

PROPERTIES OF FLEXIBLE FILMS MADE OF HEMICELLULOSE

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ABSTRACT

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Hemicellulose is the second most abundant component of plant cell walls after cellulose. It has received increasing interest as an alternative to petroleum based polymers for packaging applications because of its abundance, renewability and biodegradability. However, there are some challenges in the utilization of hemicellulose as a packaging material. Hemicelluloses are complex heteropolysaccharides with varied compositions and structures depending on the hemicellulose source (e.g., plant species, location and growth stage); they can also be influenced by the chemical, physical and biological isolation processes used to isolate them, and by any pretreatment used before isolation. It is critical to understand the influence of these factors (hemicellulose source, isolation approach, and pretreatment) on the final hemicellulose properties, such as mechanical and barrier properties, which are important for packaging applications. In addition, pure hemicellulose obtained from plants is water sensitive, brittle and weak, making it unsuitable for most packaging applications even though it is a good barrier for oxygen. Modification of hemicellulose is needed to meet the requirements of packaging materials such as protection against chemical, mechanical, physical and biological damage, and good barrier against water, oxygen, odors, etc.

This research focuses on the fabrication and characterization of hemicellulose based films with adequate properties to enable their potential application as packaging materials. Three types of raw materials, aspen ChemiThermoMechanical Pulp (CTMP), spruce CTMP and hybrid poplar powder, with different pretreatments (bleaching and no bleaching) were employed to

obtain hemicelluloses by an alkaline extraction method. The extracted hemicellulose was further formed into film by solvent casting in water with the addition of sorbitol and glutaraldehyde. These two chemicals were used as a plasticizer and a cross-linking agent, respectively, to improve the properties of hemicellulose films.

Mechanical and barrier properties of the hemicellulose based films were determined. Hemicellulose sources and pretreatments played an important role in the properties of hemicellulose based films. Hemicellulose based films from less treatment (powder samples, no bleaching) displayed better properties than the films from more treatment (pulp samples, bleaching) in general. Hemicellulose based films prepared from hybrid poplar powder without bleaching exhibited the highest tensile strength (76.5 ± 7.0 MPa) and elongation at break ($5.4 \pm 0.9\%$), which were higher than the values obtained from other studies of similar hemicellulose based films. Glutaraldehyde was suggested to be responsible for this improvement. The modulus of elasticity (MOE) (3.5 ± 0.4 GPa) was comparable with those obtained for similar hemicellulose based films in other studies. The differences in molecular weight, lignin content and crystallinity for the hemicellulose film obtained from different approaches were believed to result in the differences in tensile properties. No significant improvement in the barrier properties (water vapor and oxygen barrier properties) of the hemicellulose based films was observed in this study, which is similar to the results obtained in other studies. Hemicellulose based films prepared from both unbleached spruce CTMP and hybrid poplar powder had better barrier properties than the other films as indicated by the lower water vapor transmission rate (WVTR) values obtained at 23 °C and 100% RH, but not as good as most current commercial packaging films whose WVTR values were several orders of magnitude lower.

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1 BACKGROUND AND MOTIVATION

1.1 Introduction and research motivation

Multitudinous petroleum derived plastic materials are in widespread use in many areas nowadays; about 34% of these are used as packaging materials (American Chemistry Council, 2014). This gives rise to increasing concern about the shortage of fossil fuels in the foreseeable future, since fossil resources are considered non-renewable due to the long time period and critical conditions required in their formation. Meanwhile, a strong concern about environmental issues is caused by the wide utilization of non-degradable petroleum derived plastic materials resulting in an intensive increasing of their disposal in landfills. Furthermore, the release of greenhouse gases (e.g., CO₂) when they are burned has attracted significant attention related to global climate change.

An important approach to overcome the negative feedback from utilization of petroleum derived plastics is to use degradable polymers from renewable resources as an alternative. Biopolymers obtained from a variety of renewable resources have been investigated for biodegradable packaging applications. The most well-known biopolymers are cellulose, starch, soy protein, polylactic acid (PLA) and polyhydroxyalkanoates (PHAs), which have been successfully commercialized (Table 1) (Martín-Closas and Pelacho, 2011).

Table 1 Examples of commercially utilized biopolymers. Adapted from Mart ín-Closas and Pelacho (2011).

Biopolymer	Trademark	Manufacturer
Cellulose	Naturflex™	Innovia Films (UK)
	Biograde®	FKuR Kunststoff (Germany)
Starch	Mater-Bi®	Novamont (Italy)
	Bioplast®	Biotec (France)
Soy protein	PRO-FAM®	ADM (Netherlands)
PLA	Ingeo™	NatureWorks LLC (USA)
	Bio-Flex®	FKuR Kunststoff (Germany)
PHAs	Goodfellow PHB	Goodfellow (UK)
	Biomer®	Biomer (Germany)

Wood, as an important renewable and biodegradable natural resource, has been used as a fuel and as a construction material throughout history. The total timber volume in the US had risen to 1013 billion cubic feet in 2007 (Smith et al., 2009). It represents great storage of a renewable and biodegradable resource in the world. There are three main components in wood, cellulose, hemicellulose and lignin; each of them represents an abundant renewable source of biodegradable polymers. For the past few decades, cellulose as well as lignin has been the subject of intensive research, development and commercialization, while hemicellulose, as the second most abundant component in wood, is not well explored. For example, in the paper and pulping industry, a substantial amount of hemicellulose is just treated as waste or simply burned for energy.

Recently, the utilization of hemicellulose as a renewable biopolymer for biodegradable packaging materials has become of great interest from the economic efficiency viewpoint. Many studies have been carried out on the fabrication of hemicellulose based packaging materials with sufficient mechanical and barrier properties. These research objectives are mostly focused on the hemicellulose isolation, characterization, identification, and modification methods. Few studies are available in the open literature dealing with the influence of different hemicellulose sources, isolation methods and pretreatments on the final product properties such as tensile strength and water vapor barrier, which are important properties for packaging applications.

The exploitation of hemicellulose as an alternative to petroleum based plastics for packaging materials will earn more output value for wood industry, and therefore have a positive impact on the utilization of wood resources and also the sustainability of packaging development.

Some people may refer to hemicelluloses in their studies, but I will use the singular form “hemicellulose” in this study.

1.2 Objectives

The objectives of this dissertation are:

- 1) To set up an isolation method for extraction of hemicellulose from woody materials.
- 2) To fabricate hemicellulose based films using the extracted hemicelluloses.
- 3) To improve the properties of the hemicellulose based films for potential use in food packaging.
- 4) To characterize the physical, mechanical and barrier properties of the modified hemicellulose based films.
- 5) To study the influence of different hemicellulose sources and pretreatment on the properties of hemicellulose based films.

2 LITERATURE REVIEW

2.1 Introduction

Plastics, as a specific category of polymer with many good characteristics such as light weight, convenience of use and good barrier properties, have been dominant in the packaging market for decades. At present, an overwhelming majority of plastic polymers are derived from natural gas and petroleum, which are non-renewable fossil resources. They are either burned or dumped into landfills after short time use, causing serious public environmental concerns with respect to littering issues and the lack of landfill space because of their non-biodegradability (Selke et al., 2004). Therefore, enhancing recycling/reusing of plastics or replacing plastics by new biodegradable polymers have become the two strategies to solve these problems. For developing new biodegradable polymers, biological resources attract the most attention due to their renewability and biodegradability.

So far, many kinds of renewable resources have been investigated to produce biodegradable polymers for replacement of petroleum based packaging polymers. However, it is difficult to say that developing biodegradable polymers from renewable resources is the best scenario for “green” materials and processing techniques. Without a life-cycle environmental impact analysis, the energy required and material consumed for treatment and various wastes disposed during the production process may not be taken into consideration sufficiently. Therefore, developing biodegradable polymers from renewable resources might not be as “green” as it appears. However, from the point of view of landfill space saving and alternatives for non-renewable fossil resources, it could still be an advantage. Furthermore, if the energy required for developing biodegradable polymers from renewable resources comes from a “new energy”

source, like solar power, wind energy, water/tidal power, etc., this approach could still be more sustainable based on the carbon dioxide balance point compared with petroleum based polymers (Jiang and Zhang, 2013) .

2.2 Biodegradable polymers from renewable resources currently used in packaging

In general, three groups of renewable resources currently provide polymers for production of biodegradable packaging materials. The first group are naturally occurring biodegradable polymers, such as polysaccharides, proteins, and lipids, which can be directly obtained from biomass (Plackett et al., 2010; Nussinovitch, 2012; Peelman et al., 2013; Kuorwel et al., 2013; Félix et al., 2014; Shi and Dumont, 2014). The second group is synthesized using monomers from renewable resources, such as polylactic acid (PLA). PLA is synthesized from its monomer, lactic acid (LA), which can be obtained by bacterial fermentation of carbohydrates like corn, sugarcane, potatoes, etc. (Gruber et al., 1992). The third group is synthesized by certain microorganisms through fermentation, such as polyhydroxyalkanoates (PHAs). These are the carbon and energy storage materials produced by certain bacteria in a situation of limited nutrients but excess carbon sources (Byrom, 1994; Steinbüchel, 1991).

2.2.1 Cellulose

Cellulose is a natural homopolysaccharide belonging to the first group. It is the most abundant biopolymer in the world with an annual production of over 75 billion tons (Habibi et al., 2010). It can be found in various natural resources in the world, such as wood, abaca, bamboo, jute, flax, hemp, etc. The purest natural cellulose comes from cotton, which is about 90% cellulose. Cellulose molecules are composed of β -D-glucopyranose units linked together by β -(1-

4)-glucosidic bonds, forming a completely linear structure (Azizi Samir et al., 2005). Its molecular chain has an average degree of polymerization (DP) of at least 9000-10,000. The repeat unit of the molecular chain (Figure 1) consists of two glucose residues that contain three free hydroxyl groups on each anhydroglucose ring.

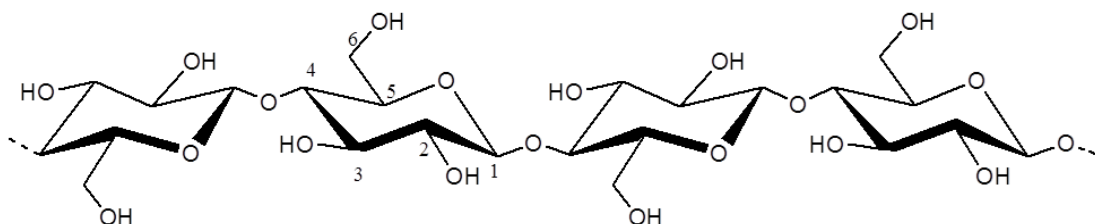


Figure 1 Schematic representation of cellulose molecule. Figure was adapted from Azizi Samir et al. (2005) (Azizi Samir et al., 2005).

