generating films of more even thickness which will increase reproducibility and decrease experimental error.
- Study a wider range of temperatures and humidities. Since humidity is relative, increasing both parameters at the same time will introduce a higher absolute humidity, which might yield a larger effect than what was found in the present work.
- Measure the effect of storage conditions on molecular weight and aldehyde content. Previous studies suggested a considerable change in both M_W and PDI, as well as the aldehyde content, which might then be related to changes in mechanical properties.

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