

IMPROVEMENT OF WATER SENSITIVITY, MECHANICAL PROPERTIES
AND UTILIZATION OF HEMICELLULOSE BASED
POLYMERIC MATERIALS

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POLYMERIC MATERIALS

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ABSTRACT

IMPROVEMENT OF WATER SENSITIVITY, MECHANICAL PROPERTIES AND UTILIZATION OF HEMICELLULOSE BASED POLYMERIC MATERIALS

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Hemicelluloses are sustainable resources of biopolymers with a huge potential to be converted into materials substituting petroleum-based products, but their hydrophilic characteristics pose a challenge to their industrial adoption. The main aim of this study is to decrease the water sensitivity of alkaline extracted xylan-based corn cob hemicelluloses (xylans) by heat-treatment and acetylation also by addressing their extrusion processing with sorbitol, glycerol and blends. Heat-treatment resulted in extruded strips with less moisture uptake, less normalized water vapor transfer rate (NWVTR) and enhanced mechanical properties, but without any significant change in their water solubilities. Acetylation was studied by exploiting the potassium acetate (KAc) salt that is formed during the alkaline extraction, which is usually removed. Moisture uptake, water solubility, and NWVTR of KAc containing acetylated xylans decreased significantly, with an increase in mechanical properties and thermal stability, showing that acetylation with KAc is an efficient method without salt purification steps and toxic catalysts like pyridine. Extrusion of xylans with sorbitol and glycerol was studied alternative to the plasticization by moisture conditioning where both plasticizers rendered xylans extrudable. Similar to the effect of KAc,

acetylation carried out in the presence of sorbitol and glycerol resulted in reduced water solubilities; however the mechanical properties were only enhanced for glycerol containing strips. Xylan and polyvinyl alcohol (PVA) blends and their heat treatment and acetylation were also studied to reduce their water sensitivity. Extrusion of xylan/PVA blends was successful which might increase the industrial utilization of xylans, but their heat treatment and acetylation resulted in brittle strips.

Keywords: Corn cob xylan, extrusion, heat treatment, acetylation, plasticizer, blending

ÖZ

HEMİSELÜLOZ TEMELLİ POLİMERİK MALZEMELERİN SU HASSASİYETİNİN, MEKANİK ÖZELLİKLERİNİN VE KULLANIM ALANLARININ GELİŞTİRİLMESİ

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Hemiselüloz, petrol temelli polimerik ürünlerin yerine kullanılabilme potansiyeli yüksek, yenilenebilir bir biyopolimer kaynağıdır; fakat hemiselülozun hidrofilik yapısı endüstriyel uygulamalarını kısıtlanmaktadır. Bu çalışmanın asıl amacı, mısır koçanından alkali özütleme tekniği ile izole edilmiş ksilan temelli hemiselülozların (ksilanlar) ısıtma işlemi ve asetilasyon yöntemleri ile su hassasiyetlerinin azaltılması ve bununla beraber plastikleştiriciler ve polivinil alkol (PVA) ile beraber ekstrüzyon metodu ile işlenmesiyle uygulama alanlarının artırılmasıdır. Isıtma işlemi sonrası, daha az nem miktarı ve daha az su buharı geçirgenliğine sahip, ayrıca daha yüksek çekme mukavemeti gösteren ekstrüde şeritler elde edilmiştir; fakat ısıtma işleminin ksilan şeritlerin su çözünürlüğüne önemli bir etkisi görülmemiştir. Asetilasyon çalışmaları, alkali özütleme işlemi sırasında oluşan ve genelde uzaklaştırılan potasyum asetat tuzu (KAc) varlığında yapılmıştır. KAc içeren ksilanların asetilasyonu sonucunda ksilanların su çözünürlükleri, nem miktarları ve su buharı geçirgenlikleri önemli bir şekilde azalmış, mekanik özellikleri ve ısıtma kararlılıkları ise belirgin bir şekilde artmıştır. Bu çalışmalar sonucu, KAc varlığında asetilasyon reaksiyonunun, piridin

gibi toksik katalizörler ya da maliyetli tuz ayrıştırma işlemleri olmadan, etkili bir yöntem olarak kullanılabilceđi gösterilmiştir. Koşullandırma vasıtasıyla ekstrüzyona alternatif olarak, ksilanların sorbitol ve gliserol varlığında ekstrüzyonu da çalışılmıştır. İki plastikleştiricinin de ksilanları ekstrüde edilebilir hale getirdiđi gözlemlenmiştir. KAc'nin etkisine benzer şekilde, sorbitol ve gliserol varlığında gerçekleştirilen asetilasyon vasıtasıyla su çözünlüğünde önemli azalmalar görölmüş; fakat mekanik özelliklerde iyileşme sadece gliserol içeren şeritler için gözlemlenmiştir. Ksilanın endüstriyel uygulamalarına yönelik olarak ksilan ve PVA harmanlama çalışmaları da yürütölmüş, ısıl işlem ve asetilasyon çalışmaları ile birleştirilmiştir. Ksilan/PVA harmanlarının ekstrüde edilebilirliđi gösterilmiş, fakat ısıl işlem ve asetilasyonun ksilan/PVA şeritlerin kırılğan olmasına sebep olduđu gözlemlenmiştir.

Anahtar Kelimeler: Mısır koçanı ksilanı, ekstrüzyon, ısıl işlem, asetilasyon, plastikleştirici, harmanlama

To my beloved family,

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LIST OF SYMBOLS

e_b	Elongation at break	%
E	Elastic modulus	MPa
MC	Moisture content	%
M_v	Viscosity average molecular weight	g/mol
NWVTR	Normalized water vapor transfer rate	(g/day.m ²)/ μ m
UTS	Ultimate tensile strength	MPa
RH	Relative Humidity	%
WG	Weight gain	%
WVTR	Water vapor transfer rate	g/day.m ²

Abbreviations

A	Acetylated samples
KAc	Potassium acetate
S	KAc salt containing xylan
DS	Desalted xylan
Sorb	Sorbitol
Gly	Glycerol
PVA	Polyvinyl alcohol

CHAPTER 1

INTRODUCTION

Petroleum is the major source for many crucial products like fuels and chemicals including polymers, which makes it vital in every aspect of our life. With the growing human population, the demand for petroleum based raw materials and energy is rapidly increasing. By 2050, the energy demand is expected to increase more than 50% of the demand in the early 2000's (Ragauskas *et al.* 2006). When the finite petroleum sources are considered, a petroleum based economy is not a sustainable policy in long term. Besides the increasing demands and depletion of petroleum resources, the concerns on the CO₂ emissions, environmental pollution, national resource sufficiency and rural economy increased the demand for sustainable sources of energy, chemicals and materials (Zhang *et al.* 2008).

Biomass has attracted considerable attention as an abundant, carbon-neutral and renewable alternative to petroleum, not only in terms of fuel production but also its potential to present many kinds petroleum-based polymers. Concepts to utilize biomass as a feedstock for fuels and products are referred as the biorefinery (Figure 1.1) (Ragauskas *et al.* 2006). Majority of the biorefineries focus on the ethanol production from starchy biomass which are referred as first generation biorefineries. During the last decades, considerable attention was given to the secondary plant sources like by-products and wastes (wheat straw, sunflower husk, corn cobs, rice bran, olive stones, brewer's spent grain) due to competition between food and non-food applications, which paved the way to second generation biorefineries using lignocellulosic biomass (Fischer *et al.* 2006; Waltz, 2008). Lignocellulosic biomass, which refers to the plant biomass like hardwood, softwood, herbaceous plants, crop residues and agricultural wastes comprises 50% of the world biomass and is considered to be one of the most important renewable resource (Claassen *et al.* 1999).

A typical lignocellulosic biorefinery concept is based on the production of cellulosic ethanol from the isolated sugars and the generation of electricity and steam by burning the residues; however effective co-utilization of the constituents of lignocellulosic biomass; cellulose, hemicellulose and lignin, is vital from the point of a realistic lignocellulose biorefinery (Zhang, 2008). As in the case of petroleum refineries, biorefineries should also produce multiple products to distribute the risk and to strengthen the economy of the biorefinery (Kamm *et al.* 2004). In many lignocellulosic refining processes, hemicelluloses are burnt or degraded to be used as raw materials. Methods for isolation of high molecular mass hemicelluloses have been developed and researchers are aiming to find potential uses for it. In that sense, current research activities on hemicelluloses focus on their utilization close to their native form as biopolymers which might partially substitute petroleum based polymers.

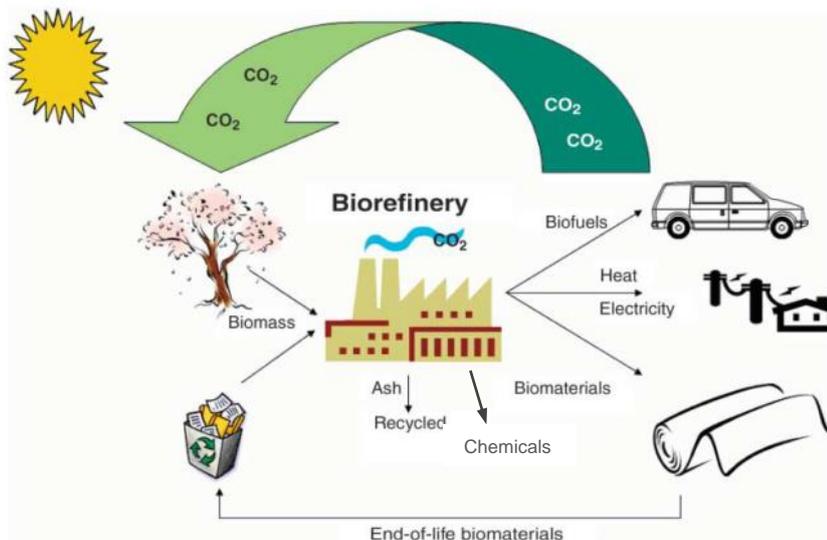


Figure 1.1 An integrated biorefinery approach for sustainable fuels and materials (Ragauskas *et al.* 2006)

The global consumption of polymers was around 160 million tonnes in 2003 (which is expected to be more than 300 million tons in 2017), 40 million tonnes of which

was consumed in the form of films (Pardos, 2004; Plastics Europe, 2015). Films are generally defined as self-supporting thin materials that can be folded without cracking and packaging industry is the main end-user of polymer films with its 40% share in all other applications (Plackett, 2011). In line with the modern lifestyle, food packaging comprises more than 60% of the packaging industry which is based on the petroleum based polymers (Plackett, 2011). Biopolymers arise as an alternative to petroleum based polymers by the utilization of renewable resources as sustainable raw materials. Hemicelluloses received a great interest due to their film forming ability and superior barrier properties against oxygen and aroma, making them a sustainable alternative to petroleum-based polymers for the food packaging industry. The production of hemicellulose based films can also be integrated to multi-product biorefineries. More efforts should be made to disclose potential of hemicellulose in packaging industry by addressing their processability and functional limitations.

Moisture tolerance of hemicelluloses is known to be a problematic issue due to their hydrophilic nature. This hydrophilicity makes hemicellulose films sensitive to water which affects their functionality negatively. Low water vapor permeability is mostly required for the packaging applications but due to the hydrophilicity of the native films, water vapor permeability values are usually high. Besides, mechanical properties, oxygen barrier properties and the integrity of the materials are also deteriorated by high water vapor uptake and water solubility (Peresin *et al.* 2012). Characteristics of these hydrophilic materials can be modified by composite approach, blending, surface modifications or bulk modifications. Generally, enhancements through the composite approaches are insignificant compared to the chemical modifications. Materials with chemical surface modifications may lose their property with time because grafted groups are susceptible to hydrolysis, where bulk modifications ensure better moisture tolerance. Although studies on hemicellulose modifications are fairly few when compared to cellulose and starch, analogous modifications are applicable to each (Plackett, 2011).

Besides their hydrophilic nature, commonly adopted solvent casting technique for the production of hemicellulose films arises as another obstacle through their commercialization. “Although solvent casting is the dominant method used in the literature for the production of hemicellulose films, melt processing by extrusion is one of the most important processing methods for other types of biopolymers, such as polylactic acid, which play a vital role in their commercialization (Lim *et al.* 2008). Alternative processing techniques for the utilization of hemicelluloses should also be studied to make hemicellulose based materials competitive with both synthetic and natural biopolymers. The extrusion of sugar beet pulp, which consists of hemicellulose, cellulose and pectin in equal amounts, has been achieved (Rouilly *et al.* 2006) and recently, extrusion processing of xylan-based hemicelluloses emerged as a promising technique paving the way to their potential industrial applications (Bahcegul *et al.* 2012)” (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry).

The major aim of this study was to decrease the moisture uptake and the water solubility of xylan-based hemicelluloses (xylans) in order to refer their utilization in packaging applications. Heat treatment and acetylation methods were utilized to improve the aforementioned water solubility and moisture sensitivity problems of xylans since both treatment methods were widely utilized for cellulose or related products but not adequately exploited for xylans. Acetylation of xylans was carried out in the presence of potassium acetate salt that is inherently produced during the alkaline extraction of xylans to find a facile method for acetylation by avoiding the use of toxic catalysts and costly salt removal steps. Within this scope, their extrusion processing in the presence of plasticizers and blends were also studied in order to show the possibilities to facilitate their potential industrial uptake. Adhering to this main framework, this study addressed;

- i) the heat treatment of xylan strips at different temperatures,
- ii) acetylation of xylans and extruded xylan strips in the presence of potassium acetate at different reaction conditions for improved mechanical and water solubility properties,

- iii) extrusion processing of xylans in the presence of sorbitol and glycerol at different concentrations and extrusion temperatures,
- iv) acetylation of plasticized xylan strips at different reaction conditions for improved mechanical and water solubility properties,
- v) xylan/polyvinyl alcohol blends and their heat treatment and acetylation

and the characterizations in terms of moisture uptake, water solubility, mechanical, chemical, thermal, morphological and barrier properties.

CHAPTER 2

LITERATURE SURVEY

2.1 Lignocellulosic Biomass

Biomass refers to the “biological materials derived from living or recently living organisms”, covering a broad range of potential renewable sources from animal wastes to forestry residues. Nearly 50% of the world biomass is composed of lignocellulosics, hence lignocellulosic biomass is considered to be one of the most important renewable resource (Claassen *et al.* 1999). Lignocellulosic biomass generally refers to a plant biomass like crop residues (corn cob, corn stover, wheat straw, cane bagasse, cotton stalk etc.), softwood (spruce, pine, etc.), hardwood (aspen, poplar, etc.) and herbaceous plants (switchgrass, reed canary grass, etc.). Among them, corn cobs are considered to be one of the most important sources of lignocellulosic biomass. Being one of the most important agricultural countries, the largest planted area in United States belongs to corn fields (USDA, NASS, 2015). Corn is also among the major crops that are being planted in Turkey with a production around 6 million tons/year, nearly half of which is considered as a waste (Celebioglu *et al.* 2012; TUIK, 2014).

Lignocellulosic biomass has a complex structure consisting of polysaccharides, phenolic polymers, proteins, volatile organic compounds and inorganics with three major constituents; cellulose, hemicellulose and lignin. Celluloses are bundled through hydrogen bonding to form cellulose fibrils. Hemicelluloses are complex, branched and heterogeneous polymeric networks, based mainly on xylose, arabinose, mannose and galactose and it has a lower molecular weight than cellulose. Lignin is a structurally complex amorphous polymer which is made up of different phenolic compounds and holds cellulose and hemicelluloses fibers together to support the plant.

A typical representation of the structure formed by these three major elements can be seen in Figure 2.1.

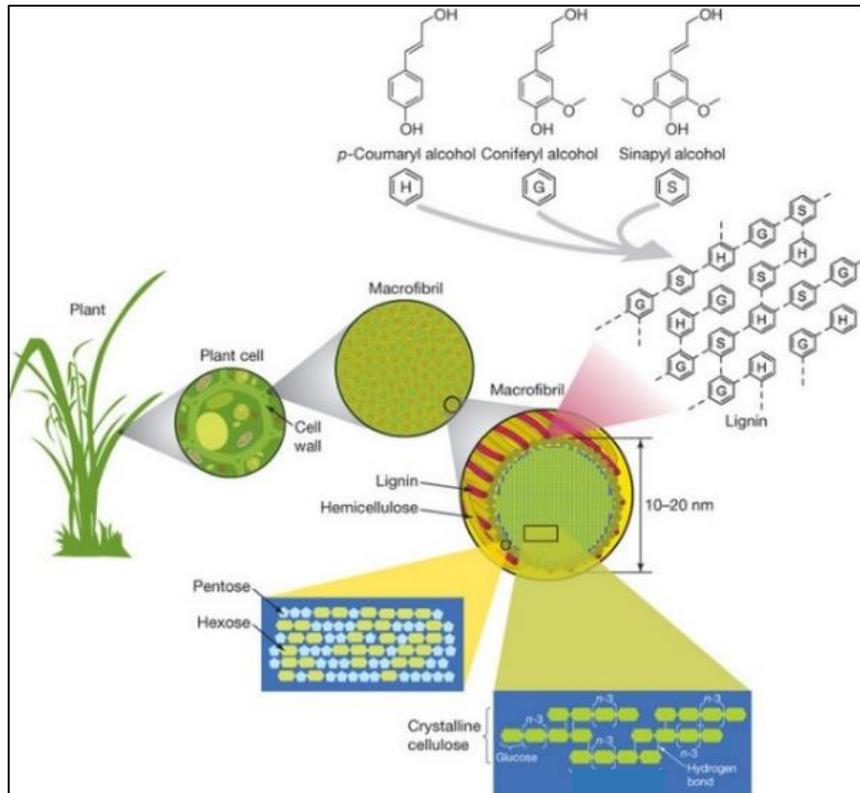


Figure 2.1 Representation of cellulose, hemicellulose and lignin in plant cell-wall structure (Rubin, 2008).

The relative compositions of cellulose, hemicelluloses and lignin in lignocellulosic structure depend on the plant species, site of harvesting, age and season; however the distribution of them can roughly be generalized to be 30-50% cellulose, 20-40% hemicellulose and 20-35% lignin (Sun *et al.* 2011). The composition of various lignocellulosic feed stocks in terms of cellulose, hemicellulose and lignin are given in Table 2.1.

Table 2.1 Cellulose, hemicellulose, and lignin contents of the common lignocellulosic feed stocks (Kumar *et al.* 2009).

Lignocellulosic Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40-55	25-40	18-25
Softwood stems	45-50	25-35	25-35
Nut shells	25-30	25-30	30-40
Corn cobs	35-45	35-40	6-15
Grasses	25-40	35-50	10-30
Wheat straw	30	50	15

2.1.1 Cellulose

Cellulose is the principal component of the lignocellulosic biomass consisting of linear $\beta(1\rightarrow4)$ linked glucose units with a degree of polymerization between 300-15000 residues (Ragauskas *et al.* 2006). Hydroxyl groups of glucose molecules form hydrogen bonds with oxygen molecules on the same or neighboring chains forming organized networks (Figure 2.2). These hydrogen bonds are mainly responsible for their poor solubility in water and in many other solvents and the recalcitrance of cellulose is considered as one of the most important challenges towards the pretreatment of biomass.

Cellulose can be both sub-crystalline and crystalline, where crystalline structures are responsible for the resistance against microbial and enzymatic attack. Depending on the source and the pretreatment method, cellulose has a degree of crystallinity between 40% and 60%. Celluloses can be present in the form of seven different polymorphs (I_α , I_β , II, III₁, III₁₁, IV₁, IV₁₁) that can be converted to each other with pretreatment methods. I_α and I_β correspond to natural crystalline forms of cellulose with triclinic and monoclinic unit cells, respectively. These two forms can be found

together but their proportions depend on the source of cellulose; I_{β} being dominant for higher plants (Yamamoto *et al.* 1994). Cellulose I can be transformed to cellulose II by regeneration, where rayon fibers and cellophane films are among the commercial applications of regenerated cellulose. Cellulose III can be obtained by harsh fragmentation of the Cellulose I or II crystal structure. Cellulose IV can be transformed from Cellulose III by thermal treatment methods (Aspinall, 1983).

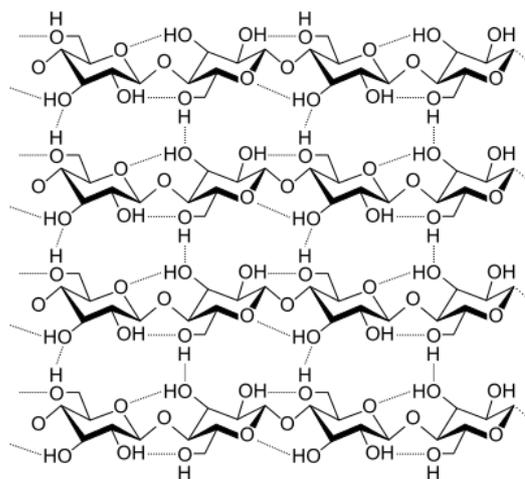


Figure 2.2 Chemical structure of cellulose with hydrogen bonds between them (Cabiac *et al.* 2011).

Reactivity of cellulose is strongly related with the morphology of cellulose since the hydroxyl groups of the amorphous regions are more accessible than those in the crystalline domains (Krassig, 1993). The crucial parameters that have an effect on the accessibility of cellulose are the pore dimension, surface area and crystallinity. Several methods are being utilized to increase the reactivity and accessibility of cellulose by swelling and de-crystallization. Interfibril bonds can be disrupted by mechanical treatments which are usually used in paper and pulp industry (Lejeune and Deprez, 2010). Chemical methods break the hydrogen bonds by the use of different solvents to have a less ordered structure. Enzymatic treatment methods attract most of the attention due to being advantageous in providing mild treatment conditions, high specificity and continuous processing. Recently, ionic liquid

pretreatment methods have emerged as a promising environmental friendly method, which is capable of dissolving cellulose in an efficient way.

Cellulose is the main raw material in paper and pulp industry and textiles. Many derivatives of cellulose are also being used utilized for pharmaceuticals applications and as adhesives. Recent applications of cellulose covers their utilization as a reinforcing element in composite materials and also as an environmental friendly and sustainable resource for the production of cellulosic ethanol with the potential to replace the depleting fossil fuels. Cellulosic ethanol is produced by the conversion of cellulose to glucose mainly via enzymatic hydrolysis and the fermentation of the produced glucose. Glucose can also be used for the production of various chemicals. Being a non-food feedstock, utilization of cellulose is important in terms of the production of sustainable products.

2.1.2 Hemicellulose

Constituting nearly one third of the plant cell wall, hemicellulose is the second most abundant type of polysaccharide in nature. Hemicellulose is a complex, branched and heterogeneous polymeric network, with a lower molecular weight than cellulose. Hemicelluloses are not the energy reserve for the plant but act as a linkage between cellulose and lignin (Popa, 1996). Unlike cellulose, hemicellulose has an amorphous structure with diversified degree of branching and molecular weight ranges (Table 2.2).

Table 2.2 Differences between cellulose and hemicellulose in lignocellulose structure

	Cellulose	Hemicellulose
Monomer	Glucose	Mixed sugars
Polymer Chain Length	Long	Short
Polymer Topology	Linear	Branched
Side groups	-	On C ₂ , C ₃ , C ₆
Crystallinity	Crystalline+Amorphous	Amorphous
Water solubility	Low	High

Hexoses and pentoses are the monomeric units of hemicelluloses, where their compositions and different pendant groups increase the complexity (Figure 2.3).

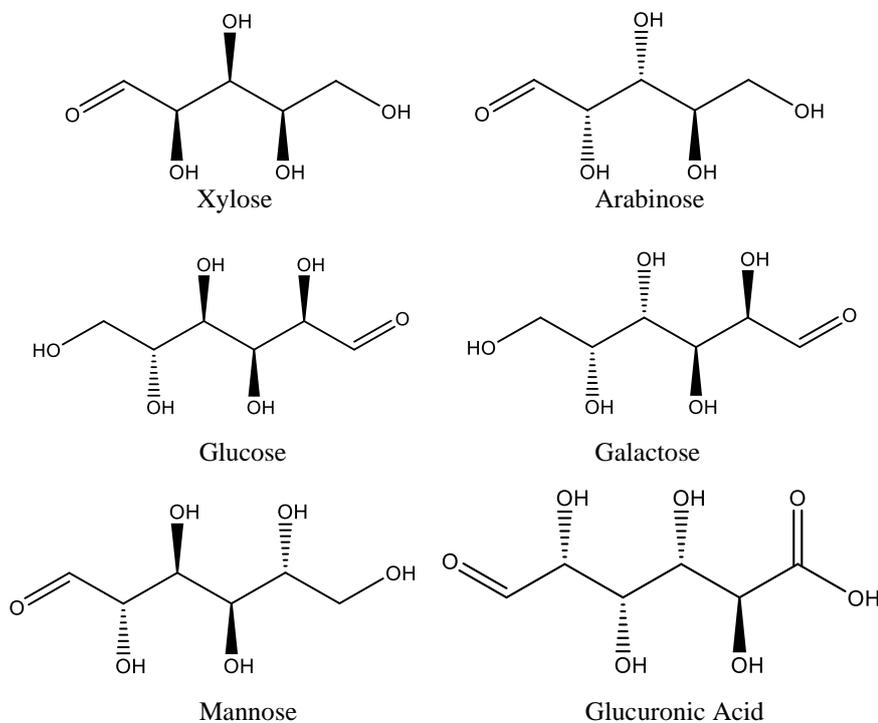


Figure 2.3 The main monomeric units of hemicellulose

Based on the macromolecular backbone, hemicelluloses are divided into four main groups; xylans, mannans, β -glucans with mixed linkages and xyloglucans (Figure 2.4). Xylans are the most abundant group of hemicelluloses in nature and the main hemicellulosic component in hardwoods and herbaceous plants. They are characterized by a xylopyranosyl backbone with (1 \rightarrow 4) β -linkages with typical side chains of sugar units and acetyl groups in the C-2 and/or C-3 positions. Homoxylans are linear hemicelluloses of xylopyranosyl residues with (1 \rightarrow 4) β -linkages and (1 \rightarrow 3) β -linkages or (1 \rightarrow 4) and (1 \rightarrow 3) mixed β -linkages. Substituted xylans such as arabinoxylans, glucuronoxylans and arabinoglucuronoxylans are known as heteroxylans (Figure 2.5) and they represent higher plant hemicelluloses since the occurrence of homoxylans are extremely rare in higher plants (Aspinall, 1983).

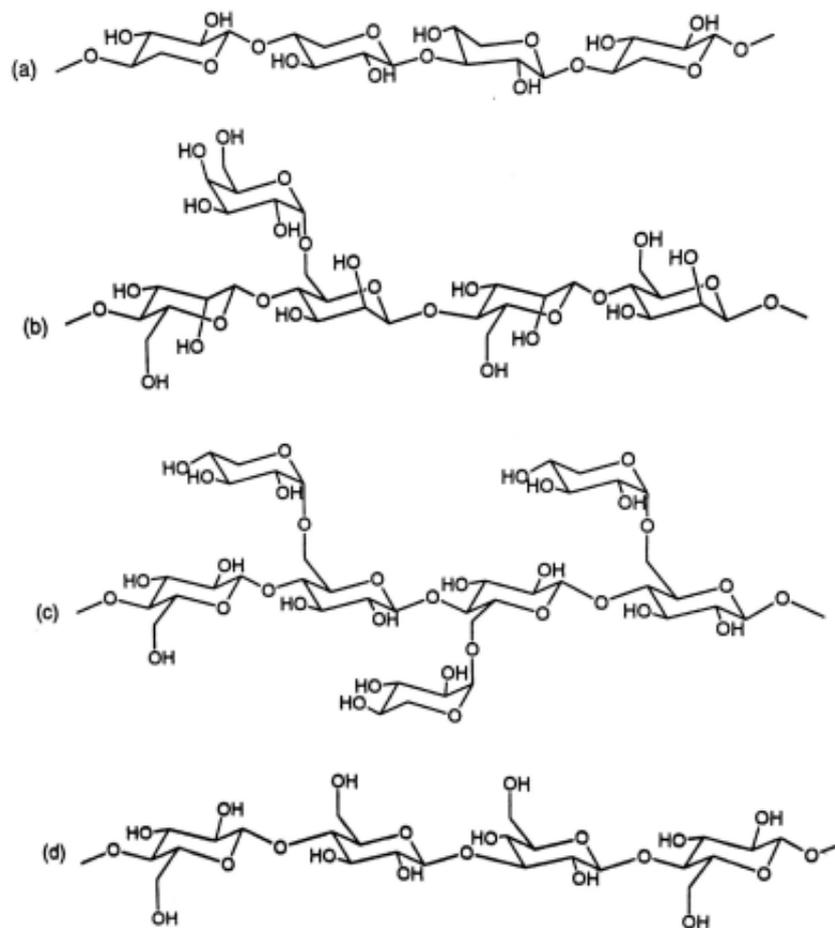


Figure 2.4 Representative structure of homoxylan (a), galactomannan (b), xylo-D-glucan (c), mixed (1→3, 1→4 linkage) β-D glucan (Plackett, 2011).

Glucuronoxylans, having a single α-D-glucuronic acid side chain, are the main component of secondary cell walls of the woody plants. Arabinoglucuronoxylans have one more additional side chain, α-L-arabinofuranosyl. They can be extracted from various wheat species, sisal and corn cobs by alkaline solutions after the delignification step (Ebringerova and Thomas, 2005). A study on the structure of corn cob xylans revealed the occurrence of a water insoluble part that is nearly unsubstituted and a water soluble part with more than 15% of the backbone substituted. Uronic acid content of the corn cob arabinoglucuronoxylans was determined as 4-9% (Ebringerova *et al.* 1992). Arabinoxylans are the main hemicellulosic components of the starchy plants. They are mainly extracted by

alkaline solutions, where they can also be extracted by water depending on their accessibility on the plant tissue. The relative ratio of arabinose to xylose of the arabinoxylans affect their solubility properties. Water soluble arabinoxylans have arabinose:xylose ratio around 1:1-2, where the ratio is around 1:3-5 for water insoluble arabinoxylans (Fischer *et al.* 2006).

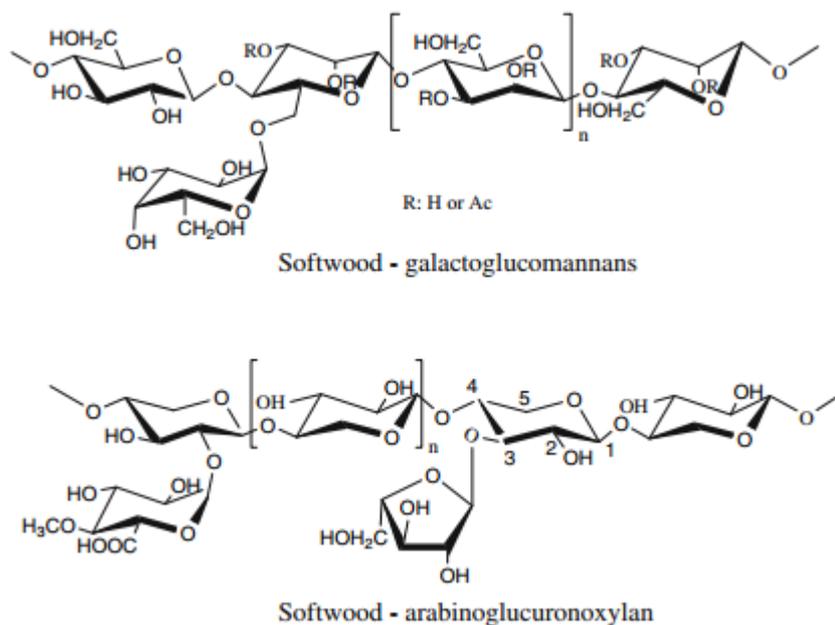


Figure 2.5 Representative structure of softwood and hardwood hemicelluloses (Pu *et al.* 2011).

Mannans, generally known as softwood hemicelluloses, can occur in the form of galactomannans and glucomannans. Galactomannans have D-mannopyranosyl backbone with $(1\rightarrow4)$ β -linkages with branches of D-galactopyranosyl, where glucomannans have β -D-glucopyranosyl units (Ebringerova and Thomas, 2005). Xyloglucans primarily occur in hardwood and grasses and they are the primary cell wall component of all higher plants. The strong interaction of xyloglucans with cellulose negatively affects their extraction. They vary according to their side groups substituted on the $(1\rightarrow4)$ β -linked D-glycopyranose backbone (Plackett, 2011).

Mixed linkage β -glucans are linear hemicelluloses resembling cellulose, but with (1 \rightarrow 3) and (1 \rightarrow 4) substitutions on the β -glucan backbone.

Hemicellulose types and their monomer compositions differ from one plant species to other and also from one part to the other part within the same plant (branches, fibers, roots). Monomer compositions for a variety of hemicellulose sources can be found in Table 2.3.

Table 2.3 Monosaccharide compositions of hemicelluloses from various lignocellulosic sources (Plackett, 2011).

Plant Source	Xylose (%)	Arabinose (%)	Glucose (%)	Galactose (%)	Mannose (%)
Spruce mannan	-	-	15	1	62
Spruce arabinogalactan	-	11	8	35	30
Larch arabinogalactan	-	16	1	79	1
Pine arabinogalactan	-	14	3	69	7
Birch xylan	92.6	1.2	2	-	-
Birch mannan	1	2	28	1	68
Beech xylan	91.6	1.2	2	-	-
Aspen xylan	95	-	0.7	0.6	-
Aspen mannan	2	1	41	1	55
Sugarcane bagasse	55	13	28	2.6	1.5
Wheat straw xylan	56.9	17.1	12.1	5.6	-
Rye straw xylan	78.3	12.4	5.9	2.5	0.4
Passion fruit rind	29	1	42	15	9
Date palm leaf	75	6.3	0.3	1	-
Flax xylan	83.2	1	2.8	3.4	0.6
Flax mannan	7.4	3.9	42.2	8.8	37.8
Corn cob xylan	66.4	19.5	-	5.4	-

As most of the plant polysaccharides, molecular weight determination of hemicelluloses is tricky due to their different solubility properties which depends on the type, degree of substitution, distribution and linkages with the surrounding network. Measurement methods also have a strong influence on the estimated molecular weight values which are usually reported by referring a very wide range.

Molecular weight of the cereal arabinoxylans and arabinoglucuronoxylans was estimated to be between 50.000 and 400.000 g/mol, where softwood and hardwood hemicelluloses have lower molecular mass (Fischer and Heinze, 2006); however molecular weight values as high as millions were also reported which might be related the chain aggregation (Ebringerova and Thomas, 2005). The thermal properties of hemicelluloses also change according to their type and interactions with the lignin network and they do not exhibit distinct thermal transitions. Arabinoglucuronoxylans extracted from wheat straw exhibited an onset of degradation around 200°C, where lignin rich fractions exhibited the first maximum around 280°C.

Hemicelluloses have very diverse industrial applications depending on their macromolecular structure after isolation from the lignocellulosic biomass (Figure 2.6).

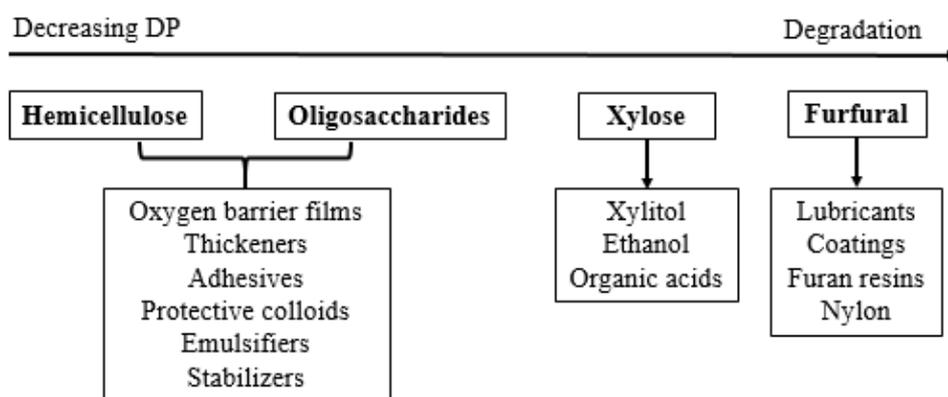


Figure 2.6 Common application areas of hemicelluloses according to their degree of polymerization (DP) (Zhang, 2008).

Hemicelluloses in polymeric form are utilized as thickeners, adhesives and recently as biodegradable oxygen barrier films (Zhang, 2008). Monomeric hemicellulose sugars can be fermented to produce organic acids and ethanol. They can also be used to produce chemicals like furfural, which is mainly used for coatings, lubricants and nylon production (Kamm *et al.* 2006).

Previous research activities on the application of hemicelluloses have focused on the production of sugars, chemicals and fuels. Conversion of hemicelluloses into high value added products like ethanol, hydrogen, succinic acid and other sugar based polyesters involves multiple steps of pretreatment, enzymatic hydrolysis and fermentation of monomeric hemicellulose sugars (Peng *et al.* 2012). They can also be used to produce chemicals like furfural, which is mainly used for coatings, lubricants and nylon production (Kamm *et al.* 2006). Current research activities focus on the utilization of hemicelluloses close to their native form as biopolymers due to their structural variety and diversity without the need of hydrolysis and fermentation steps. In particular, utilization of hemicelluloses for the production of food packaging has received special interest due to their film forming ability, low oxygen permeability and due to the ecological problems of the petroleum based packaging materials.

2.1.3 Lignin

Lignin is responsible for strengthening the plant cell wall by interacting with cellulose and hemicellulose binding the fibers together. It also plays role in the transportation of nutrients and water; and act as a defense against degradation. Lignin is formed by oxidative coupling of sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol and it is the only cell-wall polymer that does not contain carbohydrate monomers (Figure 2.7). Lignin is soluble in alcohols, ketones and ethers but insoluble in water (Sun *et al.* 2011). 90% of softwood lignin comprises coniferyl alcohol, where hardwood lignin is made up of 50% coniferyl alcohol and 50% sinapyl alcohol. Corn cob lignin is rich in coniferyl alcohol and sinapyl alcohol (Huang *et al.* 2012). Lignin structure contains various methoxyl or benzyl functional groups that defines the conformation of lignin with ether or carbon-carbon bonds between subunits with a very small percentage of unsubstituted hydroxyl groups (Sjöström, 1993). A representation of this aromatic molecule can be seen in Figure 2.8. Although many studies are going on, the native structure of lignin is still unclear (Sannigrahi *et al.* 2010). Lignin also forms covalent bonds with cell wall polysaccharides, which are called lignin-

carbohydrate complexes (LCC), rendering full yield isolation of hemicelluloses difficult. The issue can be very important when pulping is considered due to the chemical interaction between lignin and cellulose.

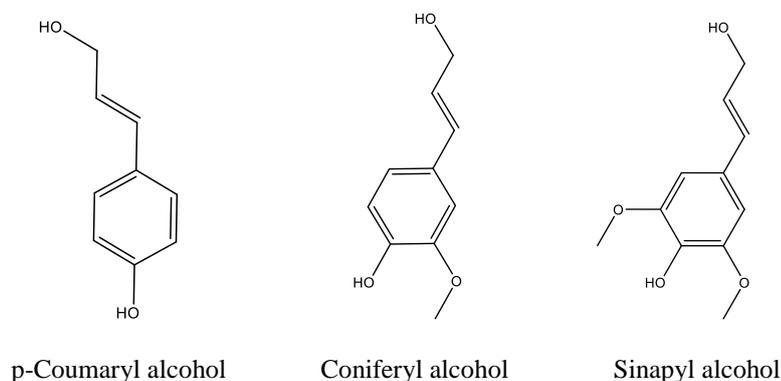


Figure 2.7 Structure of the phenolic monomers of the lignin.

Lignin is used as a precursor for many chemicals like dimethyl sulfoxide (DMSO) and ethylene and also used for many applications in polymer industry such as a replacement for epoxy and phenolic resins (Lora and Glasser, 2002) (Figure 2.9). Besides, lignin is also being used for synthetic diesel production through gasification (Zhang, 2008). Technical lignins are classified into sulfur containing (kraft lignin, lignosulfonate lignin) and sulfur-free (alkali lignin and organosolv lignin), where the production of high quality sulfur-free lignins are low (Zhang *et al.* 2008). The majority of kraft lignin is used for fuel and the alkali lignin is used as phenolic powder resins, epoxy, polyurethane and polyisocyanurate foams.

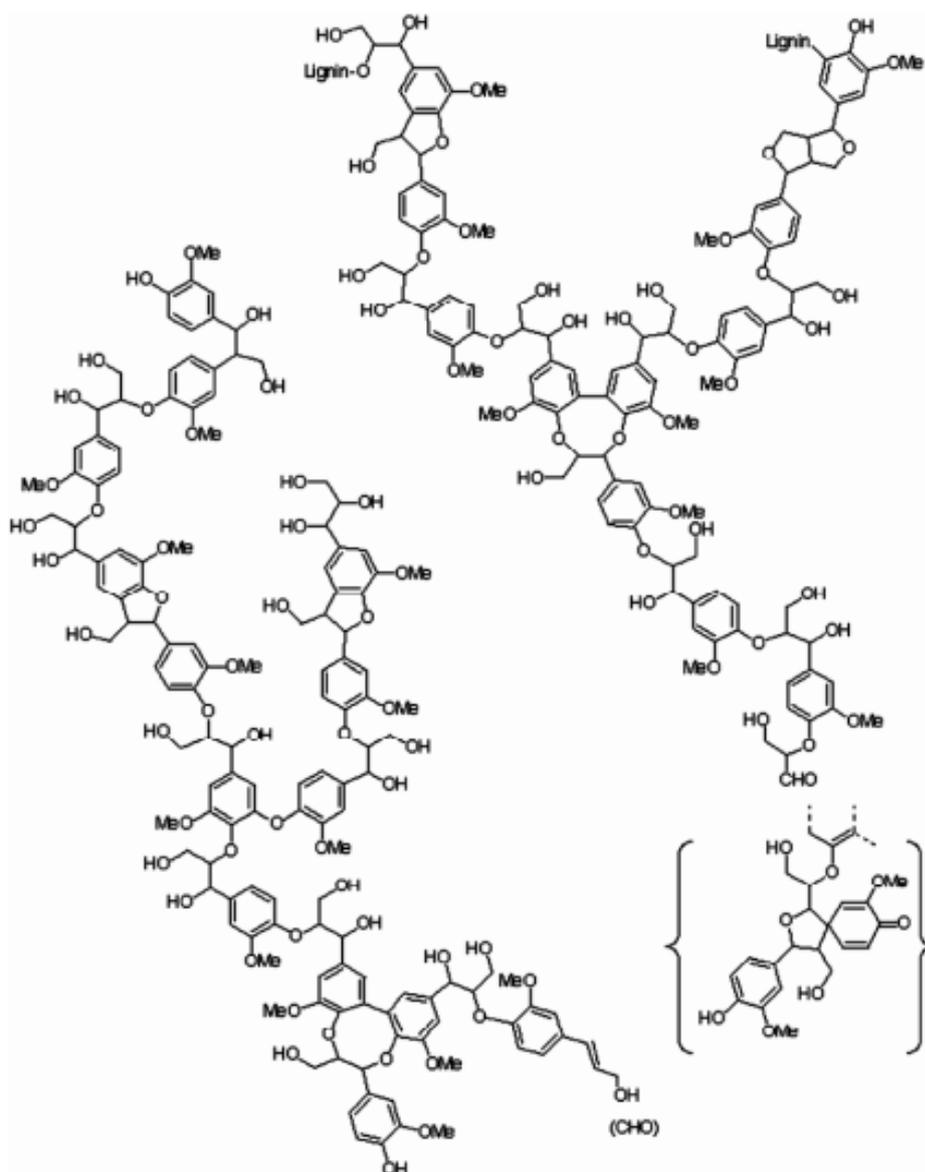


Figure 2.8 Representative structure of the softwood lignin (Adler, 1977).