Therefore cellulose molecules are peculiarly prone to form intra and intermolecular hydrogen bonds. Such hydrogen bonds connect cellulose molecules to form microfibrils, which possess both crystal regions (cellulose molecules are highly ordered) and amorphous regions (cellulose molecules are less ordered). The microfibrils are bonded together in the same manner to form fibrils and eventually cellulose fibers. Because of the supermolecular structure and strong hydrogen bonds, cellulose has high tensile strength and is difficult to dissolve in most solvents. But it also has a major disadvantage: it is very hydrophilic because of the presence of a large number of hydroxyl groups in the molecular chain. This feature limits its utilization in various applications, especially in the food packaging area, without modification.

Many efforts have been made to improve its properties for satisfaction of the requirements for packaging materials. Cellulosic polymers are classified into three main groups: regenerated cellulose (e.g. cellulosic fibers and cellophane), cellulose esters (inorganic cellulose esters, e.g. cellulose nitrate, and organic cellulose esters, e.g. cellulose acetate) and cellulose

ethers (carboxymethyl cellulose). Cellulosic fibers have been used in packaging as paper and paperboard for a long time in a broad range of food categories (Kirwan and Strawbridge, 2003). Cellophane, a regenerated cellulose product, was patented in 1912 and found immediate commercial use in packaging due to its good properties, such as low permeability to air, oils, greases etc. It is obtained by dissolving cellulose in an alkali and carbon disulfide solution, then reconverting to cellulose using a sulfuric acid/ sodium sulfate solution and finally softening using glycerol (Carlisle, 2004). Nowadays, its products have broadly registered trademarks in many countries. It can be laminated with paper, aluminum foil, PET and PE for food packaging application (Kirwan 2003; Kirwan and Strawbridge 2003). A recent research hotspot is cellulose derivatives, which can be obtained by esterification or etherification of the hydroxyl groups on cellulose molecules. These cellulose derivatives can be used to produce thermoplastic materials processable by injection molding or extrusion. Most of them display great film-forming properties, but have not been exploited on an industrial scale (Cyras et al., 2009; Shen et al., 2009). Another newly developed cellulose application involves generating nanoscale cellulosic materials, like cellulose nanofibers (CNs), cellulose nanowhiskers (CNW) and cellulose nanocrystals (CNC) or microfibrillated cellulose (MFC), which could be used as packaging film substrates or additives resulting in good barrier and excellent mechanical properties (Pääkkö et al., 2008; Plackett et al., 2010; Spence et al., 2010; Stevanic et al., 2012).

2.2.2 Starch

Starch, a major carbohydrate used for energy storage in higher plants, is another substance belonging to the first group. It has two types of macromolecules in its native state in plants: linear amylose (20%-25%) and branched amylopectin (75%-80%) (Galliard and Bowler,

1987; Jenkins et al., 1993; Gallant et al., 1997). Amylose has a similar molecular structure to cellulose; it predominantly consists of (1→4)-linked D-glucopyranose units as its backbone but with α -glycosidic linkages; amylopectin is a highly branched macromolecule with the same backbone units (α -D-glucopyranose units) but linked by (1→4) and (1→6) linkages and possessing high molecular weight (Whistler and Daniel, 1984; Kainuma, 1984), as shown in Figure 2 (Carvalho, 2013). These features make starch possess different stereochemical characteristics, resulting in different physical and chemical behaviors from that of cellulose.

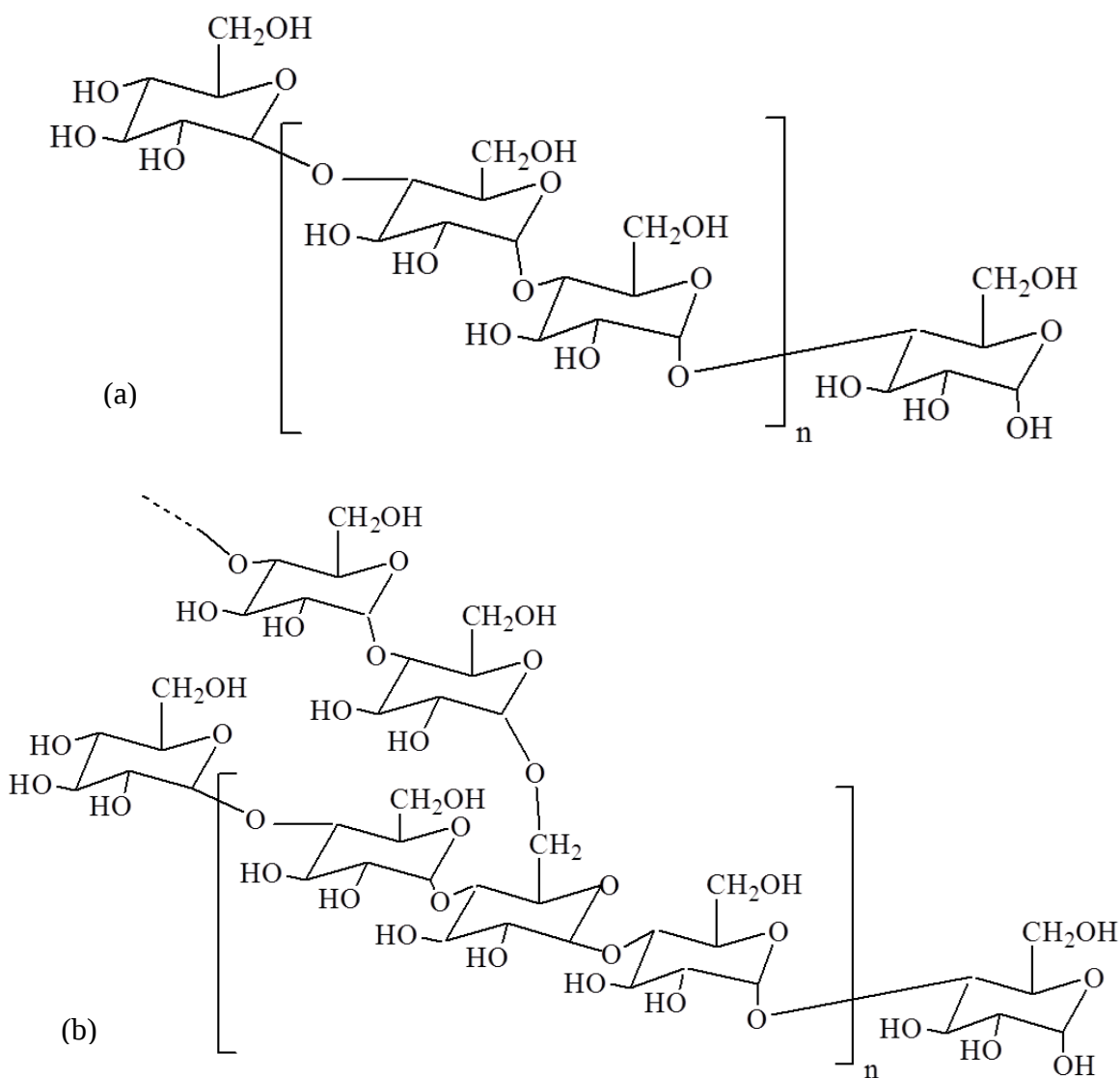


Figure 2 Amylose (a) and amylopectin (b) structures. Adapted from Carvalho (2013).

There are several crops commercially used for the production of starch. Maize, wheat, and rice were the top three crops for starch production in 2005, with about 712, 631, and 622 million metric tons produced, respectively (FAO, 2007). Starch is not meltable and becomes soluble in hot water; therefore unmodified starch films cannot meet the requirements for most applications. To be useful as a food packaging material, it needs modification to adjust its properties. Two strategies are commonly applied for starch use: 1) as a raw material for the synthesis of other polymers; 2) directly as the target polymer macromolecule without changing the molecular structure. The first strategy includes: i) using starch to produce monomers for synthesis of other polymers, such as nonbiodegradable polyethylene or biodegradable polylactic acid (Otey and Doane, 1984; Garlotta, 2001); ii) as a raw material for hydroxyl-containing monomers like glucose or dextrin for the production of mixed compositions with other monomers (Otey and Doane, 1984; Koutinas et al., 2004); iii) and as a raw material for biopolymer production by fermentation using microorganisms (Kennedy et al., 1987; Robertson et al., 2006). The second strategy is to modify starch by combination with other polymers, esterification, etherification, grafting and reactive or melt extrusion of thermoplastic starch (TPS) (Carvalho, 2013). Many types of polymers are blended with TPS to overcome its disadvantages, such as moisture susceptibility, brittleness and low strength for packaging polymer or foam applications (Fang and Hanna, 2001, 2002; Willett and Shroengen, 2002; Rodriguez-Gonzalez et al., 2003; Huneault and Li, 2007; Parulekar and Mohanty, 2007). Starch can also be acetylated for water resistance and used in packaging foams (Ganjyal et al., 2004). Commercial starch-based materials have been successfully used for packaging applications (Bastioli et al., 1991), and are even tolerant to high water activity levels (Robertson, 2008; García et al., 2009).

However, edible and soluble packages for flavor components also effectively utilize starch in packaging (Allen et al., 1963; USDA, 1971).

2.2.3 Protein

Besides cellulose and starch, protein is another abundant renewable biopolymer having great potential for replacement of petroleum based polymers in food packaging applications. These are heteropolymers that usually contain most of the 20 amino acids. Soy is the most abundant source for this application with potential annual production of 60 billion pounds of soy protein in US, followed by gluten from wheat (about 14 billion pounds), and zein from corn (about 7.8 billion pounds) (Shukla and Cheryan, 2001). Besides plants, there are also proteins from animals, such as whey and casein from milk for edible film applications (Mabesa et al., 1980; Sensidoni and Peressini, 1997).

2.2.4 Other biopolymers

Animals can also supply biopolymers used as edible coating materials in food packaging, such as gelatin, shellac and collagen (Robinson, 1953; Kuntz, 1964; Antoniewski and Barringer, 2010; Soradech et al., 2012) etc. In addition, polysaccharides such as pectin, carrageenan and algin are types of carbohydrates obtained from plants and used for edible coating applications (Kang et al., 2007; Baldwin, 1994; Keshri and Sanyal, 2009).

In addition, polylactic acid, belonging to the second group, is commercially available on a large-scale for different applications. Its consumption in 2012 was about 187,600 tons per year, according to the European Bioplastics Association. The most important market in volume for packaging application is biodegradable packaging (Auras et al., 2004). It is mainly used as a food

packaging for fresh products, which usually have short shelf-life, such as vegetables and fruit (Domenek et al., 2011).

Poly-3-hydroxybutyrate (PHB), the polyester produced by certain bacteria processing glucose, is an important member of the polyhydroxyalkanoate (PHA) family. Large-scale commercial production of PHAs uses fermentation technologies. Homopolymer PHB is a brittle, crystalline thermoplastic material and it undergoes thermal decomposition just at its melting point. Therefore, extensive efforts have been made to overcome its drawbacks by synthesis of copolymers for biodegradable applications (Rudnik, 2013 a).

2.3 Hemicellulose

Although modified biopolymers such as cellulose derivatives, thermoplastic starches or soy protein based films have been successfully used in packaging, renewable biopolymers are still currently of central interest due to the potential of replacement of conventional petroleum based polymers typically used in food packaging (De Vlieger 2003; Sommer and Kunz, 2012). Hemicelluloses recently have gained increasing interest in this type of application, not only due to their biorenewability and biodegradability, but also their lower cost and avoidance of competition with food supplies. In the past, the application of hemicellulose involved their conversion into sugars, chemicals and fuel or directly as sources of heat energy (Dumitriu, 1996). Even though other uses of hemicellulose in high-technology products have been investigated and developed, the commercial utilization of hemicellulose is still limited. Thus, adding extra value by using the hemicellulose as an alternative to petroleum based packaging materials would benefit the development of sustainable packaging and reduction of environmental issues.

2.3.1 Hemicellulose sources

As the second most abundant family of polymers after cellulose, estimated global annual production of hemicellulose is around 60 billion tons. It can be obtained from various sources, not only from wood, but also from bamboo, grass, banana stems, agricultural residues, etc. It broadly exists in the plant kingdom; you can even find it in the ocean and other aquatic systems (Sun et al., 2004). For a large scale supply, in addition to the herbaceous plants that are attracting more and more interest from researchers due to the large amount of agricultural residues, wood plays an important role as a source of high quality hemicellulose. Not only sawdust from the wood industry, but the side streams during production of thermomechanical pulp could be sources for hemicellulose for value-added products or byproducts. This is called value prior to pulping (VPP) in the paper and pulping industry. Additionally, paper grade pulp can be another large scale source of hemicellulose.

2.3.1.1 Wood sources

2.3.1.1.1 The state of wood resources

Wood, as a precious renewable resource, has supplied a huge amount of raw materials since ancient times before recorded history. It is the most important biological and renewable resource in the world. For a long time, the utilization of wood remained at the macro level, such as use as a fuel and as a raw material for construction and furniture. The growth of the wood pulp and paper manufacturing industry led to use of wood as fiber. With increasing interest in bio-based materials, there is interest in utilizing wood at the micro level. New technologies have been developed to convert various components of wood into high value products, such as lignin glue, biodegradable food packaging, alternative agents for rubber tires, anti-bacterial medical agents,

and high strength fabrics or nanocomposites. Considering the benefits of wood to society as well as the interest in sustainable development, it is critical to utilize wood more effectively and efficiently.

Wood is a hard and fibrous structural tissue consisting of three main components: cellulose (40%-45%), hemicellulose (20%-30%) and lignin (20%-25). Besides these three main components, wood also contains other minor components, ash and extractives, which include wax, pectin, resin acids, etc. (Sjöström, 1993). Since most research efforts have focused on cellulose and lignin, these two components of wood have been extensively explored and utilized.

Cellulose based products are broadly used. As mentioned before, cellulose fibers in the form of paper and paperboard, from one of the largest chemical industries in the world, the pulp and paper industry (Wise and Jahn, 1952), have been used in packaging for a long time in a wide range of food categories including fresh, dry, frozen, and liquid foods or beverages (Kirwan and Strawbridge 2003). Besides packaging applications, cellulose is also used in liquid crystal displays (Sohn et al., 2003), hollow fibers for artificial kidney dialysis (Sargent, 2007), and components or additives in pharmaceutical and food applications (Felton and Porter, 2013; Mikkelsen et al., 2011), among others. Recently, TEMPO-oxidized cellulose nanofibers (TOCN) were investigated for potential application in ion-exchange materials for water and high-performance air-filters (Isogai et al., 2011).

Lignin accounts for only 30% of the biomass weight but it contributes 40% of the fuel value, which makes it a strong candidate for biofuel products (Holladay et al., 2007). Based on its phenolic functionalities and properties, lignin attracts more attention in higher value-added renewable product applications. Lignin is a good source for valuable chemicals (aromatic aldehydes and phenolic products) after it is broken into smaller molecular units because of its

sustainable, abundant, phenolic and carbon-neutral characteristics. A series of approaches have been applied to generate biofuels and valuable compounds from lignin, including enzymatic degradation (Xia et al., 2003), photo-catalyzed degradation (Kansal et al., 2008), ionic liquids degradation (Binder et al., 2009), electrochemical degradation (Tian et al., 2010), microwave irradiation oxidation (Ouyang et al., 2010), hydrothermal conversion and pyrolysis (Wang et al., 2009; Jiang et al., 2010a, b; Mu Wei et al., 2013). Among these approaches, hydrothermal conversion of lignin has been extensively investigated (Kang et al., 2013).

2.3.1.1.2 Internal environment of hemicellulose in wood

In wood cell walls, the three main components do not exist in isolation. Cellulose fibrils are embedded in hemicellulose and lignin matrix. The basic structure/composition analysis and the application of these wood components as raw materials require as far as possible to isolate them completely from wood with as little as possible damage or change to the component structure or molecular weight. The extractions of these components all involve the breakage of the connection among these components. It is necessary to fully understand the properties of the three main components (e.g., composition, structure, physical and chemical interactions) in order to isolate high quality components.

2.3.1.1.2.1 Cellulose

As mentioned earlier in this chapter, cellulose, as the primary component in the wood cell wall, accounts for approximately 40-45% of the dry weight of wood in most species. It is a linear polymer with a rigid backbone that crystallizes and can be loadbearing (Sjöström, 1993).

Cellulose is a hydroxyl group-rich homopolymer with 3-dimensional supermolecular structure.

Figure 3 shows the molecular and supermolecular structure of cellulose from wood (Dodson, 2012).

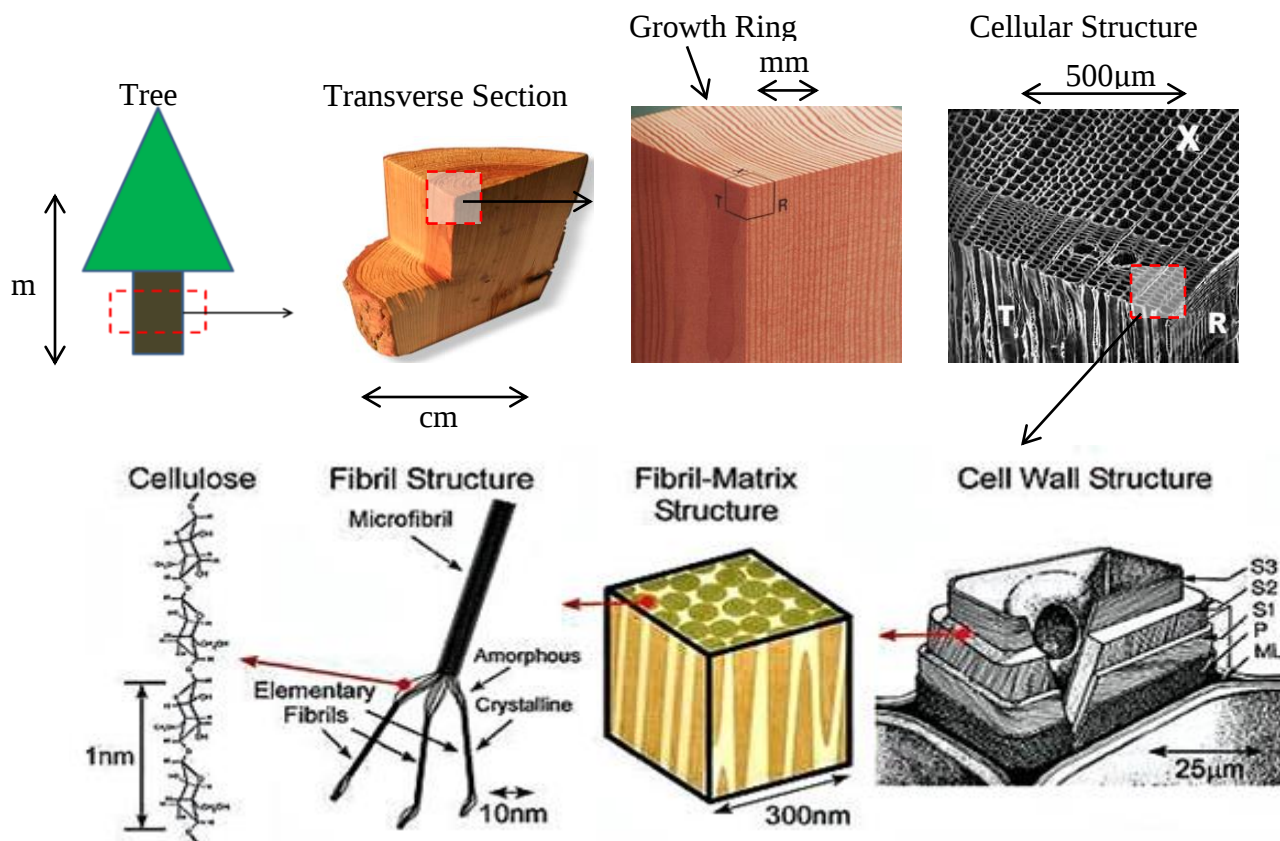


Figure 3 Cellulose structures in trees from logs to molecules. Adapted from Dodson (2012).

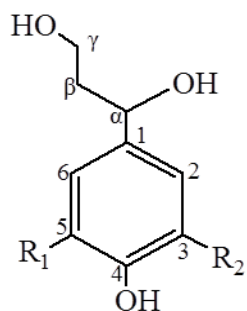
2.3.1.1.2.2 Lignin

Lignin is a carbon-rich heterogeneous biopolymer containing aromatic structural units. It is the only renewable source of aromatics, and represents an important constituent of biomass. The estimated potential lignin production is more than 50 million tons per year from the pulp and paper industry (Gosselink et al., 2004). Lignin has three basic structural units: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Hardwood lignin is primarily derived from sinapyl alcohol and coniferyl alcohol. Softwood lignin is mainly derived from coniferyl alcohol.