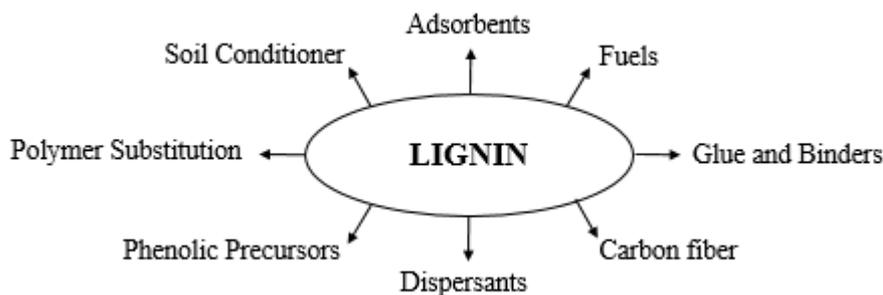


Figure 2.9 Common application areas of lignin (Zhang *et al.* 2008)

2.2 Isolation of Hemicelluloses

Plant cell walls have been evolved to serve as a barrier providing resistance to external effects like microbial attack and mechanical forces, thus pretreatments to overcome the recalcitrance of the plant cell walls are essential to utilize the lignocellulosic biomass. Recalcitrance of the biomass is handled by destructing the three dimensional structure of the biomass and fractionating it into lignin, hemicellulose and cellulose. Evidently, there is not any general pretreatment method to overcome this recalcitrance due to the structural diversity of lignocellulosic biomass. In addition to this, pretreatment methods have an important impact on the physical and chemical properties of the pretreated biomass, thus methods can also vary according to the desired end product or products (Kubicek, 2013). Number of methods outlined below can be used to utilize different fractions of lignocellulosic biomass (Kumar *et al.* 2009).

- Physical (mechanical, irradiation, ultrasonication)
- Physicochemical (steam explosion, CO₂ explosion, wet oxidation),
- Chemical (alkali, acid, organosolv, ammonia explosion)

Since hemicelluloses are bound to both cellulose and lignin, multi-step isolation procedures are necessary to separate them from the lignocellulosic biomass. Prior to hemicellulose isolation, lignocellulosic biomass can be delignified by acidic treatments, but these steps bear the risk of hemicellulose degradation. Delignification is not considered as compulsory for hemicellulose isolation; however it effects the efficiency of the isolation. Hemicelluloses in annual plants can be extracted easier than wood due to the lower amount of lignin present in their structure (Ebringerova and Hromadkova, 1999).

Physical treatment methods do not give satisfactory results when used alone and are generally used in combination with the other techniques to improve the efficiency of the isolation. Physical treatments like chipping, milling, or grinding increase surface area of the biomass allowing easy liquid penetration and the final particle size depend on the method used (Plackett, 2011). Milling and grinding results in particle sizes between 0.2-2 mm, where chipping results in bigger particle sizes (Sun *et al.* 2002). Ultrasonication can be combined with alkaline extraction methods to increase the isolated hemicellulose yield. Positive effect of ultrasonication on the extractability of corn bran hemicelluloses was shown by Ebringerova and Hromadkova (2002). Higher yields were achieved by sonication assisted NaOH extraction with similar structural and molecular properties of the alkaline extracted corn bran hemicelluloses. Power and duration of the ultrasonication should be adjusted to avoid excessive degradation of hemicelluloses. Microwave irradiation, which can also be complementary used with other techniques, has many advantages in terms of the duration of the isolation process and the amounts of chemicals used (Peng *et al.* 2012).

Steam explosion is a commonly used physicochemical treatment technique which involves the utilization of high pressure steam to fractionate lignocellulosic biomass upon a sudden reduction of the pressure causing an explosive degradation (Peng *et al.* 2012). Steam explosion has particularly received interest to obtain cellulose by effective separation of hemicelluloses and then lignin through extractions with alcohol and water and is applicable to a various biomass resources like wood and

agricultural residues. The temperature and pressure of the process changes between 160 °C and 260°C, and 0.7 MPa and 5 MPa, respectively. Steam explosion has a drawback of generating toxic derivatives which might be problematic if a successive enzymatic step is being utilized. CO₂ explosion technique, which involves the utilization of supercritical CO₂, is considered to be more advantageous than steam explosion due to the lower operation temperatures and less release of toxic compounds compared to steam explosion (Srinivasan and Ju, 2010).

Chemical methods cover the extraction of hemicelluloses via the treatments with acidic, alkali or organic solvents. Dilute or concentrated acid hydrolysis by H₂SO₄, HCl, HNO₃ or H₃PO₄ is being used for biomass treatment; but the method is not commonly adopted due to the corrosive nature of the acids and the excessive degradation of the products. Treatment with organic solvents are promising for the isolation of hemicelluloses which yields mainly xylan type hemicellulosic fractions (Shatalov and Pereira, 2002). Dimethyl sulfoxide (DMSO) is the most commonly used solvent for the extraction of hemicelluloses and DMSO or DMSO/water solutions was shown to be very effective solvents for the extraction of heteroxylans (Ebringerova and Heinze, 2000).

A range of extraction methods have been proposed for hemicellulose isolation; however alkaline extraction procedures are often preferred to isolate high molecular mass hemicelluloses (Benko *et al.* 2007). Alkali pretreatment is said to be the most promising process to break the ester bonds between lignin, hemicellulose and cellulose without fragmenting hemicelluloses (Gaspar *et al.* 2007). Alkaline hydrolysis causes the saponification of intermolecular ester bonds crosslinking hemicelluloses and lignin and breaks the structural linkages between them (Sun *et al.* 2002). It is also known that acetyl groups of hemicelluloses, which are present in higher plants at ratio between 2% and 4%, are cleaved during alkaline extraction (Aspinall, 1983).

Parameters like alkali type and concentration, temperature, time and the type of biomass have a significant effect on the yield of hemicelluloses. Aqueous solutions of calcium hydroxide, barium hydroxide, sodium hydroxide and potassium hydroxide

are being utilized, where sodium and potassium hydroxides are being the frequently used ones (Lawther *et al.* 1996). Addition of boric compounds at around 2 to 5% can be used to reduce the degradation of hemicelluloses. The effect of raw materials (corn peels, corn stalks and sugar beet pulp wastes), particle size and alkali extraction methods on hemicelluloses yields were investigated by Celebioglu *et al.* (2012). The hemicellulose yield was highest for corn residues (1.1 mm) compared to the sugar beet pulp with direct alkaline extraction method. Direct alkaline extraction method also gave higher purity levels of hemicellulose than the combined alkaline and acidic extraction methods. The optimum extraction conditions were found as 15% NaOH concentration at 40°C for 24 h. The results revealed that alkaline concentrations around 15% and mild temperatures can give high hemicellulose yields and purity. Alkaline pretreatment approaches for the co-production of glucose and hemicellulose was studied by Bahcegul *et al.* (2012). Cotton stalks were treated with 10% (w/v) KOH solution at 25°C, 60°C and 90°C for 3 hours. Alkaline insoluble cellulosic fraction was recovered by filtration and alkali soluble hemicellulosic fraction was recovered by precipitation. It was found that the hemicellulosic film forming process was much more affected by the changes in the pretreatment temperature compared to the glucose yields from cellulose. It was also shown that the higher pretreatment temperatures were detrimental to the properties of hemicellulose based films.

Although isolation of hemicelluloses can be achieved by several methods, isolated hemicelluloses are in the form of a mixture of different hemicellulosic polysaccharides. Several approaches, such as column chromatography, ammonium sulfate precipitation and ethanol precipitation, can be utilized if homogeneous hemicellulose fractions are needed. Recovery of hemicelluloses by neutralization with acetic acid and precipitation with ethanol is a commonly used fractionation procedure (Peng *et al.* 2012). A very early study by O'Dwyer (1926) classified hemicelluloses according to the fractionation steps during the extraction. Three types of hemicelluloses were outlined where hemicellulose A is the water insoluble part that is precipitated during the neutralization, hemicellulose B is precipitated by ethanol and hemicellulose C is the portion that cannot be isolated from the biomass.

As mentioned before, recalcitrance of lignocellulosic biomass can be overcome by several methods and development of efficient isolation and purification methods of hemicelluloses is crucial in terms of an integrated bio-refinery approach covering the production of chemicals and biopolymers together with bio-based fuels.

2.3 Hemicellulose Based Films

The use of synthetic polymers are ubiquitously increasing and it is predicted that 25% of the petroleum produced will be used to manufacture commodity polymers by the year 2100 (Plackett, 2011). Bio-based polymers arise as an alternative to petroleum-based polymers by the utilization of renewable bioresources as sustainable raw materials. Degradation of petroleum-based polymers in nature takes excessively long periods creating a huge environmental pollution, which can also be overcome by the utilization of bio-based polymers. Both research and industrial development of bio-based polymers covering a broad range of applications are essential for sustainability.

Food packaging industry is among the main industries dominated by petroleum-based synthetic polymers due to their easy processability, functional advantages like thermo-sealability, microwavability, optical properties and low cost (Lopez-Rubio *et al.* 2004). Many classes including polyolefins, polyesters and polyvinyl chloride have been used where polyolefins (polyethylene and polypropylene) are the most common petroleum-based polymers used in packaging industry. High-density polyethylene is used for bottles and grocery bags due to its stiffness and strength. Low-density polyethylene is used for film applications like frozen food and bread bags, due to their transparency, flexibility and moisture resistance (Marsh and Bugusu, 2007).

The essential role of food packaging material is to preserve food quality by the controlled mass transfer between the food and the atmosphere. Oxygen barrier properties of materials are important as the oxygen has a major role in degradation kinetics. Materials should serve as a barrier to aroma to preserve the taste and water vapor to preserve the texture (softness, crispiness). Mechanical properties are also

crucial for packaging applications since the physical integrity is essential to assure barrier properties. Ultimate tensile strength, elongation at break and elastic modulus are among the most widely used mechanical properties to evaluate the performance of the hemicellulose based films. “Ultimate tensile strength is the maximum tensile stress that a material can withstand before failure” and it is crucial to ensure the integrity of the packaging materials (Nielsen, 1974). Elongation at break value also determines the materials resistance to failure and denotes the percentage increase in length compared to the initial length before the material fails under tension. Elastic modulus is the ratio of stress to strain in the elastic region which indicates the stiffness of the packaging material (Nielsen, 1994).

Hemicellulose based films receive interest due to their barrier properties against oxygen and aroma, making them a sustainable alternative to petroleum-based polymers for the food packaging industry. A pilot-scale production of xylan was established by the company “Xylophane AB” with the aim of applying xylan based coatings on other packaging materials to enhance oxygen barrier properties. Research studies on hemicellulose based materials are increasing by focusing on different lignocellulosic sources, isolation and production techniques. Various lignocellulosic resources such as agricultural crops, wastes or wood have been utilized for hemicellulose based film production. Aspen wood (Gabrielii *et al.* 2000), oat spelts (Mikkonen *et al.* 2009), barley husks (Hoije *et al.* 2005), rye (Hoije *et al.* 2008), cotton stalks (Goksu *et al.* 2007), corn hull (Zhang, 2004) and corn cobs (Bahcegul, 2009; Egüés *et al.* 2014) have been utilized for hemicellulose based films. Xylans and mannans are widely used hemicellulose types for the oxygen barrier applications, where xylan is the dominating type. Tejinder (2003) prepared hemicellulose films from barley and oat β -glucans but they were less effective barriers than the xylan films.

2.3.1 Processing Methods

As stated in the previous sections, hemicelluloses recently received a great interest due to their potential to substitute petroleum-based packaging materials. From an

economical point of view, hemicelluloses should be processed by the same methods as the other conventional petroleum-based polymers for realistic scenarios. The dominant method in literature for hemicellulosic film production is the solvent casting method since there is no need for specific equipments for laboratory scale studies. Although it is a facile method for basic research, there are many handicaps at industrial scale applications.

From an industrial point of view, solvent casting method is a time consuming and energy intensive process, since it is based on the dissolution and evaporation steps (Embuscado and Huber, 2009). In solvent casting procedure, the polymer is dissolved in an appropriate solvent, casted as a thin layer on usually polycarbonate or teflon supports and dried. Drying parameters like temperature and duration affect the film structure and low temperature-long drying time enhance chain mobility to attain more crystalline structure (Rindlava *et al.* 1997). In industrial scale applications, solvents are removed through a continuous process by drum or tunnel dryers and the films are released by a blade (Müller *et al.* 2012).

Solution of hemicelluloses in water or in other solvents might be problematic due to the inherent complex structure of hemicelluloses. When large scale productions are considered, a stable solution with optimum solid content and viscosity might not be prepared causing non-homogeneous films (Siemann, 2005). Alternative to solvent-casting, extrusion method has recently come up as a potential processing method to produce hemicellulose based films. Extrusion is among the mostly used processing method for conventional polymers, which allows processing without the presence of solvents. During extrusion, polymers conveyed through a barrel in the form of a melt with the help of heat and shear. The melt material is passed through a die to obtain the extrudate. Extruders can be single-screw or twin-screw, with feeder, barrels and die as the main parts. There is a set of appropriate extruder type, screw diameter, length-to-diameter ratio and die according to the desired end products. The screw is the most important part of the extruder not only conveying the material to the die, but also effecting mixing and heat transfer to the polymer inside the barrel and the mixing efficiencies of the single and twin screw extruders differ substantially. In single screw

extruders, materials flow is induced by the screws and materials slip at the barrel walls, which might result in back flows (Harper, 1989). In twin screw extruders, the slip at the wall is prevented by the movement of screws. Counter-rotating screws are more efficient than the co-rotating screws in terms of preventing back flow. Twin-screw extruders are preferred for heat-sensitive materials with high capacity and enhanced mixing which makes them suitable for biodegradable polymer processing. Studies on extrusion of hemicelluloses are very few, but bear a huge potential for the scale-up of hemicellulose film production to industrial scale. In addition to this, extruded hemicellulose films were shown to have better mechanical properties than solvent-casted films (Bahcegul *et al.* 2012). The appearances of solvent casted (a) and extruded (b) hemicellulose films can be seen in Figure 2.10.



Figure 2.10 Hemicellulose based materials from agricultural wastes (a) Solvent casted hemicellulose films from cotton stalk (Bahcegul *et al.* 2012) (b) Extruded hemicellulose strips from corn cob (Akkus *et al.* 2014).

2.3.2 Plasticized Hemicellulose Based Films

Self-supported and flexible hemicellulose films are generally obtained by utilizing additives like plasticizers. Although the mechanism behind the plasticization is not fully known, the phenomenon is being explained by lubricity, gel and free volume theories. According to lubricity theory, internal resistance to deformation is reduced

by the presence of plasticizers facilitating the movement of macromolecules just like a lubricant (Barron, 1945) where the gel theory states that the weak bonds between the macromolecular chains are responsible for the rigidity and the plasticization effect is explained by the mechanistic theory of solvent action (Bruins, 1965). According to the theory, cross-linked gel structure is formed by secondary or van der Waals forces (not primary forces) and the flexibility increases as the distance between the cross-links increase. The free volume theory relates the movement of the polymer chains with the internal space, free volume. Theories are being overlapped to explain the plasticization mechanism, and a compatibility (stability within the polymer structure) –efficiency (the amount of plasticizer needed to achieve the desired property) concept is considered to be more reliable in determining plasticizer polymer interactions than the theories (Wilson, 1995). A plasticizer is said to be compatible with the polymer if the plasticizer contains structural groups which reversibly bind to the polymer and creates free volume together with the unattached molecules to allow flexibility. The compatibility of the plasticizer with the polymer also depends on the other factors like linearity, polarity, molecular weight and solubility parameters. Yet, there is not any universally accepted rules to exactly determine the performance of a potential plasticizer.

Plasticizers can be classified in two classes, external and internal plasticizers. Internal plasticizers are bulky structures that chemically interact with the polymer either by co-polymerization or reaction of the functional groups, whereas external plasticizers interact with the polymer chains by weak primary bonds. Although external plasticizers are susceptible to evaporation or migration due to the weak interactions; it is advantageous in obtaining various plasticizer-polymer combinations according to the needs (Vieira *et al.* 2011).

Effective conventional plasticizers are known to have sticky ends that bind them to the polymer and floppy ends to allow the movement, however conventional plasticizers used for synthetic polymers are not compatible with bio-based polymers and may lead to reduced performances due to phase separation. Polar molecules have much better plasticization effect on bio-based polymers than the amphiphilic ones

(Xu *et al.* 2012). Water is a commonly used plasticizer for polysaccharide and protein films and various plasticizers such as glycerol, low-molecular weight PEG, sorbitol, xylitol are generally used to facilitate molecular motion and decrease internal friction within the structure for flexible film production (Nielsen, 1974) (Figure 2.11).

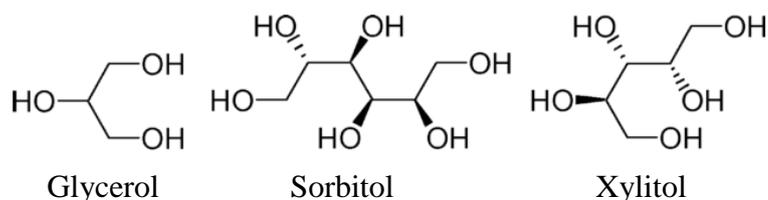


Figure 2.11 Commonly used plasticizers for the formation of intact and flexible hemicellulose films.

Water is the main solvent for many bio-based polymers and thus rather than being accumulated on the surface, it is absorbed into the bulk structure. Absorbed water molecular changes the physicochemical properties of the polymer by weakening the attracting forces between the chains and increasing the free volume. Water-hydrophilic polymer interaction lowers the glass transition temperature due to this plasticizing effect however the use of water alone might result in brittle materials in relation with the ambient relative humidity (Forssell *et al.* 1997; Szakonvi and Zenko, 2012). Polyols like glycerol and sorbitol are among the most widely used polysaccharide plasticizers as they resemble the structure of the hydrophilic biopolymers. They can easily penetrate to the structure and weaken the polymer-polymer interactions. Zhang *et al.* (2004) studied the mechanical properties and water vapor permeability of corn hull arabinoxylan films with respect to different plasticizer types. Glycerol, sorbitol and propylene glycol were used as plasticizers at different concentrations up to 20 wt%. Mechanical properties were almost independent of concentration when propylene glycol was used as a plasticizer. Propylene glycol containing films were brittle, however films containing glycerol and

sorbitol were much more flexible. All plasticized films showed lower water vapor permeability (WVP), where sorbitol plasticized films exhibit the lowest WVP values. Gröndahl *et al.* (2004) compared sorbitol and xylitol in terms of their plasticization effect for the production of aspen wood glucuronoxylan films and it was reported that the intact films could not be formed without the presence of plasticizers. Both plasticizers were added to film forming aqueous solutions at a concentration between 20% and 50%. In the range tested, sorbitol exhibited better performance than xylitol with higher elongation at break values, since xylitol had a tendency to crystallize at higher loadings. 35% sorbitol containing films were also tested for their oxygen barrier properties, which were found similar to that of a widely used ethylene vinyl alcohol food packaging films.

Mikkonen *et al.* (2009) examined the film forming properties of oat spelt arabinoxylan by the addition of external plasticizers. Preliminary experiments with xylitol, sorbitol and glycerol showed xylitol's adverse effects on mechanical and visual properties due to their migration/crystallization, so only sorbitol and glycerol were further compared. Self-supporting films could not be achieved without sorbitol or glycerol, where tensile strength decreased and elongation at break values increased with increasing plasticizer concentrations as expected. Glycerol plasticized films showed higher strength values at low concentrations, but when concentration of plasticizers increase to 40%, sorbitol plasticized films showed higher strength than glycerol plasticized films. Elongation at break values were similar for both plasticizers at all concentrations tested. WVP of films increased with increasing plasticizer concentration, where the effect was much more prominent in glycerol plasticized films. 40% glycerol containing films were most sensitive to changes with the highest water content. WVP of 40% sorbitol containing films was similar to 10% glycerol containing films for each relative humidity conditions tested. 40% sorbitol containing films also exhibited better oxygen barrier properties than glycerol containing films. Similarly, storage stability of sorbitol plasticized films were better than glycerol plasticizer films, indicating sorbitol as a better plasticizer for the formation of arabinoxylan films.

Besides the plasticizers, several additives have been used for the formation of continuous hemicellulose based films. Gabriellii *et al.* (2000) observed that chitosan addition to aspen wood hemicelluloses induces intact film formation at 10% ratio; however concentrations higher than 10% chitosan resulted in more brittle films than the pure hemicellulose films. Effect of lignin in film formation of cotton stalk xylan was shown by Goksu *et al.* (2007) where 1% lignin was found to be sufficient to achieve self-supporting continuous films. Bahcegul *et al.* (2014) observed the positive effect of potassium acetate salt, which is inherently produced during alkaline extraction, in obtaining smooth, continuous and tough hemicellulose films (Figure 2.12).

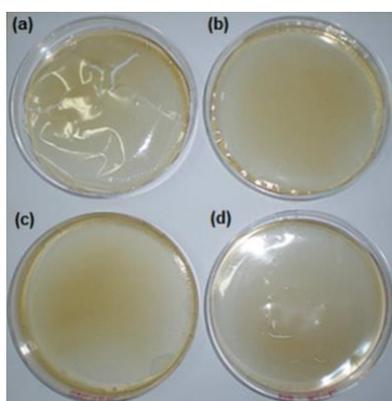


Figure 2.12 Appearance of (a) pure xylan film, (b) xylan film containing 10% commercial potassium acetate as an additive, (c) xylan films with inherently produced potassium acetate during the extraction, (d) xylan film with 10% sorbitol as an additive (Bahcegul *et al.* 2014).

Plasticizers also have a very significant impact on the processibility of hemicelluloses through extrusion. One of the pioneering studies was conducted by Rouilly *et al.* (2006) on melt viscosity measurements of sugar beet pulp, which consists of arabinoxylans, arabinans, pectins and cellulose microfibrils, with a single screw extruder. They investigated the influence of water on the glass transition temperature to understand the thermomechanical processing of biopolymers. Experiments were performed at 110°C, 120°C and 130°C at moisture contents of 20%, 25%, 30% and 35%. Low moisture content of sugar beet pulp necessitated higher die temperatures

to flow, where high moisture content caused sugar beet pulp to be too sticky preventing the feeding to the extruder. Optimum working conditions were obtained when the moisture content of sugar beet pulp was around 26%. Authors stated that the experiments could only be conducted at a limited temperature and moisture content due to the nature of the sugar beet pulp. They concluded that polysaccharides can undergo a plastic transition through a right combination of temperature, moisture content and pressure.

A follow-up study was conducted by Rouilly *et al.* (2009) on the extruded films from sugar beet pulp with plasticizers and cross-linkers. Film like strips were produced by a twin-screw extruder and the tensile properties were evaluated according to the plasticizer type (Figure 2.13). Sorbitol, adipic acid and fructose showed an anti-plasticizing effect for sugar beet pulp film strips where xylitol and glycerol was determined to be the best plasticizer tested. Water sensitivity of plasticized film strips were circumvented by utilization of glycidyl-methacrylate as a cross-linker.



Figure 2.13 Glycerol plasticized flexible and continuous extruded films from sugar beet pulp (Rouilly *et al.* 2009)

Bahcegul *et al.* (2013) showed that corn cob arabinoxylans can be extruded if they have sufficient water content, acting as a plasticizer, paving a way to their industrial production. Three different extrusion temperatures 60°C, 90°C and 120°C were used to process arabinoxylans with moisture contents around 7%, 12% and 27%, which were achieved by conditioning polymers in desiccators for different time intervals. Among the conditions tested, arabinoxylans with 27% moisture content was

successfully extruded at 90°C. Mechanical properties of the extruded strips were compared with polylactic acid (PLA) strips that were extruded with the same twin-screw extruder and extruded arabinoxylan strips exhibited higher tensile strength and elongation at break values. For packaging applications of hemicelluloses, mechanical properties are also crucial since physical integrity is essential to assure barrier properties. An overview of mechanical properties of hemicellulose based films from various resources can be seen in Table 2.4.

Table 2.4 Mechanical properties of hemicellulose based films in the presence of various plasticizers

Biomass / Hemicellulose Type	Plasticizer	Tensile Strength	Elongation at break	Young's modulus	Reference
Corn hull Arabinoxylan	-	54 MPa	6.2 %	1316 MPa	Zhang et. al 2004
	5-22% glycerol	10-47 MPa	5.6-12.1%	365-1148 MPa	
	5-22% PG*	53-61 MPa	6-8%	1225-1320 MPa	
	5-22% sorbitol	20-48 MPa	5.5-8.9%	463-1161 MPa	
Barley husk Arabinoxylan	-	50 MPa	2.5 %	2930 MPa	Höije <i>et al.</i> 2005
Oat Spelt Arabinoxylan	50% sorbitol	2 MPa	20%	-	Saxena <i>et al.</i> 2009
Spruce wood Galactoglucomannan	29% glycerol	12 MPa	3.1%	489 MPa	Mikkonen <i>et al.</i> 2010
Aspen wood Arabinoxylan	xylitol	5-40 MPa	2.8%	100-900 MPa	Gröndahl <i>et al.</i> 2004
Aspen wood Arabinoxylan	20-50% sorbitol	6-40 MPa	2-11 %	200-5000 MPa	Gröndahl <i>et al.</i> 2004
Maize bran Arabinoxylan	glycerol	72.4 MPa	26.5%	7.4 MPa	Peroval <i>et al.</i> 2002
Cotton stalk Xylan	glycerol	0.76 MPa	88%	1 MPa	Goksu <i>et al.</i> 2007
Cotton stalk Xylan	-	51.2 MPa	3.1 %	3086 MPa	Bahcegul <i>et al.</i> 2012
Corn cob Arabinoglucoronoxylan*	%26 moisture	76 MPa	35%	1073 MPa	Bahcegul <i>et al.</i> , 2013

*Prepared by extrusion. All the other films were prepared by solvent casting methods.

2.3.3 Hemicellulose Based Blends

The history of bio-based polymers are much older than the history of the synthetic ones; but the poorer performances and higher costs of natural polymers caused an increase in the utilization of synthetic ones in the past. Blending is among the mostly utilized approaches to achieve low cost bio-based materials with better properties for replacing petrochemical plastics back with sustainable natural polymers.

As mentioned before, hemicelluloses are one of the most abundant natural raw materials with a great industrial potential, but currently do not have enough industrial applications. In literature, hemicellulose blends are being prepared with other natural polymers, polysaccharides, proteins, and synthetic polymers with the aim of enlarging potential applications of them. Among the variety of hemicellulose types, xylans and mannans are the focus of bio-based packaging research. Although being few compared to the most conventional bio-based polymers like cellulose and starch, there are studies on hemicellulose based blends with cellulose, carboxymethyl cellulose, starch, gluten and chitosan (Mikkonen, 2013). In addition to this, there are studies in literature which also focus on the utilization of hemicelluloses as an additive to other biodegradable films to reduce the cost.

Kayserilioglu *et al.* (2003) showed that xylans can be added to wheat gluten films as much as 40% (w/w) without any decrease in film forming quality. Xylans and wheat gluten were mixed and dispersed in water with glycerol for film casting. It is reported that water vapor transfer rate and tensile strength is not affected by xylan gluten ratio; however elongation at break values decreased with increased xylan content.

Phan The *et al.* (2009) studied the blends of agar, cassava starch and arabinoxylan. The main film-forming components were agar and starch, in which arabinoxylan was added at low ratios as an additive and the films were cast from the aqueous solutions of them. Water vapor permeability of agar-based films was reduced by the addition of arabinoxylan; however mechanical performance was decreased with the addition

of arabinoxylans. Authors concluded that arabinoxylan can be considered as an additive for agar-based films to increase moisture barrier properties.

Gabrielii *et al.* (1998) blended alkali extracted birch glucuronoxylan with chitosan at 5-30% chitosan content in acidic conditions. Pure glucuronoxylan was not able to form films; however upon 10% chitosan addition, self-supporting films were obtained. Lower contents than 10% resulted in flakes and contents between 10% and 30% resulted in hydrogels. Interaction between chitosan and glucuronoxylan was proved by FTIR analysis; however atomic force microscopy results showed that xylans and chitosan formed two distinct phases.

Xiao *et al.* (2001) blended konjac glucomannan with sodium carboxymethyl cellulose (CMC) and obtained transparent films. Interaction of COO⁻ and OH groups of CMC and OH and COCH₃ groups in mannan was tracked by FTIR analysis. At 10wt% CMC content, tensile strength and elongation at break values of the blends were maximum with high miscibility showed by SEM. Higher CMC contents induced phase separation and increased the roughness of the films.

Chen *et al.* (2008a) studied the structure and properties of the starch films by blending starch with mannan in the presence of glycerol as a plasticizer. Melting temperature of the starch decreased as the mannan content increased. Addition of mannans increased both the tensile strength and the elongation at break values; however the presence of mannans increased the moisture uptake of the films. Blended films were reported to be a potential food packaging.

Compatible blends of hemicelluloses can be formed with other bio-based polymer due to their structural similarities; however blends with synthetic polymers can mostly be problematic due to the incompatibility between them. Although being a synthetic polymer, polyvinyl alcohols (PVA) differ from most of the petroleum based polymers being water soluble and biodegradable. These properties of PVAs make them ideal candidates as blending components with bio-based polymers. PVA has been used in blends with wheat gluten (Dicharry *et al.* 2006), collagen (Alexy *et al.*

2003), chitosan (Park *et al.* 2001), carboxymethyl cellulose (Gupta *et al.* 2013) and starch (Yang *et al.* 2008; Yun *et al.* 2006) to address possible applications for packaging industry. There are studies in literature on hemicellulose and PVA blends, but very few studies focuses on the potential applications in packaging industry. The compatibility between PVA and hemicelluloses depend on the hemicellulose type and the additives.

Mikkonen *et al.* (2008) studied the improvement in mechanical properties of galactoglucomannan (GGM) type hemicelluloses upon blending with PVA, arabinoxylan and konjac glucomannan. Different blend ratios at 3:1, 1:1, and 1:3 (w/w) were prepared with glycerol as a plasticizer at 40% (w/w) of the polymer. Polymers and glycerol was dissolved in deionized water and casted on petri-dishes. Tensile strength of the casted films increased with PVA concentration, however phase separation was detected according to optical light microscopy and scanning electron microscopy. Dynamic mechanical analysis (DMA) also exhibited two separate loss modulus for GGM and PVA blends confirming the immiscibility of the GGM and PVA.

Wang *et al.* (2014) produced xylan and PVA films with citric acid and studied the effect of PVA and citric acid contents on the mechanical, thermal, solubility and permeability properties of the blend films. FTIR and SEM results indicated a good compatibility between xylan and PVA. Authors stated that the interaction between xylan and PVA increased with citric acid possibly due to the formation of hydrogen and ester bonds. With the addition of citric acid, tensile strength of the blend films significantly reduced, whereas elongation at break values increased.

2.4 Modification of Hemicelluloses

Just like the other biopolymers, hemicelluloses are inherently hydrophilic in nature which makes films produced from these materials hygroscopic. Their hydrophilic nature is one of the main obstacles in the industrial applications of hemicelluloses. As mentioned previously, hemicellulose films have excellent oxygen barrier

properties, however due to their hydrophilicity; mechanical strength and physical integrity of hemicellulose films can be deteriorated by the absorption of water molecules acting as a plasticizer. At high humidity conditions, materials result in poor water vapor and oxygen barrier properties. Thanks to the presence of reactive hydroxyl groups, hemicelluloses are ideal targets for chemical modifications (Ebringerova *et al.* 2000). Substitution of hydroxyl groups of hemicelluloses with hydrophobic substituents reduces the water solubility and moisture uptake by decreasing the possibility of hydrogen bonding between the hydroxyl groups of hemicelluloses with water. Research on modifications of hemicelluloses are significantly lower than the other polysaccharides like cellulose or starch, however analogous modifications can be applied to each of these. Chemical modifications like esterification, etherification, cross-linking or surface modifications have been used to overcome problems with increased moisture uptake and decreased mechanical properties at humid environments, where modifications via acetylation and alkylation being the most common (Figure 2.14).

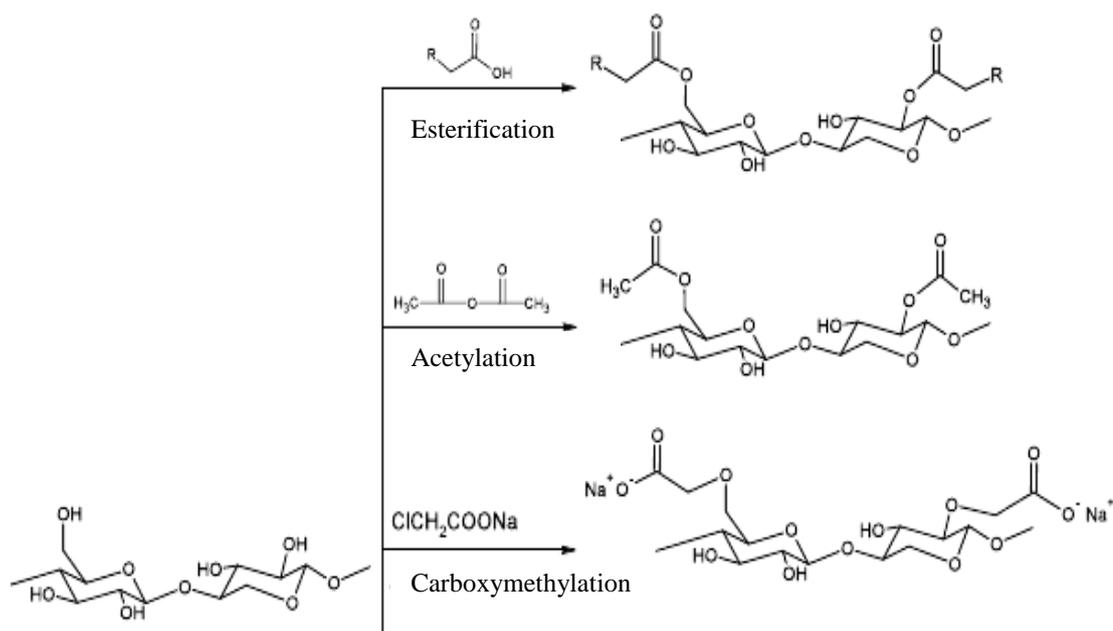


Figure 2.14 Schematic representations of the most common hemicellulose modifications (Plackett, 2011).

2.4.1 Esterification

Very first efforts on making hydrophobic hemicelluloses focused on the esterification of hydroxyl groups by the straightforward carboxylic acid chemistry. A classical procedure involves the use of an acid anhydride in the presence of a basic catalyst to produce acetate, propionate, butyrate, laurate or palmitate esters of hemicelluloses. Acetylation is among the most attractive approaches for increasing the hydrophobicity of hemicelluloses since it is already a widely known technique used for the commercial production of many products including cellulose acetates.

Fang *et al.* (1999) studied the esterification of wheat straw hemicelluloses with acyl chlorides (C3-C18) in N,N-dimethylformamide/lithium chloride solution with dimethylamino pyridine as a catalyst. Products were characterized by FTIR and their solubility in dimethylsulfoxide, tetrahydrofuran, toluene, chloroform, and dichloromethane was studied as an evidence for hydrophobic modifications. Thermal stability was increased with esterification and no degradation occurred during the reaction according to gel chromatography analysis.

Various catalysts were studied for the esterification reactions of hemicelluloses. Fang *et al.* (2008) lauroylated wheat straw hemicelluloses under mild conditions with 4-dimethylaminopyridine, N-bromosuccinimide, N-methyl pyrrolidine, N-methyl pyrrolidinone and pyridine as catalysts. Performance of all the tertiary amine catalysts was better than pyridine. With 5% 4-dimethylaminopyridine addition at 40°C and 35 minutes of reaction, a very high degree of substitution values of 1.54 was obtained. Authors noted that the modified hemicelluloses were suitable for food packaging industry to replace commodity plastics due to their hydrophobic nature.

Microwave assisted synthesis of xylan esters was studied by Xu *et al.* (2008) using N-bromosuccinimide as a catalyst in N,N-dimethylformamide and lithium chloride as a solvent. Microwave irradiation caused degradation of the hemicellulose reducing the molecular weight of the modified hemicelluloses; however increased the speed of

the reaction without any changes in chemical structure of the hemicelluloses that were modified without microwave irradiation.

Fundador *et al.* (2012) studied the synthesis of xylan esters with alkyl chain lengths between C2 and C12 and their xylan acetate, xylan propionate, xylan butyrate, xylan valerate, xyland hexanoate, xylan decanoate and xylan laurate were synthesized by the use of suitable acyl chlorides, anhydrides or carboxylic acids. NMR technique was used to analyze the structural differences of the esters. TGA analysis were conducted to elucidate their thermal characteristics, where only slightly higher degradation temperatures were reported for longer chain lengths. Esterification changed the solubility characteristics of xylans rendering xylan esters chloroform soluble. As an example of an alternative application, xylan esters were electrospun into nanofibers. Dependence of strength, modulus and elongation values on the chain length of the esters were presented, where Young's modulus and tensile strength decreased and elongation at breaks increased with increasing chain length.

A very different method of approach to esterification of hemicellulose was presented in Stepan *et al.*'s work (2013a). They reported the enzyme catalyzed surface modification of solvent cast rye arabinoxylan films by acetylation with vinyl acetate and by steartation with vinyl stearate. Different enzymes were evaluated for surface modifications and surface analysis (FT-IR, TOF-SIMS, ESCA, CA) showed that lipases from *Mucor javanicus*, *Rhizopus oryzae* and *Candida rugosa* successfully surface steartated, and a cutinase from *Fusarium solani pisi* surface acetylated the hemicellulose films after 3 days of reaction period. However, contact angle measurements showed that only initial hydrophobicity of surfaces was increased by modifications and contact angles started to decrease significantly after 20 seconds for all samples.

2.4.1.1 Acetylation

Many esterification systems have been published for the modification of lignocellulosic biomass, but none of them was as successful as acetylation in terms of up-scaling from research to commercial scale (Rowell, 2006). Acetylation of wood was first carried out in 1928 (Fuchs, 1928) and after 1940's acetylation was started to be studied widely with various kinds of lignocellulosic biomass and agricultural resources. Now, acetylation is a widely known technique for the commercial production of many products including cellulose acetates; however it is not comprehensively studied for the modification of hemicelluloses yet.

A classical procedure of acetylation involves the use of acetic anhydride in the presence of pyridine as a catalyst to produce acetylated hemicelluloses. One of the very first studies on acetylation of hemicelluloses were conducted by Smart and Whistler (1949) where acetylation was achieved by a mixture of acetic anhydride and pyridine, after swelling hemicelluloses in formamide. Sulfuric acid (Zhang *et al.* 2013), *N*-bromosuccinimide (Sun *et al.* 2004), 4-dimethyl aminopyridine (Sun *et al.* 2002) and iodine (Ren *et al.* 2007) are also being used as a catalyst in acetylation of hemicelluloses. The reaction between accessible hydroxyl groups and acetic anhydride esterifies the hemicellulose with the production of acetic acid as a by-product (Figure 2.15).

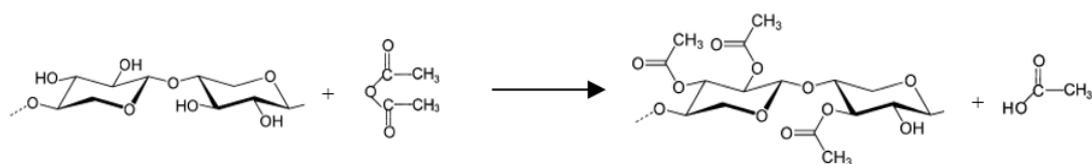


Figure 2.15 Hydroxyl groups of hemicelluloses react with acetic anhydride producing acetylated hemicelluloses with acetic acid as a by-product (Sun *et al.* 2002).

Acetylation reactions are mostly differentiated as homogeneous and heterogeneous systems in literature. Standard procedures for homogeneous systems include the dissolution of hemicelluloses in organic solvents, but greener approaches are also developed by the use of ionic liquids. A standard use of solvents was exemplified in

Fang *et al.*'s (2000) study. They studied the acetylation of wheat straw hemicellulose in dimethylformamide (DMF) and lithium chloride (LiCl) system with acetic anhydride. Hemicellulose was completely dissolved in DMF/LiCl solution with a solid content of % 2 (w/v) and the reaction was catalyzed by dimethylaminopyridine. Effect of different acetylation conditions (temperature between 60°C-85°C and reaction time between 2 hours-72 hours) were investigated and optimum reactions conditions was determined to be 85°C and 60 hours with a degree of substitution of 1.25. Instead of conventional solvents, Ren *et al.* (2007) demonstrated the first use of ionic liquids as a solvent in acetylation of hemicelluloses. Wheat straw hemicelluloses were acetylated with acetic anhydride in 1-butyl-3-methylimidazolium chloride ionic liquid. Complete dissolution of wheat straw hemicelluloses in ionic liquid was achieved at a concentration of 2.6% (w/w) at 90 °C after 1.5 hours. Optimum reactions conditions were determined to be at 100°C and 30 minutes with a degree of substitution of 1.53. They concluded that the present method has obvious advantages in that higher reaction rates can be achieved with complete conversion and greener approaches can be used.

Homogeneous systems are usually preferred in order to have high degrees of substitutions; however the use of a solvent reduces the reaction rate because modifiers are diluted in the reaction medium and very low amounts of product can be modified due to low solid loadings to achieve complete dissolution (Sun *et al.* 2002). Also, it is best to eliminate the use of organic solvents due to their harmful effects on the environment. Ionic liquids can be utilized to overcome this problem but yet, it is not a feasible way to replace organic solvents. Considering those disadvantages, heterogeneous reaction systems are also being studied. Sun *et al.* (2004) studied the acetylation of sugarcane bagasse hemicellulose with acetic anhydride using *N*-bromosuccinimide as a catalyst. They obtained different degree of substitution values between 0.27 and 1.15 by varying the reaction time between 0.5 and 5 hours and temperature between 18 °C to 80 °C. Belmokaddem *et al.* (2011) has studied both heterogeneous and homogeneous conditions for the acetylation of birchwood xylan. Homogeneous reaction took place in dimethylformamide and lithium chloride solution with acetic anhydride and heterogeneous reaction took place in slurry of

birchwood xylan and acetic anhydride. When acetylated xylans in both systems are compared, they reported that even if the mass yields of heterogeneous conditions were higher, a decrease in degree of substitution was observed. However, when only the higher degree of substitution values were considered; no significant effect of the difference in systems was observed. They stated that thermal stability is improved by acetylation under both conditions without any difference and concluded that esterification in heterogeneous conditions can be an efficient and environmentally friendly method that could be scaled-up.

A small number of the studies on hydrophobic modifications of xylans by acetylation address the material properties of them, all of which was focused on the solvent casting of films. One of the main difficulties that is encountered during the formation of solvent casted films from acetylated xylans is related with their solubility in casting solutions. Rahn *et al.* (1996) emphasized that the solvent must be compatible with the product's degree of acetylation to ensure adequate film formation. Samples with low degree of substitution are more soluble in DMSO and N,N-dimethylacetamide (DMA), samples with moderate degree of substitution are generally soluble in tetrahydrofuran, while samples with high degree of substitution are more soluble in hexane or carbon tetrachloride. Thus, it is not expected to obtain flawless film forming solutions since there is not any solvent which is compatible with a wide range of acetylation degrees. A study by Fang *et al.* (2000) on acetylation of wheat straw hemicelluloses addressed the preliminary studies on the film formation of hemicellulose acetates in DMSO. Ayoub *et al.* (2013) developed a method for acetylation of switchgrass hemicellulose in ionic liquid and produced solvent casted films of acetylated hemicelluloses using THF which were brittle. Stepan *et al.* (2013) studied the acetylation of rye arabinoxylan and spruce arabinoglucuronoxylan in ionic liquid systems and briefly mentioned their film formation abilities. They have reported the appearances of the film fragments that were produced by acetylated xylans and casted from dimethyl carbonate (DMC) and chloroform. Although most of the xylan acetates were able to form films, some of the samples were not soluble either in DMC or chloroform. The most comprehensive study on the material properties of xylan acetates were conducted by Egües and his co-workers (2014) who

studied homogeneous acetylation of corn cob arabinoxylans by formamide, acetic anhydride and pyridine and casted films from chloroform solutions. Chemical and thermal characterizations of films were done together with tensile testing and contact angle analysis. It is shown that the acetylation process allowed the highest values of tensile at 67 MPa and elongation at break at 13.4%. Dynamic mechanical analysis at different relative humidity conditions revealed that acetylation allowed xylan to be independent of the surrounding humidity.