It is a natural polyphenol with a 3 dimensional network structure constituted of the three basic structural units linked by C-C and ether bonds (Hüttermann et al., 2001), as shown in Figure 4 (Kang et al., 2013).

No effective analytical method has yet been employed to characterize the natural structure of lignin. Its structural model can be deduced by biosynthesis or chemical degradation combined with NMR and FTIR or Raman spectra analysis. Figure 5 shows a structural model of spruce lignin with 18 phenyl propane units (Freudenberg and Neish, 1968).

P-coumaryl: $R_1, R_2=H$
 Coniferyl alcohol: $R_1=H, R_2=OMe$
 Sinapyl alcohol: $R_1, R_2=OMe$



Lignin structure units

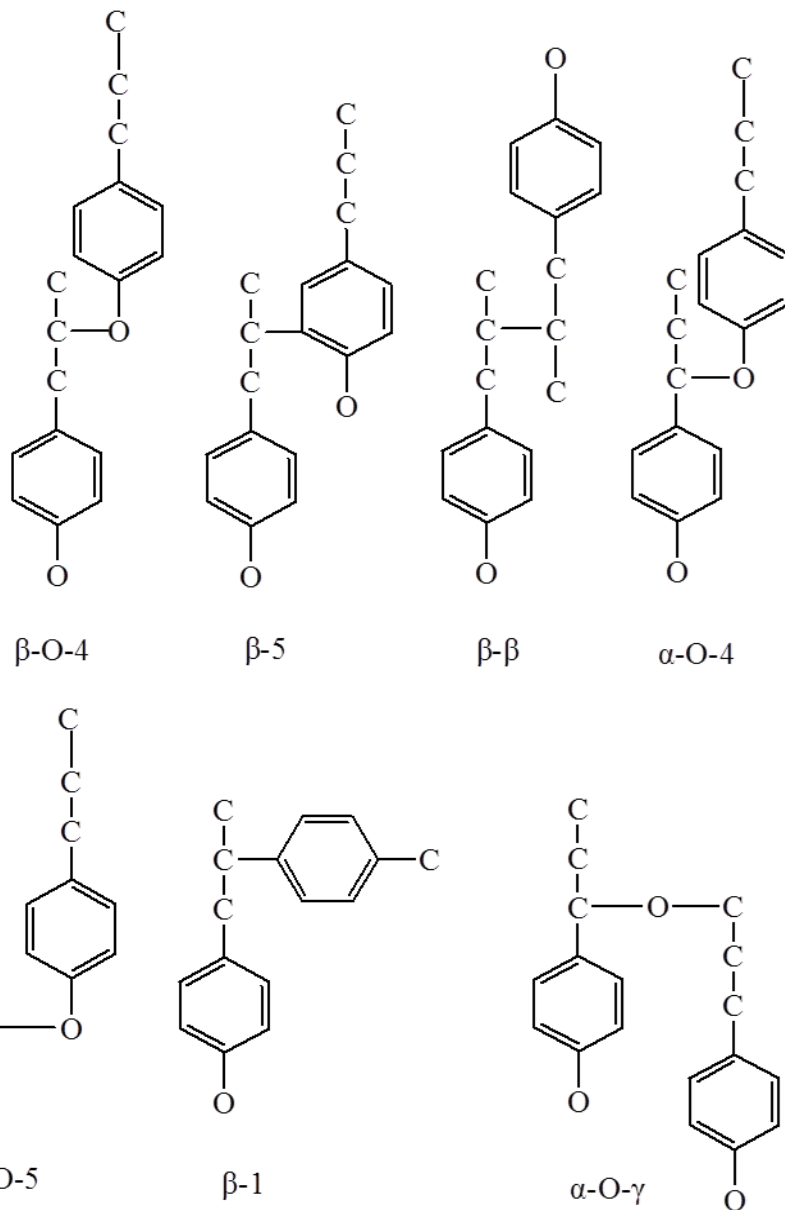


Figure 4 Lignin structure units and the linkage. Adapted from Kang et al. (2013).

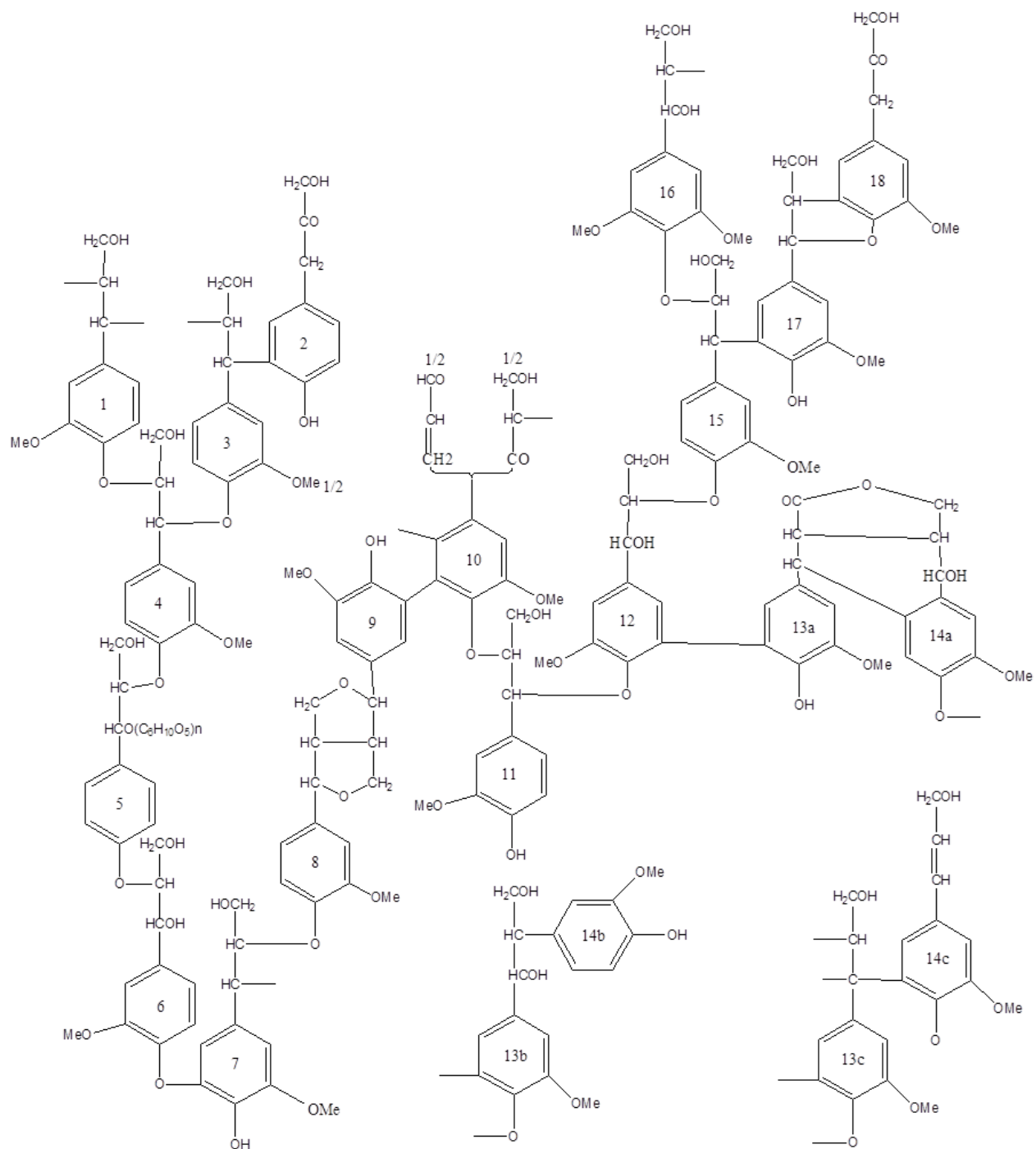


Figure 5 Structural model of spruce lignin with 18 phenyl propane units. Adapted from Freudenberg and Neish (1968).

2.3.1.1.2.3 Hemicellulose

Hemicellulose from wood is a heteropolysaccharide with a series of hexose and pentose units that are linked in an irregular manner, in contrast to the regular arrangement in cellulose. It is entirely amorphous with no crystal structure in its natural state. It has a low degree of polymerization compared with cellulose, usually between 100 and 200 (Rowell, 2012). It mainly contains the following sugar residues: D-glucopyranose, D-mannopyranose, D-galactopyranose, L-arabinofuranose, D-xylopyranose, D-glucopyranosyluronic acid and D-galactopyranosyluronic acid with minor amounts of other sugars (Timell, 1967; Sun et al., 2004; Spiridon and Popa, 2008), as shown in Figure 6 (Hansen and Plackett, 2008). The high variability of hemicellulose composition and structure makes it very challenging to characterize.

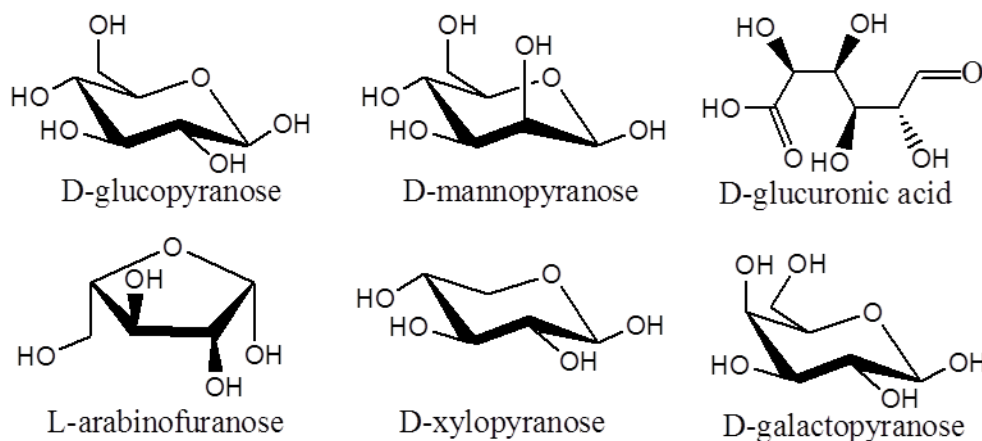


Figure 6 Main constituents of hemicellulose. Figure was adapted from Hansen and Plackett (2008) (Hansen and Plackett, 2008).

The general composition of hemicellulose varies between hardwoods and softwoods. Figure 7 shows the main hemicellulose in hardwood, O-acetyl-(4-O-methylglucurono) xylan (Hartman, 2006), while the predominant hemicellulose type in softwood is O-acetyl-galactoglucomannan (AcGGM), as shown in Figure 8 (Hartman, 2006).