2.4.2 Etherification

Etherification is one of the common methods used to modify polysaccharides to alter their solubility, film-forming and stability characteristics. Alkoxy moieties are being substituted with hydroxyl groups by various etherification reactions like carboxymethylation, alkylation, or benzylation (Hansen *et al.* 2008). There is a vast number of cellulose ethers, where the carboxymethyl cellulose and benzyl cellulose are being the widely known examples that have industrial uses.

Carboxymethylation of hemicelluloses can be achieved analogously and a common carboxymethylation method by the use of sodium hydroxide and sodium monochloroacetate was studied by Ren *et al.* (2008). Alkaline extracted sugarcane baggase hemicelluloses was carboxymethylated in ethanol/water under various reaction conditions. Authors noted that alkaline activated two step reaction was necessary in order to have high degree of substitution values. Unfortunately, results also showed that hemicelluloses are significantly degraded during the reaction at alkaline conditions. Carboxymethylation of xylans was recently studied by Alekhina *et al.* (2014) to investigate barrier properties of the films produced from carboxymethylated xylan. Tensile testing results disclosed the plasticizing effect of carboxymethylation was observed and films with higher degree of substitution values exhibited improved water vapor and oxygen permeability.

Fang *et al.* (2002) studied the methylation of hemicelluloses with methyl iodide in dimethylsulphoxide. Thermal profile of the modified hemicelluloses showed that methylation resulted in a significant thermal stability. Methylation of xylan was also achieved by Petzold *et al.* (2008) using excess amounts of methyl iodide and methyl chloride in 40% NaOH containing aqueous solutions.

Benzylation also offers better plasticity and high mechanical properties for a wide range of polysaccharides. It also serves as a method to endow hydrophobic properties and high thermal stability. Thermoplastic properties and lower water solubility of hemicelluloses can be achieved by benzylation. One of the most successful studies in literature is conducted by Hartman *et al.* (2006) to produce O-acetylgalactogluco mannan (GM) films that show high resistance in high humidity conditions. Benzylated GM was found to form self-supporting, strong, transparent films. The resulting films were excellent oxygen barrier and their barrier properties were significantly less sensitive to moisture than their unmodified counterparts. Ren *et al.* (2012) prepared hydrophobic hemicelluloses by benzylation with benzyl chloride in ethanol/water system with sodium hydroxide as a catalyst. FTIR and NMR studies proved that benzyl groups were attached to the backbone of the hemicelluloses (Figure 2.16).

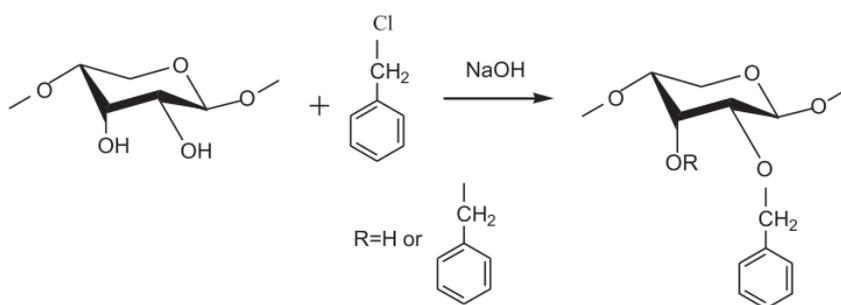


Figure 2.16 Benzylation of hemicellulose with benzyl chloride (Ren *et al.* 2012).

2.4.3 Cross-linking

Cross-linking is another type of hemicellulose modification interconnecting hemicellulose molecules by covalent linkages altering their molecular weight, mechanical and swelling behaviour. Most of the studies on cross-linking of hemicelluloses address their hydrogels examining their swelling behaviour. Although being relatively few, there are studies in literature mentioning cross-linking for film applications. Mikkonen *et al.* (2012) used glyoxal as a cross-linking agent which was proved to increase the mechanical strength, rigidity and moisture sorption of the extruded starch. Self-supporting films of spruce O-acetyl-galactoglucomannans (GGM) were formed by glyoxal-crosslinking where cohesive films cannot be formed with GGM. Cross-linking with 5% glyoxal was sufficient for cohesive films with increased tensile strength, modulus and glass transition temperature. Upon modification, water vapor permeability of the films were reduced at higher humidity conditions. The lowest oxygen permeability values were obtained for crosslinked plasticized GGM films with 20% sorbitol. Zoldners *et al.* (2013) utilized polycarboxylic acids that are widely used as cross-linkers for biopolymers like cellulose and starch. Citric acid, maleic acid and butane tetracarboxylic acid (BTCA) was used as linking agents with sodium hypophosphite as a catalyst. Films with significantly reduced water sensitivity were obtained for 10% BTCA cross-linked and 20% citric acid cross-linked hemicelluloses. Moisture sorption of the films decreased twice fold between 0% and 100% relative humidity conditions compared with the unmodified films.

2.4.4 Surface Modifications

Surface modifications of many biopolymers can be achieved by grafting for a wide range of applications. Cellulose and starch substrates are the most common polysaccharides grafted with hydrophobic substituents. As analogous modifications can be applied among the polysaccharides, modification of hemicelluloses by grafting also attracted attention. The free reactive hydroxyl groups of hemicellulose serve as

excellent sites to form grafts (Lindblad *et al.* 2005). Many studies on grafting of hemicelluloses have been focused on modification of gums, but there are also examples surface modifications of hemicellulose based films. Water sensitivity of hemicellulose based films can be significantly increased by grafting, however the affects may not last long due to the susceptibility of grafted molecules to hydrolysis and leach out of the surface. Various fatty acids were grafted on arabinoxylan films by plasma and electron beam irradiation treatment (Peroval *et al.* 2003). Upon treatment, contact angles of the films increased from 70° to 115°C, but with a tendency to reduce with time. Gröndahl *et al.* (2006) fluorinate the surfaces of arabinoxylan films by gaseous trifluoroacetic anhydride as in Figure 2.17. Although hydrophobic characteristics were introduced to the surfaces, the change was relatively insignificant most probably due to the hydrolysis of trifluoroacetate groups upon contacting with water.

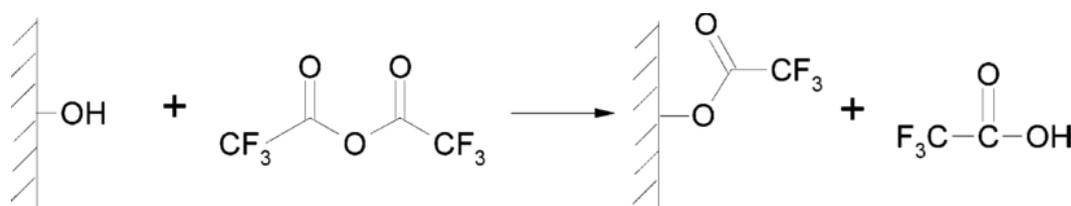


Figure 2.17 Reaction of arabinoxylan based films surface with trifluoroacetic anhydride (Gröndahl *et al.* 2006).

Hartman *et al.* (2006) studied three different strategies by plasma treated grafting of styrene, vapor-phase grafting of styrene and lamination of unmodified galactoglucomannan with a benzylated galactoglucomannan to produce less moisture sensitive oxygen barrier films. Authors reported that humidity tolerance of vapor-phase-grafted surfaces were better than their plasma treated counterpart. In line with the contact angle analysis, lamination with a hydrophobic benzylated layer was also disclosed as an efficient method for protection against water.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Xylan-based hemicelluloses (xylans) were extracted from corn cobs provided from Hatay, Turkey. Potassium hydroxide, acetic acid, potassium acetate, sorbitol, glycerol, triacetin, polysorbate (Tween[®] 80), polyvinyl alcohol (Mowiol[®] 4-88, Mw~31,000, 88% hydrolysis), alkali lignin, calcium carbonate, D-(+)-glucose and L-(+)-arabinose was purchased from Sigma-Aldrich (St.Louis, Missouri, USA). Acetic anhydride was purchased from Merck with the permission of Turkish Drug and Medical Device Institution, Turkey. Sulfuric acid, D-(+)-xylose and D-(+)-galactose were purchased from Merck (Darmstadt, Germany). Ethanol was purchased from Colony Sugar Mills (Lahore, Pakistan)

3.2 Alkaline extraction of xylans

Corn cobs were milled by a laboratory hammer mill (Arthur Thomas Co., Philadelphia, USA) and sieved (Analytical Sieve Shaker, Retsch GmbH, Haan, Germany) to a particle size between 1.19 mm and 0.15 mm with 16 and 100 mesh screens. Xylans were alkaline extracted from the milled corn cobs according to previously reported methods with minor changes (Zilliox *et al.* 1998; Bahcegul *et al.* 2014). The experimental steps for alkaline extraction procedure was given in Figure 3.1. 50 grams of milled corn cob was used for each extraction. The milled corn cobs were swollen in 1000 ml deionized water for 15 minutes at room temperature and filtered by a cheesecloth. Swollen xylans were mixed with 10% KOH or 24% KOH (w/v) extraction solutions at a solid loading of 10% (w/w) and stirred by a magnetic stirrer (RCT Basic Safety Control, IKA Werke, Staufen, Germany) at 500 rpm for two

hours at room temperature. Undissolved solid residues were again filtered off by a cheesecloth and the xylan rich extraction solution was centrifuged (Hettrich, Rotina 380R, Germany) using 50 ml centrifuge tubes at 5000×g for 5 minutes to completely remove the insoluble particles. 1250 ml ethanol-acetic acid solution containing 10% (v/v) acetic acid was prepared beforehand and kept in refrigerator for 1 hour prior to use. Ethanol-acetic acid solution was poured on the xylan rich solution to neutralize and precipitate the xylans.

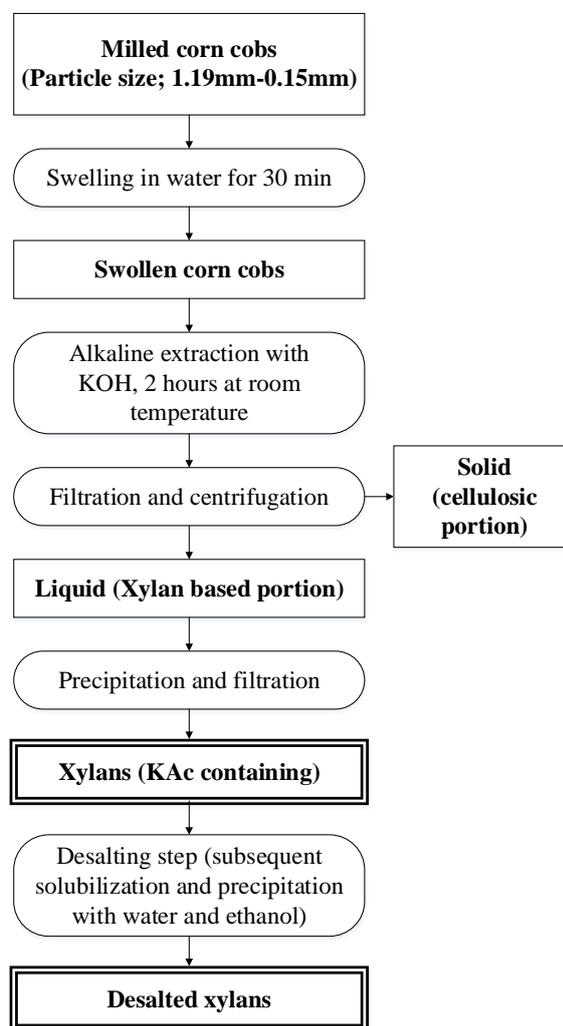


Figure 3.1 Procedure for alkaline extraction of xylans from corn cobs, including the desalting step.

Precipitated xylan rich portion was recovered from the solution by cheesecloth. Extracted xylans were either purified by three cycles of solubilization and precipitation with 3:1 (v/v) ethanol and water to remove potassium acetate that is formed during the neutralization step (desalted) or used without any treatment (KAc containing). Purification step was carried out by first dissolving the extracted xylans in 100 ml of deionized water and then precipitating them by the addition of 300 ml. of ethanol. Precipitated xylans were filtered using cheesecloth and the cycle was repeated two more times. Extracted xylans were spread on the petri dishes and dried at room temperature. Extracted xylan polymers can be seen in Figure 3.2.



Figure 3.2 Appearances of xylans isolated from corn cobs by alkaline extraction

3.3 Compositional Analysis

Alkaline extracted xylan residues were characterized in terms of their lignin content, salt content and the monosaccharide composition representing the hemicellulosic portion by UV/Visible Spectrophotometry, conductivity and high performance liquid chromatography (HPLC), respectively.

3.3.1 Monosaccharide analysis

Monosaccharide compositions of the extracted xylan residues were determined by HPLC according to the National Renewable Energy Laboratory (NREL, Golden, Colorado) analytical procedure of biomass (NREL, 1996; 2011). Monosaccharide compositions were analyzed by Shimadzu LC-20A HPLC system (METU Chemical

Engineering Department) equipped with a transgenomics CARBOSep COREGEL-87P column at 85°C.

For each sample, 0.3 g of extracted residue were hydrolyzed in 3 ml of 72% (w/w) sulfuric acid solution in a water bath at 30°C for 1 hour. Sulfuric acid concentration in the hydrolyzation solution was diluted to 4% (w/w) with the addition deionized water and the suspensions were poured into autoclave bottles. The bottles were autoclaved (Hirayama, Hiclave HVE-50) at 121°C for 1 hour for further digestion. The pH of the hydrolyzation solution was adjusted to 6-7 by mixing 20 ml portion of it with CaCO₃. Neutralized solution was filtered by a 0.22 µm syringe filter into the HPLC vials for the analysis. Samples were fed to the system with a flow rate of 0.6 ml/min and an injection volume of 40 µl. Degassed deionized water after filtration with 0.45 µm filter was used the mobile phase. Calibration curves were prepared by the standard solutions of D(+)xylose, D(+)glucose, D(+)galactose and L(+)arabinose at different concentrations in the range between 0-2 mg/ml (Appendix A). The concentration analysis were carried out using the software (LC Solution) accompanying the HPLC and with the assistance of a peak separation program (PeakFit v4.12).

3.3.2 Lignin content

Lignin contents of extracted xylan residues were determined by UV/Visible spectrophotometer (Nicolet Evolution 100, Thermo Fisher Scientific Inc., USA) at 280 nm as suggested by Westbye *et al.* (2007). Xylans were dissolved in 5 ml of 4% NaOH solution at a solid loading of 2% (w/v) overnight. The solution was filtered through a 0.22 µm filter. Standard lignin solutions were prepared using commercial alkali lignin in 4% (w/v) NaOH in the range between 0-0.1 mg/ml. Lignin content in extracted residues were estimated according to the calibration curve fitted to the absorbance vs. lignin concentration graph (Appendix B).

3.3.3 Potassium acetate content

Potassium acetate content of the xylans were determined by conductivity-meter analysis. Xylans were dissolved in 40 ml of deionized water at a solid loading of 1% w/v and stirred by a magnetic stirrer for 1 day at room temperature. Standard potassium acetate solutions were prepared by dissolving potassium acetate in deionized water in the range between 0-0.2 mg/ml (Appendix C). Conductivities of the solutions were determined by conductivity meter (Inolab, WTW Cond 720, Germany) and concentrations were estimated according to the calibration curve prepared by the standard potassium acetate.

3.4 Extrusion

Extracted xylan polymers were extruded with a twin-screw, co-rotating extruder (Thermo Scientific HAAKE MiniCTW, USA) shown in Figure 3.3. A rectangular die with 5×0.5 mm (width × thickness) dimensions was used to obtain extrudates in the form of a strip. 4 to 5 grams of polymer was manually fed to the extruder and the strip moving out of the die was collected on a moving belt. Extrusion was performed by setting extrusion temperature and screw speed as parameters. Extrusion settings together with the torque values were controlled and recorded via the software supplied with the extruder. Residual xylans were thoroughly removed from the screws and the die with distilled water after the extrusion. Extrusion was performed by either conditioning xylans at 90 ± 5 % relative humidity or in the presence of plasticizers to render xylans extrudable. Conditioning took place at room temperature for 24 hours prior to extrusion in a desiccator containing water to load xylans with around 26% moisture. Unless otherwise stated, a typical extrusion procedure was conducted by a conditioning step prior to extrusion at 90°C and 50 rpm screw speed (Bahcegul *et al.* 2013). Extrusion of xylans in the presence of sorbitol or glycerol was conducted without the conditioning step. Prior to extrusion, plasticizers and xylans were partially dissolved in a small amount of deionized water and stored at room temperature to allow evaporation of water, since preliminary studies on the

introduction of these plasticizers into the xylans showed that plasticization effect was better when the plasticizer and xylans were mixed by partially dissolving them in water compared to directly mixing them. Xylan and PVA blends were prepared by directly mixing them in their native forms. Xylan and PVA mixtures were also conditioned at 90 ± 5 % relative humidity at room temperature for 24 hours prior to extrusion to render them extrudable.

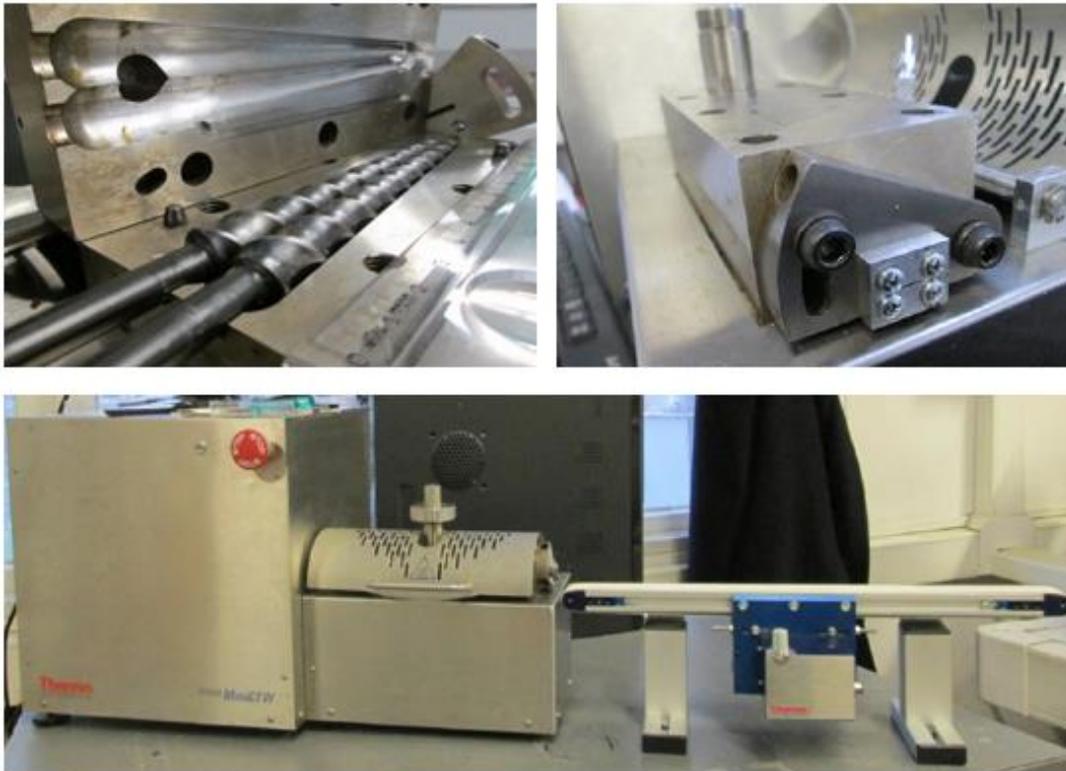


Figure 3.3 Twin-screw extruder used for the extrusion of xylans.

3.5 Modification Methods

3.5.1 Heat treatment

Extruded xylan strips were cut into 6 cm pieces and subjected to heat treatment at 60°C, 90°C, 120°C and 150°C for 1 hour in an oven. Percent moisture loss of the strips upon heat treatment were determined by weighing strips before and after the

treatment. Dimensional changes of the strips upon treatment and conditioning were measured by a digital micrometer (40 EXL, Mahr GmbH, Germany).

3.5.2 Acetylation

Acetylation reaction was carried out by utilizing acetic anhydride as an acetylating agent using a solid loading of 1:6 g xylan/ml acetic anhydride. Reaction took place by mixing either xylans or extruded xylan strips with acetic anhydride at designated temperatures and durations in the range between 60°C-120°C and 10 minutes-8 hours, respectively, in an oil bath, under reflux and stirring (RCT Basic Safety Control, IKA Werke, Staufen, Germany, equipped with a PT 1000.60 temperature sensor) (Figure 3.4). All the glassware used for the reaction were completely dried since acetic anhydride is not stable in water and decomposes to acetic acid. Samples were recovered from the reaction solution using a filter paper and washed thoroughly three times with ethanol to remove the residual acetic anhydride and the by-product acetic acid. Acetylated samples were dried at ambient conditions.



Figure 3.4 Acetylation of xylans under reflux and stirring

3.6 Characterizations

3.6.1 Weight gain analysis

Weight gain (WG) values regarding the exchange of hydroxyl groups with acetyl groups were calculated gravimetrically. Weight gain values were based on the dry weight of acetylated xylans and their unreacted counterparts dried at 105 °C for 24 hours. %WG values were reported as the average of three samples and calculated according to following the formula:

$$\text{Weight gain (\%)} = \frac{(\text{Dry weight after} - \text{Dry weight before}) \text{ the reaction}}{\text{Dry weight before the reaction}} \times 100$$

3.6.2 Molecular weight determination

Viscosity average molecular weight of the xylans were determined by capillary viscometry as described by Bahcegul *et al.* (2014). Native and acetylated xylans were dissolved in 4% (w/v) NaOH solution for 1 day and 2 days, respectively, at room temperature, due to their different solubility characteristics. 20 ml of solution was poured to the reservoir of the Ubbelohde viscometer at room temperature and the time it took for the solution to pass through the two calibrated marks were recorded. The procedure was repeated three times for concentrations between 0-0.8 g/dl. Several viscosity functions are defined to study viscosity average in molecular weight. Relative viscosity (η_{rel}) is defined to be the ratio of the viscosity of the solution with a defined concentration and the viscosity of the solvent which can be simplified to the ratio between the time it takes for polymer solution to flow (t) to the time it takes for the solvent to flow (t_0).

$$\eta_{rel} = \frac{t}{t_0} \quad (t_0 \text{ for 4\% (w/v) NaOH})$$

Specific viscosity (η_{sp}) reflects the fractional increase in viscosity without the solvent viscosity.

$$\eta_{sp} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$$

The reduced viscosity (η_{red}) is the increase in fluid viscosity per unit of polymer solute concentration, c (g/dL).

$$\eta_{red} = \frac{\eta_{sp}}{c}$$

The intrinsic viscosity, $[\eta]$, is found by extrapolating the plots of specific viscosity/concentration (η_{sp}/c) versus concentration (c) and the natural logarithm of the relative viscosity/concentration $\ln(\eta_{rel})/c$ versus concentration (c) to extract the "intrinsic" properties of the polymer chain by eliminating influence of entanglements on viscosity. $[\eta]$ values from the two plots were determined and the average of them was used to find the molecular weight of the samples.

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad [\eta] = \lim_{c \rightarrow 0} \frac{\ln(\eta_{rel})}{c} \quad \text{where } \eta_{rel} = \frac{t}{t_0} \quad (t_0 \text{ for 4\% (w/v) NaOH) and}$$

$$\eta_{sp} = \eta_{rel} - 1$$

$$[\eta] = KM_v^a$$

For non-spherical particles including polymeric molecules, Mark-Houwink-Sakurada equation relates the intrinsic viscosity to the viscosity average molecular weight where K and a are experimentally determined empirical constants, which were determined as $K = 2.67 \cdot 10^{-4}$ and $a = 0.73$ for xylans (Eremeeva *et al.* 1993). Sample data sets are given in Appendix D.

3.6.3 Moisture content analysis

The moisture content of the xylans or xylan strips were determined gravimetrically. Samples were kept inside a climatic chamber (MMM Medcenter Climacell 111,

Germany) at designated relative humidity conditions and dried at 105 °C for 24 hours. The strips were weighed at the end of the moisture conditioning and drying steps. The percentage moisture contents are reported as the average of two samples on a wet basis and were calculated as follows:

$$\text{Moisture Content (\%)} = \frac{\text{Weight after conditioning} - \text{Dried weight}}{\text{Weight after conditioning}} \times 100$$

3.6.4 Water solubility

Water solubility values were determined by mixing the xylans or xylan strips with distilled water at a solid content of 1% (w/v) at room temperature under stirring for 1.5 hours. Undissolved solid particulates were separated from the solution by filter paper and the remaining solution was centrifuged at 8000×g for 10 minutes to recover the suspended particles. The recovered samples were dried at 105 °C for 24 hours. Water solubility (%) values were calculated using the following formula below and reported as the average of two samples.

$$\text{Water solubility (\%)} = \frac{\text{Initial weight} - \text{Final weight after dissolution}}{\text{Initial weight}} \times 100$$

3.6.5 Water vapor transfer rate

Water vapor transfer rates (WVTR) of the extruded xylan strips were determined gravimetrically. Strips with 0.5 cm × 2.5 cm dimensions were sealed on the glass bottles filled with dried silica gels with an aluminum tape. The glass bottles were placed inside the desiccators with 90 ± 5 % relative humidity at room temperature. The bottles were weighed in every 24 hours and the difference between the initial weight of the bottle and the weight of the bottle at any interval were used to determine the WVTR of the strips. Net weight gain of the bottles were found by subtracting the weight gain due to the absorption of water by the strips. WVTR of the strips were

calculated by the formula given below and the normalized values with respect to film thickness (NWVTR) was reported as the units of gram per day and volume.

$$\text{WVTR} = \frac{\text{Net weight gain per day}}{\text{Area of the film (m}^2\text{)}}$$

$$\text{NWVTR} = \frac{\text{WVTR(g/day.m}^2\text{)}}{\text{Film thickness}(\mu\text{m)}}$$

3.6.6 Tensile testing

Mechanical properties of the extruded hemicellulose strips were tested using a universal testing machine located in METU Central Laboratory (Zwick/Roell Z250, Zwick GmbH & Co., Ulm, Germany) equipped with 10 kN load cells with wedge grips (Figure 3.5). The extruded strips were cut into pieces with a length of 6 cm. and conditioned in a climatic chamber (MMM Medcenter Climacell 111, Germany) at 23°C at specified relative humidity conditions 1 day prior to testing. Unless otherwise stated, tensile tests were conducted at 50% relative humidity conditions since most of the ASTM standards for polymers refers to 50% relative humidity environments. The thickness of the test specimens were measured after the conditioning step prior to testing using a digital micrometer (40 EXL, Mahr GmbH, Esslingen, Germany). The tests were performed at a cross-head speed of 5 mm/min and the grip separation was 20 mm. The grip separation was set to 29 mm. for the cases where an extensometer was used to determine elastic modulus values of the strips. The tests were conducted in an environment in which the temperature and relative humidity conditions were controlled using a climatic room conditioner (Tecnaire LV, Italy). Each test was conducted by 3-5 samples and the test results including the ultimate tensile strength (UTS), percent elongation at break (e_b) and elastic modulus (E) were obtained using testXpert 2 software accompanying the testing machine.

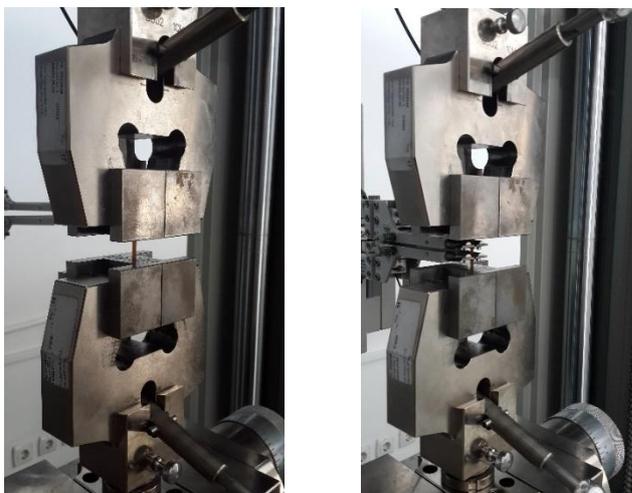


Figure 3.5 Strips are being tested with 10 kN load cells with wedge grips (left) and with extensometer attached (right).

3.6.7 Attenuated total reflection-Fourier transform infrared spectroscopy

The Fourier transform infrared spectra of xylans and xylan strips were obtained by Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) Spectroscopy (Shimadzu IR Prestige 21, Japan) equipped with a diamond-germanium ATR crystal (METU Chemical Engineering Department). The spectra were recorded between 700 cm^{-1} and 4000 cm^{-1} spectral width with a resolution of 4 cm^{-1} and an accumulation of 10 scans.

3.6.8 Thermogravimetric analysis

Thermal degradation behaviors of xylans and the xylan strips were investigated by thermogravimetric analyzers (Shimadzu DTG-60H, Japan or Perkin Elmer Pyris1, USA) located in METU Chemical Engineering Department and METU Central Laboratory, respectively, between 20°C and 800°C at a heating rate of 10°C/min under nitrogen atmosphere.

3.6.9 Optical transmission light microscopy

The upper surfaces of the xylans strips were analyzed by an optical transmission light microscope (Leica CM E, Meyer Instruments, USA) without any treatment. The photographs of the surfaces were obtained by a digital camera.

3.6.10 Scanning electron microscopy

The fractured surface morphologies of the xylan strips were examined by scanning electron microscopy (QUANTA 400F, METU Central Laboratory). Prior to analysis, the strips were broken in liquid nitrogen for smooth cross-sections. The cross-sectional fractured surfaces were coated with gold–palladium and mounted vertically on the four sides of the metal cubic holders with the help of double-sided carbon tapes.

CHAPTER 4

RESULTS AND DISCUSSION

This study mainly focused on reducing the moisture uptake and water solubility of xylan based corn cob hemicelluloses (xylans) by,

- i) Heat treatment
- ii) Acetylation
- iii) Blending

to increase their industrial utilization. Xylans were isolated from corn cobs by alkaline extraction utilizing two different alkaline concentrations. Extracted xylan residues initially contain potassium acetate salt (KAc) that is inherently produced during the alkaline extraction which can then be purified by a desalting step to obtain desalted xylans. Studies on the acetylation of xylans in the presence of potassium acetate were carried out by utilizing both alkaline concentrations without the desalting step; whereas studies on heat treatment, acetylation in the presence of sorbitol and glycerol and xylan/polyvinyl alcohol blends were conducted by utilizing 24% KOH extracted desalted xylans. An outline of the experimental steps together with the type of xylans utilized were shown in Figure 4.1.

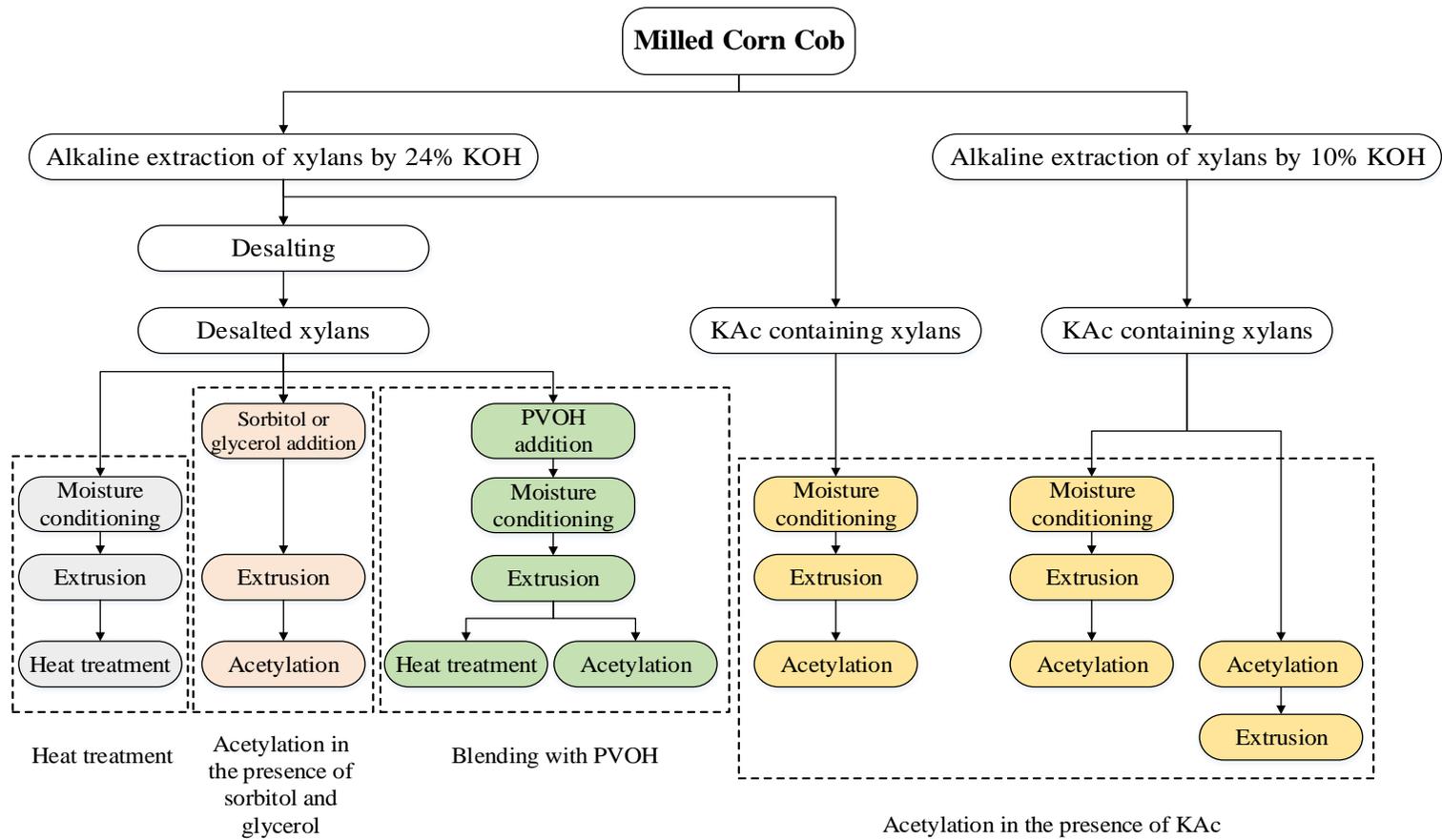


Figure 4.1 Outline of the main experimental steps followed.

As can be inferred from the Figure 4.1, experimental steps differ for each study which necessitates the involvement of different parameters. The classification of parameters used throughout the whole study was given in Table 4.1. The relevant parameters for each study were outlined at the beginning of the sections.

Table 4.1 Parameters used throughout the whole study.

Xylan Extraction	Purification	Additive& Concentration	Extrusion Temperature	Heat Treatment	Acetylation		
10% KOH	Desalted	Sorbitol	10%	75°C	60°C	60°C	10 min
24% KOH	No desalting*	Glycerol	20%	90°C	90°C	90°C	15 min
			30%	120°C	120°C	120°C	30 min
			40%	150°C	150°C		1 h
			40%	200°C			2 h
		PVA	20%				2.5 h
			40%				4 h
			60%				8 h
			80%				

*KAc containing xylans

The results of the studies were outlined in five sections. Compositional analysis of the extracted xylan residues were given in the first section. Heat treatment, acetylation of xylans in the presence of potassium acetate and acetylation of xylans in the presence of plasticizers were covered in the second part. Xylan and polyvinylalcohol blends were studied in the third part including the application of heat treatment and acetylation methods to the xylan/polyvinyl alcohol blend strips. Strips with reduced water sensitivities and improved mechanical properties from each part were further analysed by their water vapor transfer rates which is outlined in the fourth section and the comparison of the results were given as a summary in the last section.

4.1 Compositional analysis of alkaline extracted residues

The relative compositions of cellulose, hemicellulose and lignin can vary among different lignocellulosic biomass. Similarly, extracted residues from these

lignocellulosic resources also differ in composition according to the pretreatment methods and isolation procedures. In this study, corn cob, one of the major agricultural residue produced in Turkey, was utilized as the lignocellulosic resource. In literature, studies on the constituents of lignocellulosic structure of corn cob report the relative compositions of cellulose, hemicellulose and lignin to be between 35-45%, 35-40% and 6-15%, respectively (Jorgensen *et al.* 2007; Kumar *et al.* 2009).

Xylan based hemicellulosic fractions of corn cob were isolated by the alkaline extraction method adapted from Zilliox and Debeire (1998) and Bahcegul *et al.* (2014) with minor changes using two different alkaline concentrations, 10% KOH and 24% KOH, with or without salt purification steps as explained in Section 3.2. Compositional analysis were performed to determine monosaccharide composition, lignin content and residual salt concentrations of the extracted fractions by HPLC, UV/Visible spectrophotometry and conductivity analysis, respectively. Results of the analysis were outlined in Table 4.2.

Table 4.2 Compositional data of the xylan based hemicellulosic portion isolated from corn cobs by different alkaline extraction conditions.

	10% KOH KAc containing	10% KOH desalted	24% KOH KAc containing	24% KOH desalted
Yield (wt%)*	20±2	16±2	32±2	25±2
Lignin (wt%)	12.4±0.9	11.3±0.7	12.9±0.3	12.4±0.2
Residual salt (wt%)	16.0±0.8	1.0±0.4	32.0±0.8	1.0±0.2
Monosaccharide composition of the extracted xylan based hemicellulosic portion(%)**				
Xylose	65±1	62±3	66±2	68±5
Arabinose	21±2	26±4	24±4	20±5
Galactose	11±2	9±1	7±2	9±4
Glucose	3±1	3±1	2±1	3±1

*Ratio of the extracted residue to the initial weight of the corn cob

** Ratio of each sugar to the total sugar amount of the xylan based hemicellulosic portion

As can be seen from the table, extracted residues have a lignin content around 12%, which is in line with the literature since alkaline extraction methods are known to carry some of the lignin in the lignocellulosic biomass to the extracted residue (Brienzo *et al.* 2009). Concentration of the alkaline extraction solution did not affect the residual lignin concentration, however a slight decrease in lignin contents was observed accompanying the washing step, which can be explained by the removal of the lignin together with salts (Egües *et al.* 2014).

Neutralization step during the alkaline extraction of xylan based hemicelluloses (xylans) results in formation of salts which depends on the type of the alkaline solution and acid used. During the current procedure of alkaline extraction, potassium acetate (KAc) is formed by the neutralization of potassium hydroxide with acetic acid. As can be inferred from the Table 4.2, KAc contents of the extracted xylans were significantly affected by the concentration of alkaline solution and the washing step, as the higher alkaline concentrations results in formation of higher amount of salts during neutralization. Extracted xylans were purified by three cycles of solubilization and precipitation steps with 3:1 (v/v) ethanol and water to remove potassium acetate. For 24% KOH extracted xylans, KAc contents were sequentially reduced from 32% to 12%, 12% to 5% and 5% to 1% after the first, second and third washing steps, respectively. Both 10% and 24% KOH extracted xylans retained only 1% KAc after the purification step showing that the desalting step was successful in removing KAc from the xylans.

All four extraction conditions yielded similar monosaccharide compositions, where xylose, arabinose, galactose and glucose contents of the xylan based hemicellulosic portion were around 65%, 23%, 9%, and 3%, respectively. The results were also compared statistically by 2-sample t-test which also indicated that the differences in monosacchaharide compositions with respect to the designated extraction conditions were insignificant (Appendix E). Erdemir (2015) studied the effect of alkaline concentration on the extraction of xylans from corn cob considering their compositional properties, showing that the concentration of the potassium hydroxide in the 5-24% range did not affect the monosaccharide composition of the isolated

xylan based hemicellulosic portion. Concentration of the xylose, as monomer, was the highest which was followed by arabinose as an evidence of the xylose backbone with arabinose substitutions. The presence of galactose and glucose was expected, since the corn cob hemicelluloses are known to be rich in arabinoglucuronoxylan type hemicelluloses (Ebringerova *et al.* 1992). Arabinose to xylose ratio of the extracted residues were around 0.35, indicating that every 3 moles of xylose in the xylan backbone is substituted with an arabinose molecule. Glucose and galactose concentrations showed that every 6 moles of xylose in the xylan backbone is substituted with pyranoses. A representative structure of the extracted xylans can be seen in Figure 4.2.

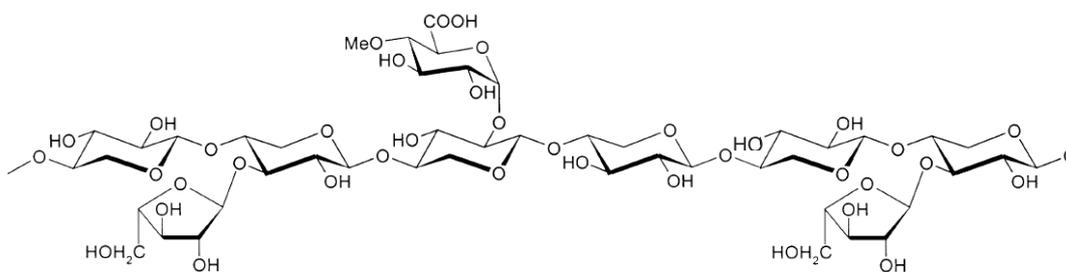


Figure 4.2 A representative sketch for the extracted corn cob hemicelluloses showing a xylan backbone with arabinose and galactose substitutions

Compositional analysis showed that the extracted xylan based hemicellulosic portions in four different conditions yielded similar lignin and monosaccharide compositions but they were significantly different in terms of their potassium acetate content.

4.2 Modifications to improve the water sensitivity of the xylans

4.2.1 Heat treatment of extruded xylan strips

“Plasticization effect of water molecules has been widely reported in the literature and high moisture uptake can negatively affect the mechanical response of the bio-

based materials (Levine *et al.* 1988; Dammström *et al.* 2005; Egües *et al.* 2014). In addition to this, humid conditions might be detrimental to barrier properties due to the increase in free volume. Therefore, relationship between the moisture induced properties of the xylan based materials must be understood and controlled for realistic applications. Although studies that address the moisture sensitivity of hemicelluloses are fairly few when compared to cellulose and starch, analogous modifications are applicable to each of the polysaccharides (Plackett, 2011). Heat treatment is usually used for cellulosic materials like wood to increase dimensional stability and durability by decreasing their moisture tolerance” (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry).

The present study combines the recently developed extrusion processing of xylans (Bahcegul *et al.* 2013) with a simple heat-treatment step in order to reduce the moisture sensitivity and to enhance the mechanical properties of the extruded xylan strips in a simple and applicable manner. The effects of heat treatment temperature on the moisture uptake behaviors of the extruded xylan strips were investigated together with the volume change of the strips to elucidate the changes in the mechanical properties upon heat treatment. The parameters used in the study was outlined in Table 4.3.

Table 4.3 Parameters used for the heat treatment of desalted xylan strips

Xylan Extraction	Purification	Additive& Concentration	Extrusion Temperature	Heat Treatment	Acetylation
24% KOH	Desalted	-	120°C	60°C 90°C 120°C 150°C	-

4.2.1.1 Effect of heat treatment on the moisture sensitivity and mechanical properties of the xylan strips

Following the alkaline extraction and desalting step of xylans from corn cobs by 24% KOH extraction solution, extracted xylan residues were conditioned at 90% relative humidity for 1 day to render them extrudable by the plasticization effect of moisture (Bahcegul *et al.* 2013). Xylan strips were extruded from these conditioned polymers using a twin-screw extruder operated at 90°C and 50 rpm (Figure 4.3).

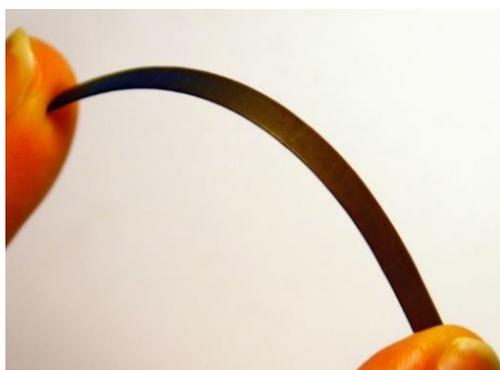


Figure 4.3 Appearance of the strips extruded from 24% KOH extracted desalted xylans.

Tensile testing results of the extruded strips that were conditioned at specified relative humidity (RH) conditions for 24 hours was shown in Figure 4.4. The ultimate tensile strength (UTS) of the strips decreased more than 50%, from 85 MPa to 40 MPa, by an increase in the surrounding relative humidity from 35% to 70%. But still ultimate tensile strength values around 40 MPa at 70%RH can be considered to be satisfactory when compared with the relevant literature results reported for solvent casted films between 1-25 MPa (Goksu *et al.* 2007; Mikkonen *et al.* 2009).

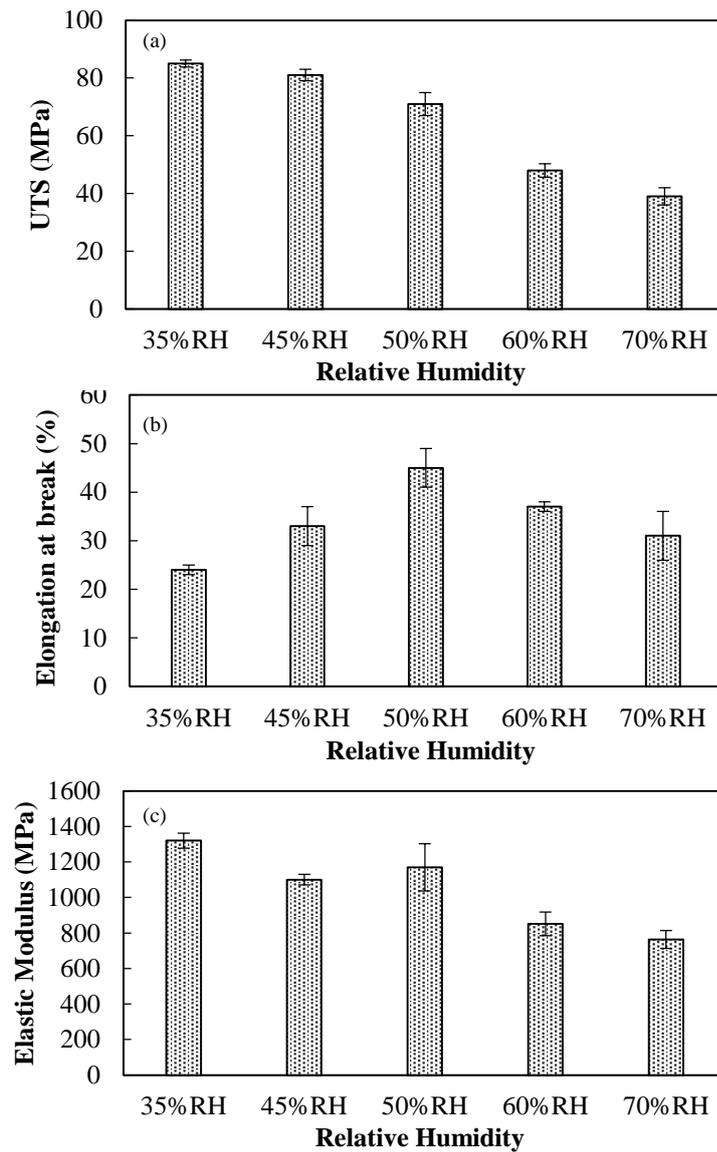


Figure 4.4 Ultimate tensile strength (a), elongation at break (b) and elastic modulus values (c) of the strips extruded from 24% KOH alkaline extracted, desalted xylans, conditioned at designated relative humidity conditions at 23°C for 24 hours prior to tensile testing.

Elastic modulus values (E) also decreased with the increase in the surrounding relative humidity most probably due to the plasticization effect of moisture. Elongation at break (e_b) values increased up to a certain point and then decreased due to the adverse effect of higher relative humidity conditions. The decrease in the

elongation values can be related with excessive plasticization and the strength of the strips reduced significantly causing premature failure with less elongation.

Several researchers reported the effect of heat treatment, specifically drying, on the mechanical, chemical and physical properties of the bio-based polymers and materials. Extruded strips were heat treated at four different temperatures, 60°C, 90°C, 120°C and 150°C, and characterized by moisture uptake and tensile testing in order to determine the possible effects of heat treatment on their moisture content and mechanical properties.

Preliminary experiments, which were conducted with a wider temperature and duration range, revealed that the heat treatment temperature has a more profound effect than the treatment duration so the duration was kept constant at 1 hour. The maximum heat treatment temperature was kept at 150°C in line with the degradation temperature of the hemicellulose which starts around 180°C (Lv *et al.* 2009). Besides, 180°C heat treatment deformed the strips which also resulted in strips with lower strength and elongation values.

As shown in Figure 4.5, “different heat treatment temperatures not only caused the strips to have different moisture contents after the moisture conditioning period but also affected the moisture absorption behavior of the strips, increasing the time necessary for the moisture content of the strips to reach equilibrium. In other words, moisture uptake took place at a slower rate and to a lesser extent as the heat treatment temperature was increased. The untreated strips attained equilibrium at the first day of conditioning and the water content of these strips was 12% both at the end of one day and seven days of conditioning. On the other hand, the strips heat-treated at 150°C had a water content of only 7% at the end of one day of conditioning, which increased to 8.5% at the end of the fifth day and stayed constant. The moisture uptake of the 150°C heat-treated strips were further tracked for 30 days to ensure that they reached their equilibrium moisture content no increase in moisture content” was observed at the end of 30 days (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry).

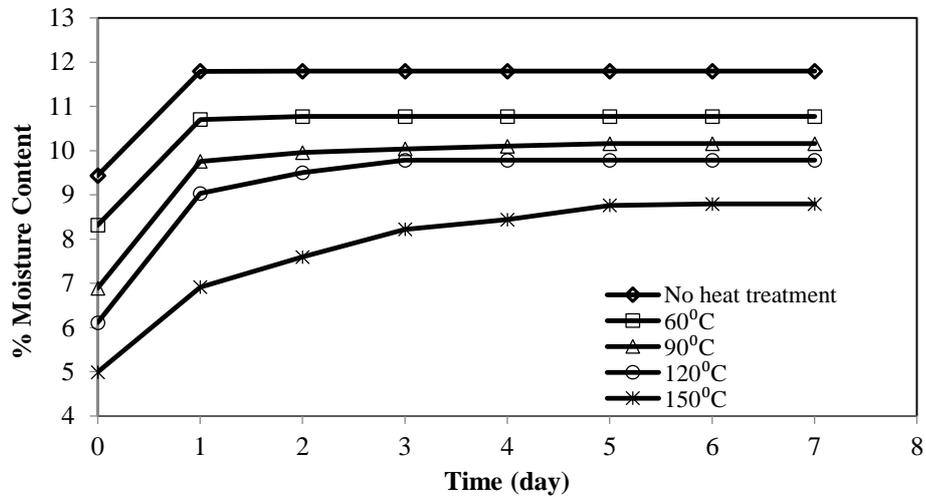


Figure 4.5 Moisture absorption behavior of the 24% KOH extracted, desalted xylan strips upon conditioning at 50% RH and 23°C that were heat treated at different temperatures for 1 hour together with their untreated counterpart. The 0th day data show the initial moisture contents of the strips at ambient conditions (25% RH at the time of the experiment)

The ultimate tensile strength (UTS), elongation at break (e_b) and elastic modulus (E) values of the xylan strips that were heat treated at four different temperatures for 1 hour are shown in Figure 4.6. The strips were conditioned at 23°C and 50% RH for a period of one day as in the usual procedure and seven days to ensure that all the strips had reached their equilibrium moisture content. As shown in Figure 4.6a, increasing the heat treatment temperature resulted in increased UTS values. This effect was more substantial for the strips conditioned for one day compared to those conditioned for seven days, since the moisture contents of the strips were lower at the first day compared to the seventh day (Figure 4.5). Following the heat treatment conducted at 150°C for 1 h, UTS of the strips increased from approximately 70 MPa to 120 MPa and 100 MPa for the strips conditioned for one day and seven days, respectively.

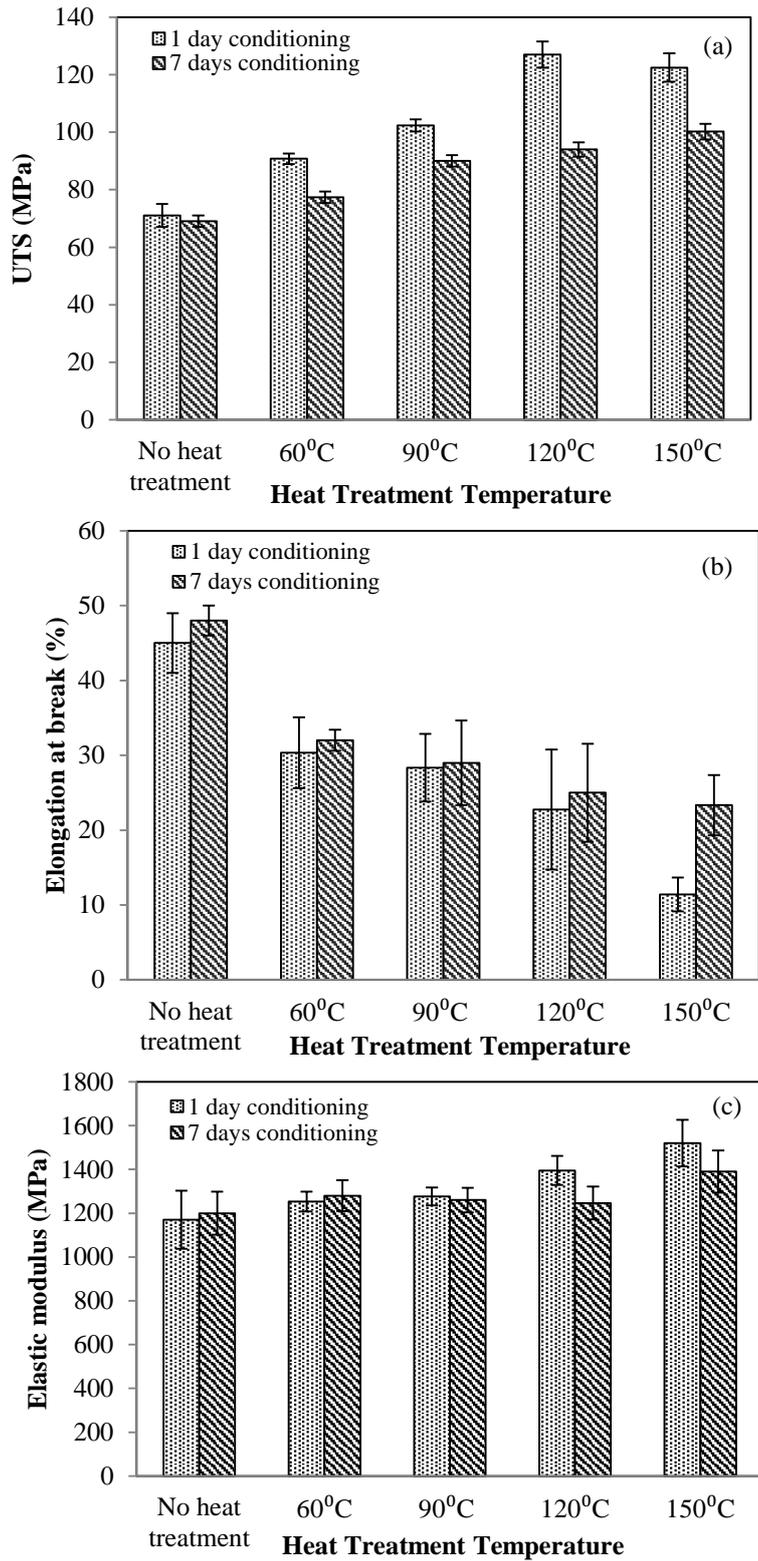


Figure 4.6 Ultimate tensile strength (a), elongation at break (b) and elastic modulus values (c) of the 24% KOH extracted, desalted xylan strips with and without heat treatment. Prior to tensile testing, the strips were conditioned at designated periods at 23°C and 50% RH.

A similar trend to that of the UTS took place for the modulus of the strips (Figure 4.6c) although the increase in the E values with increasing heat treatment temperature was relatively small compared to the increase in the UTS values.

The effect of heat treatment on the strips' modulus was most notable at a heat treatment temperature of 150°C. It should be noted that the tensile testing was conducted without an extensometer which resulted in underestimated E values; however the trend of the E values were not expected to change and it reflects the changes in the flexibility of the strips upon heat treatment.

“Unlike the UTS and E values, increasing the heat treatment temperature resulted in lower e_b values for the strips (Figure 4.6 b). This was especially notable for the strips conditioned for one day prior to tensile testing where the strips heat-treated at 150°C had the lowest e_b value. On the other hand, the e_b values of the strips conditioned for seven days did not decrease considerably between heat treatment temperatures of 90°C and 150°C” (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry).

“Xylan type hemicelluloses are highly hydrophilic polymers and the plasticizing effect of water on such polymers is well-known. Considering this issue, the changes induced on the mechanical properties of xylan strips by heat treatment and different conditioning periods should likely be related to the water content of strips. Heat treatment did not have an additional effect on the mechanical properties of the strips, other than introducing moisture content differences, which was disclosed by comparing the mechanical properties of a native and a heat treated strip at the same moisture content” (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry). Native xylan strips conditioned at 35% relative humidity for one day and 90°C, 1 hour heat treated strip conditioned at 50% relative humidity for seven days had the same moisture content around 9.5% and the ultimate tensile strength values of the strips were 85 MPa and 90 MPa, respectively, which were statistically the same according to 2-sample t-test ($p=0.16>0.05$).

“On the basis of the previously mentioned plasticizing effect of water, the differences in the moisture contents of the strips are crucial for understanding the differences in the mechanical properties of the strips that took place following the heat treatment. Increasing the heat treatment temperature increased the UTS and E values most likely because the strips had less water in them, which resulted in a decreased plasticization of the strips. This decreased plasticization had an opposite effect on the ductility of the strips where increasing the heat-treatment temperature led to lower e_b values. The differences in the mechanical properties of the strips treated at the same temperature but conditioned for different periods of time also deserve attention. These differences were most remarkable for the strips treated at 120°C and 150°C, which were the strips that needed the most time to reach to equilibrium water content. Thus these two types of strips had the greatest difference between their water contents recorded at the first and the seventh day of conditioning, which eventually resulted in larger differences to occur in their mechanical properties with respect to conditioning period compared to the strips treated at lower temperatures” (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry). Although, decrease in moisture contents of the strips upon heat treatment reduced the elongation at break values due to less plasticization with moisture, materials with higher strength and stiffness can be obtained.

4.2.1.2 Effect of heat treatment on the chemical, thermal and the morphological properties

“In order to further understand the relation between the moisture content of the strips and their mechanical properties, the dimensions of the strips after heat-treatment and after seven days conditioning period were recorded to calculate the strips’ volume after each step. Heat treatment had a major impact on the volume of the strips recorded after the heat-treatment and the conditioning periods. As shown in Table 4.4, increasing the heat-treatment temperature resulted in increased shrinkage of the strips where the swelling of the strips during the subsequent conditioning period took place at a lesser extent with increasing heat-treatment temperature. In line with the

previous results, the effect of heat-treatment temperature on the shrinkage and swelling of the strips was most evident after the heat-treatment performed at 150°C. These strips shrunk the most after the heat-treatment and volume was decreased by 7.5% where the volume increase was recorded as 6.3% after the seven days conditioning period, which was less than all the other strips. The shrinkage and swelling of the strips is related to water evaporation and absorption, respectively. Thus it appears that higher heat-treatment temperatures decrease the moisture uptake of the strips leading to lower equilibrium moisture contents and hence, lower plasticization, which results in a more closely packed structure with less free volume in macroscopic level compared to the strips treated at lower temperatures. As expected, these differences associated with the volume of the strips eventually affect their mechanical properties due to the different levels of interactions between the xylan polymer chains. Increasing the heat treatment temperature results in lower free volumes in macroscopic level leading to increased chain interactions, which further results in increased ultimate tensile strength and decreased elongation at break values” (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry).

Table 4.4 Volume changes of the 24% KOH extracted, desalted xylan strips by heat treatment and subsequent conditioning steps

Heat Treatment Temperature	Volume change at the end of heat treatment (%)	Volume change at the end of conditioning (%)^a
No heat treatment	-	17.2±1.8
60°C	-1.7±0.1	14.1±2.5
90°C	-4.0±0.4	11.0±1.5
120°C	-5.2±1.2	8.5±1.1
150°C	-7.5±1.2	6.3±1.7

^aStrips were conditioned at 23°C and 50% RH for seven days.

Water solubility properties of xylan based materials are among the most important properties that play a vital role for potential packaging applications due to the requirement of low water solubility for the integrity of the materials. Although

moisture sensitivities of the strips decreased upon heat treatment; water solubility values were not significantly affected as can be seen in Figure 4.7. Methods which only induce conformational changes might not be as effective as chemical modifications since the solubility is strongly related with the interaction between xylan and water, so heat treatment at the temperatures tested might not be sufficient to ensure low water solubility.

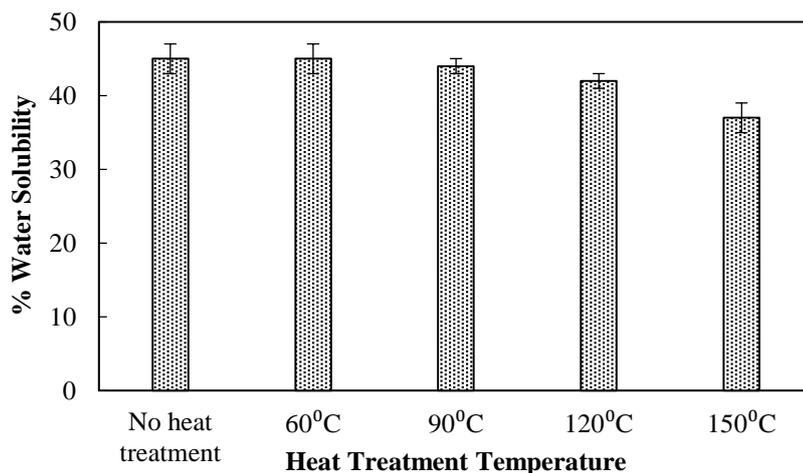


Figure 4.7 Water solubility of the strips extruded from 24% KOH alkaline extracted, desalted xylans, that were heat treated at designated temperatures for 1 hour. The tests were conducted at room temperature after 1.5 hours of dissolution at a solid loading of 1% (w/v).

“Heat treatment is used to increase the dimensional stability and durability of wood based materials by decreasing their moisture uptake; the changes induced by the heat-treatment at higher temperatures are generally attributed to the chemical transformations taking place in the wood internal structure (Esteves *et al.* 2009). As shown in Figure 4.8, both the untreated and 150°C, 1 hour heat-treated strips had the same infrared spectrum, indicating that degradation of xylans did not occurred upon heat treatment. The absorption peaks seen in Figure 4.8 are characteristic bonds of xylan structure. Intense peaks around 1040 cm^{-1} are attributed to C-O and C-O-C stretching of xylans (Kacurakova *et al.* 1994) and small peaks around 1160 cm^{-1} indicate arabinose residues (Egües *et al.* 2014) verifying a xylan backbone with

arabinose substitutions. Smaller but sharper peak around 890 cm^{-1} is attributed to the β -glycosidic linkages between the sugar units (Gupta *et al.* 1987). The broad peak around 3350 cm^{-1} and the peak around 2850 cm^{-1} are assigned to C-H stretching and -OH stretching of the xylans, respectively (Ma *et al.* 2012)” (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry).

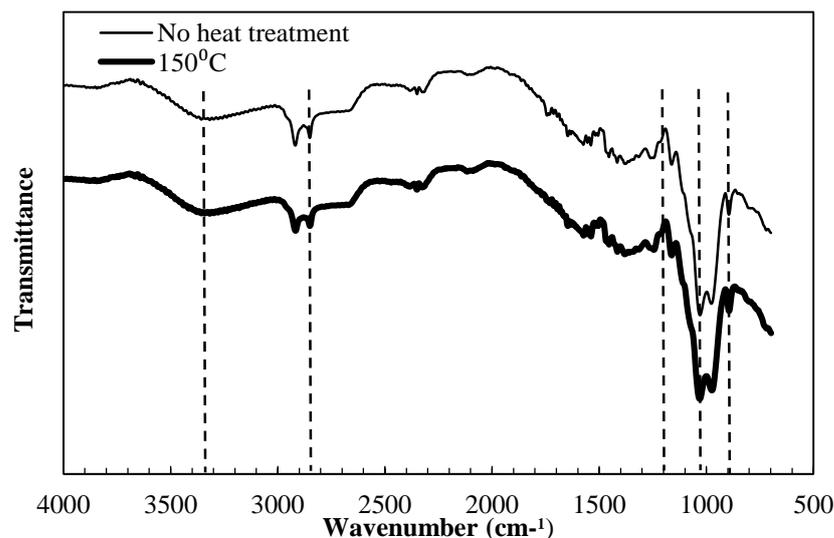


Figure 4.8 Infrared spectra of untreated and 150°C, 1 hour heat treated strips extruded from 24% KOH alkaline extracted, desalted xylans

The impact of heat treatment differs depending on the temperature and duration of the treatment. Heat treatment temperatures above 150°C causes permanent changes in the physicochemical properties of wood materials (Korkut *et al.* 2008). High temperature heat treatments result in reduced hydrophilicity mainly due to the increased crystallinity of cellulose, (Petrisans *et al.* 2003; Chen *et al.* 2011, Kacikova *et al.* 2013), cross-linking of lignin (Acharjee *et al.* 2011) or degradation of hemicelluloses (Brito *et al.* 2008, Rowell *et al.* 2008). Heat treatment at lower temperatures has also been shown to reduce the hydrophilicity of wood due to the conformational changes in the wood polysaccharides without chemical modifications (Hakkou *et al.* 2005). Changes in moisture uptake behaviours and mechanical properties of the strips might be related with the conformational changes of the xylans.

As shown in Figure 4.9, “thermal analysis of the untreated and 150°C, 1 hour heat treated strips also represent similar thermal degradation curves under nitrogen atmosphere. Maximum weight loss rates due to the degradation of hemicelluloses were observed at 293°C for both of the strips showing that thermal behaviors of the strips do not change by heat treatment” (Reproduced from Akkus *et al.* 2014 with permission from the Royal Society of Chemistry).

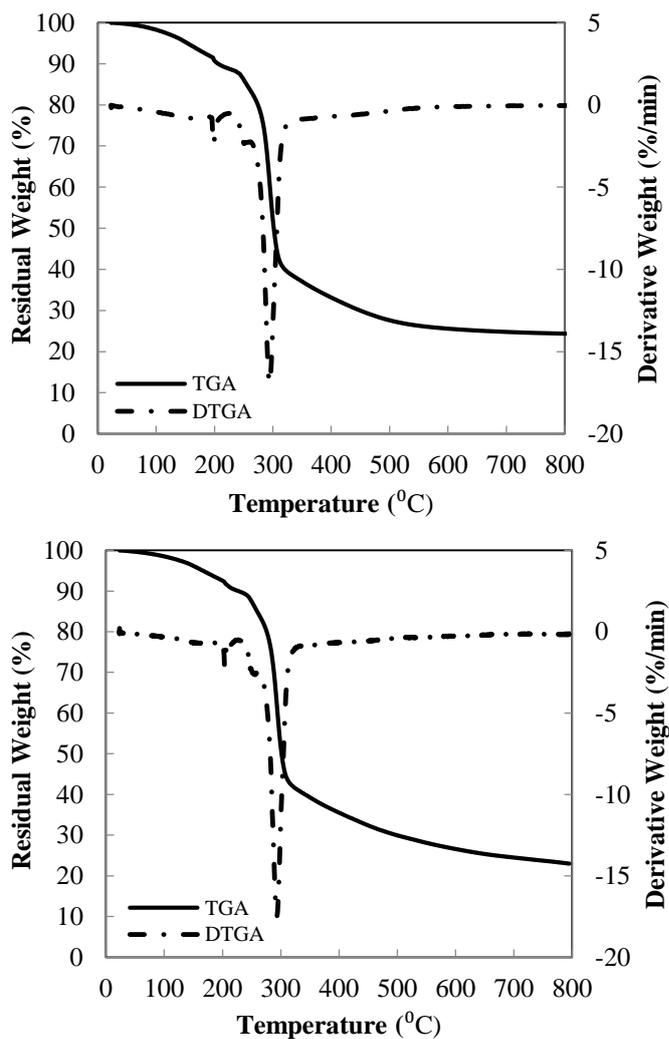


Figure 4.9 Thermogravimetric (TGA) and differential thermogravimetric (DTGA) curves of the untreated (a) and 150°C, 1 hour heat treated (b) strips extruded from 24% KOH extracted, desalted xylans.

Analogous to the similarities observed between the untreated and heat treated strips regarding the infrared spectra and thermogravimetric analysis, heat treatment resulted

in a similar morphology with that of the untreated strips (Figure 4.10). Both the untreated and heat treated strips had a quite homogenous surfaces indicating that the evaporation of water during heat-treatment did not cause any defects, which would negatively affect the mechanical properties of the films. The slight difference in the roughness of the fractured surfaces might be related with the changes in mechanical properties upon heat treatment. Decrease in elastic modulus and the elongation at break values of the strips upon heat treatment might be responsible for the difference in fracture mechanisms since the morphology of untreated strip exhibited more ductile behaviour than the heat treated strip.

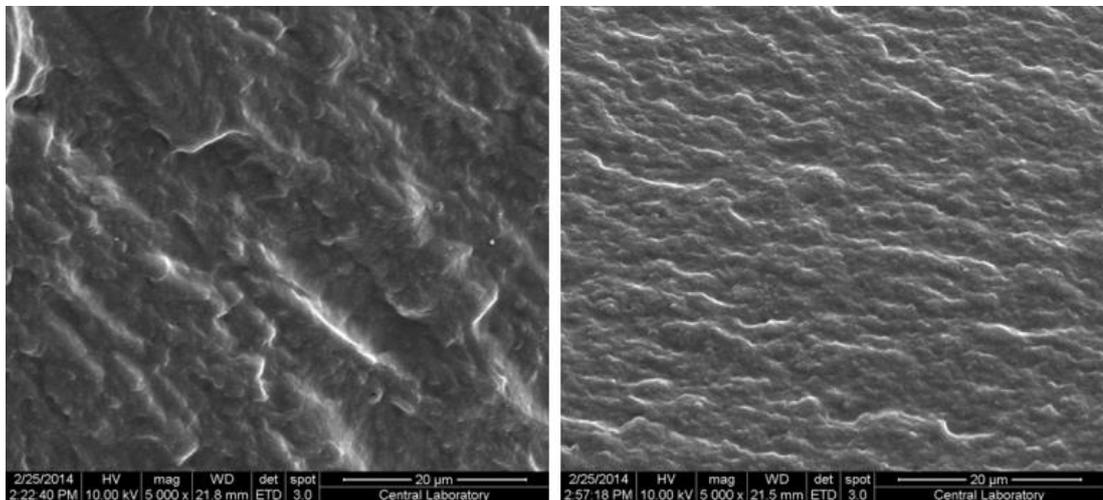


Figure 4.10 Scanning electron microscopy of the fractured surfaces for untreated and 150°C, 1 hour heat treated strips from 24% KOH alkaline extracted, desalted xylans. Left image represents the native strips and the right image represents the heat treated strips. Strips were broken in liquid nitrogen.

As a summary, the effect of heat treatment on the moisture sensitivities of the extruded xylan strips were investigated by utilizing treatment temperatures between 60°C and 150°C. Moisture sensitivities of the strips were reduced upon heat treatment and the equilibrium moisture contents of the strips was reduced as the heat treatment temperature was increased. Although moisture uptake of the strips at 50% relative humidity conditions decreased nearly 30% upon 150°C heat treatment, water

solubility values of the heat treated materials was not affected significantly, since heat treatment did not induce any changes in chemical structure of the xylans. Decrease in moisture contents of the strips upon heat treatment also provided materials in higher strength but reduced flexibility due to reduced plasticization with moisture. Upon heat treatment at 150°C, elongation at break values were reduced from 45% to 25%; however the ultimate tensile strength values increased from 70 MPa to 100 MPa at 50% relative humidity conditions. Although water solubility problem still remain as an issue as the physical changes introduced by heat treatment are not as effective as chemical modifications, the method can be still be utilized for short-term usage applications that are not in direct contact with water but still requires less moisture sensitive materials. By applying heat treatment, xylan based materials with enhanced mechanical properties and moisture sensitivities can be obtained particularly if materials with high tensile strength and reasonable elongation at break values are desired (Akkus *et al.*, 2014).

4.2.2 Acetylation of xylans in the presence of potassium acetate

Extraction procedures with alkaline solutions are often preferred to isolate high molecular mass hemicelluloses (Benko *et al.* 2007), which consist of dissolution, neutralization and ethanol precipitation steps (Bahcegul *et al.* 2012; García *et al.* 2013; Jiang *et al.* 2014). Besides those steps, an additional purification step is usually applied to remove the salts that are formed during the neutralization step, since the presence of salts may deteriorate mechanical properties of hemicellulose based materials (Egüés *et al.* 2014; Mikkonen *et al.* 2009). However, a recent study by Bahcegul *et al.* (2014) showed that potassium acetate (KAc), which is formed during the neutralization of potassium hydroxide (KOH) and acetic acid, improves both film formation and mechanical properties of xylan-based films revealing that an additional purification step might not always be necessary depending on the type of salt. The present section shows that KAc, which is inherently produced during the alkaline extraction of hemicelluloses, is also helpful to fulfill the acetylation reaction showing

an efficient way to obtain more hydrophobic acetylated xylans without the use of toxic catalysts such as pyridine. A commonly applied purification step to remove KAc was also eliminated, proving the significance of utilizing KAc in the acetylation of xylans. The parameters used throughout acetylation of xylans in the presence of KAc was outlined in Table 4.5

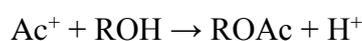
Table 4.5 Parameters used for acetylation of KAc containing xylans and the strips

Xylan Extraction	Purification	Additive & Concentration	Extrusion Temperature	Heat Treatment	Acetylation
10% KOH	Desalted	-	-	-	60°C 10 min
24% KOH	No desalting*		90°C		90°C 30 min
					120°C 1 h
					2 h
					2.5 h
					4 h
					8 h

*KAc containing xylans

The extent of the acetylation reaction was determined by weight gain analysis and the effect of KAc on the acetylation was verified by ATR-FTIR analysis. Native and acetylated xylans were characterized by their water solubility, moisture uptake and thermal degradation behaviors to verify the effect of KAc in obtaining hydrophobically modified xylans without the use of catalysts.

A classic procedure of acetylation involves the use of catalysts like sulfuric acid or pyridine (Sato *et al.* 2003; Xu *et al.* 2010; Zhang *et al.* 2013 and Egiés *et al.* 2014). N-bromosuccinimide, 4-dimethyl aminopyridine, iodine (Ren *et al.* 2007), potassium carbonate and potassium acetate were also used as a catalysts in acetylation of hemicellulose and wood (Sun *et al.* 2002; Sun *et al.* 2004; Ren *et al.* 2007; Obataya *et al.* 2008; and Özmen *et al.* 2013). Different mechanisms are involved in acid or based catalyzed acetylation, however both mechanisms necessitate the ionization of the acetic anhydride and the substitution of functional groups (Schenk, 1968).



Salts are known to serve as basic catalysts for acetylation and act as a nucleophile accelerating the ionization of acetic anhydride (Schenk, 1968), but currently not utilized for the acetylation of hemicelluloses. Acetylation of xylans were studied by taking the advantage of inherently produced potassium acetate during the alkaline extraction. Xylans were alkaline extracted by two different alkaline concentrations 10% and 24%, which represent the lowest alkaline concentration to obtain a reasonable xylan yield and a relatively high alkaline concentration, to investigate the effect of the amount of the residual salt on the acetylation. As explained in Section 4.1, extracted xylans had similar lignin content and monosaccharide composition and only differ in terms of their salt contents which were around 16 wt% and 32 wt%. Acetic anhydride was used as an acetylating reagent and the method was adopted from Sun *et al.* (2002) with some modifications. Initially, the reaction temperature and duration was set to 120°C and 30 minutes and xylans were mixed with acetic anhydride in a flat bottom round flask at 120°C under reflux without any additional solvent or catalysts. Water solubilities of the acetylated KAc containing xylans that were extracted with two different alkaline concentrations were determined and compared with their desalted counterparts (Figure 4.11)

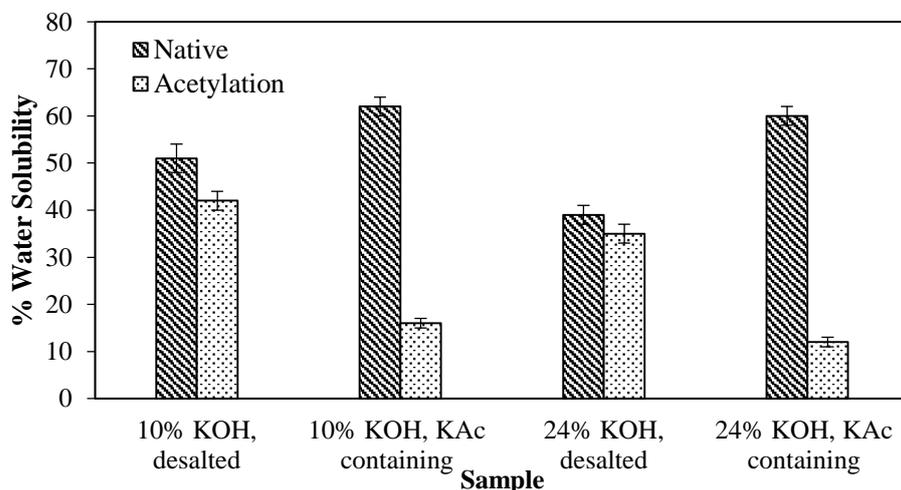


Figure 4.11 Water solubilities of native and acetylated xylans that were extracted at different conditions (10% KOH and 24% KOH extracted xylans contain 16% and 32% potassium acetate, respectively, where desalted xylans contain 1% potassium acetate.)

As can be inferred from the Figure 4.11, native xylans were highly soluble in water regardless of the extraction conditions, where the water solubility of KAc containing samples being higher due to their KAc content. Upon acetylation, water solubilities of KAc containing xylans were significantly decreased by around five fold. A slight decrease in water solubility of desalted xylans upon acetylation can be explained by the effect of heat applied during reaction in line with the results of the Section 4.2.1. At the reaction conditions tested, the increase in salt concentration did not significantly affect the solubility values of the acetylated KAc containing xylans, so the use of lower alkaline concentrations seems more favorable. These preliminary results showed the possibility of converting xylans into more hydrophobic forms by a very simple acetylation procedure in the presence of KAc. Parametric studies on acetylation of xylans were further conducted by utilizing 10% KOH extracted xylans.

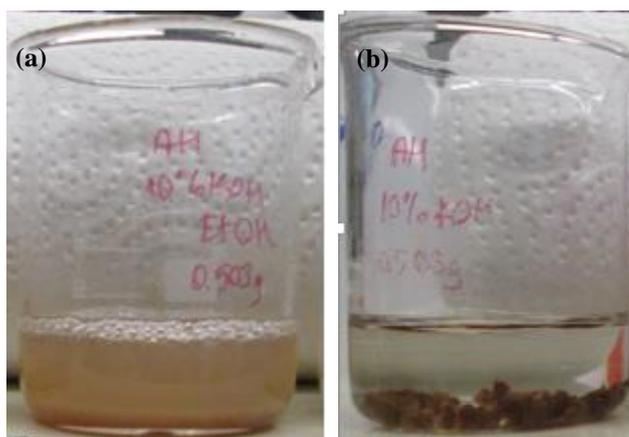


Figure 4.12 Appearances of the native and acetylated xylans in water after 1.5 hours of mixing. (a) represents 10% KOH extracted, KAc containing native xylans and (b) represents 10% KOH extracted, KAc containing acetylated xylans.

4.2.2.1 Effect of reaction parameters on the acetylation of xylan polymers

Acetylation reaction was carried out by reacting 10% KOH extracted xylans in the presence or absence of KAc with acetic anhydride as the acetylating agent. The reaction was simply followed by determining weight gain (WG) values regarding the

exchange of hydroxyl groups with acetyl groups which had been addressed in many studies as a facile method to discuss the success of acetylation (Xie *et al.* 2007; Stefke *et al.* 2009). Table 4.6 shows the percent weight gain values of xylan polymers upon acetylation together with the reaction conditions and their corresponding sample codes.

Table 4.6 Percent weight gain values of 10% KOH extracted desalted or KAc containing xylans at different reaction temperatures and durations.

Sample Code	Sample Type	Reaction Temperature	Reaction Time	% Weight Gain
S	KAc containing xylan	-	-	-
DS	Desalted xylan	-	-	-
Effect of KAc				
S A120-1h	KAc containing xylan	120°C	1 hour	17.6±0.6
DS A120-1h	Desalted xylan	120°C	1 hour	0.1±0.2
DS IA120-1h*	Desalted, KAc impregnated xylan	120°C	1 hour	18.1±1.0
Effect of reaction temperature				
S A60-1h	KAc containing xylan	60°C	1 hour	0.2±0.1
S A90-1h	KAc containing xylan	90°C	1 hour	4.6±0.6
S A120-1h	KAc containing xylan	120°C	1 hour	17.6±0.6
Effect of reaction duration				
S A120-15	KAc containing xylan	120°C	15 min.	6.7±0.7
S A120-30	KAc containing xylan	120°C	30 min.	13.5±0.7
S A120-1h	KAc containing xylan	120°C	1 hour	17.6±0.6
S A120-2h	KAc containing xylan	120°C	2 hours	20.5±0.8
S A120-4h	KAc containing xylan	120°C	4 hours	22.7±0.5
S A120-8h	KAc containing xylan	120°C	8 hours	23.5±0.7

* Xylans were first desalted and then impregnated with KAc as a control experiment.

The effect of KAc on acetylation was revealed when S A120-1h and DS A120-1h were compared, which were obtained by reacting the KAc containing and desalted xylans with acetic anhydride at 120°C for 1 hour, respectively. According to the weight gain values of S A120-1h and DS A120-1h, the presence of KAc triggered the reaction leading to a substantial increase in the weight gain values of modified xylans from 0.1% to around 18%. The positive effect of KAc was further confirmed by acetylating desalted xylans that were subsequently impregnated with 16%

commercial KAc (DS-I A120-1h) to resemble the salt content of the inherently KAc containing xylans. Both S A120-1h and DS-I A120-1h gave similar weight gain values verifying that KAc has a significant effect on acetylation. The weight gain values directly reflect the degree of acetylation because neither KAc leached out nor acetic anhydride or any other by-products retained within the acetylated xylans. Optimum reaction conditions for acetylation of xylans in the presence of KAc were determined in terms of temperature and time. As expected, WG values increased with the increasing of temperature. WG of KAc containing acetylated xylans at 60°C, 90°C and 120°C (S A60-1h, S A90-1h and S A120-1h) were 0.2%, 4.6% and 17.6% respectively, showing that the reaction did not take place at 60°C but considerably speed up at 120°C. The differences in the increments of WG values can be attributed to the temperature induced breaking of hydrogen bonds, rendering reactive chemical sites available (Rana *et al.* 1997; Sun *et al.* 2004) and enhancing the reaction synergistically with KAc. The effect of time on the reaction efficiency was also investigated by keeping the reaction temperature constant at 120°C (Figure 4.13). WG values of S A120-15, S A120-30 and S A120-1h increased significantly with increasing reaction time but the weight increase proceeded at slower rates for the reaction durations longer than 1 hour. WG values of 20.5%, 22.7% and 23.5% for S A120-2h, S A120-4h and S A120-8h, respectively, showed that continuing the reaction at 120°C more than 4 hours was not necessary, since doubling the reaction time did not significantly affect WG values of the modified xylans.

Weight gain values are around 20% is considered reasonable, where the values for most of the pyridine catalyzed acetylation reactions of hemicelluloses were around also around 20% at most. Rana *et al.* (1997) reported the maximum weight gain as 18% for the acetylation of jute fiber in an acetic anhydride-pyridine system at 120°C for 4 hours. Sun *et al.* (2002) studied the acetylation of rice straw at 100 and 120 °C for different durations between 1 hour and 4 hours in the presence of tertiary amine catalysts, pyridine, 4-dimethylaminopyridine, N-methylpyrrolidine, and N-methylpyrrolidinone. They reported various weight gain percentages over the range 4% to 15%, where the maximum gain was found to be 15.4% for dimethylaminopyridine catalyzed acetylation of rice straws.

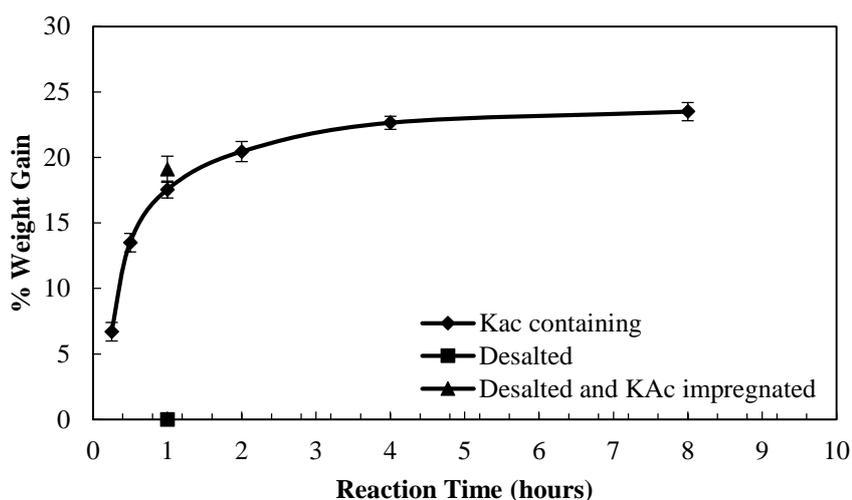


Figure 4.13 Reaction progress curves of 10% KOH extracted potassium acetate containing, desalted and KAc impregnated xylans acetylated at 120°C for different durations (S A120's, DS A120-1h and DS IA120-1h, respectively).

Besides weight gain analysis, molecular weight determination is another tool to measure the success of acetylation. Viscosity average molecular weight of the samples DS, DS A120-1h, S, S A120-1h and S A120-4h were determined by capillary viscometer (Eremeeva *et al.* 1993) and shown in Table 4.7. Higher molecular weight of the desalted xylans could be associated with the loss of smaller molecular weight xylans during desalting step. In line with the weight gain values, molecular weight of the KAc containing xylans increased due to the introduction of acetyl groups. As desalted samples (DS) can not be acetylated, no change in their molecular weight was expected. Although molecular weight determination of hemicelluloses is debatable due to their uncontrollable solubility characteristics which depend on the type, degree of substitution, and linkages with the surrounding network; the change in the molecular weight values might provide information about the possible increases in molecular weight by the introduction of acetyl groups or indicate any degradation during the reaction. When %WG values of S A120-1h and S A120-4h were considered, theoretical molecular weights were expected to be around 30,000 g/mol and 31,000 g/mol, with a 17.6% and 22.7% increase in the molecular weight of the

KAc containing xylans (25,000 g/mol), respectively. The theoretical molecular weight were close to the values found by capillary viscometry, which might indicate that there was no significant degradation upon reaction.