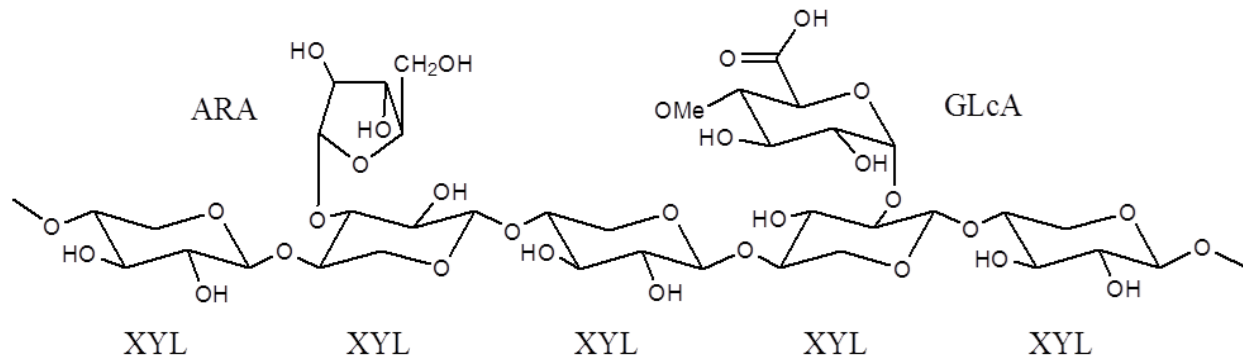


Figure 7 General structural formulas of arabino-(4-O-methyl-glucurono)-xylan. (XYL=xylose, GLcA=methylglucuronic acid, ARA= arabinose). Figure was adapted from Hartman (2006) (Hartman, 2006).

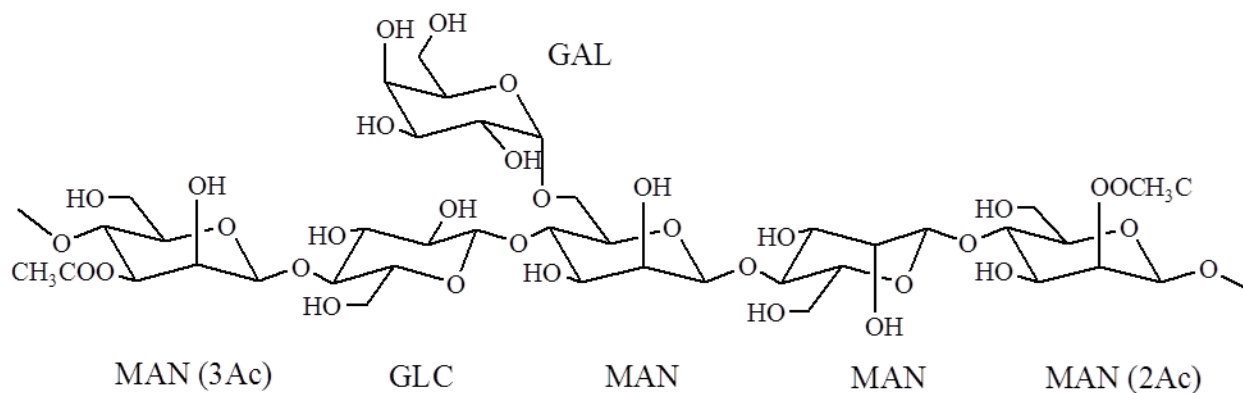


Figure 8 General structural formulas of AcGGM. (GAL=galactos, GLC=glucose, MAN=mannos, Ac=acetyl group). Figure was adapted from Hartman (2006) (Hartman, 2006).

As the compositions and structures of hemicelluloses above show, they, like cellulose, are rich in hydroxyl groups, but they also can possess acetyl groups.

As a result of these functional groups and their macromolecular structures, the three main components of wood are connected to each other tightly and systematically by physical binding

and chemical interaction. Between cellulose and hemicellulose, hydrogen bonding and molecular chain intermixing are the main forms of binding (Scheller and Ulvskov, 2010); while covalent bonds (mainly R-benzyl ether linkages) are the primary connections between hemicellulose and lignin (Deniaud et al., 2003).

2.3.1.2 Pulp source

In the modern pulping industry, the steam liquid after pulping and also the pulp itself are important sources for hemicellulose due to the large volume available in the world. Total production of wood pulp (air dried pulp) for paper and paperboard in the US was reported to be 50301×10^3 metric tons in 2012; market wood pulp (air dried pulp) was reported as 8392×10^3 metric tons (FAO, 2012-2017). Pulp has become an abundant raw material worldwide.

Several pulping processes are currently used in today's industry: mechanical pulp (RMP), thermomechanical pulp (TMP), chemithermomechanical pulp (CTMP), chemical pulp (mostly Kraft pulp), recycled pulp, organosolv pulp and other alternative pulping methods. The chemithermomechanical pulp process is to pretreat wood chips with sodium carbonate, sodium hydroxide, sodium sulfite and other chemicals before refining them with refiner plates which are similar to mechanical pulp equipment. The conditions during the chemical treatment are much milder than in a chemical pulping process, such as lower temperature, shorter time, and less extreme pH. So the fiber will have less degradation and the lignin will not be removed as much as in a chemical pulping process. Organosolv pulping uses organic solvents, such as methanol, ethanol, formic acid and acetic acid often in combination with water at temperatures above $140\text{ }^{\circ}\text{C}$ to break down lignin and hemicellulose into soluble fragments in the solvent liquor. It nearly removes all the hemicellulose in the pulp. Therefore, organosolv pulp cannot be a hemicellulose source. Overall, chemical pulping predominates in world pulp production (more

than 80%), and bleached Kraft pulp accounted for more than half of chemical pulp production in 2012 (FAO, 2012).

2.3.2 Hemicellulose definition and utilization

The term hemicellulose was originally proposed to designate polysaccharides that can be extracted from higher plants by alkaline solution (Schulze, 1891). Hemicellulose can be divided into four classes of polysaccharides with different structures, based on the current stage of knowledge (Ebringerová et al., 2005): (a) xylans, (b) mannans, (c) β -glucans with mixed linkages, and (d) xyloglucans.

Based on the primary structure of various plant xylans, xylan-type polysaccharides can be divided into two types, homoxylans and heteroxylans. Homoxylans are found in seaweeds and green algae, and have a backbone consisting of xylopyranose residues linked by (1 $\rightarrow$ 3) or mixed (1 $\rightarrow$ 3, 1 $\rightarrow$ 4) glycosidic linkages (Ebringerová and Heinze, 2000; Yamagaki et al., 1997). Xylans from terrestrial plants are heteroxylans with a β -(1-4)-D-xylopyranose backbone with branches comprised of short carbohydrate chains. These side chain groups include L-arabinose, D-glucuronic acid or its 4-O-methyl ether, and/or various oligosaccharides. D-glucose, L-arabinose, D- or L-galactose and D-xylose are commonly the main constituents of these oligosaccharides. This type of xylans include glucuronoxylans, (arabino)glucuronoxylans, arabinoxylans, (glucurono)arabinoxylans and other complex heteroxylans (Ebringerová et al., 2005).

In the past, utilization of hemicellulose was mainly focused on converting it to sugars and chemicals, such as sweetening agents, thickeners, and emulsifiers used in the food industry (Dumitriu, 1996). One industrial scale use of hemicellulose is to convert xylan to xylose, xylitol and furfural. Xylitol has been applied in a variety of food products (Ebringerová and Heinze, 2000). In the pulp and paper industry, retaining the hemicellulose in the pulp has been shown to

improve both the mechanical properties of the paper and the yield (Schönberg et al., 2001; Ban et al., 2011; Oksanen et al., 2011). Recently, more attention has been placed on the application of hemicellulose as a raw material for high-technological products (Hansen and Plackett, 2008) such as cationic polymers (Ebringerova et al., 1994), hydrogels (Gabrielii et al., 2000), long-chain ester derivatives (Sun et al., 1999; Gabrielii et al., 2000; Petzold-Welcke et al., 2014), and thermoplastic hemicellulose derivatives (Sun et al., 1999; Jain et al., 2000). Meanwhile, hemicelluloses used as ingredients in the formulation of flexible packaging films attract more and more attention from researchers. The definition of flexible packaging is a package or container made of flexible or easily yielding materials that, when filled or closed, can be readily changed in shape. The construction may be of paper, plastic film, foil or any combination of these, including rollstock, bags, pouches, labels/wraps, lidding, shrink sleeves and stretch film (Schottland, 2004). The flexible packaging market in U.S. is about \$20 billion per year. Film is defined as an optional term for sheeting having a nominal thickness no greater than 0.25 mm (0.010 in, ASTM D883).

2.4 Problems for exploitation of hemicellulose in flexible packaging films

Applicable food packaging materials must have adequate mechanical properties and provide a sufficient barrier to oxygen, water vapor, light, bacteria and/or other contaminants in order to prevent food deterioration to provide a shelf life that is sufficiently long. So for hemicellulose to be used as a packaging material, feasible and reliable hemicellulose extraction and modification techniques are essential because of the inherent characteristics of hemicellulose.

1) Hemicellulose has a complicated composition and structure in contrast to cellulose; it is a series of hexose and pentose units that are linked in an irregular manner. Different plant species, plant locations, growth stages and isolation processes can result in significant variation in hemicellulose composition and structure (Schröder et al., 2001; Sun et al., 2005; Lai et al., 2006). The high variety of hemicellulose composition and structure from different sources and processes make it very challenging to process hemicellulose in a competitive and guaranteed industrial scale; hence hindering the extension of the utilization of hemicellulose.

2) In general, hemicellulose from wood has a much lower degree of polymerization than cellulose, usually between 100 and 200 (Rowell, 2012). It is branched, and difficult or impossible to crystallize. Thus, hemicellulose comparatively has lower strength than cellulose.

3) Hemicellulose has an abundance of hydroxyl groups in its structure, resulting in strong hygroscopicity. This makes hemicellulose based films have a strong tendency to absorb moisture from the air, resulting in not only low water vapor barrier but also negatively impacting its physical and mechanical properties. Additionally, the moisture content promotes the growth of microorganisms, and reduces the protection for the food.

4) The inherent nature of hemicellulose and its film forming procedure also mean hemicellulose based films have an oxygen transmission rate that needs to be improved for applications with higher requirements.

5) Hemicellulose is a nutrient for microorganisms. Anti-bacterial and anti-mold agents are therefore necessary for some specific food packaging applications.