Table 4.7 Viscosity average molecular weight of the samples determined by capillary viscometry

Sample Code	Molecular Weight
DS	40,000 g/mol
DS A120-1h	39,000 g/mol
S	25,000 g/mol
S A120-1h	31,000 g/mol
S A120-4h	32,000 g/mol

4.2.2.1.1 Attenuated total reflectance-Fourier transform infrared spectroscopy

Infrared spectroscopy is extensively used for plant cell wall analysis and has been very useful for studying hemicelluloses, celluloses and their functional groups (Kacurakova *et al.* 2001). The acetylation of xylans can be easily verified by FTIR analysis since the characteristic peaks for acetyl groups can be clearly identified in the spectrum. The spectra of desalted, KAc containing and acetylated xylan samples can be seen in Figure 4.14. The characteristic peaks of xylan structure can be seen in the spectra of DS (a) and S (c). Sharp but small peaks around 890 cm^{-1} are attributed to the β -glycosidic linkages between the sugars units (Gupta *et al.* 1987). C-O and C-O-C stretching of xylans can be attributed to intense peaks around 1040 cm^{-1} (Kacurakova *et al.* 1994) and small peaks around 1160 cm^{-1} indicate arabinose substitutions (Egüés *et al.* 2014). The peak around 2850 cm^{-1} are assigned to the C-H stretching and the broad peak around the 3350 cm^{-1} represents -OH stretching. The spectrum of the xylan containing KAc (S) has two additional peaks that are absent in the spectrum of the desalted xylan (DS) around 1530 cm^{-1} and 1360 cm^{-1} . Those peaks can be correlated with the salts of carboxylates and is an evidence of KAc salt in the structure (Smith, 1998).

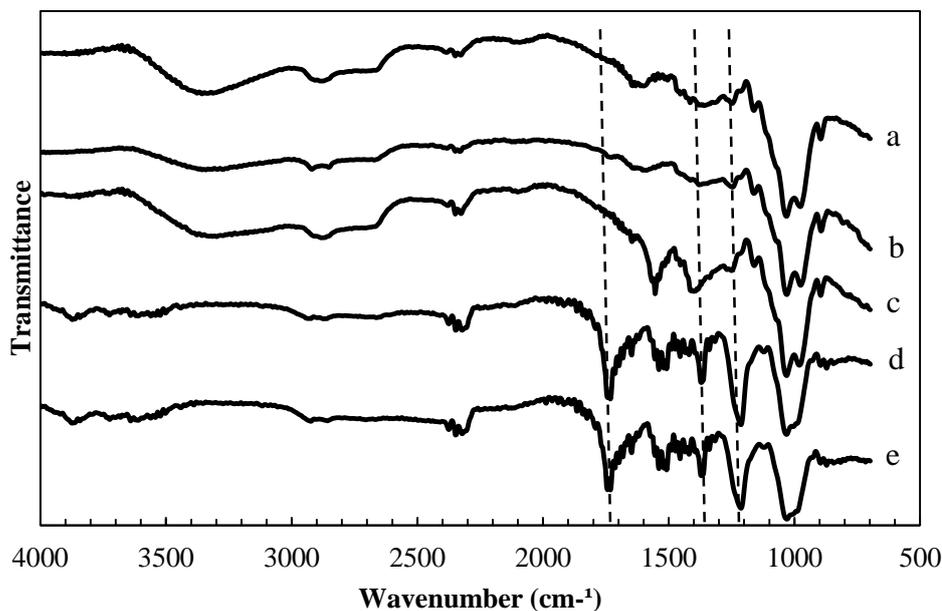


Figure 4.14 The infrared spectra of the 10% KOH extracted desalted samples DS (a), DS A120-1h (b), and the potassium acetate containing samples S (c), S A120-1h (d) and S A120-4h (e). “A” stands for the acetylated samples together with the reaction conditions.

The acetylation of KAc containing samples, S A120-1h (d) and S A120-4h (e), were clearly identified by three distinct peaks around 1730 cm^{-1} , 1375 cm^{-1} and 1220 cm^{-1} which are attributed to the three important ester peaks, C=O, -C-CH₃ and -C-O-, respectively (Egüés *et al.* 2014; Sun *et al.* 2004). These three important peaks did not exist in the spectra of DS A120-1h, showing that acetylation can only be achieved for KAc containing samples for the reaction conditions tested. Also, the disappearance of broad band around 3350 cm^{-1} verified the successful exchange of hydroxyl groups with acetyl groups. Results were compared with the conventional pyridine catalyzed acetylation to reveal the effect of KAc. Desalted xylans were acetylated in the presence of pyridine at two different reaction conditions and the reaction was followed by ATR-FTIR.

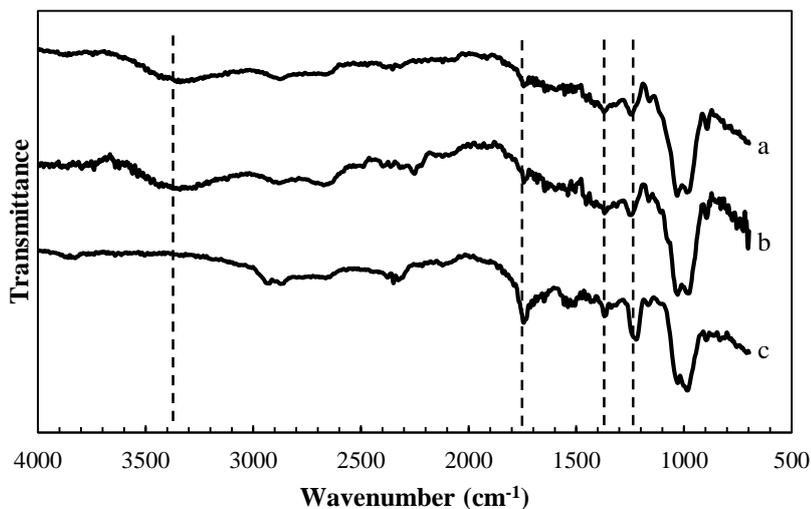


Figure 4.15 The infrared spectra of the 10% KOH extracted desalted sample DS (a) and its acetylated counterparts at 120°C for 1 hour (b) and 120°C for 4 hours (c) in the presence of pyridine as a catalyst.

As can be seen in Figure 4.15, characteristic peaks of acetyl groups were not present in the spectrum (b). Pyridine catalyzed reaction at 120°C for 1 hour did not result in acetylated xylans, whereas KAc containing xylans were successfully acetylated at the same reaction conditions. Acetylation was achieved when the reaction duration was increased to 4 hours (c), but the intensities of the peaks were significantly lower than the sample S A120-4h in Figure 4.14, disclosing the effective acetylation in the presence of KAc.

Weight gain values and FTIR analysis complement each other further solidifying the positive effect of KAc presence on the acetylation of xylans. KAc is known to act as a plasticizer by reducing the intermolecular forces within the polymer (Bahcegul *et al.* 2014). The changes in the molecular packing of the polymer due to the plasticization affect several properties of the materials like their transport properties. These changes were also speculated to effect the occurrence of reactions (Riquelme *et al.* 2015). Previous studies showed that swelling of starch molecules increased the diffusibility of acetic anhydride (Bayazeed *et al.* 1998) and facilitated the

nucleophilic attack by activating hydroxyl groups (Jeon *et al.* 1999). Hill *et al.* (2004) also suggested that wood polymers should be previously swollen to break the intermolecular hydrogen bonds for successful acetylation and the acetylation of xylans in the presence of KAc is thought to be associated with these phenomena.

4.2.2.1.2 Water solubility

Water solubility characteristics of xylans can be altered by the changes in their chemical structure through acetylation (Gröndahl *et al.* 2003). Figure 4.16 shows the percent water solubility values of the KAc containing and desalted xylans together with their acetylated counterparts. Both the KAc containing (S) and the desalted (DS) samples are soluble in water, where the water solubility of S being higher due to its KAc content. As expected, the water solubility of S significantly decreased from 46% to 4% after its acetylation at 120°C for 1 hour (S A120-1h). Although the difference between the water solubilities of S A120-1h and S A120-4h was not significant, further increasing reaction time to 4 hours decreased the water solubility to 2.4%, suggesting that the modified xylans were nearly water insoluble. Contrary to S, the water solubility of DS was only slightly reduced from 35% to 29% as a result of the acetylation reaction at 120°C for 1 hour. Although the acetylation of DS was not successful, the samples experienced a heat treatment during reaction which probably led to a slight decrease in water solubility values (Akkus *et al.* 2014). In line with the previously discussed weight gain values and chemical analysis; water solubility results show that xylans can be converted into more hydrophobic forms by a very simple acetylation procedure in the presence of KAc.

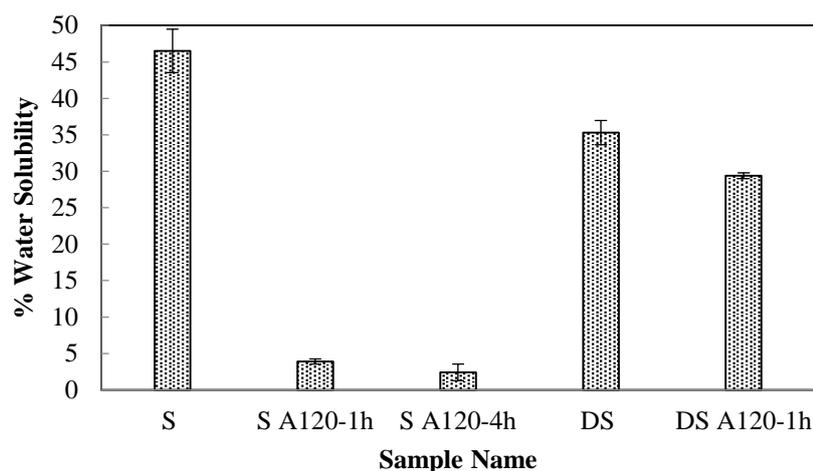


Figure 4.16 Water solubility values of 10% KOH extracted potassium acetate containing (S) and desalted xylans (DS), and their acetylated counterparts at 120°C for 1 hour and 4 hours (S A120-1h, S A120-4h and DS A120-1h).

4.2.2.1.3 Moisture uptake isotherm

Moisture uptake of xylans can be reduced by decreasing the possibility of hydrogen bonding between the hydroxyl groups of xylans with water. The exchange of hydroxyl groups with hydrophobic acetyl groups decreases the tendency of xylan polymers to absorb moisture from the environment as a result of the decrease in the number hydroxyl groups that are available for hydrogen bonding. The equilibrium moisture contents of the samples S, S A120-1h, S A120-4h were recorded at different relative humidity conditions together with DS and DS A120-1h to track the changes in the moisture uptake of the samples induced by acetylation in the presence of KAc. As shown in Figure 4.17, the moisture uptake curves for the non-acetylated samples (S and DS) exhibit the characteristic sigmoidal shape for hydrophilic polysaccharides (Stevanic *et al.* 2012). Both samples had similar equilibrium moisture contents for relative humidity conditions between 0% and 70%. For relative humidity values higher than 70%, the moisture content of S increased at a higher extent than DS due to the presence of KAc, which additionally absorbs moisture (Bahcegul *et al.* 2014). The moisture uptake curves of DS and DS A120-1h showed the same characteristics with a minor decrease in moisture contents of DS A120-1h. Although acetylation

could not be achieved for DS A120-1h, decrease in moisture contents can be attributed to the heating effect that took place during the acetylation reactions (Akkus *et al.* 2014). The thicknesses of the xylan films reduced when they were heat treated due to the permanent reduction in the volumes of the xylan films, which can cause reduction in the moisture uptake of xylans (Akkus *et al.* 2014). The characteristic sigmoidal shape of moisture uptake curve was diminished for S A120-1h and S A120-4h verifying the hydrophobic modifications by acetylation. S A120-1h and S A120-4h have significantly lower moisture contents than S for all of the conditions tested. The difference between the moisture content values increases as the humidity increases. At 90% relative humidity, the equilibrium moisture contents of S, S A120-1h and S A120-4h were determined as 63%, 19% and 12%, respectively. The sample S has moisture content around 12% at 30% relative humidity; whereas S A120-4h attained that value after being conditioned at 90% relative humidity, showing a significant reduction in the moisture uptake of acetylated samples.

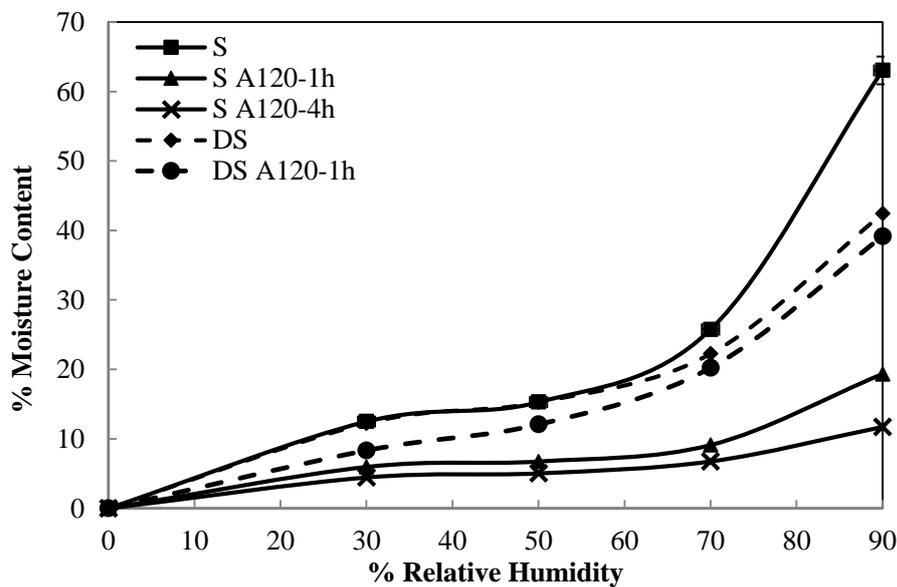


Figure 4.17 Moisture absorption isotherms of 10% KOH extracted potassium acetate containing (S) and desalted xylans (DS), and their acetylated counterparts at 120°C for 1 hour and 4 hours (S A120-1h, S A120-4h and DS A120-1h).

4.2.2.1.4 Thermal Degradation Analysis

Effect of acetylation on the thermal degradation behaviors of KAc containing and desalted xylans were characterized using thermogravimetric analysis under nitrogen atmosphere (Figure 4.18).

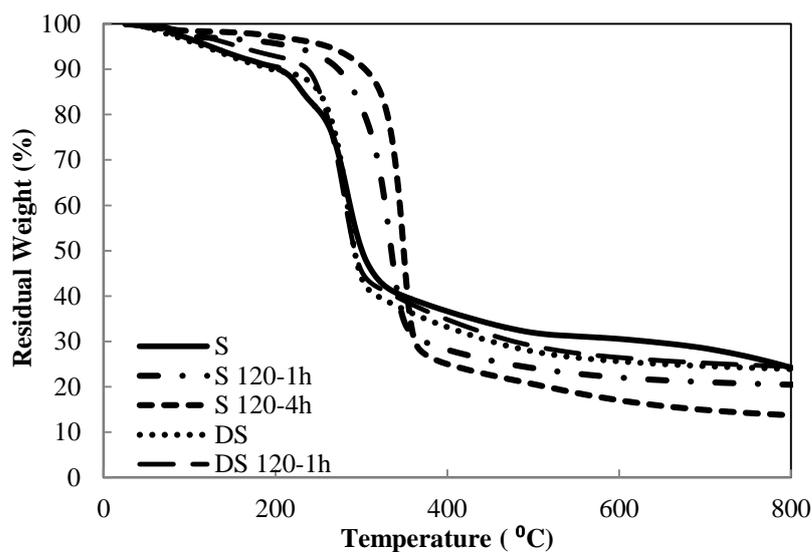


Figure 4.18 Thermal degradation curves of potassium acetate containing (S) and desalted xylans (DS) and their acetylated counterparts at 120°C for 1 hour and 4 hours (S A120-1h, S A120-4h and DS A120-1h).

The initial weight losses of the samples below 150°C can be related to the loss of moisture verifying that acetylated samples, S 120-1h and S 120-4h have lower moisture contents than the non-acetylated samples S, DS and DS 120-1h. The temperatures at which the maximum weight loss occurred for KAc containing xylans, S, S 120-1h, S 120-4h, were determined as 283°C, 333°C, 349°C, respectively. As can be deduced from these results, the thermal stabilities of xylans were greatly enhanced by acetylation in the presence of KAc. Higher thermal stability of the acetylated xylans can be explained on the basis of decreased hydroxyl content since hydroxyl groups takes place in degradation reactions leading to lower thermal stability (Aburto *et al.* 1999; Fundador *et al.* 2012). Increase in the degradation

temperature of acetylated xylans might improve their processing ability by melt processing techniques. The temperatures at which the maximum weight loss occurred for desalted xylans, DS and DS 120-1h, were determined as 284°C and 282°C, respectively. Thermal stability of DS did not change upon reaction with acetic anhydride since acetylation could not be achieved without KAc under these conditions.

Acetylation of xylans by exploiting the inherently produced KAc gave promising results in terms of hydrophobic modifications. These hydrophobically modified xylans must lead to materials with enhanced moisture sensitivities for realistic applications. Preliminary studies on the extrusion of acetylated xylans showed that acetylated xylans crumbled into dust on the screws of the extruder and could not be extruded. To investigate the processibility of acetylated xylans, extrusion was studied in the presence of polysorbate 80 (Tween 80), triacetin, sorbitol and glycerol as plasticizers, the results of which can be seen in Appendix F in details. During the extrusion of acetylated xylans without any additive, maximum torque of the extruder was reached within a few seconds following the feeding. With the use of Tween 80, maximum torque was reached after a couple of minutes. No torque limitation was when triacetin was used and polymers were able to pass through the die, but the strips were fragmented into pieces just after coming out of the die. Continuous strips were formed by the extrusion of acetylated xylans in the presence of sorbitol and glycerol; however the resulting strips were very weak with an ultimate tensile strength around 0.7 MPa at 50% relative humidity. Problems regarding the extrusion of acetylated xylans were by-passed by carrying out the acetylation reaction after the extrusion of native xylans to end up with xylan strips with reduced water sensitivity.

4.2.2.2 Acetylation of extruded xylan strips

Extrusion of acetylated xylans did not give satisfactory results, therefore as an alternative to the extrusion of acetylated xylans, acetylation of extruded native xylans were studied. KAc containing xylans that were extracted by two different alkaline

concentrations were extruded and then acetylated by acetic anhydride. Sample codes of the xylan strips together with their corresponding extraction and acetylation conditions can be seen in Table 4.8.

Preliminary studies showed that acetylation in the presence of lower KAc concentrations necessitate longer reaction times or higher temperatures which caused strips to deform during the reaction. Therefore acetylation studies were conducted with two different alkaline solutions, 10% KOH and 24% KOH. As given in Section 4.1, the salt concentrations of the xylans were 16 wt% and 30 wt%, respectively. Acetylation was followed by ATR-FTIR and the spectra of the samples 10% KOH extracted KAc containing strips (S-10's) and 24% KOH extracted KAc containing strips (S-24's) were shown in Figure 4.19 and Figure 4.20, respectively.

Table 4.8 The sample codes of potassium acetate containing strips extracted by different alkaline concentrations and acetylated at various reaction conditions.

Sample Code	Alkaline concentration	Reaction Temperature	Reaction Time
S-10	10% KOH	-	-
S-10 A90-10	10% KOH	90°C	10 minutes
S-10 A90-30	10% KOH	90°C	30 minutes
S-10 A90-2.5	10% KOH	90°C	2.5 hours
S-10 A120-10	10% KOH	120°C	10 minutes
S-10 A120-30	10% KOH	120°C	30 minutes
S-24	24% KOH	-	-
S-24 A90-10	24% KOH	90°C	10 minutes
S-24 A90-30	24% KOH	90°C	30 minutes
S-24 A120-10	24% KOH	120°C	10 minutes
S-24 A120-30	24% KOH	120°C	30 minutes

The addition of acetate groups can be simply verified by tracking the peaks around 1730 cm⁻¹, 1375 cm⁻¹ and 1220 cm⁻¹. According to Figure 4.19, acetylation of 10% KOH extracted KAc containing strips can only be achieved when longer reaction times are used at 90°C or at higher reaction temperatures, but defects were formed on the surface of the acetylated strips under those reaction conditions. According to

Figure 4.20, 24% KOH extracted, KAc containing strips were successfully acetylated at 90 °C upon 30 minutes of reaction due to their higher KAc content. Acetylation at 120 °C for 10 minutes (S-24 A120-10) and 30 minutes (S-24 A120-30) was also successful but the strips deformed during the reaction by curling up. Mechanical properties and moisture contents of 10% KOH extracted and 24% KOH extracted KAc containing strips at different relative humidity conditions were shown in Figure 4.21. Mechanical properties of the samples S-10 A90-2.5, S-24 A120-10 and S-24 A120-30 could not be determined due to their defects which prevented to conduct reliable measurements.

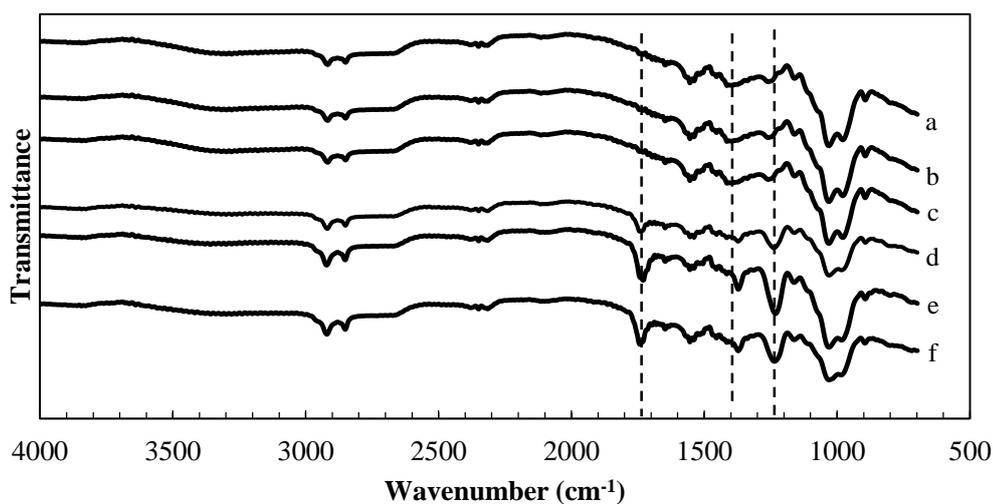


Figure 4.19 The infrared spectra of the 10% KOH extracted potassium acetate containing strips; (a) native (S-10) and their acetylated counterparts (b) at 90°C for 10 minutes (S-10 A90-10), (c) at 90°C for 30 minutes (S-10 A90-30), (d) at 90°C for 2.5 hours (S-10 A90-2.5h), (e) at 120°C for 10 minutes (S-10 A120-10), and (f) at 120°C for 30 minutes (S-10 A120-30).

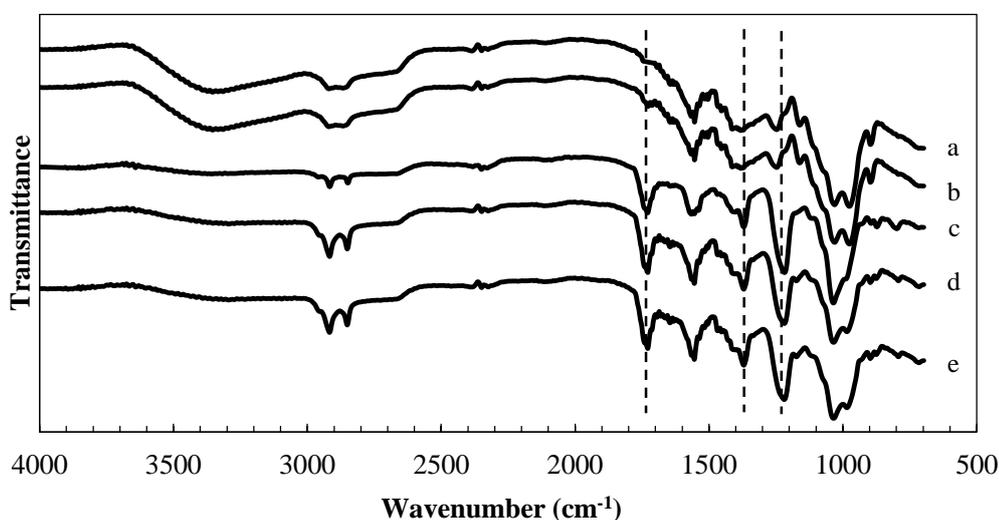


Figure 4.20 The infrared spectra of the 24% KOH extracted potassium acetate containing strips; (a) native (S-24) and their acetylated counterparts (b) at 90°C for 10 minutes (S-24 A90-10), (c) at 90°C for 30 minutes (S-24 A90-30), (d) at 120°C for 10 minutes (S-24 A120-10), and (e) at 120°C for 30 minutes (S-24 A120-30).

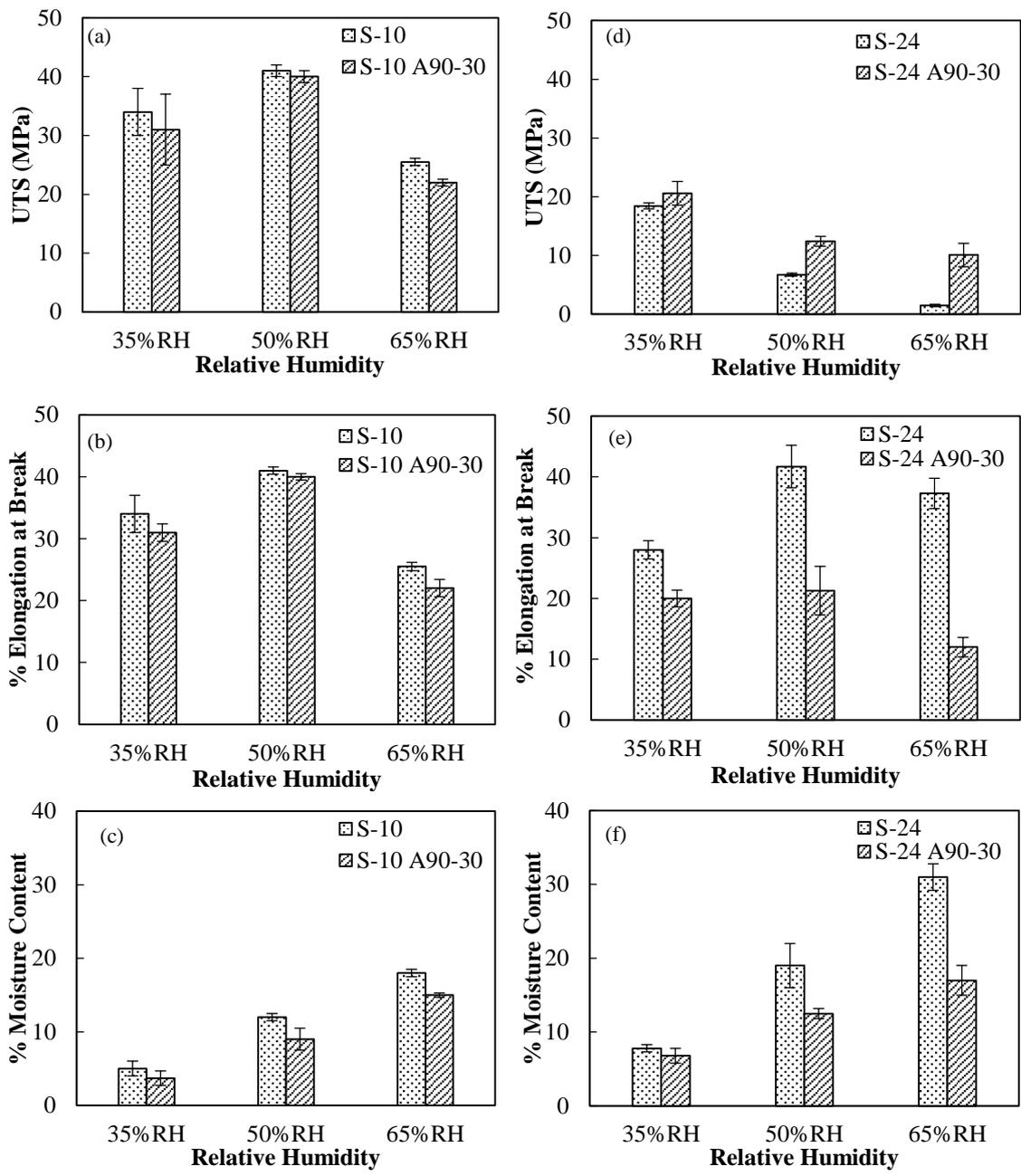


Figure 4.21 Ultimate tensile strength, elongation at break values and moisture contents of the 10% KOH and 24% KOH extracted potassium acetate containing native xylan strips, S-10 and S-24, and their counterparts acetylated at 90 °C for 30 minutes, S-10 A90-30 and S-24 A90-30, respectively. The tests were conducted under 35%, 50% and 65% relative humidity conditions.

First of all, the mechanical properties of the KAc containing xylan strips are significantly lower in strength and higher in moisture content compared to the desalted strips. As outlined in the previous sections (Figure 4.4), desalted xylan strips have ultimate tensile strength values around 70 MPa at 50% relative humidity, which was reduced to 40 MPa and 7 MPa for 10% KOH and 24% KOH KAc containing strips, respectively (Figure 4.21 (a) and Figure 4.21 (d)). Decrease in ultimate tensile strength values of KAc containing strips, especially at high humidity conditions, can be explained by the synergistic plasticizing effect of KAc and the moisture.

As can be inferred from the Figure 4.21 (a), (b) and (c), mechanical properties and the moisture contents of the 10% KOH extracted KAc containing strips did not significantly changed upon acetylation. The results were consistent with the IR spectra results in Figure 4.19 showing that acetylation reaction carried out at 90°C for 30 minutes was not successful. As can be seen from Figure 4.21 (d), ultimate tensile strength values of S-24 significantly decreased by increasing relative humidity. The decrease in ultimate tensile strength values of the S-24 was nearly ten fold when relative humidity increased from 35% to 65%; however this decrease reduced to two fold upon acetylation at 90°C for 30 minutes (S-24 A90-30) most probably due to the changes in moisture sorption behavior of the strips. Elongation at break values in Figure 4.21 (e) decrease upon acetylation which can also be related with their lower moisture contents. As can be in seen in Figure 4.21 (f), S-24 A90-30 absorbs nearly 40% less moisture when conditioned in 65% relative humidity compared to its native counterpart S-24. Those results indicate a decrease in the response of material properties of acetylated xylan strips to different relative humidity conditions, leading to enhanced moisture sensitivities. Water solubilities of the strips were shown in Figure 4.22. In line with the previous results outlined in Figure 4.21, the water solubility characteristics of S-10 also did not altered by acetylation at 90°C for 30 minutes. Despite the lower mechanical properties of 24% KOH extracted KAc containing strips compared to 10% KOH extracted counterparts, almost water insoluble xylan strips can be obtained upon acetylation of them at 90°C for 30 minutes (S-24 A90-30).

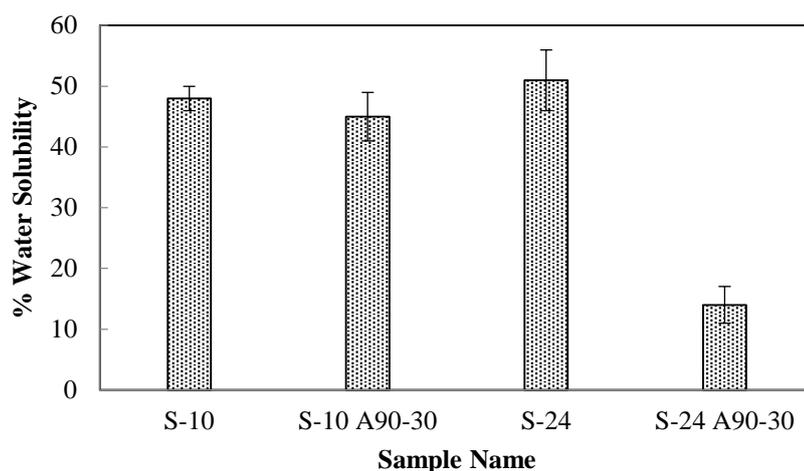


Figure 4.22 Water solubility values of 10% KOH and 24% KOH extracted potassium acetate containing native xylan strips, S-10 and S-24, and their counterparts acetylated at 90 °C for 30 minutes, S-10 A90-30 and S-24 A90-30.

As a summary, acetylation of xylans was studied in the presence of KAc that is formed during alkaline extraction, by retaining them together with xylans without an additional purification step. Effect of KAc content, reaction temperature and reaction time on the xylan polymers were investigated and the acetylation in the presence of KAc was shown to be an easy and efficient method to obtain xylans with low water solubilities and moisture uptake values. Extrusion of KAc containing acetylated xylans were studied, but due to the difficulties regarding their processibility, the resulting strips were very weak. Problems regarding the extrusion of acetylated xylans were by-passed by carrying out the acetylation reaction after the extrusion of native xylans. Significantly less water soluble and less moisture sensitive strips with enhanced mechanical and thermal properties were achieved through the acetylation of KAc containing xylan strips. Optimum mechanical properties with lowest water solubility values were achieved upon the acetylation of 24% KOH extracted KAc containing strips at 90 °C for 30 minutes. Ultimate tensile strength and elongation at break values at 50% relative humidity, and water solubilities of the acetylated strips were around 13 MPa, 23% and 14%, which were reported as 6 MPa, 40% and 50% for their native counterparts, respectively.

4.2.3 Acetylation of xylan strips extruded in the presence of sorbitol and glycerol

Extrusion processing of xylans has been addressed in previous sections and referred as an important step that paves the way to their commercialization. As most of the biopolymers, hemicelluloses in their native forms have poor melt-processing ability and have to be plasticized before processing. Water is the best known plasticizer for biopolymers and hemicelluloses, however the use of water alone might result in brittle materials since the water content of the hemicellulose based materials strongly depend on the moisture content of the storage conditions (Forssell *et al.* 1997). Less volatile plasticizers like glycerol, sorbitol or xylitol are among the most widely used plasticizers to obtain flexible hemicellulose films by solvent casting method (Hansen *et al.* 2008), where glycerol and sorbitol usually outperforms the xylitol plasticized films (Mikkonen *et al.* 2009).

Extrusion of xylans in the presence of sorbitol and glycerol, which are widely used for solvent casting of hemicelluloses, was studied to address utilization of xylans by investigating their melt processing abilities. In addition to this, acetylation of the extruded plasticized strips were also studied to obtain less moisture sensitive and less water soluble materials. In Section 4.2.2, the presence of KAc positively affected the acetylation reaction, which was explained by the reduced intermolecular forces within the polymer increasing the diffusibility of acetic anhydride and facilitating the nucleophilic attack by activating hydroxyl groups. In line with these results, sorbitol and glycerol was also thought to effect the success of acetylation by reducing the intermolecular forces upon plasticization. Acetylation of sorbitol and glycerol plasticized strips were studied by utilizing desalted xylans to eliminate the effect of KAc on mechanical properties and on acetylation. The experimental parameters used in this part of the study is given in Table 4.9.

Table 4.9 The parameters used for the acetylation of xylans in the presence of sorbitol and glycerol

Xylan Extraction	Purification	Additive& Concentration		Extrusion Temperature	Heat Treatment	Acetylation	
24% KOH	Desalted	Sorbitol	10%	90°C	-	120°C	15 min
		Glycerol	20%	120°C			30 min
			30%	150°C			1 hour
			40%				

4.2.3.1 Extrusion of xylans in the presence of sorbitol and glycerol

Extrusion of 24% KOH extracted desalted xylans was studied in the presence of sorbitol and glycerol at different plasticizer concentrations and extrusion temperatures with a constant screw speed at 50 rpm. 10 wt%, 20 wt%, 30 wt% and 40 wt% plasticizer containing desalted xylans were fed to a twin-screw extruder to explore their extrudability at 90°C, 120°C and 150°C. Extrudability of xylan polymers and the sample codes of the experimental sets can be seen in Table 4.10.

As can be seen in Table 4.10, 20 wt% sorbitol addition was not enough to render xylans extrudable for the temperatures tested. Contrary to the 20 wt% sorbitol addition, 20 wt% glycerol containing xylans were extrudable indicating that glycerol exhibited a better plasticizing effect for xylans. For the case of 30 wt% sorbitol containing xylans, extrusion temperatures higher than 90°C enabled the flow of xylans within the extruder, where 40 wt% sorbitol containing xylans were extrudable for all the temperatures tested. Xylans plasticized with glycerol were extrudable for all the extrusion temperatures and concentrations tested except at 10 wt%.

The mechanism of plasticization is being explained by different theories, where the mechanism related with small polar molecules like water, glycerol and sorbitol has been explained by the free volume theory. Although these molecules lead to plasticization through the same mechanism, the difference in their structure may

evoke different plasticization characteristics. The lower molecular weight plasticizers enabling them to easily incorporate into the polymer, which can be correlated with the better plasticization through by glycerol than sorbitol. The difference in their plasticizing effects could also be related with their hydrophilicity since glycerol, being more hydrophilic, is known to be a better plasticizer for many polysaccharide films (Tapia-Blácido *et al.* 2011).

Table 4.10 Extrudability of sorbitol and glycerol plasticized desalted xylans at different plasticizer concentrations and extrusion temperatures.

Sample Code	Plasticizer	Plasticizer Amount (w/w)	Extrusion Temperature	Extrudability
20-Sorb-90	sorbitol	20%	90°C	-
20-Sorb-120	sorbitol	20%	120°C	-
20-Sorb-150	sorbitol	20%	150°C	-
30-Sorb-90	sorbitol	30%	90°C	-
30-Sorb-120	sorbitol	30%	120°C	√
30-Sorb-150	sorbitol	30%	150°C	√
40-Sorb-90	sorbitol	40%	90°C	√
40-Sorb-120	sorbitol	40%	120°C	√
40-Sorb-150	sorbitol	40%	150°C	√
10-Gly-90	glycerol	10%	90°C	-
10-Gly-120	glycerol	10%	120°C	-
10-Gly-150	glycerol	10%	150 °C	-
20-Gly-90	glycerol	20%	90°C	√
20-Gly-120	glycerol	20%	120°C	√
20-Gly-150	glycerol	20%	150 °C	√
30-Gly-90	glycerol	30%	90°C	√
30-Gly-120	glycerol	30%	120°C	√
30-Gly-150	glycerol	30%	150 °C	√
40-Gly-90	glycerol	40%	90°C	√
40-Gly-120	glycerol	40%	120°C	√
40-Gly-150	glycerol	40%	150 °C	√

Sample sets that yielded extrudable xylans were further used to determine their mechanical properties. Ultimate tensile strength, elongation at break and elastic modulus values of sorbitol and glycerol plasticized desalted xylan strips were compared in the Figure 4.23 together with their moisture contents at the time of testing in Figure 4.24.

The effects of all the experimental parameters on the ultimate tensile strength of the parameters strips were shown in Figure 4.23(a). For a clear comparison, the results can be discussed in three cases considering extrusion temperature, plasticizer concentration or plasticizer type. At constant extrusion temperature, ultimate tensile strength of the strips decreased with the increasing plasticizer content at all temperatures for both of the plasticizer type. The effect of extrusion temperature on the ultimate tensile strength at constant glycerol concentration showed that the extrusion temperature did not have any effect on the tensile strength of the glycerol plasticized xylan strips. On the other hand, tensile strength of the sorbitol plasticized xylan strips increased with increasing extrusion temperature. Keeping the plasticizer concentration and extrusion temperatures constant, sorbitol plasticized strips exhibited higher ultimate tensile strength values than glycerol plasticized strips and the difference in values increased as extrusion temperature increases. Ultimate tensile strength values of glycerol plasticized strips changed in the range between 1.3 MPa and 14.7 MPa, whereas sorbitol plasticized samples exhibited higher strength values between 8.3 MPa and 38.5 MPa. Compared to the ultimate tensile strength of the desalted xylan strips extruded at 90°C after the moisture conditioning step, which were around 70 MPa (Figure 4.4), presence of sorbitol and glycerol caused a decrease in the ultimate tensile strength of the strips.

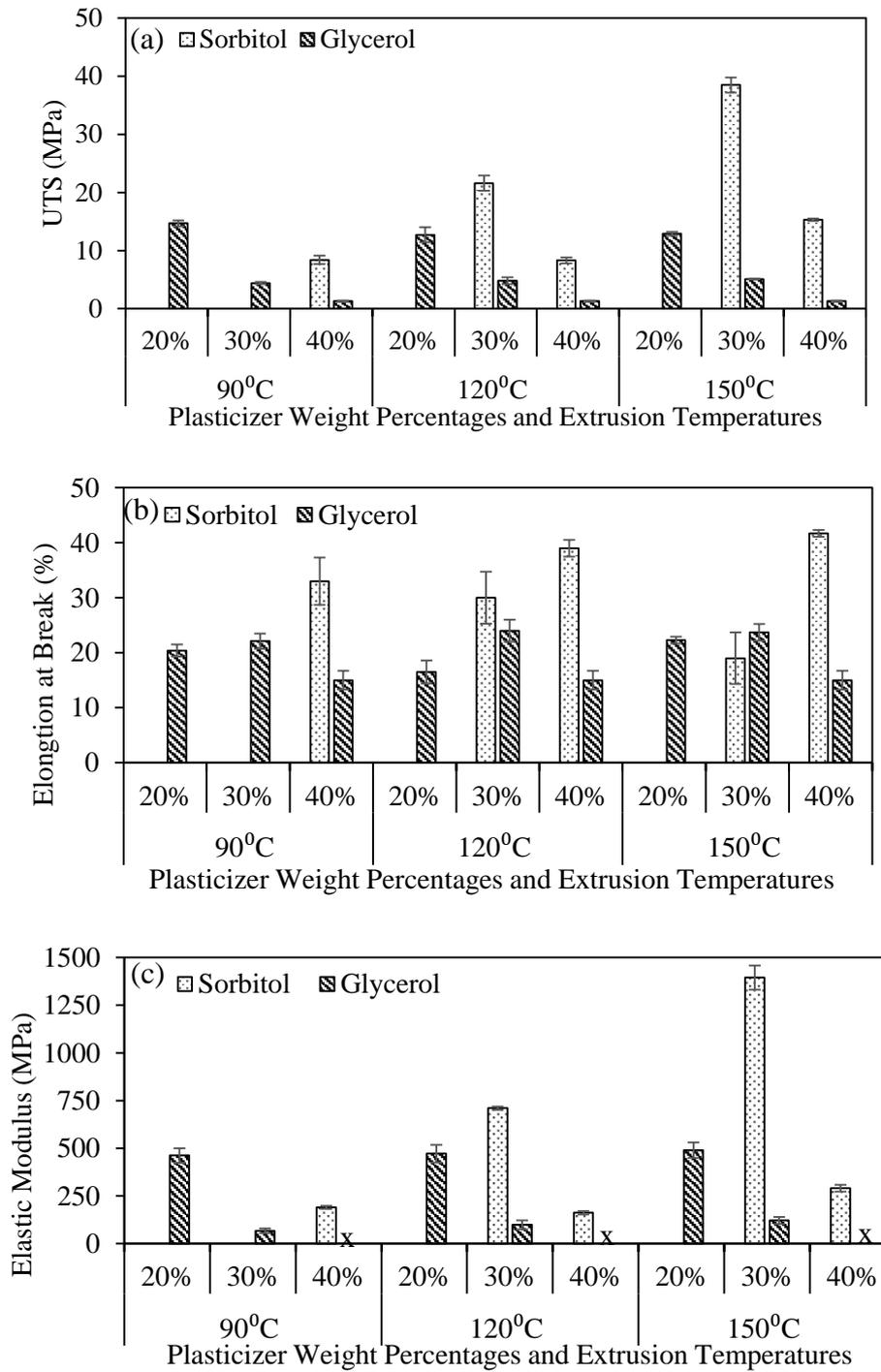


Figure 4.23 Ultimate tensile strength (UTS), elongation at break and elastic modulus values of the sorbitol and glycerol plasticized desalted xylan strips. Missing bars refer to the conditions which xylans were not extrudable. Symbols "x" in (c) refer to the strips that could not be tested due to the deformations caused by the extensometer.

According to Figure 4.23(b), elongation at break values of the sorbitol plasticized xylans increased with an increase in the plasticizer concentration at constant extrusion temperature. On the other hand, elongation at break values of the glycerol plasticized xylans were initially increased with the increase in the plasticizer concentration from 20 wt% to 30 wt%, but then decreased with further increase in the concentration to 40 wt%. The reduction in elongation at break values were accompanied by the very low tensile strength values around 1.5 MPa indicating a weakening effect due to extensive plasticization at higher glycerol concentrations. Parallel with trends of tensile strength values, elongation at break values of the glycerol plasticized xylans were not significantly affected by the extrusion temperature. Maximum elongation at break values were obtained for the strips extruded at 150°C which were around 42% and 24% for sorbitol and glycerol plasticized strips, respectively.

A contact type measurement extensometer was attached to the tensile testing instrument for an accurate determination of the elastic modulus values of the strips. As can be inferred from the Figure 4.23(c), determination of the elastic modulus of 40 wt% glycerol containing samples was not possible as they were instantly damaged by the knife edges of the sensor arms. Elastic modulus of the glycerol plasticized strips were much lower than their sorbitol plasticized counterparts. Elastic modulus of strips with both plasticizers decreased with an increase in the plasticizer concentration in line with the plasticization effect. At constant plasticizer concentration, extrusion temperature did not affect the elastic modulus of glycerol plasticized strips, however for sorbitol plasticized strips, elastic modulus increased with an increase in extrusion temperature.

Glycerol and sorbitol are hydrophilic plasticizers and the presence of them in a readily hydrophilic matrix might further increase the water content of the polymer. Considering the effect of water molecules as a plasticizer, moisture contents of the strips were also recorded to investigate a possible synergistic effect of water and the plasticizers on the mechanical properties. According to Figure 4.24, moisture contents of the strips increased as the sorbitol and glycerol concentrations increase indicating an additional moisture uptake in their presence. This effect is more

pronounced in glycerol than sorbitol. Sorbitol plasticized strips have lower moisture content values than their glycerol plasticized counterparts, due to the lower hydrophilicity of sorbitol than glycerol, which is also one of the main reasons for their higher mechanical properties. Extremely weak behavior of the 40 wt% glycerol containing strips might be a result of the synergistic effect of glycerol and water, as the moisture contents of the samples were also high. Through different combinations of plasticizers and extrusion temperatures, mechanical properties can be tuned to obtain various strength and flexibility combinations.

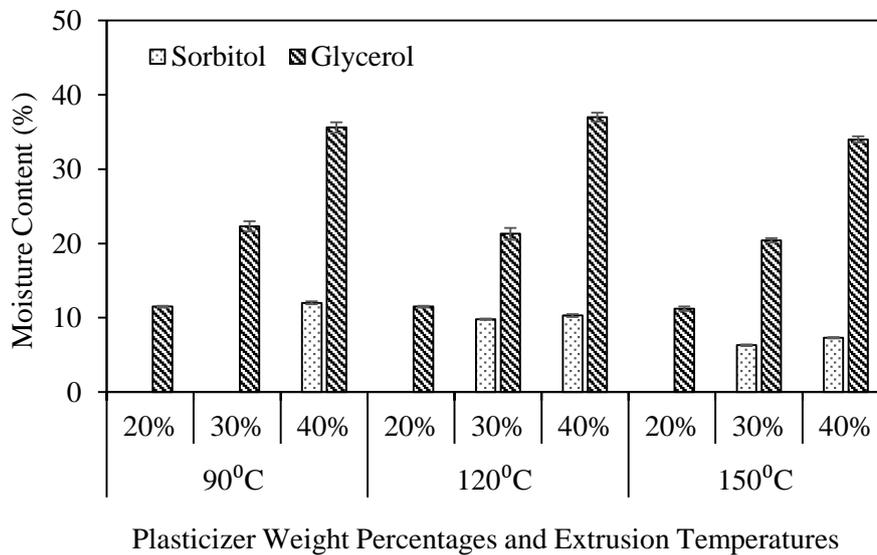


Figure 4.24 Moisture uptake values of the sorbitol and glycerol plasticized desalted xylan strips at the time of testing upon conditioning at 50% RH. Missing bars refer to the conditions which xylans were not extrudable.

Besides the mechanical properties, the physical appearance of the materials is also important that has to be considered for potential applications. It was observed that at high sorbitol concentrations (40 wt%), white spots were formed on the surfaces of the strips in time. Migration and crystallization of plasticizers is a known issue as reported in various studies in the literature. Talja *et al.* (2007) observed the

crystallization of sorbitol and xylitol on starch films at relative humidity conditions below 50%. This may affect the long term stability of the materials causing their mechanical properties change with time. The white spots observed on the sorbitol plasticized strips might be associated with the solidification of sorbitol, where glycerol plasticized strips preserved their appearance (Figure 4.25). The changes in physical appearance of 40 wt% sorbitol containing strips and the very low mechanical properties of 40 wt% glycerol containing strips made the use of these plasticizers at 40 wt% unfavorable. Since the sorbitol containing desalted xylans were not extrudable at 20 wt% sorbitol concentration, further studies were conducted by comparing sorbitol and glycerol containing strips at 30 wt% concentration.



Figure 4.25 Appearances of the sorbitol and glycerol plasticized desalted xylan strips extruded at 90°C after a week of storage. The strip on the top represents the 40 wt% sorbitol containing and the bottom represents 40 wt% glycerol containing strips.

4.2.3.2 Attenuated total reflectance-Fourier transform infrared spectroscopy

According to the results of the previous section, 30 wt% sorbitol or glycerol plasticized strips were further utilized for acetylation studies. Acetylation of sorbitol and glycerol containing xylan strips was studied at different reaction durations at 120°C. Constant reaction temperature at 120°C was used since it was shown in Section 4.2.2 that the acetylation degree was highest at 120°C. Sorbitol and glycerol plasticized xylan strips were acetylated by acetic anhydride at the specified conditions given in the Table 4.11.

Table 4.11 Specifications and sample codes of sorbitol and glycerol plasticized desalted xylan strips acetylated at specified conditions.

Sample Code	Plasticizer	Plasticizer Amount (w/w)	Extrusion Temperature	Acetylation Duration
30-Sorb-120	Sorbitol	30%	120°C	-
30-Sorb-120-A15	Sorbitol	30%	120°C	15 minutes
30-Sorb-120-A30	Sorbitol	30%	120°C	30 minutes
30-Sorb-120-A60	Sorbitol	30%	120°C	60 minutes
30-Gly-120	Glycerol	30%	120°C	-
30-Gly-120-A15	Glycerol	30%	120°C	15 minutes
30-Gly-120-A30	Glycerol	30%	120°C	30 minutes
30-Gly-120-A60	Glycerol	30%	120°C	60 minutes

Acetylation of the strips were tracked by the substitution of hydroxyl groups with acetyl groups, which is verified by the ATR-FTIR spectra shown in

Figure 4.26. Acetylation of both glycerol and sorbitol plasticized xylan strips were clearly identified by three distinct peaks around 1730 cm^{-1} , 1375 cm^{-1} and 1220 cm^{-1} which are attributed to the three important ester peaks, C=O, -C-CH₃ and -C-O-, respectively (Egüés *et al.* 2014; Sun *et al.* 2004). These three important peaks did not exist in the spectra of 30-Gly-120 and 30-Sorb-120, showing that acetylation was achieved at designated reaction conditions. The lack of peaks at $1840\text{-}1760\text{ cm}^{-1}$ indicated that the product was free of unreacted acetic anhydride (Sun *et al.* 2004). The disappearance of broad band around 3350 cm^{-1} also verified the successful exchange of hydroxyl groups with acetyl groups.

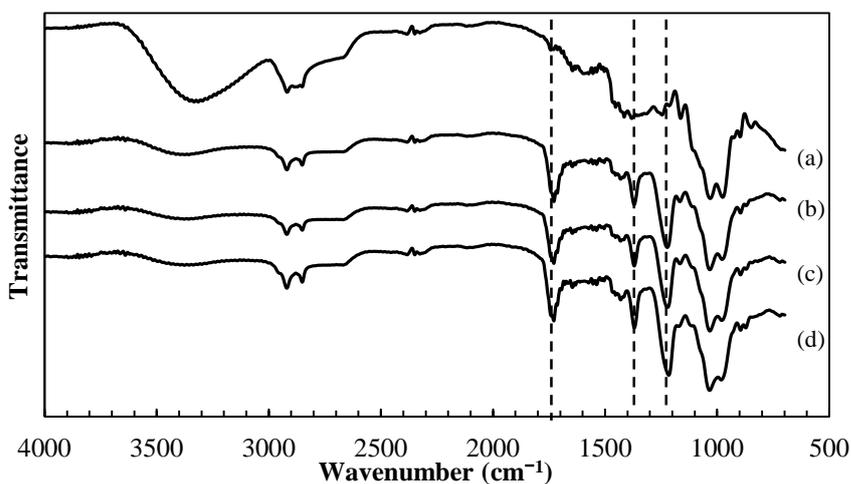
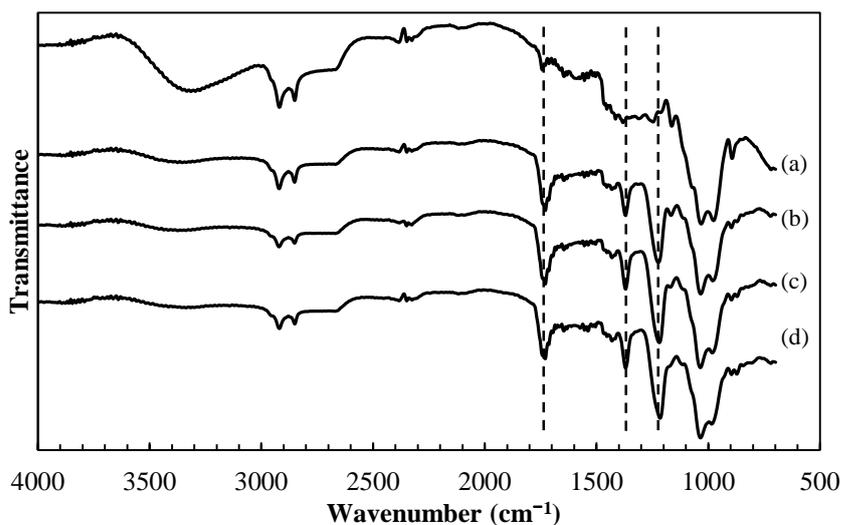


Figure 4.26 Infrared spectra of the 30 wt% sorbitol and glycerol containing desalted xylan strips. The spectra at the top represents the 30 wt% sorbitol containing strips without acetylation (a), and after acetylation at 120°C for 15 minutes (b), 30 minutes (c) and 60 minutes (d). The spectra at the bottom represents the 30 wt% glycerol containing strips without acetylation (a), and after acetylation at 120°C for 15 minutes (b), 30 minutes (c) and 60 minutes (d).

As discussed throughout the previous sections, acetylation of xylans and xylan strips could be achieved in the presence of KAc, which also acts as a plasticizer, without the need of an additional catalyst. Similar results were also observed for the

acetylation of plasticized xylans as the acetylation was successful for sorbitol and glycerol containing strips. Plasticizers soften the material by reducing the intermolecular forces within the polymer and these changes were also speculated to effect the occurrence of reactions (Riquelme *et al.* 2015). Acetylation of xylan strips in the presence of sorbitol and glycerol is thought to be associated with this phenomena similar to the acetylation of xylan strips in the presence of KAc. Acetylation of xylan strips can also be achieved in the presence of sorbitol and glycerol by a simple reaction procedure.

4.2.3.3 Effect of acetylation on the mechanical and solubility properties of the sorbitol and glycerol plasticized strips

Ultimate tensile strength, elongation at break and elastic modulus values of sorbitol and glycerol containing strips specified in Table 4.11 were determined at different relative humidity conditions to elucidate the effects of hydrophobic modifications introduced by acetylation on the mechanical properties. Ultimate tensile strength, elongation at break and elastic modulus values of the strips were compared in Figure 4.27 and Figure 4.28 for glycerol and sorbitol containing strips, respectively. Moisture contents at the time of testing were also determined to enlighten the changes in mechanical properties at different relative humidity conditions.

Figure 4.27(a) shows the ultimate tensile strength values of the glycerol plasticized strips as reference (30-Gly-120) and their acetylated counterparts at 30-50-70% relative humidity conditions. As expected, ultimate tensile strength of the non-acetylated 30-Gly-120 decreased drastically as the relative humidity increased. The decrease in the ultimate tensile strength values were accompanied with an increase in moisture contents of the strips as expected (Figure 4.27 d), which is typical for hydrophilic materials. At 70% relative humidity, 30-Gly-120 had a moisture content around 30% which lead to extremely poor mechanical properties restricting their functionality with elastic modulus values around 17 MPa and elongation at break values around 8%.

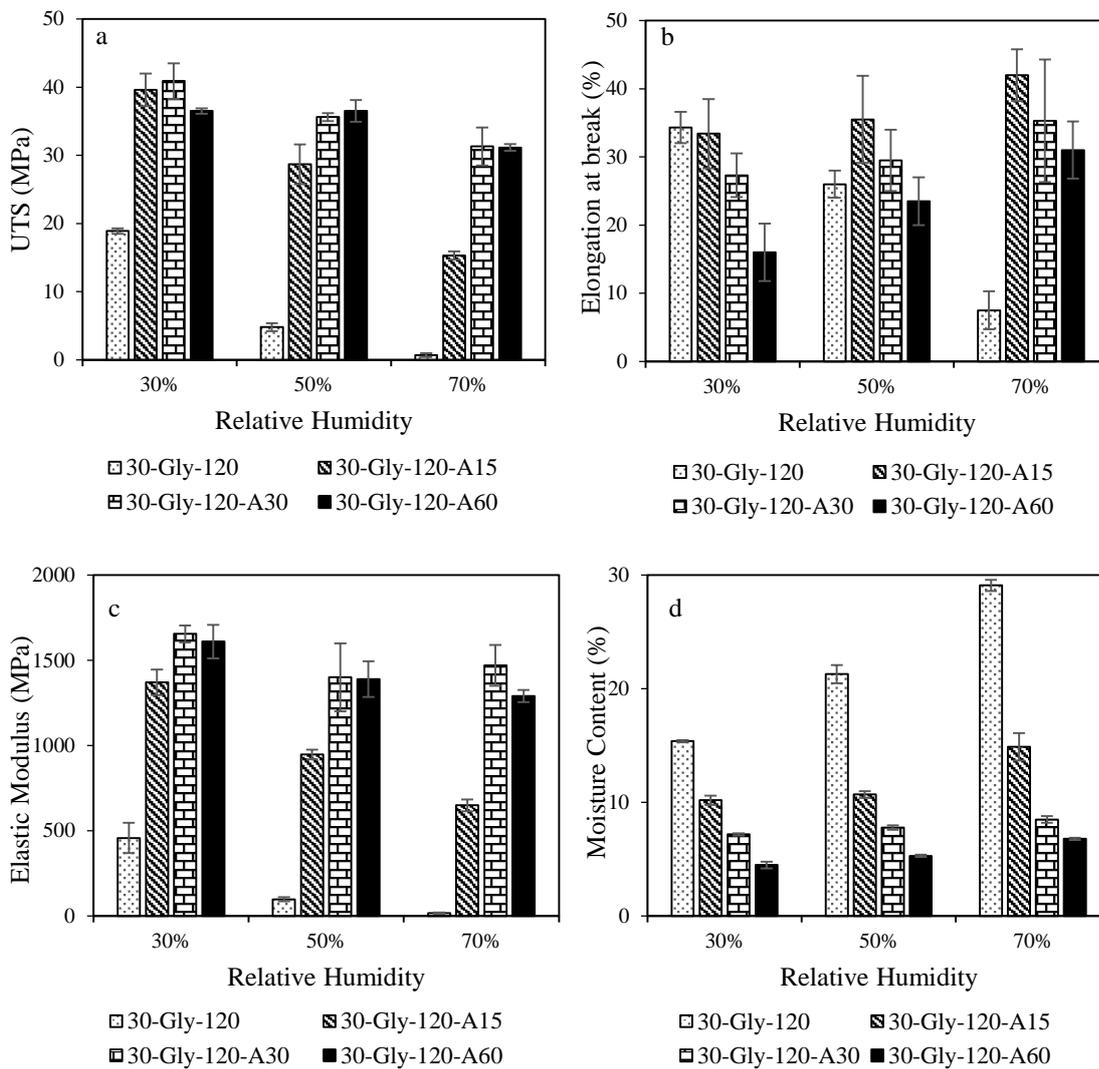


Figure 4.27 Ultimate tensile strength, elongation at break, elastic modulus and moisture contents of the 30 wt% glycerol containing desalted xylan strips (30-Gly-120) and their counterparts acetylated at 120 °C for 15 minutes (30-Gly-120-A15), 30 minutes (30-Gly-120-A30), and 60 minutes (30-Gly-120-A60). The tests were conducted under 30%, 50% and 70% relative humidity conditions.

Acetylated samples exhibited significantly better mechanical properties at all relative humidity conditions tested. Ultimate tensile strength and elastic modulus values increased with an increase in reaction duration from 15 minutes (30-Gly-120-A15) to

30 minutes (30-Gly-120-A30), but the difference was insignificant between 30 minutes (30-Gly-120-A30) and 60 minutes (30-Gly-120-A60). As can be seen in Figure 4.27 (b), elongation at break values of acetylated strips decreased by the increase in reaction durations, however they still outperformed 30-Gly-120 at high relative humidity conditions. Upon 30 minutes of acetylation (30-Gly-120-30A); ultimate tensile strength, elongation at break and elastic modulus of glycerol plasticized strips at 70% relative humidity increased from 0.7 ± 0.3 MPa to 31.3 ± 2.8 MPa, $7.5\pm 2.8\%$ to $35.3\pm 9\%$ and 17.3 ± 3 MPa to 1470 ± 120 MPa, respectively; where moisture contents decreased from $29\pm 0.5\%$ to $8.5\pm 0.3\%$.

Tensile testing results of sorbitol plasticized acetylated strips were shown in Figure 4.28 together with their moisture contents at the time of testing. The most noticeable aspect of the tensile testing results of sorbitol plasticized samples were their quite different behaviors upon acetylation compared to their glycerol plasticized counterparts. According to Figure 4.28(a), at 30% relative humidity, ultimate tensile strength of the strips drastically reduced by the acetylation regardless of the reaction duration. A decrease in ultimate tensile strength of 30-Sorb-120 was observed with an increase in relative humidity as expected. The same trend was also observed for 30-Sorb-120-A15, which indicated that 15 minutes of reaction was not sufficient to reduce the moisture sensitivity of the sorbitol plasticized strips. Ultimate tensile strength values of the 30-Sorb-120-A30 and 30-Sorb-120-A60 were independent of the relative humidity. 30-Sorb-120 and 30-Sorb-120-A15 also exhibited similar moisture contents values as shown in Figure 4.28(d). Sorbitol containing strips acetylated at 30 minutes (30-Sorb-120-A30) and 60 minutes (30-Sorb-120-A60) and outperformed in terms of strength only at high relative humidity conditions. Elongation at break values of sorbitol plasticized acetylated strips were also significantly lower than 30 Sorb-120 at all relative humidity conditions tested as can be seen in Figure 4.28(b). Stiffer materials were obtained by acetylation as can be seen in Figure 4.28(c). Significant reduction in ultimate tensile strength and elongation at break values might point out that acetylation reaction could be detrimental to sorbitol plasticized materials as small cracks and deformations were observed in the acetylated samples.

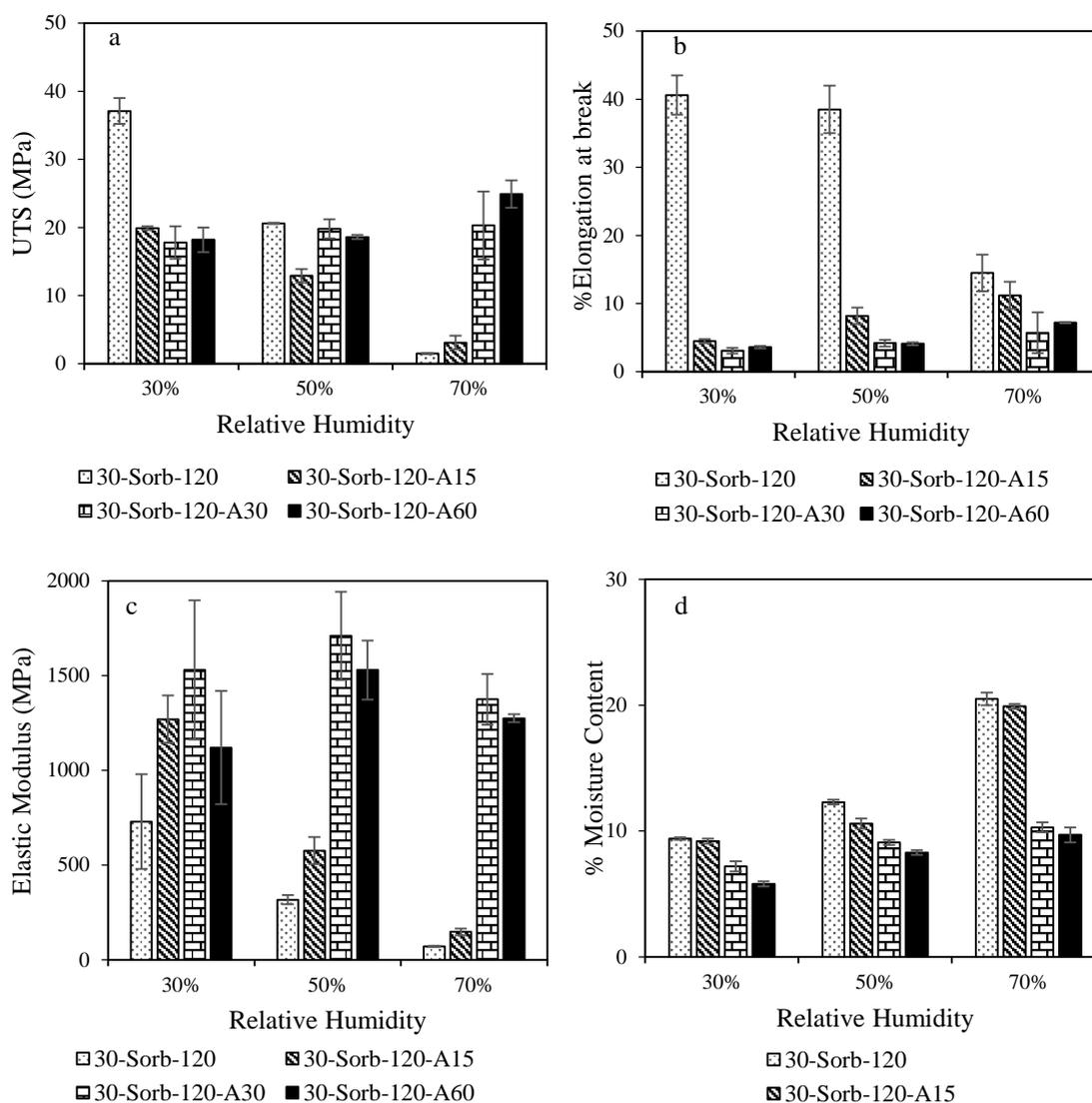


Figure 4.28 Ultimate tensile strength, elongation at break, elastic modulus and moisture contents of the 30 wt% sorbitol containing desalted xylan strips (30-Sorb-120) and their counterparts acetylated at 120 °C for 15 minutes (30-Sorb-120-A15), 30 minutes (30-Sorb-120-A30), and 60 minutes (30-Sorb-120-A60). The tests were conducted under 30%, 50% and 70% relative humidity conditions.

Acetylation creates a bulking effect due to the introduction of acetate groups instead of smaller hydroxyl groups. This bulking effect might lead to a decrease in hydrogen bonding between the chains by increasing the spacing between them (Sun *et al.* 2002), thus materials undergo permanent expansion upon acetylation (Karr *et al.* 2000,

Rowell, 1992). Although the expansion between the chains results in a possible plasticization effect, expansion of the materials might be detrimental to their integrity. In light of these, the reduction in mechanical properties of sorbitol plasticized acetylated strips was thought to be related with the cracks formed during acetylation. Native sorbitol plasticized strips were less flexible than their glycerol plasticized counterparts which might also be responsible for the crack formation in sorbitol plasticized strips upon acetylation. Nevertheless, mechanical properties of the acetylated strips become relatively independent of the changes in surrounding relative humidity upon acetylation at 120°C for 30 minutes.

Water solubilities of glycerol and sorbitol plasticized strips and their acetylated counterparts were also determined to elucidate the hydrophobic modifications introduced by acetylation (Figure 4.29). Native glycerol and sorbitol plasticized strips were highly soluble in water exhibiting nearly the same solubility values. Upon 15 minutes of reaction, water solubility of sorbitol and glycerol plasticized strips decreased nearly 30% and 70%, respectively, showing that acetylation was more successful for glycerol plasticized strips, which were also in line with the mechanical properties and moisture content analysis. At longer reaction durations (i.e 30 minutes and 60 minutes), solubility of the glycerol and sorbitol plasticized samples were very close to each other. The difference between solubilities were also insignificant for both type of strips as the reaction duration increased. After 30 minutes of reaction, solubilities of the samples 30-Sorb-120-A30 and 30-Gly-120-A30 reduced nearly 90% of its initial value without acetylation.

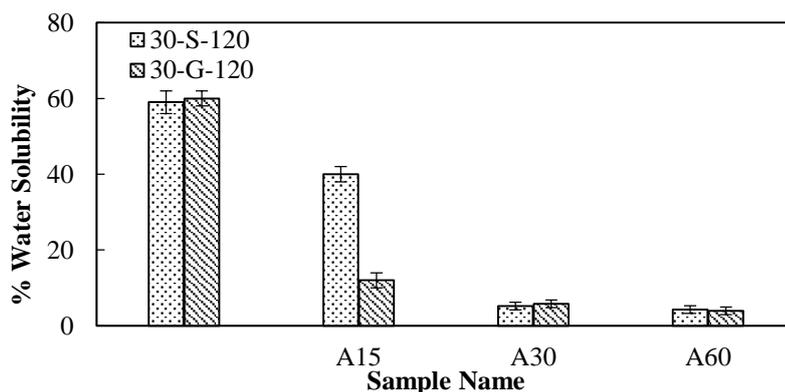


Figure 4.29 Water solubility of 30 wt% sorbitol and glycerol containing desalted xylan strips (30-Sorb-120 and 30-Gly-120) and their acetylated counterparts for 15 minutes (A-15), 30 minutes (A-30) and 60 minutes (A-60).

4.2.3.4 Thermogravimetric Analysis

Effect of acetylation on the thermal degradation behaviors of glycerol and sorbitol plasticized xylan strips were characterized by thermogravimetric analysis under nitrogen atmosphere (Figure 4.30). First of all, acetylation enhanced the thermal stabilities for both glycerol and sorbitol plasticized samples. Higher thermal stability of acetylated xylans can be explained on the basis of decreased hydroxyl content (Aburto *et al.* 1999) since hydroxyl groups takes place in degradation reactions leading to lower thermal stability (Fundador *et al.* 2012). Initial weight losses of the glycerol plasticized samples (Figure 4.30 a) below 150°C can be related with the loss of moisture verifying that acetylated samples have lower moisture contents than their non-acetylated counterparts. The same trend cannot be observed in sorbitol plasticized samples (Figure 4.30 b) possibly due to their lower moisture contents. The temperatures at which maximum weight loss occurred increased from 297°C (30-Gly-120 and 30-Sorb-120) to 320°C (30-Gly-120-A60 and 30-Sorb-120-A60) for both plasticizers upon acetylation reaction for 60 minutes. The increase in the maximum weight loss temperatures were also observed for KAc containing acetylated xylans, from 283°C to 333°C, upon acetylation at 120°C for 1 hour.

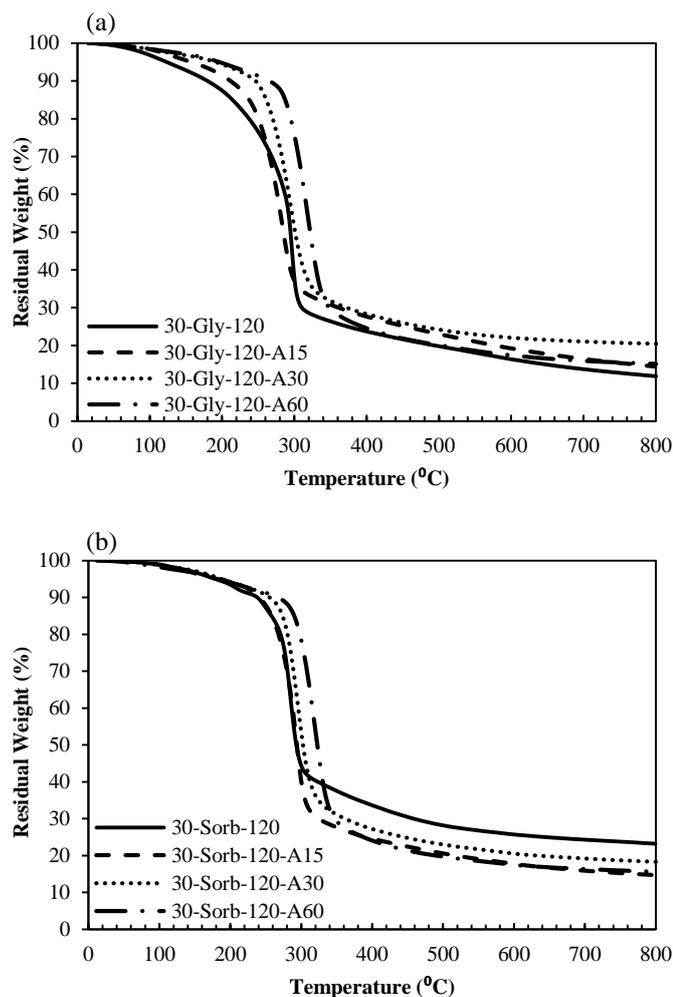


Figure 4.30 Thermal degradation curves of 30 wt% glycerol and sorbitol containing desalted xylans strips and their acetylated counterparts under nitrogen atmosphere. The figure on the top represents the 30 wt% glycerol containing strips without acetylation (30-Gly-120), and after acetylation at 120°C for 15 minutes (30-Gly-120-A15), 30 minutes (30-Gly-120-A30) and 60 minutes (30-Gly-120-A30). The figure at the bottom represents the 30 wt% sorbitol containing strips without acetylation (30-Sorb-120), and after acetylation at 120°C for 15 minutes (30-Sorb-120-A15), 30 minutes (30-Sorb-120-A30) and 60 minutes (30-Sorb-120-A30).

4.2.3.5 Scanning Electron Microscopy

As outlined in the Section 4.2.3.3, small cracks were observed on the 30 wt% sorbitol containing acetylated strips which was correlated with the significant reduction in

mechanical properties upon acetylation. The fractured surfaces of the 30 wt% sorbitol plasticized strip (30-Sorb-120) and its counterpart acetylated for 60 minutes (30-Sorb-120-A60) were further examined by scanning electron microscopy. As can be seen in Figure 4.31 (a) and (b) 30-Sorb-120 and 30-Sorb-120-A60 displayed similar morphologies being smooth and continuous at higher magnifications, however cracks were observed throughout at lower magnifications (Figure 4.31 c and d) which might be an evidence of reduced mechanical properties upon acetylation.

To sum up, extrusion of xylans in the presence of commonly used plasticizers, glycerol and sorbitol, were studied to address their processing in line with the processing techniques of the conventional polymers. Glycerol exhibited better plasticization effect compared to sorbitol rendering xylans extrudable at lower concentrations and extrusion temperatures, but under the same extrusion conditions and concentrations, sorbitol plasticized strips were better in both ultimate tensile strength and elongation at break values. In line with the effect of KAc, glycerol and sorbitol also exhibited a positive effect towards the acetylation of xylan strips without the necessity of any solvents or catalysts. Acetylation can be achieved at shorter durations for glycerol plasticized strips probably due to the positive effect of higher free volume upon better plasticization. Considering these points, glycerol was thought to be an effective plasticizer both from the point of processing and acetylation. Acetylated glycerol containing strips with ultimate tensile strength, elongation at break and moisture content values around 35 MPa, 30% and 8% were obtained, which were around 5 MPa, 26% and 22%, respectively at 50% relative humidity before acetylation.

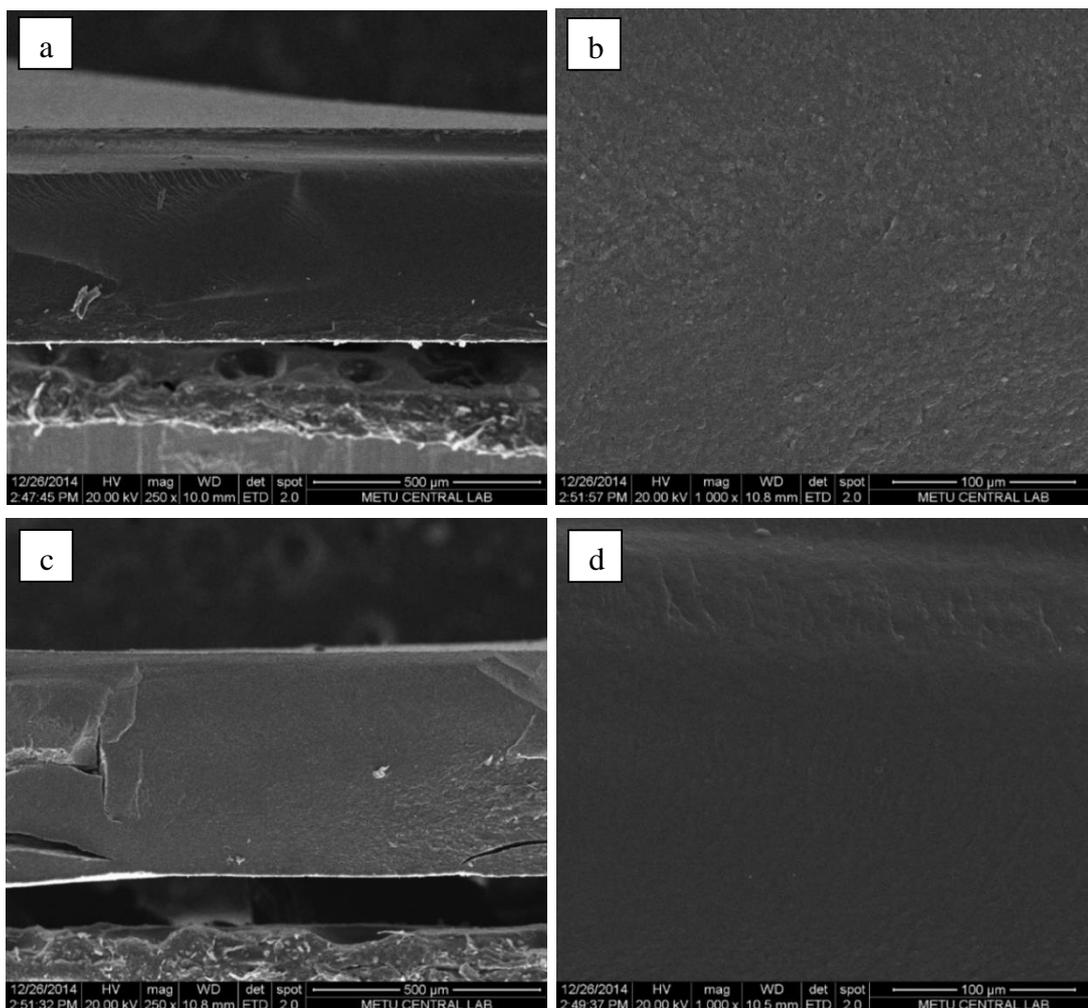


Figure 4.31 Scanning electron microscopy images of the fractured surfaces of 30 wt% sorbitol plasticized desalted xylan strips and their acetylated counterparts. Images represent the native strips (30-Sorb-120) (a) at 250X magnification, (b) 1000X magnification, and acetylated strips at 120°C for 60 minutes (30-Sorb-120-A60) (c) at 250X magnification, (d) 1000X magnification. Strips were broken in liquid nitrogen.

4.3 Xylan/polyvinyl alcohol blends

Current trends show that sustainable and bio-based plastics are getting more and more prominent to replace petrochemical plastics. Utilization of bio-based plastics can be

spread by blending with conventional polymers to provide competitive alternatives, however blends with synthetic polymers can mostly be problematic due to the incompatibility between them. Although being a synthetic polymer, polyvinyl alcohols (PVA) differ from most of the petroleum based polymers being water soluble and biodegradable. They also have potential in plastics and packaging applications (Tang *et al.* 2011), which makes them ideal candidates as blending components with hemicelluloses.

Blends of 24% KOH extracted desalted xylans with commercial PVA (Mowiol[®]4-88 Mw~31,000 and 88% hydrolysis) were studied throughout this study by extrusion processing. Heat treatment and acetylation methods outlined in the previous sections were also applied to xylan/PVA blends to decrease its water sensitivity. The parameter used in this part of the study was given in the Table 4.12.

Table 4.12 Parameters used for the xylan/polyvinyl alcohol blends

Xylan Extraction	Purification	Additive & Concentration	Extrusion Temperature	Heat Treatment	Acetylation
24% KOH	Desalted	PVA	20% 40% 60% 80%	75°C 90°C 200°C	120°C 120°C 15 min

4.3.1 Extrusion of xylan/polyvinyl alcohol blends

Commercial PVA (Mowiol[®] 4-88) with 88% hydrolysis was utilized to produce xylan-PVA blends due to their higher water solubilities compared to fully hydrolyzed PVA, to be more compatible with xylans. Preliminarily, PVA was either directly extruded or conditioned at 90% RH for 1 day prior to extrusion as in the case of conventional xylan extrusion outlined in this study to evaluate their melt processing (Table 4.13).

Table 4.13 Extrudability of polyvinyl alcohol at various extrusion temperatures with and without conditioning step prior to extrusion.

Polymer	Conditioning	Extrusion Temperature	Extrudability
PVA	-	120°C	-
PVA	-	150°C	-
PVA	-	200°C	√
PVA	+	75°C	√
PVA	+	90°C	√
PVA	+	120°C	-
PVA	+	150°C	-

Degradation temperature of PVA is very close to or slightly higher than its melting point (Tsuchiya *et al.* 1969) for which melting temperature should be controlled to have adequate melt flow without degradation. Melting temperature of the PVAs range between 180 °C to 240 °C and the PVA used in this study has a melting temperature at 200°C. As can be seen in Table 4.13, PVA could not be extruded at 120°C and 150°C, but extrusion was successful at 200°C, at its melting point, as expected. When conditioned, PVA could be extruded at temperatures as low as 75 °C, since the polymer flow was facilitated by the plasticization effect of moisture similar to the hemicellulose extrusion studies in literature. Extrusion was not successful at temperatures higher than 90°C because the polymers got too sticky to ensure the feeding to the extruder. PVA is known to have adhesive properties which increase with temperature (Gutiérrez-López *et al.* 2008) and PVA polymers got much softer and sticky in the presence of moisture synergistically with increased temperature, which might be the reason for the difficulties in feeding the polymers to the extruder.

Mechanical properties of the extruded PVA strips were listed in Table 4.14. PVA strips extruded at 200°C exhibited high modulus, tensile strength and elongation values and low moisture content at the time of testing. Resulted strips were clear and transparent at first, but get blurred and turned pale as extrusion continues possibly due to the degradation. Alternative to the extrusion at its melting point, PVA after moisture conditioning at 90% relative humidity for 1 day can be extruded at 90 °C, at

which xylans can also be extruded. PVA strips extruded at 90 °C exhibited very high elongation at break values with a moderate tensile strength around 15 MPa.

Table 4.14 Ultimate tensile strength (UTS), elongation at break (e_b), elastic modulus (E), and moisture contents (MC) of the extruded PVA strips.

Polymer	Extrusion Temp.	UTS (MPa)	e_b (%)	E (MPa)	MC** (%)
PVA	200°C	85±5	61±14	3920±71	1.6±0.3
PVA (conditioned*)	75°C	15±1	125±7	136±57	7.5±0.1
PVA (conditioned*)	90°C	15±1	200±50	89±9	8.5±0.1

* Polymers are conditioned at 90% relative humidity for 1 day prior to extrusion

** The values represent the moisture contents of the strips at the time of tensile testing at 23°C and 50% relative humidity conditions

Xylan and PVA blends at different ratios were conditioned one day prior to extrusion and extruded at 90°C to obtain materials in the form of a strip. Preliminary studies on xylan/PVA blends showed that mechanical properties of strips did not change significantly with blending procedures conducted by mixing xylan and PVA either directly or partially dissolving in a small amount of water followed by the evaporation of water at room temperature. Mechanical properties of xylan/PVA blends together with the xylan and PVA strips as a reference can be seen in Table 4.15.

PVA strips exhibited very high elongation at break values compared to xylan strips, whereas xylans strips were significantly stronger. Addition of 20 wt% PVA decreased the tensile strength from 69 MPa to around 50 MPa. The decrease was more prominent in elongation at break values which was reduced from 45% to around 11%. Tensile strengths were further decreased as PVA content increased, however elongation at break values increased substantially by 3.5 fold for every 20% PVA addition. 80% PVA containing strips exhibited somewhat higher elongation at break values than pure PVA strips on average, but the values can be regarded close to each other when standard deviations were considered. From a different point of view,

addition of 20 wt% of xylan to PVA did not affect mechanical properties of PVA as the samples 80 wt% PVA and PVA exhibited similar elastic modulus, ultimate tensile strength and elongation at break values.

Table 4.15 Ultimate tensile strength (UTS), elongation at break (e_b), elastic modulus (E), and moisture contents (MC) of 24% KOH extracted desalted xylan/PVA strips prepared at different ratios. Blends were conditioned at 90% relative humidity for 1 day prior to extrusion and extruded at 90°C.

Polymer	UTS (MPa)	e_b (%)	E (MPa)	MC * (%)
Xylan	69±2	45±4	3640±240	11.8±0.1
20 wt% PVA	50±2	11±4	2785±162	11.4±0.1
40 wt% PVA	42±2	22±2	2430±480	10.6±0.1
60 wt% PVA	22±1	75±18	420±97	10.6±0.1
80 wt% PVA	16±1	253±52	109±52	10.1±0.1
PVA	15±1	200±50	89±9	8.5±0.1

* The values represent the moisture contents of the strips at the time of tensile testing at 23°C and 50% relative humidity conditions

PVA and xylan/PVA blends were further compared by considering the conventional processing temperature of PVA at 200°C. Xylan/PVA blends at 60 wt% PVA content extruded at 90°C was fed to the extruder again for a second step of extrusion at 200°C, since xylans were not extrudable through one step extrusion at 200°C. Strips with 60 wt% PVA content was chosen for comparison due to their elongation at break values which lie between the values of pure PVA and xylan. According to the results given in Table 4.16, ultimate tensile strength and elastic modulus values of 60 wt% xylan/PVA blend strips were increased upon the second extrusion step at 200°C. Elongation at break values decreased from ~75% to ~8% which can be correlated with the decrease in moisture contents of the strips from ~11% to ~2%. PVA strips extruded at 200°C and 60 wt% PVA blend strips extruded both at 90°C and 200°C exhibited similar ultimate tensile strength and modulus values, however the presence of xylan decreased the elongation at break values from 61% to 8%. The results also

indicated that extrusion temperature might have a prominent effect on the mechanical properties and moisture contents of the xylan/PVA blends.

Table 4.16 Ultimate tensile strength (UTS), elongation at break (e_b), elastic modulus (E), and moisture contents (MC) of the PVA and 24% KOH extracted desalted xylan/PVA blend strips processed at different extrusion temperatures.