Thus it can be said that in order to transfer the potential of hemicellulose as a packaging material into reality, the characteristics of hemicelluloses from different sources and pretreatments should be clarified in order to clearly understand the influences of these

characteristics on their final performance. In addition, hemicellulose based packaging films should also possess sufficient mechanical/physical properties, adequate oxygen/moisture barrier properties and anti-bacteria/anti-mold properties (especially for some special applications). This needs suitable, reliable and cost efficient isolation methods based on a sound understanding of the influences from the different sources and pretreatments to obtain hemicellulose with as high quality as possible for fabrication of packaging materials. Then corresponding measures could be taken to modify the hemicellulose in order to obtain enhanced properties that will satisfy the requirements for packaging materials.

2.5 Review of studies on hemicellulose for packaging applications

2.5.1 Different sources for hemicellulose and their compositions and structures

Research shows that the composition and structure of hemicellulose varies between different plant species, plant locations, growth stages, and also the different isolation processes. Significant variations of hemicellulose composition and structure could be obtained and thus produce markedly different hemicellulosic products. (Gatenholm and Tenkanen, 2004; Lindblad and Albertsson, 2005; Sun et al., 2005; Lai et al., 2006).

2.5.2 Isolation methods

Hemicellulose in the plant cell wall is bound to cellulose and lignin. The interaction among these three components and also the relatively large molecular size make it difficult to diffuse out of the matrix during hemicellulose extraction. Several most commonly used extraction methods are described below.

2.5.2.1 Steam treatment

When wood is exposed to high temperature in a moisture-rich environment, the ester bonds in the hemicellulose will be cleaved and hence produce some organic acids, mainly acetic acid. The release of these organic acids further catalyzes the auto-hydrolysis of the glycosidic bonds in the hemicellulose and other wood polymers. Therefore, a partially depolymerized low molecular weight hemicellulose in aqueous solution is obtained. Due to the degradation of the hemicellulose, this treatment results in a low quality hemicellulose product with low yields and contamination of cellulose and lignin. O-acetyl groups on the hemicellulose molecular chain can be retained. A yield of 8% (wt.) of hemicellulose was reported after spruce steam treatment for 2 min at 200 °C (Palm and Zacchi, 2003).

2.5.2.2 Microwave treatment

This technique employs microwaves to irradiate wood for heating in water. The mechanism is the same as in the technique above, and bears the same disadvantage, except for the uniform heating in this treatment. Meanwhile, new problems like long time requirements for heating and cooling result (Teleman et al., 2000; Lundqvist et al., 2002).

2.5.2.3 Explosion treatment

Explosion treatment is also a hydrothermal treatment like steam treatment. Hence it leads to a similar release of acids which can promote auto-hydrolysis in the wood polymers together with the other disadvantages of steam treatment. The main difference between steam treatment

and steam explosion is the rapid depressurization that takes place at the end of steam explosion. This could break the wood materials to small size fibers or fiber bundles, increasing the exposure surface of wood materials to the cooking liquor (Ahvazi et al., 2007; Mart ín-Sampedro et al., 2011a, b). Meanwhile, it could bring more opportunities for contamination from cellulose and lignin. In other words, the parameters during the steam explosion need to be designed and controlled appropriately in order to obtain better quality hemicellulose (Wu et al., 1999; Krawczyk et al., 2008;).

So generally speaking, these hydrothermal techniques are not suitable for extraction of high quality hemicellulose owing to the disadvantages mentioned above. They are more likely to be used as a treatment to remove hemicellulose, obtaining the cellulose for other uses like in Kraft pulping (Mart ín-Sampedro et al., 2014).

2.5.2.4 Hemicelluloses from process water

In the wood industry, there is a common hydrothermal treatment step to soften the lumber before processing (Edlund et al., 2010). And in the paper and pulping industry, the extracted streams from CTMP mills are rich in hemicellulose (Saadatmand et al., 2012; Liu et al., 2012; Mikkonen and Tenkanen, 2012). Hemicelluloses can be found in various process liquors (Persson et al., 2005). Microfiltration (Krawczyk and Jonsson, 2011), ultrafiltration and diafiltration (Persson et al., 2007; Krawczyk et al., 2008) are usually the techniques that are employed to separate hemicellulose from the other substances in the process water. Thus, hemicellulose as a by-product could add extra value and facilitate reuse of the waste to reduce cost.

An economic evaluation of isolation of hemicelluloses from process streams has been done for thermomechanical pulping of spruce (Tobias Persson et al., 2007). The report stated that it is possible to produce hemicellulose based films with good oxygen barrier properties at a price that is competitive with the materials used today.

2.5.2.5 Alkaline extraction

Alkaline extraction has been proved to be a promising process for complete utilization of lignocelluloses without environment issues (Peng et al., 2009). This technique dissolves hemicellulose by cleavage of the R-ether linkages between the lignin and hemicellulose and the ester bonds between lignin and/or hemicelluloses while at the same time swelling the cellulose to promote the release of hemicellulose from the matrix (Jackson, 1977; Spencer and Akin, 1980). Hence, the hemicellulose extracted by this technique could be of high quality without severe degradation of hemicellulose or critical contamination with cellulose or lignin (Sun et al., 2001; Peng et al., 2013; Sun et al., 2013). Through this process, alkali-soluble hemicelluloses can be easily utilized for valuable products (Sun and Hughes, 1998; Gabrieli et al., 2000; Grøndahl et al., 2004; Ruzene et al., 2008; Peng et al., 2009; Agneta et al., 2009; Zhang et al., 2011; Laine et al., 2013; Alekhina et al., 2014).

2.5.3 Influence of composition and structure on the final product properties

Hemicellulose is a type of heteropolymer, with various compositions and structures. This nature makes it capable of having enormously different properties when involving interaction with other materials. The different constituents, substitution, molar mass and structures of hemicellulose can lead to diverse reactivity. Many studies have examined the influence of

hemicellulose composition and structure (substituent patterns, molar mass and crystallinity) on the final film properties, which is well correlated with the substitution ratio, for example Ara/Xyl ratios of arabinoxylan (Teleman *et al.*, 2000; Höije *et al.*, 2008; Zhang *et al.*, 2011; Stepan *et al.*, 2012).

2.5.4 Modification methods

A number of different physical and/or chemical approaches have been investigated for fabrication of flexible hemicellulose based films with enhanced mechanical and barrier properties for packaging applications, as discussed below:

2.5.4.1 Addition of plasticizer and cross-linking agents

This technique commonly employs sorbitol, glycerol, propylene glycol or xylitol as a plasticizer to make the hemicellulose based film more flexible to resolve its brittleness. The studies showed that hemicellulose film with sorbitol has better properties overall; at about 20% (wt.) addition based on the dry weight, the film had the highest tensile strength, and at the same time greater elongation compared to the other plasticizers. Cross-linking agents, such as glyoxal, glutaraldehyde and genipin, are usually used to enhance the strength of the hemicellulose based films. They can build covalent bonds within and/or between the hemicellulose molecular chains. Thus they can remarkably improve the tensile strength and potentially contribute to the oxygen and moisture barrier properties (Gabrieliia *et al.*, 2000; Zhang and Whistler, 2004; Grøndahl *et al.*, 2004; Mikkonen *et al.*, 2009; Hansen *et al.*, 2012).

2.5.4.2 Esterification and etherification

The large amount of hydroxyl groups on the hemicellulose molecular chain provides excellent opportunity for property changes by substitution reactions. Changing functional groups can result in regulation of hemicellulose solubility, stability, and film-forming ability in order to obtain the desired properties. The techniques make the hydroxyl groups of hemicellulose react under certain conditions to be esterified or etherified to obtain hydrophobic carboxymethyl hemicellulose and benzyl hemicellulose, thus improving the moisture barrier (Hartman et al., 2006; Kochumalayil et al., 2013). The theoretical reaction of benzylation of an acetylated mannose unit is shown in Figure 9 (Hartman, 2006).

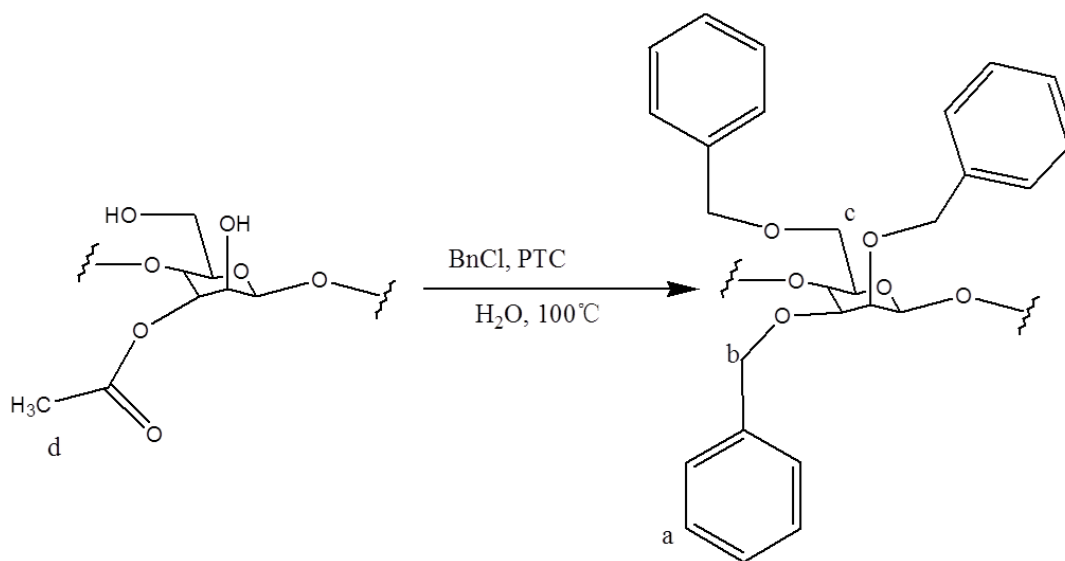


Figure 9 Theoretical reaction in which acetylated galactoglucomannan (AcGGM) is fully benzylated exemplified by an acetylated mannose unit. Figure was adapted from Hartman (2006) (Hartman, 2006).

2.5.4.3 Surface grafting

Surface grafting usually employs plasma to treat the hemicellulose film surface, producing functional groups for the next stage. The gas plasma could be oxygen, argon, nitrogen or air. After plasma treatment, the film surface is then exposed to hydrophobic materials like styrene resulting in vapor-phase grafting with styrene to make the film surface linked with hydrophobic styrene molecules, as shown in Figure 10 (Hartman, 2006). This technique allows fabrication of hemicellulose films with hydrophobic surfaces to reduce moisture sensitivity (Hartman et al., 2006; Kochumalayil et al., 2013).

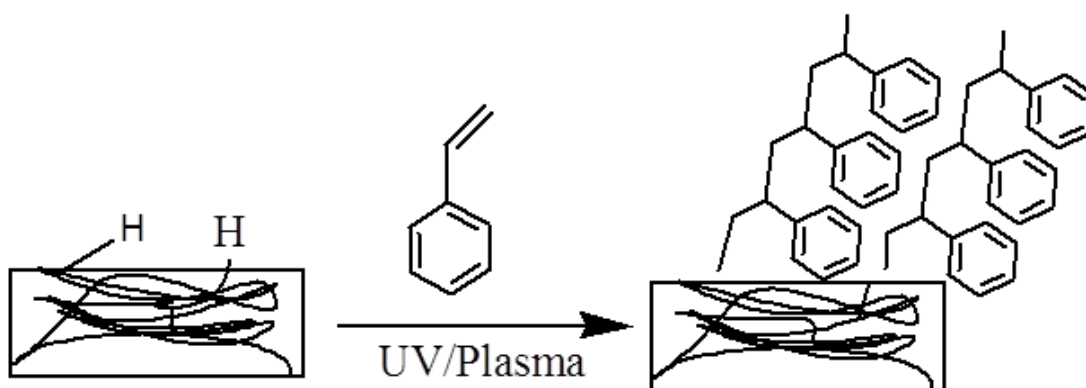


Figure 10 Theoretical styrene monomer attachment to AcGGM surface by plasma treatment or vapor-phase grafting. Figure was adapted from Hartman (2006) (Hartman, 2006).

2.5.4.4 Lamination

This method allows hemicellulose to laminate with a hydrophobic material. The hydrophobic material mostly determines the properties of the final products. By lamination of an AcGGM alginate blend film with benzylated galactoglucomannan (GGM), excellent barrier properties were obtained for water vapor with $8 \text{ cm}^3 \mu\text{m m}^{-2} (24 \text{ h}^{-1}) \text{ kPa}^{-1}$ at 83% RH (Hartman

et al., 2006).

2.5.4.5 Surface coating

This technique is aimed at improving barrier properties. For obtaining a good gas and vapor barrier layer, the coating material needs to be pore-free and it is better if it is hydrophobic. Al_2O_3 can be deposited on the surface of polymers by the atomic layer deposition (ALD) technique, forming a high-quality pore-free barrier film. Al_2O_3 coated galactoclugomannan (GGM)-coated board (GGM appr. 9g/m^2) reduced the OTR value to close to the oxygen barrier level required for dry food applications (Hirvikorpi et al., 2011). TEMPO-oxidized cellulose nanofibrils possess free carboxyl groups, which could change the cellulose nanofibrils to hydrophobic, and thus remarkably increase the barrier properties (Isogai et al., 2011).

2.5.4.6 Composites

Hemicellulose blended with nanoscale cellulose can remarkably improve the mechanical properties, such as stiffness, strength and stretch. Nearly 1.5 times the stiffness (7.3 GPa) and improved strength (143 MPa) compared to pure hemicellulose film were observed in a high molecular weight arabinoxylan based hemicellulose film, and the stress at break (7.2%) was nearly twice that of the pure hemicellulose based film. Nanoclay blending with hemicellulose reduced the water vapor transmission rate (WVTR) of the composite by about 5%. However, in combination with crosslinking agents, WVTR was reduced by about 10%. Even though the nanoscale substance addition in hemicellulose reduced the water/water vapor permeability, it was still two orders of magnitude larger than in current commercially used packaging films (Edlund et al., 2010; Doroudgarian, 2011; Stevanic et al., 2012; Sárossy et al., 2012; Saadatmand et al.,

2012).

2.5.4.7 Enzymatic modification

The properties of polymers are related to the degree of polymerization as well as to substitution. The use of enzymes can change the amounts of the side groups of hemicellulose, hence changing both its solubility and crystallinity. Removal of side groups can result in a closer association of hemicellulose molecular chains, and thus contribute to crystallization and influencing the performances of the hemicellulose products (Settineri and Marchessault, 1965; Chanzy et al., 1979).

2.6 Economic evaluation for hemicellulose application

To turn the potential use of hemicellulose as a packaging material for relieving the dependence of society on petrochemicals into reality, the isolation method of hemicellulose should be cost-efficient. As a promising hemicellulose source, the process streams in thermomechanical pulp mills have attracted much attention for hemicellulose extraction. Persson et al. in 2007 performed an economic evaluation of a hemicellulose isolation method from the process streams in thermomechanical pulp mills by membrane filtration. They proposed that using hemicellulose as an oxygen barrier could be possible at a price that is competitive with the materials used today. Nevertheless, the economic evaluation of hemicellulose isolation from other sources (wood, agricultural residues, grass) is hardly seen in the open literature.

3 MATERIALS AND METHODS

3.1 Introduction

Hemicellulose, as the second most abundant renewable biopolymer on earth, has attracted a great deal of attention for its potential in manufacturing of high-value-added products, like food packaging materials. For these materials, adequate mechanical properties (strength and flexibility), sufficient barrier to oxygen and water vapor, and in some cases, preventing light, bacteria and/or other contaminants are necessary in order to keep food from deterioration to provide a sufficiently long shelf life. Therefore, efficient measures are necessary to take in order to overcome the drawbacks of hemicellulose to provide adequate properties.

Many studies have been carried out to fabricate reliable packaging materials with sufficient mechanical and barrier properties from hemicellulose. Research objectives mostly focus on the isolation, characterization, identification, and modification methods. Few studies are available in the open literature dealing with the influence of different hemicellulose sources, isolation methods and pretreatments on the properties important for packaging materials such as tensile properties and water vapor transmission.

Efforts need to be made to fully understand the influence on the properties of hemicellulose for selection and/or adjustment of isolation methods to provide the properties needed for large industrial scale applications. And also corresponding measures could be taken to modify hemicellulose products in order to obtain enhanced properties, to satisfy the requirements as packaging materials.

Wood is extensively used for pulping to make paper and paperboard. In USA, the forest area slightly increased from 296,335 (1000 ha) in 1990 to 304,022 (1000 ha) in 2010 (FRA, 2010). Aspen (*Populus tremula*) is a very commonly seen hardwood species. Spruce is

commonly found in the northern temperate and boreal (taiga) regions of the earth. They are both important species for the pulp and paper industry. Chemi-thermo-mechanical pulp (CTMP) aspen hardwood and spruce softwood can offer ideal raw materials for the isolation of hemicellulose with high yield and reasonably high molar mass, due to their high production, and low content of lignin and other contaminants (Fuhrmann and Krogerus, 2009). Hybrid poplar, as one of the hemicellulose sources in this study, is one of the fastest growing wood species. It can be harvested from December to June. It grows broadly in temperate and cold temperate zones in the northern hemisphere. Like aspen, hybrid poplar is a popular species in many countries, including the United States. In addition, utilization of wood, unlike cereal plants such as rye, wheat, oat, corn, etc., does not compete with food for people or livestock. So, aspen CTMP (CTMP A), hybrid poplar powder (HPP) and spruce CTMP (CTMP S) are the three types of raw materials used as hemicellulose sources in this study.

Hemicellulose has many hydroxyl groups in its molecular chain. These groups make hemicellulose very hydrophilic. But also they provide the possibility to be modified by cross linking, changing them to ester bonds, to increase the intermolecular interaction/connection for improvement of the mechanical properties. Meanwhile, it would be an effective approach to improve their hydrophobic properties. For resolving the brittleness of hemicellulose based film, plasticizer is needed to increase its flexibility. Sorbitol is proved to be a promising plasticizer for arabinoxylan based film (Hansen et al., 2012). Glutaraldehyde has been used as a cross-linking agent in many applications, such as in bioprostheses, the fixation of cells, the immobilization of enzymes, and the delivery of controlled drug (Jayakrishnan and Jameela, 1996). It is also allowed to be used as a component of paper and paperboard in contact with aqueous and fatty food (21CFR176.170). EPA (Environmental Protection Agency) in 2007 published the

reregistration eligibility decision for glutaraldehyde (EPA 739-R-07-006). It is used in food handling and food storage establishments as an antimicrobial agent. Glutaraldehyde-containing products are also approved for use in aquatic areas. EPA concluded that the special hazard-based FQPA Safety Factor for glutaraldehyde should be removed.

Thus, in this study, sorbitol and glutaraldehyde were employed as additives to improve the properties of hemicellulose based films for potentially use for packaging application.

Commercial xylans (Sigma-Aldrich) as a perfect model for hemicellulose were investigated in advance to figure out the proper additive amounts and their ratio in the xylan based films. The degree of polymerization (DP) of these xylans and tensile properties of their films were tested as well, for clarification of the influence of DP on the properties. Then, hemicelluloses from different sources (hardwood & softwood; pulp & powder) and pretreatments (chemithermomechanical treatment & mechanically ground; bleached & unbleached) were used in this study to fabricate hemicellulose based films with sorbitol and glutaraldehyde as the plasticizer and cross-linking agents, respectively.

The alkaline extraction method was selected in this study for isolation of hemicellulose, because the structure of alkaline extracted hemicellulose is quite similar to its native status except for the removal of O-acetyl groups under alkaline conditions compared with the other methods (Teleman et al., 2000). The equipment used in this method is not required to support high temperature and pressure, which makes it very easy to conduct in the laboratory. Furthermore, the chemicals used in this method are relatively easy to handle.

3. 2 Materials and chemicals

Xylans from beechwood, birchwood and oat spelts purchased from Sigma-Aldrich were used as the hemicellulose models in this study. Hybrid poplar was ground to reduce its size to pass mesh #35 in order to increase its specific surface area exposure under the reaction conditions, which helps hemicellulose release from its matrix in the wood cell wall. Thus, three types of raw materials, hybrid poplar powder (HPP), aspen CTMP (CTMP A) and spruce CTMP (CTMP S), were used for alkaline extraction of hemicellulose. The raw materials were either bleached or unbleached before alkaline extraction. Hence, hemicellulose was prepared through six different approaches. Detailed preparation procedures are explained below. Ethylenediaminetetraacetic acid (EDTA, Sigma-Aldrich), ethanol (190 proof, Baker), and filter paper (Waters) were the chemicals and reagents used in the hemicellulose preparation steps. HPLC water (Baker), dextran with different molecular weights (Sigma-Aldrich), sodium nitrate (Sigma-Aldrich) and sodium hydroxide (Sigma-Aldrich) were the chemicals used in the hemicellulose analysis procedures. Sorbitol and glutaraldehyde (50%) were purchased from Sigma-Aldrich and used as the film additives. Disodium 2, 2'-bicinechoninate, sodium carbonate, sodium bicarbonate, copper sulfate pentahydrate and L-serine were purchased from Sigma-Aldrich and used for DP measurement by the reducing-end method.