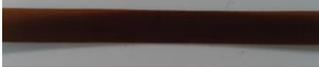
Polymer	Extrusion Parameters	UTS (MPa)	e_b (%)	E (MPa)	MC* (%)
PVA	200 °C	86±7	61±14	3920±70	1.6±0.3
60 wt%PVA	90 °C	22±1	75±18	420±97	10.6±0.1
60 wt%PVA	90 °C and 200 °C	91±7	8±1	3750±103	1.9±0.3

* The values represent the moisture contents of the strips at the time of tensile testing at 23°C and 50% relative humidity conditions

Although the forthcoming studies were conducted with PVA being a synthetic polymer, blends of xylans with other natural polymers were also investigated as a preliminary study which could be studied in details in further studies. Similar to the preparation of xylan/PVA blend strips, corn zein, wheat gluten, carboxymethyl cellulose (CMC) and chitosan blends were prepared by the 20% (wt/wt) addition of them. 20% (wt/wt) was chosen because the content was high enough to foresee the possible effects of additives on the properties xylan based strips. These biopolymers were chosen as additives for blends because all of them possess good film forming abilities and they have been already used to make blends with different kinds of natural or synthetic polymers. Corn zein is a plant based protein that is insoluble in water except at very low or high pH and has an amphiphilic nature containing more than 50% non-polar aminoacids. (Plackett, 2011). Corn zein found many commercial applications in coatings and biodegradable films. Wheat gluten is another plant based protein which is produced from wheat flour. Plasticized wheat glutens films can be formed by solvent casting, moulding or extrusion (Kayserilioglu *et al.* 2003; Hernandez *et al.* 2008). Carboxymethyl cellulose (CMC) is a cellulose derivative having carboxymethyl groups bound the hydroxyl groups of the cellulose

molecule. CMC possesses good film forming ability and their films are flexible and transparent. Chitosan is a cellulose-like biopolymer which is present in the exoskeletons of crustaceans. Chitosan films were obtained by casting from acidic solutions. It has already found many industrial applications and chitosan films are recently receiving interest for coating and packaging applications (Plackett, 2011). There are studies in the literature mentioning their blends with hemicelluloses; however hemicelluloses were used as an additive instead of being the main matrix. Appearance of the extruded strips, together with the mechanical properties and percent moisture contents at the time of testing were listed in Table 4.17.

Table 4.17 Ultimate tensile strength (UTS) and elongation at break values (e_b) of 24% KOH extracted desalted xylan blends with various biopolymers and corresponding moisture contents (MC) at the time of tensile testing.

Sample	Extruded Strips	UTS (MPa)	e_b (%)	MC (%)
Desalted xylan		69±2	45±4	11.8±0.1
20% (wt/wt) zein		54±4	21±4	12.0±0.4
20% (wt/wt) gluten		61±3	13±3	11.5±0.2
20% (wt/wt) CMC		70±4	31±7	11.7±0.3
20% (wt/wt) chitosan		54±2	9±1	11.2±0.1

According to tensile testing results, addition of gluten and CMC did not result in a significant difference in terms of elastic modulus and ultimate tensile strength. Elongation values of the blends were lower than the desalted xylan strips which was also an observed trend in literature. Chitosan blended strips gave the worst elongation values possibly due to the improper dispersion of chitosan particles. Effect can also be foreseen from the strips because chitosan particles were visible to eye inside the strips. Mechanical properties were also reduced for zein blended case, although the

strips were very smooth and homogeneous. Reduction of mechanical properties can be attributed to the nature of zein, since extruded zein samples reported to have tensile strength values between 19-30 MPa, elongation values between 5-11% and modulus between 380-480 MPa (Selling, 2010).

4.3.2 Attenuated total reflectance-Fourier transform infrared spectroscopy

Fourier transform infrared spectra of the xylan/PVA blend strips were studied to show the possible interactions between xylan and PVA. Infrared spectra of the samples were shown in Figure 4.32. The first three spectra (a,b,c) in Figure 4.32 are the characteristic peaks of an xylan structure. The intense peak around 1030 cm^{-1} were assigned to the C–O stretching. Small peaks around 1160 cm^{-1} indicate arabinose residues confirming the xylan backbone with arabinose substitutions. The smaller but sharper peak around 890 cm^{-1} was attributed to the β -glycosidic linkages between the sugar units. The broad peak around 3350 cm^{-1} and the peak around 2850 cm^{-1} were assigned to C–H stretching and –OH stretching of the xylans, respectively. Other three spectra (d, e, f) show the characteristic peaks of PVA having nearly similar features with xylans due to their structural similarities. Intensifying bands around 1730 cm^{-1} with the increasing PVA content were attributed to the inherent residual acetate groups of PVA. The spectra of the strips resemble the spectra of xylan or PVA related to their dominance in the blends. As the blending is not reactive, phases possibly interacted physically by the formation of hydrogen bonds. PVA and xylan are both hydrophilic in nature with –OH groups present, which might create an expectation of high interaction between them; however as explained in Section 4.3.1 elongation at break values of xylan strips decreased significantly by the addition of 20% PVA. PVA is commonly used for blending with starch and the compatibility between them is also contradictory as some studies address the enhancements due to their good compatibility (Chen *et. al*, 2008b) and some address the reduced elongation at break and tensile strength values due to poor interface adhesion (Liu *et al*. 1999).

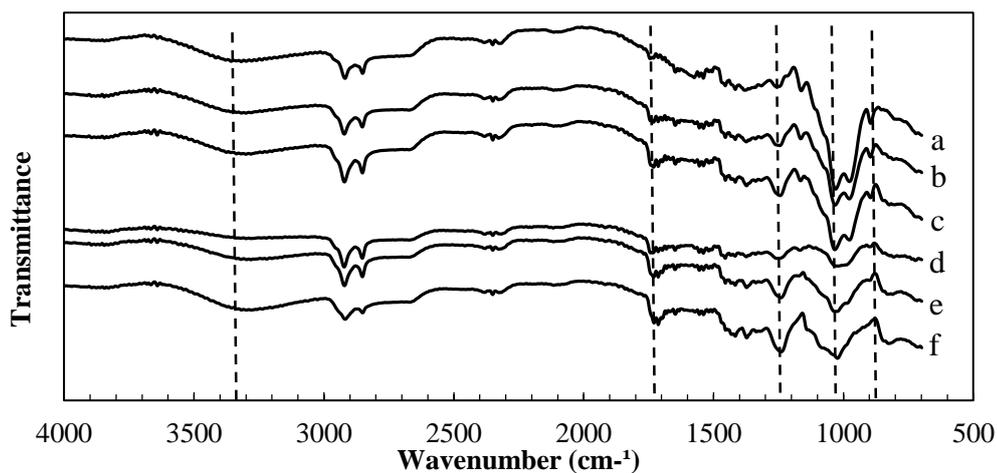


Figure 4.32 Infrared spectra of 24% KOH extracted desalted xylan/PVA strips at different blend ratios (a) xylan, (b) 20 wt% PVA, (c) 40 wt% PVA, (d) 60 wt% PVA, (e) 80 wt% PVA and (f) PVA

4.3.3 Optical Transmission Light Microscopy

Surface characteristics of extruded strips were analyzed by optical transmission light microscopy and shown in Figure 4.33. Xylan strips had a brownish color, where PVA strips were somewhat transparent and the color of the strips got lighter as the concentration of PVA increased. Localized brownish areas on a lighter matrix were observed for 80% PVA containing strips indicating that xylans were localized at low concentrations, which can be prevented by better mixing procedures. Addition of PVA resulted in rougher film surfaces than the pure xylan strips.

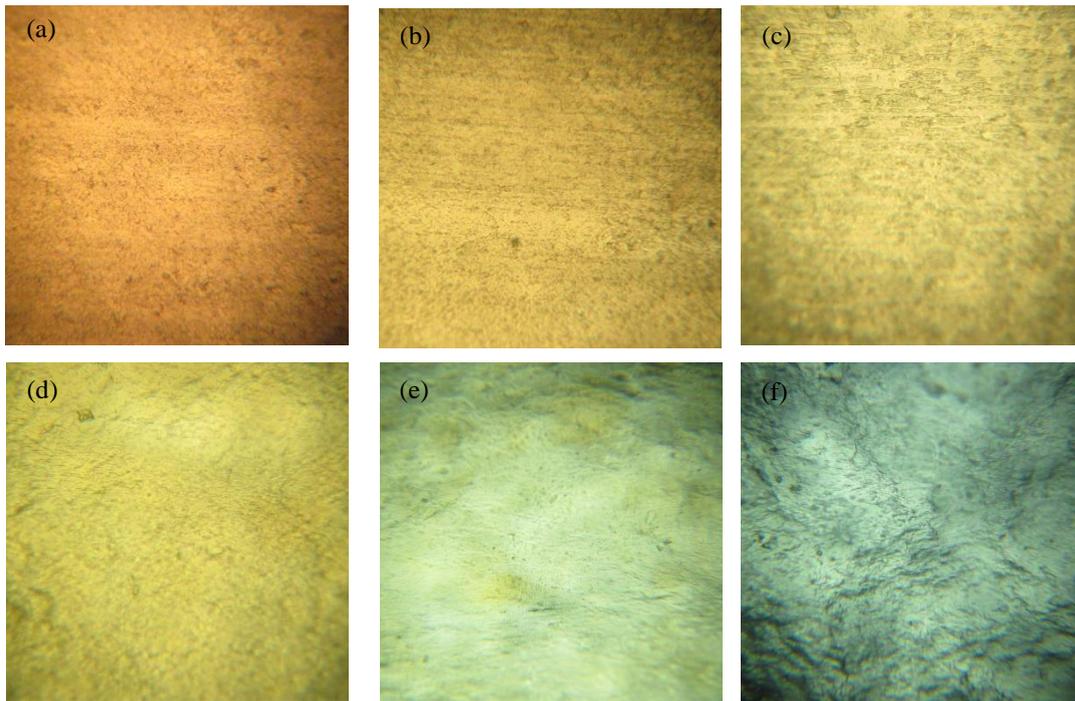


Figure 4.33 Optical transmission light microscopy images of the upper surfaces of the (a) 24% KOH extracted desalted xylan, (b) 20 wt% PVA blend, (c) 40 wt% PVA blend, (d) 60 wt% PVA blend, (e) 80 wt% PVA blend, and (f) PVA strips.

4.3.4 Scanning Electron Microscopy

Fractured surface morphologies of the xylan/PVA blend strips were compared with xylan and PVA strips by scanning electron microscopy analysis. As can be seen in Figure 4.34, fractured surfaces of the PVA strip was less grainy than the xylan strips. The morphologies of xylan/PVA blend strips were similar regardless of the blending ratio resembling more of the morphology of the xylan strips. As can be inferred from the figures, no phase separation between xylan and PVA was observed.

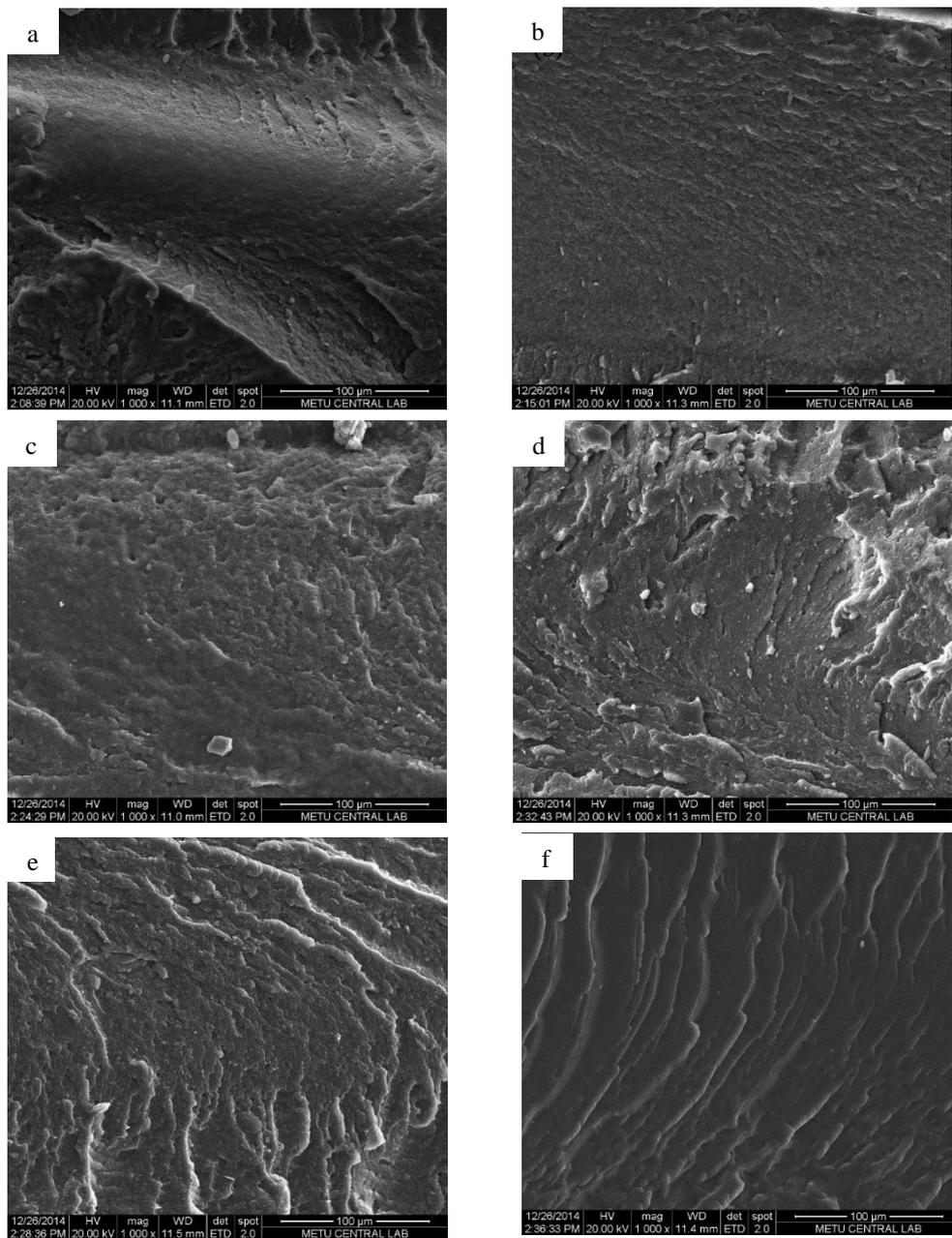


Figure 4.34 Scanning electron microscopy images of the fractured surfaces (a) 24% KOH extracted desalted xylan, (b) 20 wt% PVA blend, (c) 40 wt% PVA blend, (d) 60 wt% PVA blend, (e) 80 wt% PVA blend, and (f) PVA strips

4.3.5 Heat treatment and acetylation of xylan/ polyvinyl alcohol strips

Although PVA has a potential in forming matrices with biopolymers due to their strong hydrophilicity, the requirement of low water sensitivity is mostly required for practical applications (Kumeta *et al.* 2004). Chemical modifications leading to cross-linking (Sakurada, 1985) and the substitution of hydroxyl groups (Pan *et al.* 2014) resulted in hydrophobically modified PVA. Besides, tensile strength of the PVA was also improved upon heat treatment at 80 °C probably due to the removal of water leading more dense and arranged structures (Huang *et al.* 2000). The effect of heat treatment on the water sensitivity and mechanical properties of the desalted xylan strips were outlined in Section 4.2.1. As outlined in Section 4.2.2, hydrophobically modified xylans can be obtained by acetylation in the presence of KAc or plasticizers with significantly less water solubility, moisture sensitivity and enhanced mechanical properties. In line with these results, desalted xylan/PVA blends were heat treated at 120°C for 1 hour and acetylated at 120°C for 15 minutes to investigate their effects on xylan blends. Resulting strips were characterized by their water solubility, chemical properties and mechanical properties which were outlined in the forthcoming sections.

4.3.5.1 Heat treatment of xylan/ polyvinyl alcohol strips

Heat treatment of desalted xylan and PVA blends were studied at different PVA ratios and the strips were heat treated at 120°C for 1 hour. First of all, ATR-FTIR spectra of the strips were obtained in order to determine if heat treatment resulted in any chemical changes. As can be seen in Figure 4.35, the first three spectra (a,b,c) are the characteristic peaks of an arabinoxylan structure and the other three spectra (d, e, f) show the characteristic peaks of PVA. The spectra of the strips resemble the spectra of either xylan or PVA related to their dominance in the blends and no changes in their chemical structure is observed as expected.

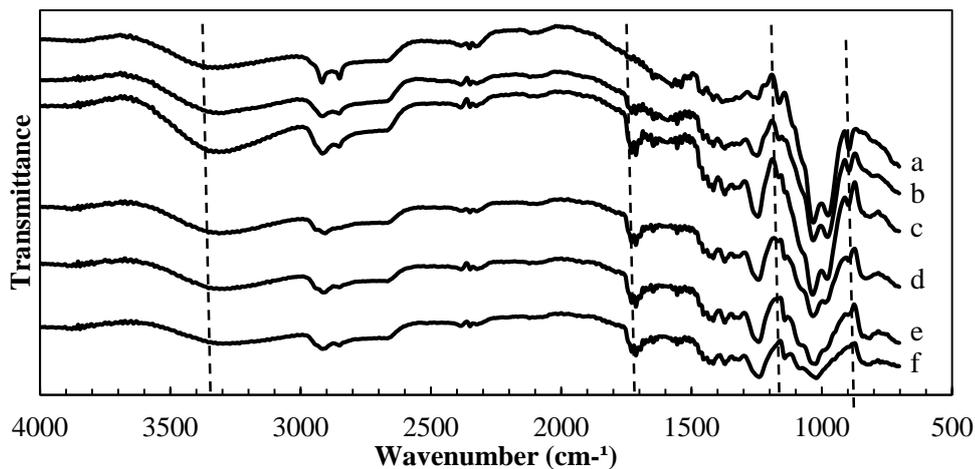


Figure 4.35 Infrared spectra of 24% KOH extracted desalted xylan/PVA strips heat treated at 120°C for 1 hour at different blend ratios (a) xylan, (b) 20 wt% PVA, (c) 40 wt% PVA, (d) 60 wt% PVA, (e) 80 wt% PVA and (f) PVA.

Mechanical properties of heat treated xylan/PVA blends were determined by tensile testing and compared with their native counterparts in Figure 4.36. In line with the results of the heat treated desalted xylan strips, tensile strength of the xylan/PVA blends increased upon heat treatment; however the decrease in elongation at break values was more significant for PVA containing strips. Compared to their native counterparts, ultimate tensile strength and elastic modulus values increased and the elongation at break values decreased as the PVA contents of the strips increased. Heat treatment has a more profound effect on PVA than xylan most probably due to its crystalline structure which probably altered during the heat treatment resulting in stronger but less flexible strips.

Moisture contents of the strips at the time of testing were also shown in Figure 4.37 to elucidate the differences in mechanical properties. Moisture contents of the strips also decreased upon heat treatment in line with the results of Section 4.2.1, however the decrease was not as dramatic as expected to cause such a significant reduction in elongation at break values. Thus the changes in mechanical properties can not only

be related with the lower moisture contents of the strips, but also related with the response of PVA to heat treatment.

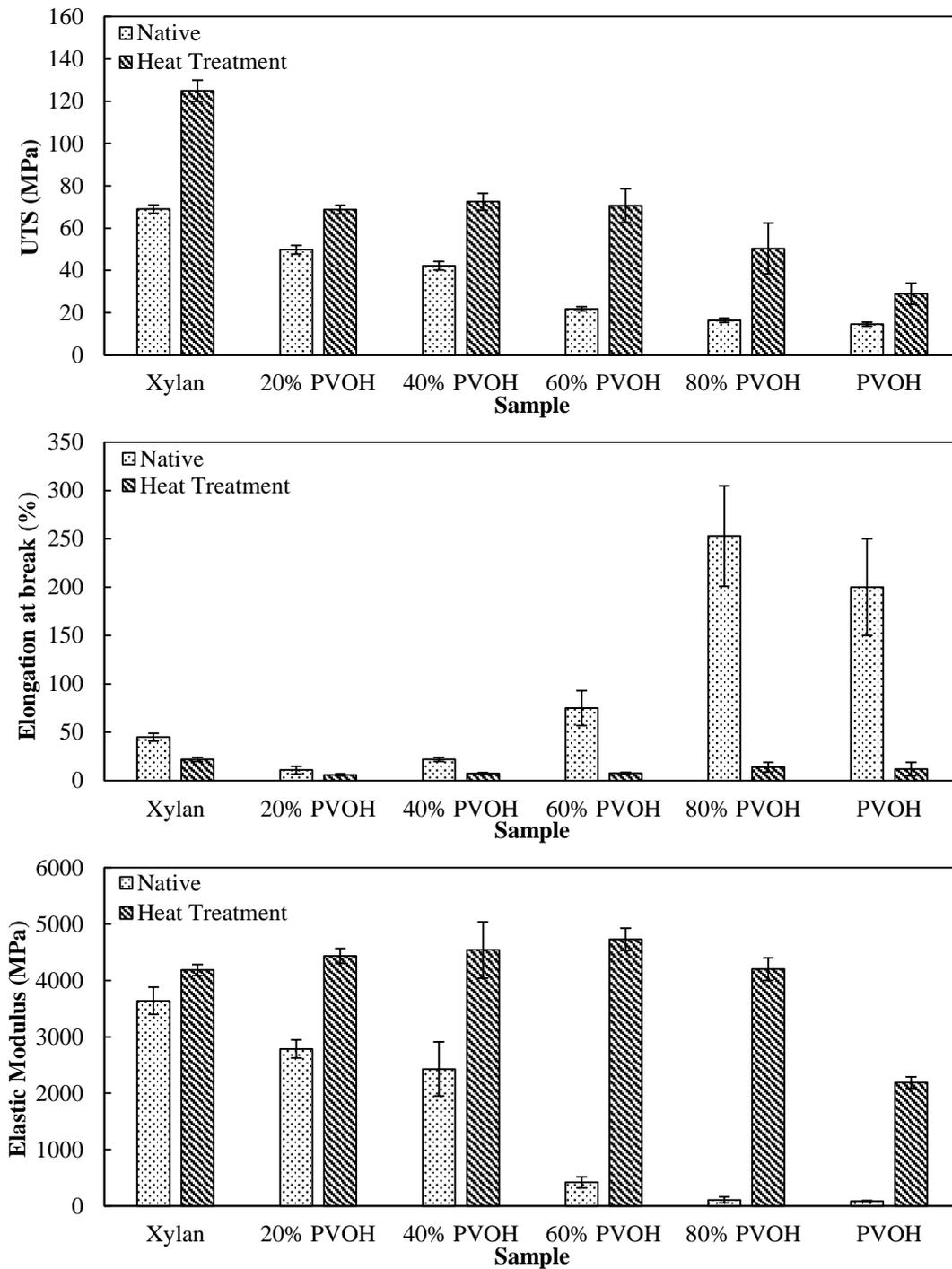


Figure 4.36 Ultimate tensile strength, elongation at break, and elastic modulus values of 24% KOH extracted, desalted xylan and polyvinyl alcohol blend strips with and without heat treatment.

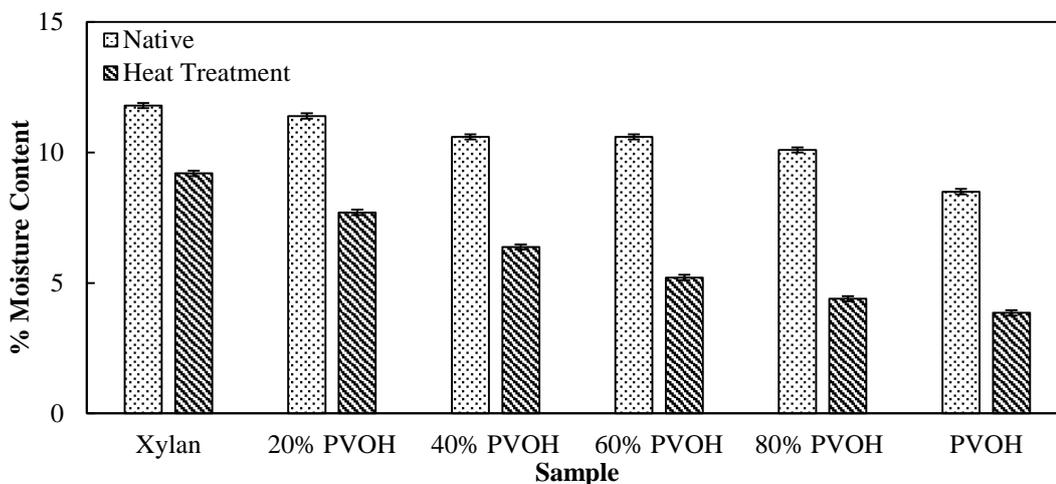


Figure 4.37 Moisture contents of the 24% KOH extracted, desalted xylan and PVA blend strips at the time of testing. Prior to tensile testing, the strips were conditioned at 23°C and 50% RH for 1 day.

Water solubility of heat treated xylan/PVA strips were shown in Figure 4.38 together with their untreated counterparts. As can be seen in the figure, native and heat treated strips did not exhibit significantly different solubility values. Studies on heat treatment of desalted xylan strips were showed that the strips with high tensile strength and reasonable elongation at break values can be obtained despite their water solubility; however neither the tensile strength nor the elongation at break values of the heat treated xylan/PVA blends were satisfactory. Acetylation of blends were studied alternative to heat treatment to address water solubility issues by introducing chemical modifications.

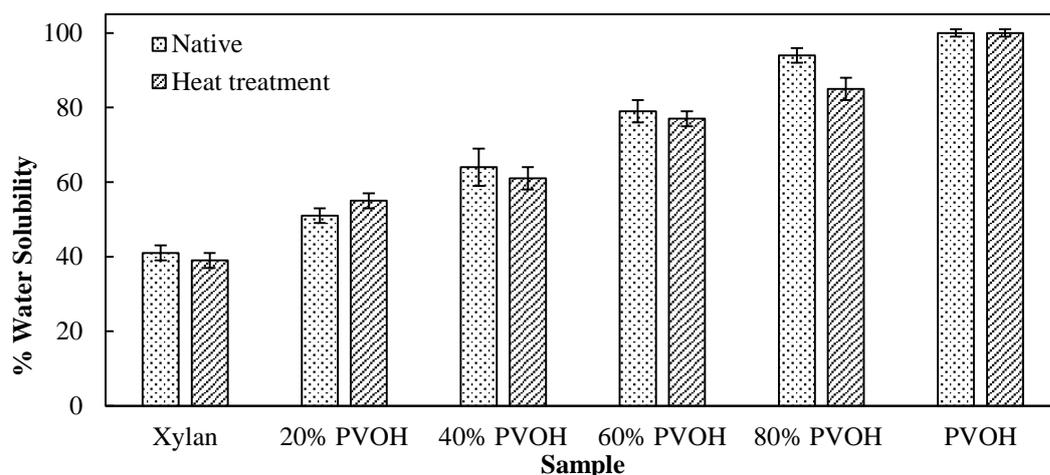


Figure 4.38 Water solubility of the 24% KOH extracted, desalted xylan and polyvinyl strips. The tests were conducted at room temperature for 1.5 hours at a solid loading of 1% (w/v).

4.3.5.2 Acetylation of xylan/ polyvinyl alcohol strips

Similar to the other hydrophilic polymers, chemical modifications of PVA, which also involves the acetylation reaction, can be utilized to improve the water sensitivity of PVA based materials. Previous studies on the acetylation of PVA showed that hydrophobicity of the PVA increased by the changes in crystallinity, hydrogen bonding and chain mobility upon acetylation (Ochiai *et al.* 1974; Zaslavsky *et al.* (1984). Acetylation of xylans in the presence of KAc, sorbitol and glycerol was studied in the previous parts and acetylation in the presence of PVA was thought to effect in a similar way by also taking the advantage of PVA acetylation. Desalted xylan/PVA strips at different blend ratios were acetylated at 120°C for 15 minutes since the strips were deformed at longer reaction durations during the preliminary experiments. The changes introduced by the acetylation of xylans, PVA and their blends at different ratios were tracked by ATR-FTIR spectroscopy (Figure 4.39). Different from the spectra of native and heat treated xylans outlined in Figure 4.32 and Figure 4.35, PVA containing strips exhibited three important ester peaks around 1730 cm^{-1} , 1375 cm^{-1} and 1220 cm^{-1} (C=O, -C-CH₃ and -C-O-, respectively) which are very intense indicating successful acetylation. Although the acetyl groups were

introduced to the xylan/PVA blends, the broad peak around 3350 cm^{-1} did not disappear showing that some hydroxyl groups are still present.

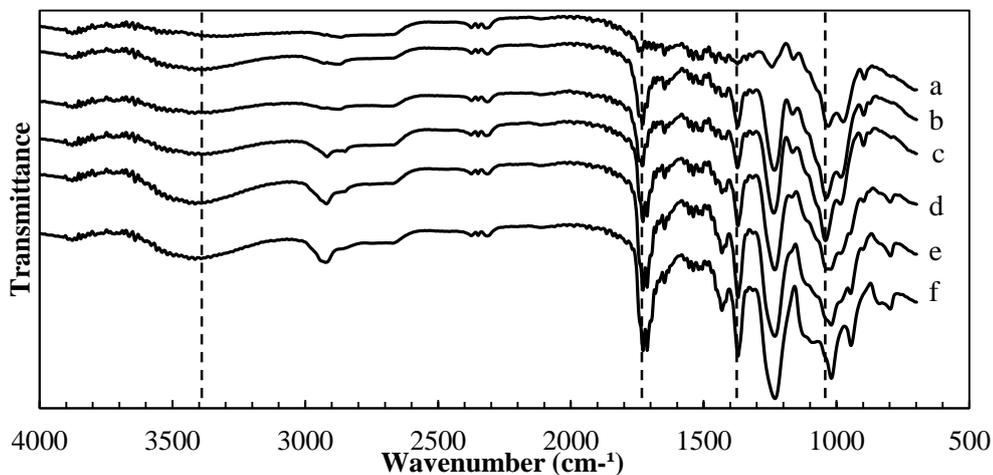


Figure 4.39 Infrared spectra of 24% KOH extracted desalted xylan/PVA strips heat treated at 120°C for 1 hour at different blend ratios (a) xylan, (b) 20 wt% PVA, (c) 40 wt% PVA, (d) 60 wt% PVA, (e) 80 wt% PVA and (f) PVA.

Mechanical properties of heat treated xylan/PVA blends were determined by tensile testing and compared with their native counterparts in Figure 4.40. Tensile testing of acetylated PVA and 80% PVA blend strips could not be determined because the strips lost their integrity during acetylation. Contrary to the previous results of the acetylated strips, tensile strength of the xylan/PVA blends were only slightly increased and elongation at break values were significantly decreased upon acetylation and resulted in stiff and brittle materials.

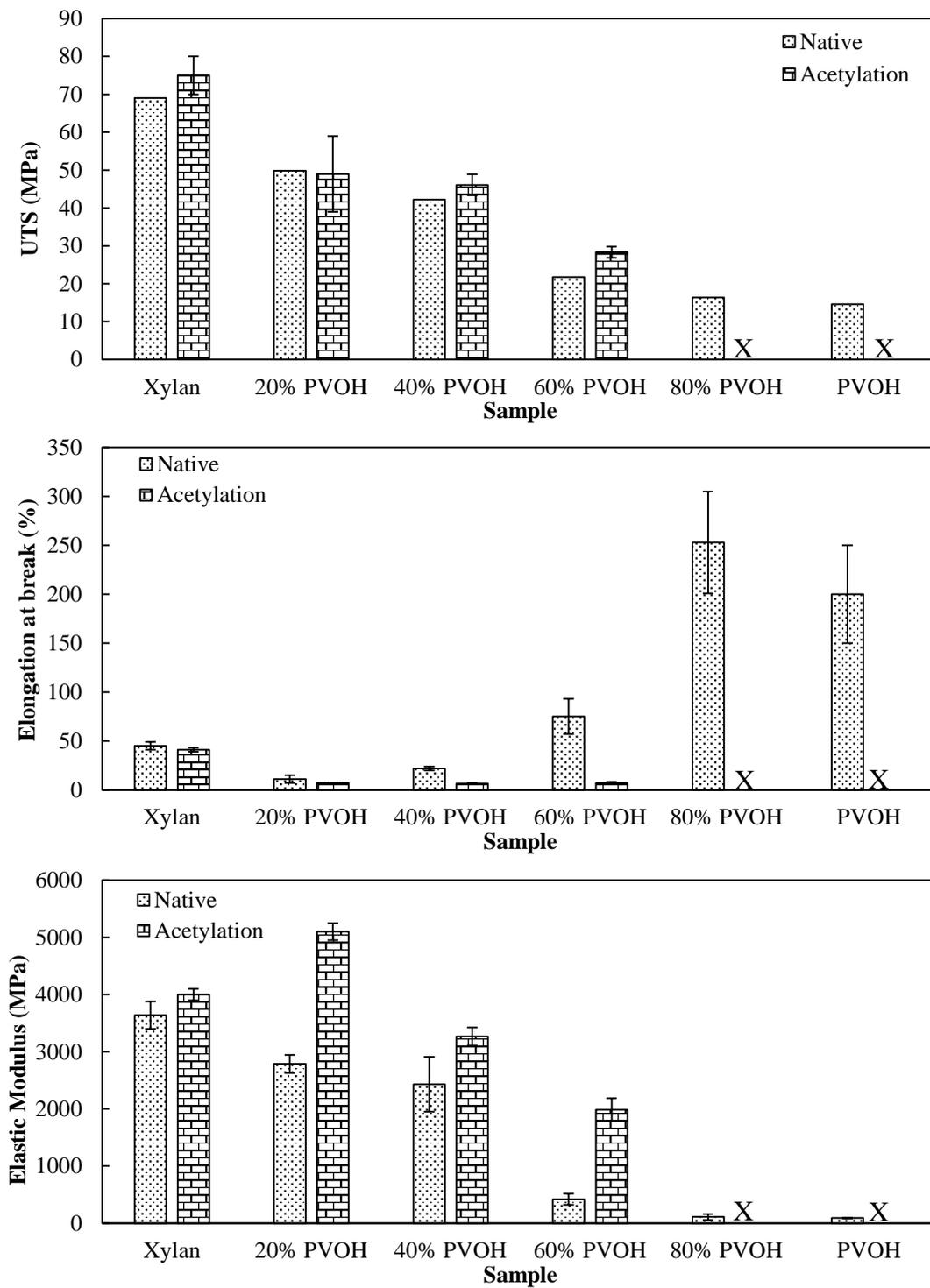


Figure 4.40 Ultimate tensile strength, elongation at break, and elastic modulus values of 24% KOH extracted, desalted xylan and polyvinyl alcohol blend strips at different ratios with and without acetylation.

Moisture contents of the strips at the time of testing decreased upon acetylation as shown in Figure 4.41; however decrease was also not significant in line with the results of the textile testing results. Water solubility values of the strips also decreased but they can be still regarded as highly water soluble (Figure 4.42). Considering the ATR-FTIR results, although the acetylation of xylan and PVA blends can be achieved upon reaction with only acetic anhydride, unexchanged hydroxyl groups were still present which is responsible for only a slight reduction in their water solubility and moisture sensitivity. All in all, blending xylans with PVA might increase the industrial utilization of xylans in their native forms but heat treatment and acetylation approaches might not contribute to their potential applications considering the slight decrease in their water solubility and the significant reduction in their elongation at break and elastic modulus values.

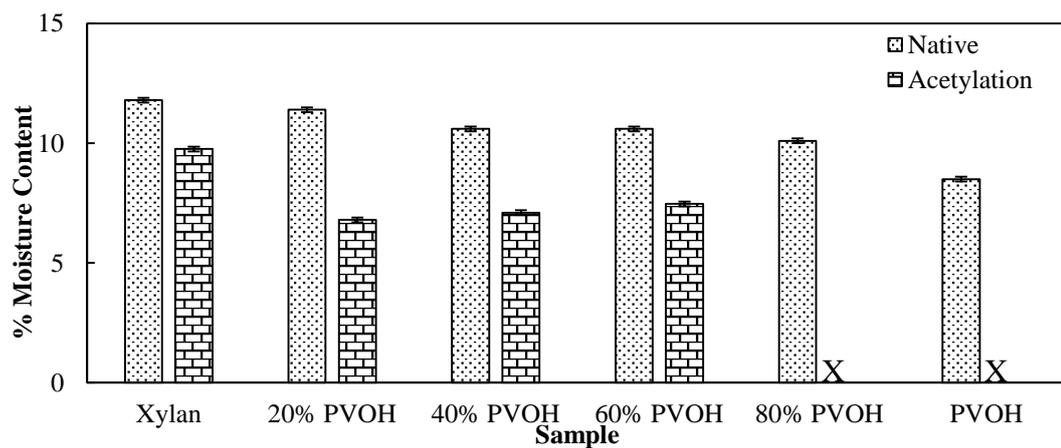


Figure 4.41 Moisture contents of the 24% KOH extracted, desalted xylan and PVA blend strips at different ratios at the time of testing. Prior to tensile testing, the strips were conditioned at 23°C and 50% RH for 1 day. Symbols “x” refer to the strips that could not be tested.

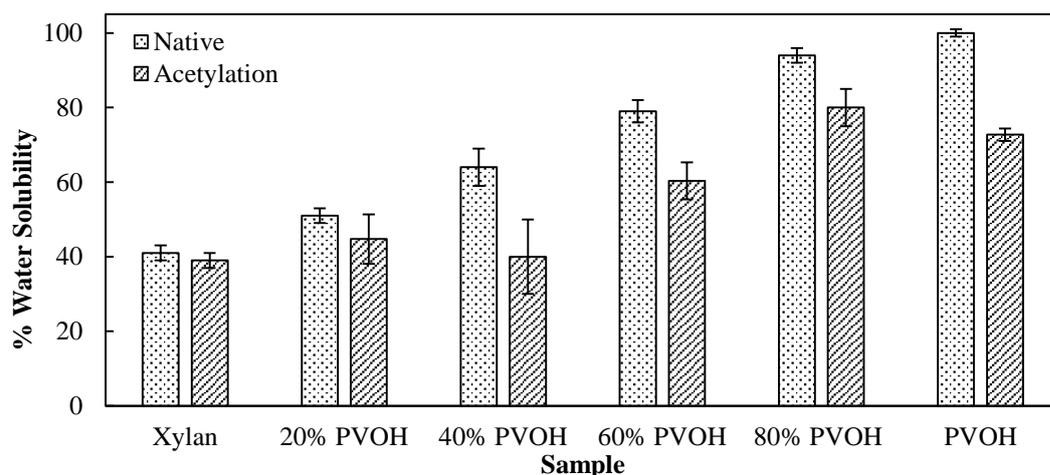


Figure 4.42 Water solubility of the 24% KOH extracted desalted xylan and polyvinyl alcohol blend strips at different ratios. Symbols “x” refer to the strips that could not be tested.

4.4 Comparison of the water vapor transfer rates of the strips

One of the major challenges faced during the utilization of xylans, especially for food packaging applications, is their low resistance to humid conditions. Barrier properties are important for food packaging applications to sustain quality and freshness of the packaged products; however xylan films fail to provide high water vapor barrier properties compared to conventional polymeric materials. Current research activities are focused on the development of xylan based materials to keep up with the water vapor barrier properties of the conventional materials (Weber, 2000). Normalized water vapor transfer rates (NWVTR) of the particular strips exhibiting improved mechanical properties or reduced water sensitivities through heat treatment and acetylation were determined and reported with their native counterparts in Table 4.18. For a clear comparison, parameters related with each strips were also outlined in the Table 4.19 according to the sample numbers.

Table 4.18 Normalized water vapor transfer rates of the xylan strips at 25°C prepared by different approaches, and the examples from the literature representing biobased and synthetic polymers.

Sample	Sample code given in the text	NWVTR (g/day.m²)/μm
1) Desalted xylan	DS	5.8
2) Desalted xylan Heat treatment at 120°C, 1h	-	3.9
3) KAc containing xylan	S-24	X
4) KAc containing xylan Acetylation at 90°C, 30 min.	S-24 A90-30	4.6
5) Desalted xylan – 30 wt% glycerol	30-Gly-120	7.2
6) Desalted xylan – 30 wt% glycerol Acetylation at 120°C, 30 min	30-Gly-120-A30	3.9
7) Polyvinyl alcohol (PVA)	-	2.0
8) Desalted xylan – 40 wt% PVA	-	2.6
9) Desalted xylan – 40 wt% PVA Heat treatment at 120°C, 1h	Heat -	2.5
10) Desalted xylan – 40 wt% PVA Acetylation at 120°C, 30 min	-	2.8
Xylan films with %1 lignin (Goksu <i>et al.</i> 2007)		8.3
Xylan films with %1 lignin+2% glycerol (Goksu <i>et al.</i> 2007)		9.0
Thermoplastic starch (Savadekar <i>et al.</i> ,2012)		3.1
PLA (Shogren, 1997)		3.2
Low density polyethylene (Peroval <i>et al.</i> 2002)		0.5

Table 4.19 Parameters related with the strips according to the sample numbers outlined in the Table 4.18.

	Xylan Extraction	Purification	Additive& Concentration		Extrusion Temperature	Heat Treatment	Acetylation	
1)	24% KOH	Desalted	-		90°C	-	-	
2)	24% KOH	Desalted	-		90°C	120°C	-	
3)	24% KOH	No desalting*	-		90°C	-	-	
4)	24% KOH	No desalting*	-		90°C	-	90°C	30 min
5)	24% KOH	Desalted	Glycerol	30%	120°C	-	-	
6)	24% KOH	Desalted	Glycerol	30%	120°C	-	120°C	30 min
7)			PVA	100%	90°C	-	-	
8)	24% KOH	Desalted	PVA	40%	90°C	-	-	
9)	24% KOH	Desalted	PVA	40%	90°C	120°C	-	
10)	24% KOH	Desalted	PVA	40%	90°C	-	120°C	15 min

* KAc containing strips

Desalted xylan strips that were extruded 90°C (1) were taken as a reference since they were extruded according to the one of the pioneering studies on extrusion of xylans (Bahcegul *et al.* 2013). NWVTR of the heat treated desalted xylan strips (2) decreased significantly probably due to the decrease in free volume in macroscopic level and increased chain interactions upon heat treatment. NWVTR of the KAc containing xylan strips (3) could not be measured because the strips disintegrated from the mask used for the experiment. The strips disintegrated from the masks most probably due to their high moisture sensitivity caused by the presence of KAc. NWVTR of acetylated the KAc containing strips (4) were lower than the desalted xylan strips which might be related with the hydrophobic properties introduced by acetylation. The higher NWVTR of the glycerol plasticized strips (5) compared to the desalted xylan strips (1) can be correlated with their higher free volumes due to the presence of glycerol. NWVTR of the acetylated desalted xylan – 30% wt. glycerol plasticized strips (6) were not only lower than their native counterparts (5) and but also from the desalted xylan strips (1) showing the success of acetylation. NWVTR of PVA were nearly 3 fold lower than desalted xylan strips which is also in line with the literature studies. Addition of 40 wt% PVA to desalted xylans significantly reduced the NWVTR of desalted xylan strips (1); however NWVTR of the samples were not significantly affected by heat treatment and acetylation.

Heat treated desalted xylan strips (2) and acetylated desalted xylan – 30% wt. glycerol plasticized strips (6) exhibited the same NWVTR values at 3.9 (g/day.m²)/μm. The NWVTR of the acetylated the KAc containing strips (4) were a bit higher at 4.6 (g/day.m²)/μm. The highest NWVTR was observed for glycerol containing desalted xylans (5) as 7.2 (g/day.m²)/μm, where NWVTR of the desalted xylans (1) were reported as 5.8 (g/day.m²)/μm. The increase in NWVTR values of the xylan films upon the addition of glycerol was also reported by Goksu *et al.* (2007). The NWVTR of the films were reported to increase from 8.3 (g/day.m²)/μm to 9.0 (g/day.m²)/μm upon the addition of 2% glycerol and correlated with the increases in the free volume. NWVTR of the low density polyethylene was significantly lower than the xylans strips as expected; however when compared with the widely used biobased polymers like thermoplastic starch and PLA, promising NWVTR values were obtained for heat treated (1) and acetylated desalted xylan – 30% wt. glycerol plasticized strips (6).

4.5 Summary of the results

This study was mainly focused on heat treatment, acetylation and blends, all of which can be regarded as separate studies with interpretations of different parameters, but they also bear results which are comparable to each other. This part summarizes the main results and conclusions of the studies on heat treatment, acetylation of xylans in the presence of KAc, acetylation of xylans in the presence of sorbitol and glycerol, and xylan/PVA blends (Table 4.20); and compares the properties of particular samples exhibiting improved mechanical properties or water sensitivities from each study (Table 4.21).

Table 4.20 An overview of the main results

		Main Results
Heat treatment	Heat treatment of desalted xylan strips at different temperatures	<p>Significantly enhanced ultimate tensile strength and moisture uptake upon heat treatment</p> <p>Moisture uptake: Decrease as heat treatment temperature increases (in the range 8.5%-12%)</p> <p>Water solubility: No significant change (in the range 37%-45%)</p> <p>Tensile testing: As heat treatment temperature increases, UTS increases and e_b decreases (in the range 70MPa-127MPa and 12%-48%, respectively)</p> <p>ATR-FTIR: No change in the chemical structure</p> <p>TGA: No change in thermal stability (293°C)</p> <p>SEM: No change in morphology</p>
Acetylation in the presence of KAc	Acetylation of desalted xylans	<p>No acetylation in the absence of KAc</p> <p>Moisture uptake: No significant change (in the range 12%-14%)</p> <p>Water solubility: No significant change (35%)</p> <p>ATR-FTIR: No change in the chemical structure</p> <p>TGA: No change in thermal stability (284°C)</p>
	Acetylation of KAc containing xylans and xylan strips	<p>Efficient acetylation in the presence of KAc.</p> <p>Enhanced water sensitivity and mechanical properties upon acetylation</p> <p>Moisture uptake: Decrease as acetylation temperature and duration increases (in the range 4%-31%)</p> <p>Water solubility: Decrease as acetylation temperature and duration increases (in the range 2%-48%)</p> <p>Tensile testing: Upon acetylation, UTS increases and e_b decreases (in the range 2 MPa-42MPa and 12%-42%, respectively)</p> <p>ATR-FTIR: Changes in the chemical structure (introduction of acetyl groups)</p> <p>TGA: Increased thermal stability (in the range 284°C-349°C)</p>

Table 4.20 An overview of the main results (cont'd)

Main Results	
Extrusion of desalted xylans in the presence of glycerol or sorbitol	<p>Extrusion of xylans can be achieved upon plasticization with sorbitol and glycerol.</p> <p>Xylans were extrudable at lower concentrations of glycerol (20 wt%) compared to sorbitol (30 wt%)</p> <p>Tensile testing: Sorbitol plasticized strips have higher UTS and e_b compared to glycerol plasticization (in the range 8 MPa-38 MPa, 19%-42% for sorbitol and 1 MPa-13 MPa, 15%-24% for glycerol, respectively)</p>
Acetylation in the presence of sorbitol and glycerol	<p>Efficient acetylation in the presence of sorbitol and glycerol.</p> <p>Enhanced water sensitivity for both type of strips, enhanced mechanical properties for glycerol plasticized strips.</p> <p>Moisture uptake: Decrease upon acetylation, more significant for glycerol containing strips (in the range 4.5%-29% for glycerol and 6%-20% for sorbitol)</p> <p>Water solubility: Decrease upon acetylation both for glycerol and sorbitol containing strips (in the range 4%-60% for both)</p> <p>Tensile testing: Upon acetylation, UTS and e_b increases for glycerol containing strips (increases in the range from 1 MPa to 40 MPa and 7% to 42% , respectively) Upon acetylation UTS and e_b decreases for sorbitol containing strips (decreases in the range from 37 MPa to 3 MPa and 40% to 4% , respectively)</p> <p>ATR-FTIR: Changes in the chemical structure both for glycerol and sorbitol containing strips (introduction of acetyl groups)</p> <p>TGA: Increased thermal stability both for glycerol and sorbitol containing strips upon acetylation (in the range 297°C-320°C)</p>
Acetylation of glycerol or sorbitol plasticized desalted xylan strips	

Table 4.20 An overview of the main results (cont'd)

Main Results		
Blending	<p>Extrusion of polyvinyl alcohol and xylan/polyvinyl alcohol blends</p>	<p>Extrudability of PVA was achieved at 90°C by moisture conditioning which was in line with the extrusion processing of desalted xylans.</p> <p>Tensile testing: Compared to the conventional extrusion temperature of PVA at 200°C, UTS decreased from 85 MPa to 15 MPa and e_b increased from 61% to 200%. Upon the addition of PVA to desalted xylans at different ratios, UTS of xylans strips decreased and e_b first decreased, then increased (in the range of 15 MPa-70 MPa and 11%-250%)</p> <p>Moisture uptake: Reduced upon increasing PVA ratio in blends (in the range 8.5%-12%)</p>
	<p>Heat treatment and acetylation of desalted xylan/polyvinyl alcohol blend</p>	<p>Acetylation of PVA and xylan/PVA blends achieved</p> <p>Enhanced ultimate tensile strength and moisture uptake, reduced elongation at break values upon heat treatment and acetylation.</p> <p>Moisture uptake: Reduced upon heat treatment and acetylation (in the range 4%-12% and 7%-12%)</p> <p>Water solubility: Increased upon increasing PVA ratio in blends (in the range 41%-100%) No change upon heat treatment (in the range 41%-100%) Decreased with acetylation (to the range 39%-73%)</p> <p>Tensile testing: Upon heat treatment, UTS increases, e_b decreases (in the range 15 MPa-120 MPa and 6%-250%) Upon acetylation, UTS increases, e_b decreases (in the range 15 MPa-75 MPa and 7%-250%)</p> <p>ATR-FTIR: No change upon heat treatment. Changes in chemical structure upon acetylation for xylan/PVA blend strips and PVA strips except for xylan strips.</p> <p>SEM: No phase separation. Morphology resembles either xylan or PVA depending on their relative concentrations.</p>

In order to correlate the results outlined in Table 4.20 and to disclose the samples that are most relevant to the goals of the study; strips exhibiting improved mechanical properties and water sensitivities upon heat treatment or acetylation were compared together with their native counterparts in Table 4.21 and in Figure 4.43. For a clear comparison, parameters related with each strip were also outlined in the Table 4.22 according to the sample numbers.

Reducing the water solubility and moisture uptake of the xylan strips was the major aim of this study. As can be inferred from the Table 4.21, this aim was accomplished better by acetylation reaction compared to heat treatment. Water solubility of acetylated KAc containing xylan strips (4) and glycerol plasticized xylans strips (6) were significantly reduced to 14% and 6%, respectively, where solubility of the heat treated xylans strips (2) were around 42%. Water solubilities of xylan/PVA blends were also reduced by heat treatment (9) and acetylation (10) but the solubility values were still quite high around 61% and 40%, respectively, most probably due to the complete water solubility values of PVA. The results also showed that water solubility of the native xylan strips (1) increased in the presence of KAc (3), glycerol (5) and PVA (8).

Parallel to the water solubility values, the presence of KAc (3) and glycerol (5) increased the moisture contents of the xylan strips (1) at 50% relative humidity. Similar trends were also seen in literature showing that the increase in moisture contents were related with the addition of hydrophilic plasticizers like glycerol and KAc (Mikkonen *et al.* 2009; Bahcegul *et al.* 2014). Both heat treatment and acetylation was successful in reducing the moisture contents of the strips that they were applied. Although the changes in moisture content values of the strips might not seem as drastic as the changes in water solubility values, their effect is more prominent on the mechanical properties. A decrease in the moisture contents of the desalted xylan strips from 12% to 9% upon heat treatment resulted in a 1.5 fold increase in the ultimate tensile strength from 69 MPa to 95 MPa.

Table 4.21 Water solubility, moisture content (MC), ultimate tensile strength (UTS), elongation at break (e_b) and normalized water vapor transfer rates (NWWTR) of the xylan strips prepared by different approaches together with the examples from the literature representing biobased and synthetic polymers.

Sample	Sample code given in the text	Water solubility (%)	MC* (%)	UTS* (MPa)	e_b * (%)	NWWTR** (g/day.m ²)/ μ m
1) Desalted xylan	DS	45%	12%	69 MPa	45%	5.8 (g/day.m ²)/ μ m
2) Desalted xylan Heat treatment at 120°C, 1h	-	42%	9%	95 MPa	23%	3.9 (g/day.m ²)/ μ m
3) KAc containing xylan	S-24	51%	16%	7 MPa	41%	X
4) KAc containing xylan Acetylation at 90°C, 30 min.	S-24 A90-30	14%	9%	13 MPa	21%	4.6 (g/day.m ²)/ μ m
5) Desalted xylan – 30 wt% glycerol	30-Gly-120	60%	21%	5 MPa	26%	7.2 (g/day.m ²)/ μ m
6) Desalted xylan – 30 wt% glycerol Acetylation at 120°C, 30 min	30-Gly-120-A30	6%	8%	36 MPa	30%	3.9 (g/day.m ²)/ μ m
7) Polyvinyl alcohol (PVA)	-	100%	9%	15 MPa	200%	2.0 (g/day.m ²)/ μ m
8) Desalted xylan – 40 wt% PVA	-	64%	11%	42 MPa	22%	2.6 (g/day.m ²)/ μ m
9) Desalted xylan – 40 wt% PVA Heat treatment at 120°C, 1h	-	61%	6%	73 MPa	7%	2.5 (g/day.m ²)/ μ m
10) Desalted xylan – 40 wt% PVA Acetylation at 120°C, 30 min	-	40%	7%	46 MPa	6%	2.8 (g/day.m ²)/ μ m

*determined at 23°C and 50% relative humidity conditions, **determined at 25°C

Table 4.21 Water solubility, moisture content (MC), ultimate tensile strength (UTS), elongation at break (e_b) and normalized water vapor transfer rates (NWVTR) of the xylan strips prepared by different approaches together with the examples from the literature representing biobased and synthetic polymers (cont'd).

Sample	Sample code given in the text	Water solubility (%)	MC* (%)	UTS* (MPa)	e_b * (%)	NWVTR** (g/day.m ²)/ μ m
Xylan films with % 1 lignin (Goksu <i>et al.</i> 2007)		99%	-	2 MPa	50%	8.3 (g/day.m ²)/ μ m
Xylan films with % 1 lignin+2% glycerol (Goksu <i>et al.</i> 2007)		98%	-	1 MPa	88%	9.0 (g/day.m ²)/ μ m
Thermoplastic starch (Thunwall <i>et al.</i> 2006; Savadekar <i>et al.</i> 2012; Ninago <i>et al.</i> 2015)		80%	17%	2-25 MPa	2-56%	3.1 (g/day.m ²)/ μ m
PLA (Shogren, 1997; Bahcegul <i>et al.</i> 2013)				52 MPa	12%	3.2 (g/day.m ²)/ μ m
Low density polyethylene (Peroval <i>et al.</i> 2002)				13-28 MPa	100-965%	0.5 (g/day.m ²)/ μ m

*determined at 23°C and 50% relative humidity conditions, **determined at 25°C

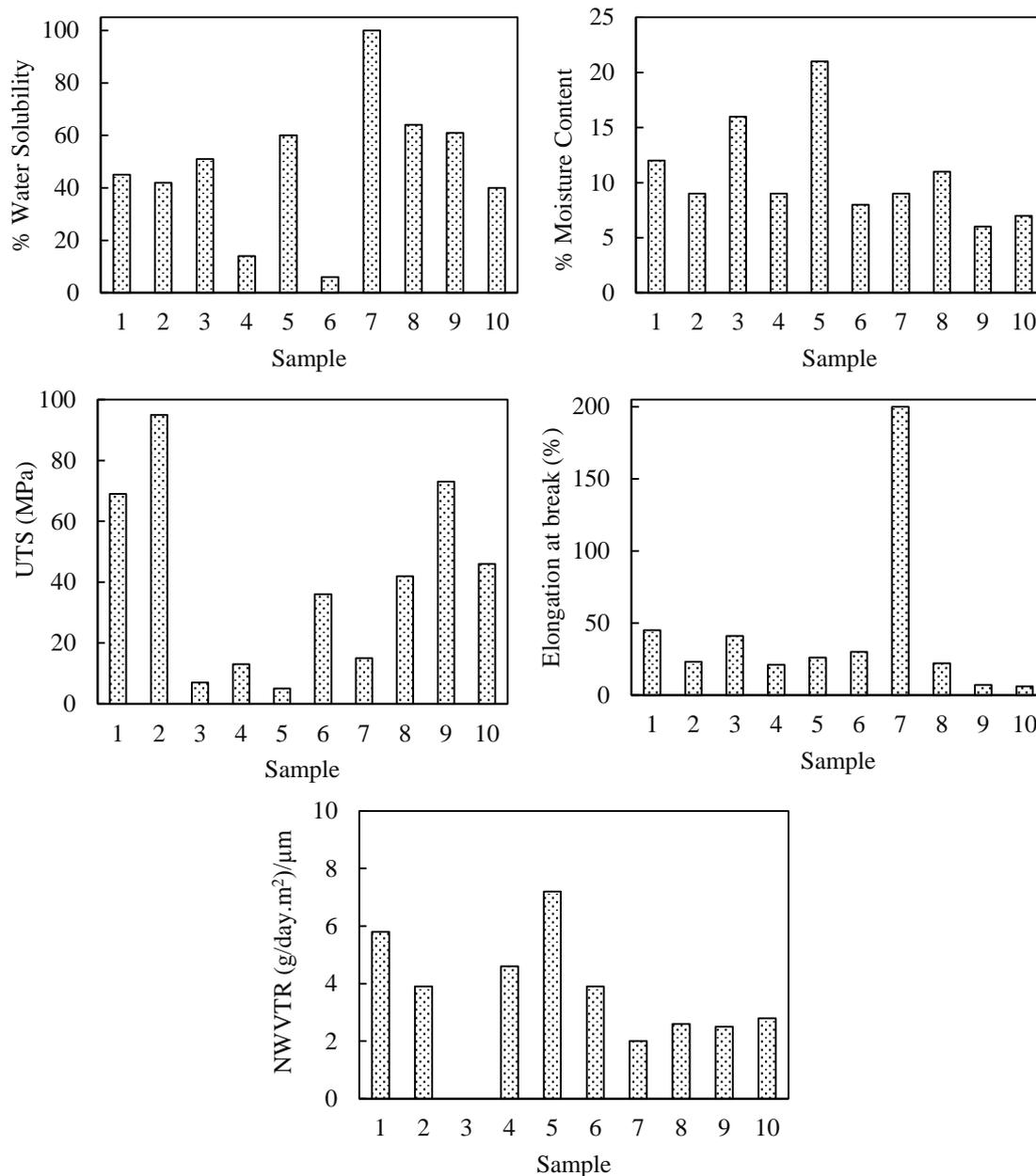


Figure 4.43 Water solubility, moisture content, ultimate tensile strength (UTS), elongation at break, and normalized water vapor transfer rates (NWVTR) of the xylan strips prepared by different approaches. The explanations of the sample numbers were given in Table 4.22.

Table 4.22 Parameters related with the strips according to the sample numbers outlined in the Table 4.21.

	Xylan Extraction	Purification	Additive & Concentration		Extrusion Temperature	Heat Treatment	Acetylation	
1)	24% KOH	Desalted	-		90°C	-	-	
2)	24% KOH	Desalted	-		90°C	120°C	-	
3)	24% KOH	No desalting*	-		90°C	-	-	
4)	24% KOH	No desalting*	-		90°C	-	90°C	30 min
5)	24% KOH	Desalted	Glycerol	30%	120°C	-	-	
6)	24% KOH	Desalted	Glycerol	30%	120°C	-	120°C	30 min
7)			PVA	100%	90°C	-	-	
8)	24% KOH	Desalted	PVA	40%	90°C	-	-	
9)	24% KOH	Desalted	PVA	40%	90°C	120°C	-	
10)	24% KOH	Desalted	PVA	40%	90°C	-	120°C	15 min

Mechanical properties of the strips at 50% relative humidity exhibit a wide range between 5 MPa and 95 MPa for ultimate tensile strength and 7% to 200% for elongation at break values. First of all, the presence of KAc and glycerol reduced the ultimate tensile strength of the xylan strips due to their plasticization effect. Ultimate tensile strength of the xylans were also reduced upon the addition of PVA which already exhibited lower ultimate tensile strength values than xylan. Compared to their native counterparts, both heat treatment and acetylation resulted in an increase in the ultimate tensile strength values. Although the highest ultimate tensile strength was exhibited by heat treated strips at 95 MPa with a 1.5 fold increase compared to its native counterpart, the increase in ultimate tensile strength upon acetylation was higher at around 2 fold and 7 fold for KAc containing and glycerol containing xylans, respectively. The presence of KAc (3) and glycerol (5) also reduced the elongation at break values of the xylan strips (1) contrary to the trends in literature showing the increase in the elongation at break values in the presence of plasticizers (Mikkonen *et al.* 2009). The results can be correlated with the reduced ultimate tensile strength of the strips causing premature failure without much elongation. PVA strips exhibited high elongation at break values; however xylan/PVA blend at 40 wt% ratio exhibited lower elongation at break values than both xylan and PVA which was further reduced

upon heat treatment an acetylation. Elongation at break values of the glycerol plasticized strips (5) increased from 26% to 30% upon acetylation (6), which was also accompanied by the increase in the ultimate tensile strength, thereby exhibiting higher ultimate tensile strength values and the elongation at break values at the same time.

The results were also compared with other studies in the literature representing properties of xylan films obtained by solvent casting, conventional biopolymers and synthetic polymers with similar application purposes. Cotton stalk xylan based films exhibited very high water solubility indicating the high hydrophilicity of xylans (Goksu *et al.* 2007). The ultimate tensile strength values of the films were very low, which was usually the case for solvent casted films (Goksu *et al.* 2007). Extruded desalted xylan strips (1) exhibited superior ultimate tensile strength, similar elongation at break values and lower NWVTR compared to xylan films showing that extrusion is a promising technique for the production of xylan based materials. The properties of all the xylan strips were also comparable with thermoplastic starch, exhibiting similar ultimate tensile strength and elongation at break values in similar ranges, but lower NWVTR (Thunwall *et al.* 2006). As expected, all xylan strips possessed lower elongation at break values and higher water vapor transfer rates compared to LDPE. Acetylated glycerol plasticized desalted xylan strips (6) exhibiting the lowest water solubility with moderate mechanical properties and water vapor transfer rates were the most relevant sample to the major aim of this study. When compared with PLA, one of the most widely utilized water insoluble biopolymer, which have ultimate tensile strength and elongation at break values around 52 MPa and 12% (Bahcegul *et al.* 2013), respectively; acetylated glycerol plasticized xylan strips can be regarded as ideal candidates as sustainable biopolymers for industrial applications.

CHAPTER 5

CONCLUSIONS

The major aim of this study was to decrease the moisture uptake and the water solubility of xylans, one of the most abundant types of hemicelluloses, by heat treatment and acetylation to refer their utilization in packaging applications. By doing so, their extrusion processing with sorbitol and glycerol, and blends with polyvinyl alcohol were also addressed to stress their potential utilization. The main conclusions of the study are outlined in the following points

- Native xylans were extrudable in the presence of KAc, sorbitol, glycerol and polyvinyl alcohol; however acetylated xylans could not be extruded effectively.
- Presence of KAc decreased the mechanical properties of native xylan strips. Mechanical properties of the KAc containing xylan strips further decreased by the increase in the KAc content.
- Use of sorbitol and glycerol as plasticizers resulted in lower mechanical properties compared to moisture conditioned native xylan strips. Glycerol exhibited better plasticization effect compared to sorbitol rendering xylans extrudable at lower concentrations and extrusion temperatures. Under the same extrusion conditions and concentrations, sorbitol plasticized strips exhibit higher mechanical properties.
- Ultimate tensile strength of the native xylan/polyvinyl alcohol blend strips decreased and elongation at break values first decreased, then increased with an increase in the polyvinyl alcohol concentration.
- Heat treatment significantly decreased the moisture uptake of desalted xylan strips providing improved ultimate tensile strength values as high as 120 MPa. Although the heat treatment did not have a significant effect on the

water solubility, the method can still be utilized for applications that do not involve direct contact with water.

- Potassium acetate (KAc), produced during the alkaline extraction was shown to have a positive effect on the acetylation reaction.
- Upon acetylation of KAc containing strips, moisture uptake, water solubilities and water vapor transfer rates were decreased and mechanical properties were increased significantly.
- Sorbitol and glycerol also exhibited a positive effect towards the acetylation of xylans. Mechanical properties of glycerol plasticized strips were significantly increased upon acetylation.
- Heat treatment and acetylation reduced the water solubility and moisture uptake of the xylan/polyvinyl alcohol blend strips, but resulted in brittle materials.
- Both heat treatment and acetylation resulted in strips with reduced water vapor transfer rates showing better barrier properties against water vapor.

Consequently, acetylation was shown to be more effective compared to heat treatment, in terms of reducing the water solubility of the xylan strips. Acetylated glycerol plasticized xylan strips yielded very low water solubility values with sufficient mechanical and enhanced water vapor barrier properties paving the way to industrial utilization of xylans.

CHAPTER 6

RECOMMENDATIONS

In the light of the results of this study,

- Further studies on the properties of the xylan strips, e.g. oxygen barrier properties, might be conducted to fully address their applicability. To achieve this, strips with higher surface areas have to be produced which might be carried out in a medium scale extruder.
- Processing of xylans other than the extrusion technique can also be studied in the presence of plasticizers to comprehensively cover the processing techniques of conventional polymers. Applicability of techniques like injection or compression molding might lead to new application areas of xylans to substitute petroleum based polymers.
- Studies on xylan blends with other biopolymers, and especially with carboxymethyl cellulose might play an important role to increase the industrial utilization of xylans. Besides, processing of xylans with polylactic acid might also be promising in terms of packaging applications.
- Biodegradability of acetylated xylans might be studied to assess the impact of acetylation reaction.
- Antimicrobial properties of acetylated xylans could also be investigated.

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APPENDIX A

CALIBRATION CURVES FOR MONOSACCHARIDE ANALYSIS

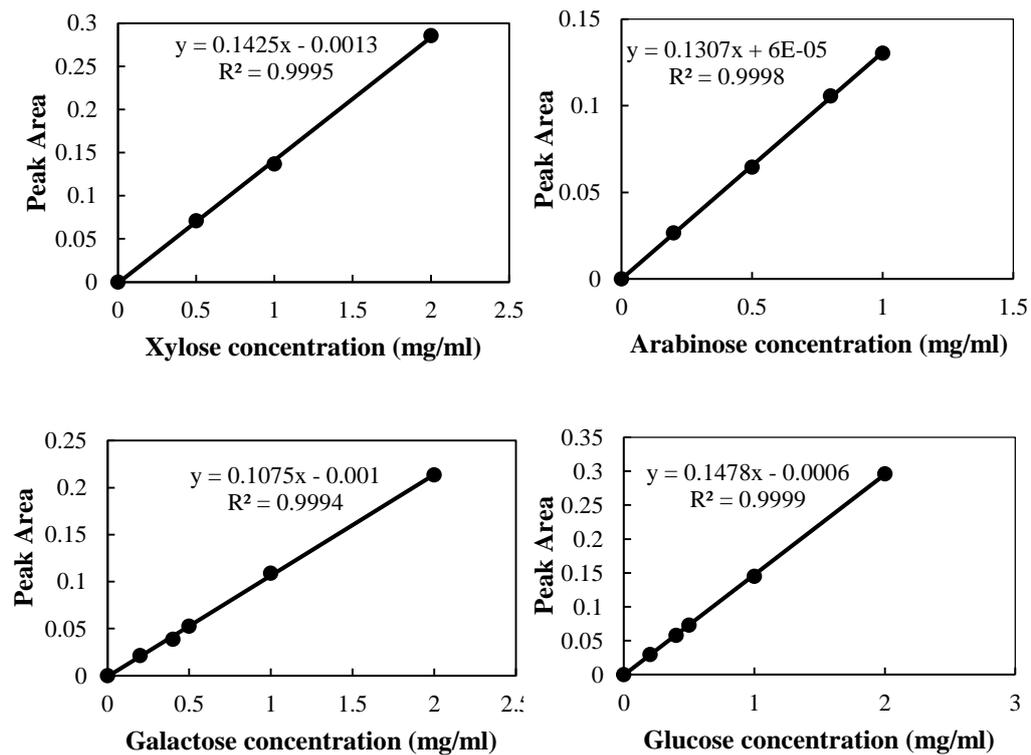


Figure A.1 Calibration curves used to determine monosaccharide compositions of extracted xylans by HPLC analysis (Shimadzu LC-20A HPLC system equipped with a transgenomics CARBOsep COREGEL-87P column).

APPENDIX B

CALIBRATION CURVE FOR ALKALI SOLUBLE LIGNIN

Commercial alkali soluble lignin (Sigma Aldrich) was used as a standard at different concentrations in 4% (w/v) NaOH solution. A linear calibration curve was fitted to the data obtained at 280 nm via UV-Visible Spectrophotometer (Nicolet Evolution 100, Thermo Fisher Scientific Inc., USA).

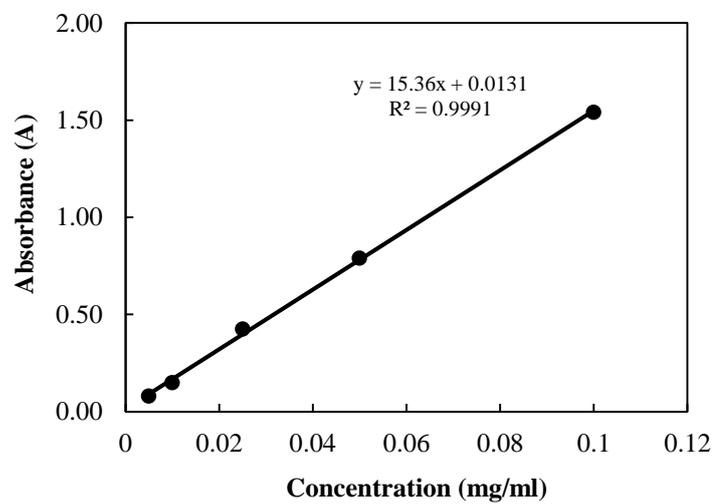


Figure B.1 Calibration curve used to determine alkaline soluble lignin concentrations in extracted hemicelluloses.

APPENDIX C

CALIBRATION CURVE FOR POTASSIUM ACETATE

Commercial potassium acetate (Sigma Aldrich) was dissolved in deionized water at different concentrations. Conductivity of the standard solutions were measured by conductivity meter (Inolab, WTW Cond 720, Germany) at room temperature and a linear calibration curve was fitted to the data.

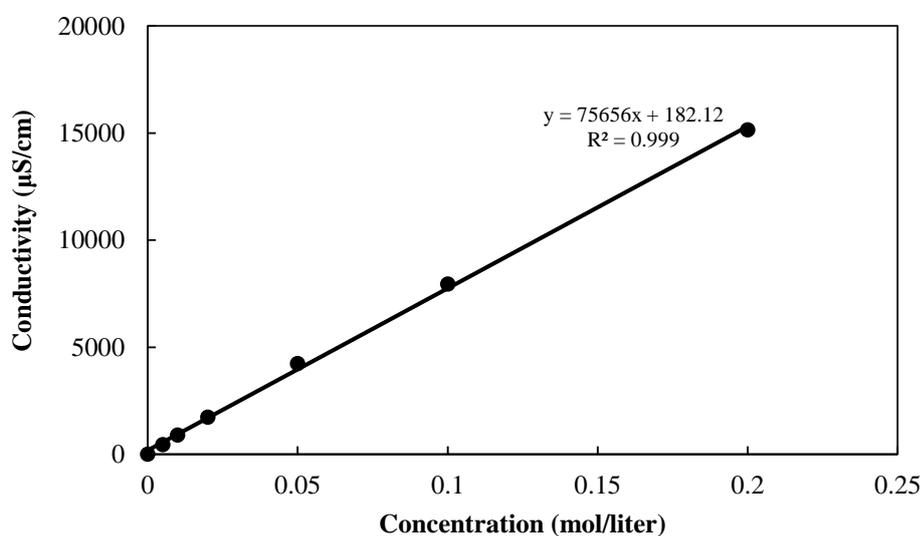


Figure C.1 Calibration curve used to determine residual salt concentrations in extracted hemicelluloses.

APPENDIX D

VISCOSITY AVERAGE MOLECULAR WEIGHTS

Viscosity average molecular weights of desalted xylans, acetylated desalted xylans (1 hour), KAc containing xylans and acetylated KAc containing xylans (1 hour and 4 hours) outlined in Table 4.7 were determined by capillary viscometry as explained in Section 3.6.2. One data set for each of the samples were given below, where the viscosity average molecular weights of the samples were reported by averaging 2 or 3 data sets for each sample.

Table D.1 Data set for desalted xylans (DS), acetylated desalted xylans (DS A120-1h), KAc containing xylans (S) and acetylated KAc containing xylans (S A120-1h and S A120-4h) where concentration and time data was recorded as the raw data. Time data refer to the average of three measurements.

	Concentration (g/dl)	Time (sec)	η_{rel}	η_{sp}	η_{red}	$\ln(\eta_{red})/c$	η_{sp}/c
Sample Code DS	0.8	462	1.92	0.92	1.15	0.81	1.15
	0.6	399	1.66	0.66	1.09	0.84	1.09
	0.4	336	1.39	0.39	0.99	0.83	0.99
	0.2	286	1.19	0.19	0.93	0.86	0.93
	0 (t_0)	240	1	0	0	0	0
	Concentration (g/dl)	Time (sec)	η_{rel}	η_{sp}	η_{red}	$\ln(\eta_{red})/c$	η_{sp}/c
Sample Code DS A120- 1h	0.8	430	1.78	0.78	0.98	0.72	0.98
	0.6	374	1.55	0.55	0.92	0.73	0.92
	0.4	327	1.36	0.36	0.89	0.76	0.89
	0.2	283	1.17	0.17	0.87	0.80	0.87
	0 (t_0)	240	1	0	0	0	0

Table D.1 (cont'd)

	Concentration (g/dl)	Time (sec)	η_{rel}	η_{sp}	η_{red}	$\ln(\eta_{red})/c$	η_{sp}/c
Sample Code S	0.8	356	1.48	0.48	0.60	0.49	0.60
	0.6	319	1.33	0.33	0.55	0.47	0.55
	0.4	287	1.20	0.20	0.49	0.45	0.49
	0.2	262	1.09	0.09	0.46	0.44	0.46
	0 (t ₀)	240	1	0	0	0	0
	Concentration (g/dl)	Time (sec)	η_{rel}	η_{sp}	η_{red}	$\ln(\eta_{red})/c$	η_{sp}/c
Sample Code S A120- 1h	0.8	360	1.49	0.49	0.62	0.50	0.62
	0.6	329	1.37	0.37	0.61	0.52	0.61
	0.4	302	1.25	0.25	0.63	0.56	0.63
	0.2	271	1.12	0.12	0.62	0.59	0.62
	0 (t ₀)	240	1	0	0	0	0
	Concentration (g/dl)	Time (sec)	η_{rel}	η_{sp}	η_{red}	$\ln(\eta_{red})/c$	η_{sp}/c
Sample Code S A120- 4h	0.8	368	1.53	0.53	0.67	0.53	0.67
	0.6	335	1.40	0.40	0.66	0.56	0.66
	0.4	302	1.26	0.26	0.65	0.57	0.65
	0.2	270	1.13	0.13	0.63	0.59	0.63
	0 (t ₀)	240	1	0	0	0	0

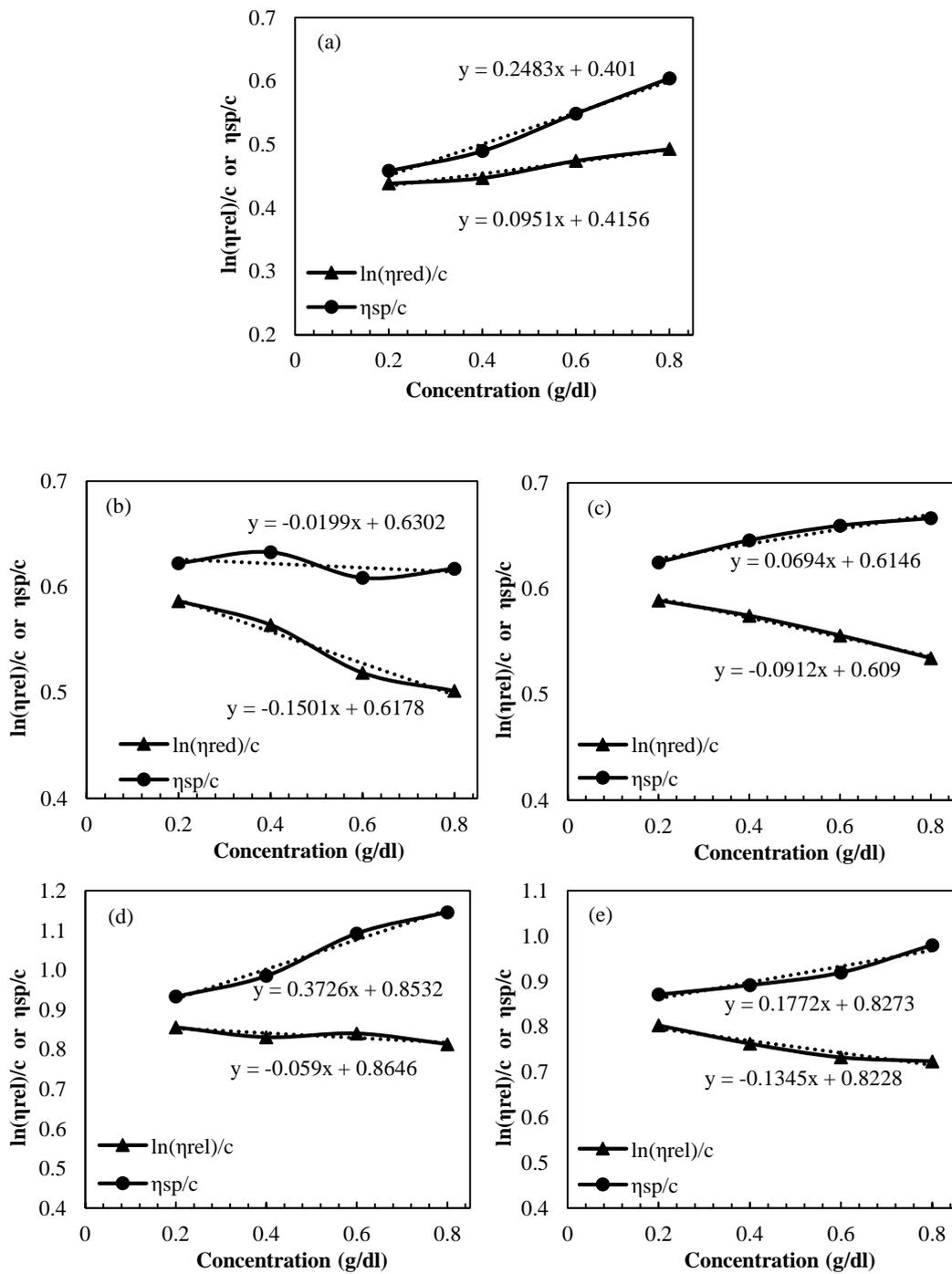


Figure D.1 Plots that were used to find the viscosity average molecular weight of S (a), S A120-1h (b), S A120-4h (c), DS (d) and DS A 120-1h (e). Intercepts of the two plots for each sample was averaged to determine the intrinsic viscosity which is used in Mark-Houwink-Sakurada equation.

APPENDIX E

STATISTICAL ANALYSIS (P VALUES) FOR MONOSACCHARIDE COMPOSITIONS AT DIFFERENT EXTRACTION CONDITIONS

Table D.1 p-values for glucose, xylose, arabinose and galactose concentrations determined by HPLC analysis at different extraction conditions.

GLUCOSE	10% KOH KAc containing	10% KOH desalted	24% KOH KAc containing	24% KOH desalted
10% KOH KAc containing	-	0.71	0.45	0.90
10% KOH desalted	0.71	-	0.56	0.60
24% KOH KAc containing	0.45	0.56	-	0.35
24% KOH desalted	0.90	0.60	0.35	-
XYLOSE	10% KOH KAc containing	10% KOH desalted	24% KOH KAc containing	24% KOH desalted
10% KOH KAc containing	-	0.15	0.53	0.51
10% KOH desalted	0.15	-	0.13	0.18
24% KOH KAc containing	0.53	0.13	-	0.74
24% KOH desalted	0.51	0.18	0.74	-
GALACTOSE	10% KOH KAc containing	10% KOH desalted	24% KOH KAc containing	24% KOH desalted
10% KOH KAc containing	-	0.23	0.25	0.58
10% KOH desalted	0.23	-	0.88	0.68
24% KOH KAc containing	0.25	0.88	-	0.65
24% KOH desalted	0.58	0.68	0.65	-
ARABINOSE	10% KOH KAc containing	10% KOH desalted	24% KOH KAc containing	24% KOH desalted
10% KOH KAc containing	-	0.09	0.48	0.90
10% KOH desalted	0.09	-	0.26	0.29
24% KOH KAc containing	0.48	0.26	-	0.64
24% KOH desalted	0.90	0.29	0.64	-

2-sample t-test was conducted by Minitab 1.6 for the results outlined in Table 4.2. (compositional data of the hemicellulose rich residues isolated from corn cobs by different alkaline extraction conditions). p-values were listed in the following tables and the values $p > 0.05$ shows that the results are in within the 95% confidence interval (not significantly different).

APPENDIX F

EXTRUSION OF ACETYLATED XYLANS

Extrusion of acetylated xylans was studied in the presence of Tween 80 (polysorbate 80) and triacetin to investigate their processibility. KAc containing xylans were extracted by 10% KOH alkaline solutions and acetylated at 120°C for 1 hour to achieve sufficient hydrophobic characteristics as shown in Section 4.2.2. Preliminary studies showed that during the extrusion of acetylated xylans without any additive, maximum torque of the extruder was reached within a few seconds following the feeding. With the use of Tween 80, this behavior was delayed for a couple of minutes. The performance of triacetin was better as the film like structures were formed on the screws although the maximum torque has been reached. Acetylated xylans without any plasticizer were crumbled into dust inside the barrel. Better film formation was observed on the screws when 150°C extrusion temperature was used (Figure F.1).

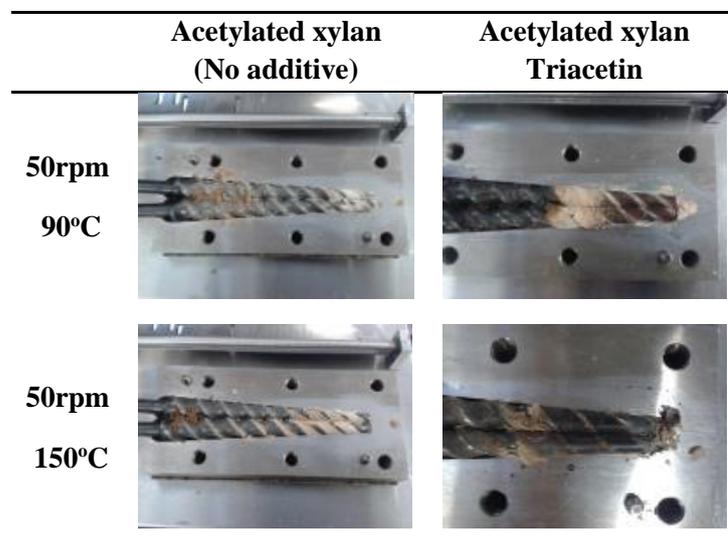


Figure F.1 Appearances of the acetylated KAc containing xylans (10% KOH extracted) inside the barrel on the screws of the extruder, just after the extrusion was terminated due to torque limitations.

In the light of the preliminary experiments, five more experimental sets were performed with triacetin by different plasticizer concentrations and extrusion temperatures (Table F.1). Extrusions of acetylated xylans at 33% triacetin content were all terminated before the product comes out of the die because screws were hardly moving and maximum torque was reached due to poor polymer flow. No torque limitation was observed when 50% triacetin was used and polymers were able to pass through the die; however the strips were crumbled into pieces just after coming out of the die.

Table F.1 Extrusion of KAc containing xylans acetylated at 120°C for 60 minutes

Plasticizer	Amount (w/w)	Extrusion Temp.	Extrudability	Comments
Triacetin	33%	90°C	X	Max. torque reached
Triacetin	33%	120°C	X	Max. torque reached
Triacetin	33%	150°C	X	Max. torque reached
Triacetin	50%	120°C	~	Strips crumbled into pieces just after coming out of the die

Acetylated xylans could not be extruded in the presence of triacetin due to poor polymer flow. Although no torque limitation was observed, 50% addition of triacetin as a plasticizer was not rational so no further studies were conducted by increasing the extrusion temperature. Alternative to triacetin, glycerol and sorbitol were utilized as plasticizers. Acetylation reaction was carried out for 30 minutes instead of 60 minutes for moderate acetylation to make use of remaining hydrophilic groups for plasticization with sorbitol and glycerol. Extrusion temperature kept constant at 150°C because previous studies showed that although strips didn't come out of the die, film like structures were formed on the screws at this temperature. Higher extrusion temperatures were not studied due to the possibility of hemicellulose degradation. Plasticizer concentration was kept constant and the sequence of plasticizer addition was changed as a parameter to find out the most compatible

interaction. Xylans were mixed with plasticizers before the acetylation reaction (BA) or after the acetylation reaction (AA) at 120°C for 30 minutes and then extruded at 150°C and 50 rpm. Parameters and the appearances of the extruded strips are listed in Table F.2

Table F.2 Extrusion of KAc containing xylans acetylated at 120°C for 30 minutes

Plasticizer	Amount (w/w)	Plasticizer Addition*	Extrusion Temp.	Extruded Strip	Comments
sorbitol	33%	BA	150°C		Brittle
sorbitol	33%	AA	150°C		Brittle
glycerol	33%	BA	150°C		Brittle
glycerol	33%	AA	150°C		Soft, flexible

*BA: Before Acetylation AA: After acetylation

First of all, notable differences in appearance between the extruded strips were created by the sequence of the plasticizer addition. Regardless of the plasticizer type, plasticizer addition after the acetylation step yielded better strips in terms of appearance. When the plasticizers were compared, strips with glycerol were much more continuous and flexible than the ones with sorbitol; however they still have rough edges and surfaces making them inappropriate for mechanical characterizations. Following experiments were conducted with glycerol by changing glycerol amount, extrusion temperature and acetylation reaction time. The appearance of the extruded strips and parameters are listed in Table E.3. As seen in the first three rows of the table, extrusion with 33% (wt/wt) glycerol addition resulted in physically better strips. With 50% (wt/wt) addition of glycerol, viscosity of the polymer probably became too low that screws were freely moving and extrudate could not come out of the die. On the other hand, 10% (wt/wt) addition of glycerol

did not provide sufficient flexibility to obtain continuous strips. Three different temperatures were tested for the extrusion of 33% (wt/wt) glycerol containing polymers. Extrusion at 90°C was terminated before the product comes out of the die because maximum torque was reached. When acetylation reaction time was increased, glycerol was no longer able to plasticize xylan polymers possibly due to the higher degree of acetylation and lower compatibility of the polymer with glycerol.

Table F.3 Extrusion of glycerol containing xylans acetylated at 120°C.

Plasticizer	Amount (w/w)	Acetylation	Extrusion Temp.	Extruded Strip	Comments
glycerol	50%	30 min	150°C	X	Not viscous enough to flow
glycerol	33%	30 min	150°C		Soft, flexible
glycerol	10%	30 min	150°C		Brittle, fragmented
Use %33 glycerol					
glycerol	33%	30 min	90°C	X	Max. torque reached
glycerol	33%	30 min	120°C		(smoother than 150°C counterpart)
glycerol	33%	30 min	150°C		Soft, flexible
glycerol	33%	60 min	90°C	X	Max. torque reached
glycerol	33%	60 min	120°C	X	Max. torque reached
glycerol	33%	60 min	150°C	X	Max. torque reached

Among all the parameters tested, best strips by appearance were obtained by the extrusion of 33% (w/w) glycerol plasticized acetylated xylans at 120°C; however the resulting strips were very weak with an ultimate tensile strength around 0.7 MPa at 50% relative humidity.

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PUBLICATIONS

Peer-reviewed Publications Indexed in SCI

Akkus, M., Bahcegul, E., Ozkan, N., Bakir, U. (2014). Post-extrusion heat treatment as a facile method to enhance the mechanical properties of extruded xylan based polymeric materials, *RSC Advances*, 4, 62295-62300.

Akkus, M., Ozkan, N., Bakir, U. (2015). Efficient acetylation of xylans in the presence of potassium acetate, *In Progress*.