3.3 Fabrication of xylan based films by solvent casting

3.3.1 Function of additives

Xylan from beechwood (0.85g, dry weight) was dissolved in 90 g DI water by heating at $69 \pm 1^\circ\text{C}$ for about 30 min with magnetic stirring. After cooling down to room temperature, a total of 0.25 g sorbitol and glutaraldehyde (GA) were added to this xylan solution at ratios of 3:1, 2:1, 1:0, 0:1, 1:1, 1:2, 1:3 sorbitol:GA. Each of these solutions was then magnetic stirred again and

transferred evenly to 3 petri dishes (100 mm diameter × 15 mm height) by passing through a #230 mesh screen to remove particles. These samples were then evaporated at room temperature (23°C) for about 3 days to form films. Then they were transferred to a room maintained at 23°C temperature and 50% relative humidity and conditioned for 2 weeks.

3.3.2 Proper amount of additives

Xylan from beechwood (0.85g, dry weight) was dissolved in 90 g DI water by heating at $69 \pm 1^\circ\text{C}$ for about 30 min with magnetic stirring. After cooling down to room temperature, different amounts of sorbitol and glutaraldehyde (GA) were added to the xylan solution at a constant ratio of 4:1 (sorbitol: GA). A series of solutions with different total additive amounts of 0.125, 0.25, 0.5 and 0.75 gram were obtained. A xylan solution without additives was the control. Each of these solutions was then magnetically stirred, transferred to 3 petri dishes after screening, evaporated to form films and conditioned as described above.

3.4 Hemicellulose extraction and film fabrication

Before hemicellulose extraction, it was necessary to remove extractives and ash so that they did not cause any interference with the further treatment. Lignin was removed as well for the bleached hemicellulose samples.

3.4.1 Extractives removal

Due to health hazards associated with the use of benzene, ethanol and hot water were used as the solvents to remove the extractives in wood, replacing the ethanol-benzene mixture used previously in accordance with NREL/ TP-510-42619. The Soxhlet method was used here. Oven dried hybrid poplar powder (10 g) was put in a pre-weighed extraction thimble and inserted to the Soxhlet tube. HPLC grade water (190 ± 5 ml) was added to the tared receiving flask and adjusted to provide about 5 siphon cycles per hour and refluxed for 24 hours; the same

amount of 190 proof ethanol (190 ± 5 ml) was used subsequently with about 10 siphon cycles per hour and refluxed for an additional 24 hours. The ethanol mainly removed wood resin material, including fatty and resin acids, sterols, waxes and fats, which can be dissolved in organic solvents. Hot water removed the water-soluble compounds such as polyphenols and low molecular weight carbohydrates, for example, tannins, gums, sugars, starches, and coloring matter. Some of the low molecular weight hemicellulose could be removed at the same time. Meanwhile, some ash was removed in the hot water extraction procedure, also.

3.4.2 Metal ion chelation

The raw materials normally contained metal ions (such as Mn^{2+} and Fe^{2+}) that could catalyze the disproportionation of hydrogen peroxide and interfere with the bleaching procedure. For example, soluble ferrous iron can be rapidly oxidized by hydrogen peroxide to ferric (Fe^{3+}), forming a rapidly settling ferric hydroxide floc. Deactivation of the metal ions is thus necessary. Ethylenediaminetetraacetic acid (EDTA) can inhibit the ability of metal ions to catalyze the disproportionation of hydrogen peroxide. Once bound to EDTA, these metal centers tend not to form precipitates or to interfere with the action of hydrogen peroxide. Therefore, ethylenediaminetetraacetic acid was used to bind those ions to eliminate their activity. Each raw material was treated with 0.2% EDTA (wood:EDTA ratio = 1:30, w/w) in a plastic bag placed in a water bath at 70 °C for 1 hr. After that, the raw materials were filtered, and washed with DI water.

3.4.3 Bleaching

A bleaching solution containing 20% sodium percarbonate (SPC), 0.05% magnesium sulfate and 3% sodium silicate was used to remove lignin from the extractive-free hybrid poplar powder, aspen CTMP and spruce CTMP. Sodium percarbonate is in fact a carbonate perhydrate with chemical formula, $2 \text{Na}_2\text{CO}_3 \cdot 3 \text{H}_2\text{O}_2$. It is a colorless, crystalline, hygroscopic and water-soluble solid. It is a source of highly concentrated hydrogen peroxide in non-aqueous systems, even if the material is not fully soluble. The addition of small amounts of water or sonication can increase the rate of oxidation. Dissolved in water, it yields a mixture of hydrogen peroxide (which eventually decomposes to water and oxygen) and sodium carbonate. It is very storage-stable if it is dried. So it is much safer to store or transport compared with liquid hydrogen peroxide. Furthermore, it contains no phosphorus or nitrogen; it is an eco-friendly chemical, and has been used as an ingredient in a number of home and laundry cleaning products. Thus, sodium percarbonate was selected as the bleaching agent in this study. EDTA treated raw materials with bleaching solution (1:50, w/w) were placed in a plastic bag kept in a water bath at 85-90 °C for 1 hr. The raw materials were then filtered and washed with DI water.

3.4.4 Alkaline extraction

After the treatment procedures above, the leftover material was mainly hollocellulose, which contains cellulose and hemicellulose. Potassium hydroxide with a concentration of 10% (w/w) was used as the alkaline extraction solution to extract hemicellulose from the hollocellulose at a sample to solution ratio of 1:50 (w/w). This extraction was conducted at room temperature for 20 hours with magnetic bar stirring. Then the supernatant liquor was collected by centrifugation (Eppendorf, 5804R, Germany) at 4500 rpm for 4 min for further treatment.

3.4.5 Hemicellulose recovery

The ethanol method was applied to precipitate the hemicellulose from its alkaline solution at a ratio of 1:1 (190 proof ethanol, w/w). The precipitate was collected by centrifugation and washed with 1:1 water-ethanol solution twice with repeated centrifugation. 190 proof ethanol (95%) was used for the final wash to remove the low molecular weight organic matter. Then, the solid remainder was dried at room temperature for film making. The used ethanol was recycled by rota-evaporation.

3.4.6 Fabrication of extracted hemicellulose films by solvent casting

One gram of hemicellulose was dissolved in 90 g DI water by heating at $69 \pm 1^\circ\text{C}$ for about 15 mins. After the temperature dropped to room temperature, 0.2 g sorbitol (plasticizer) and 0.05 g glutaraldehyde (cross-linking agent) were added into the solution. The solution was magnetically stirred for 5 min, transferred evenly to 3 petri dishes (100 mm diameter $\times$ 15 mm height) by passing through a 230 mesh screen and evaporated at room temperature to form films. A digital micrometer was used to measure the thickness of the films. For each approach, six films were made. Hemicellulose films without additives and with the same amount of sorbitol were fabricated as well for comparison.

3.5 Characterization and property analysis

3.5.1 HPLC analysis

Sugar analysis of the hemicellulose was conducted using high performance liquid chromatography (HPLC). HPLC is a technique to separate, identify and quantify the different components in a mixture. The typical detectors used for HPLC include UV-VIS detector, photo

diode array detector, fluorescence detector, mass spectroscopic detector, refractive index detector and light scattering detectors.

The composition analysis of the hemicellulose obtained from the six different approaches in this study was carried out according to modified protocol NREL/TP-510-42618. A 0.1 g hemicellulose sample was first hydrolyzed in 29 mL 4% sulfuric acid solution by placing in an autoclave at 121°C for 1 hr. The hydrolysate was then neutralized by calcium carbonate until no bubble production. The sugar content after neutralization was determined by HPLC equipped with refractive index (RI) detector and an Aminex HPX-87P 9 μm , 7.8 x 300 mm column (Bi-Rad Laboratories, Inc., CA, USA) kept at 40°C. An isocratic elution was carried out at a flow rate of 0.6 mL min⁻¹ for 17 min with a mobile phase of DI water. Acetyl groups in the hemicellulose molecular chain were determined by HPLC with an Aminex HPX-87H 9 μm , 7.8 x 300 mm column (Bi-Rad Laboratories, Inc., CA, USA) kept at 40°C. A mobile phase of 6M sulfuric acid solution was used to elute the sample at the same flow rate as in the sugar content measurement. The other conditions were the same. All the samples were filtered by a 0.45 μm membrane (Baker) before injection into the HPLC. The solid residue in the acid solution was collected by paper filtration and dried for measurement of lignin content as well as ash content contained in the extracted sample after burning. All the tests were conducted in duplicate.

3.5.2 SEC measurement

Size exclusion chromatography was used to estimate the molecular weight of the extracted hemicellulosic preparations using elution in an aqueous mobile phase solvent containing 0.1 M sodium nitrate and 0.01 M sodium hydroxide. The molecules with different molecular weights were separated based on their size during their elution through the column and

detected using a refractive index (RI) detector. The chromatogram equipment included two Waters (Milford, MA) columns (Ultrahydrogel 250, 7.8 mm X 300 mm and Ultrahydrogel 500, 7.8 mm X 300 mm) to improve the separation of hemicellulose molecules.

Dextran standards with molecular weights of 6000, 40000, 70000, 100000 and 2000000 g/mol were used to calibrate the columns. The extracted hemicellulosic preparations were dissolved in an aqueous solution similar to the mobile phase at a ratio of 1:100 (solid: liquid mobile phase) through heating for 60 minutes at a temperature of 66 ± 2 °C with sonication as well. Sonication was used to reduce the aggregation of hemicellulose molecules during dissolution (Stoklosa and Hodge, 2012).

The SEC column was kept at a temperature of 40 °C and each sample (injection volume: 20µl) was run for 48 min with a flow rate of 0.6 ml/min. All the samples were run in triplicate.

Knowing the elution time and the flow rate, the elution volume was calculated by multiplying the flow rate by the elution time as expressed in the equation below:

$$\text{Volume} = \text{Retention time} \times \text{flow rate}$$

Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PI) of hemicellulose samples based on the calibrated elution volume range were calculated from the SEC analysis results.

The number average molecular weight is the statistical average molecular weight of all the polymer chains in the sample, defined as:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

where M_i is the molecular weight of a chain, N_i is the number of chains of that molecular weight.

The weight average molecular weight takes into account the molecular weight of a chain in determining contributions to the molecular weight average. It is defined as:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

In the SEC approach, molecular weight distribution information is processed by dividing the output from the concentration detector into a number of time slices of equal width. Each of these time slices stands for a type of monodisperse molecular weight based upon the calibration curve. Next, the corresponding elution volume, molecular weight (M_i), area (A_i), cumulative area, cumulative area percent, A_i divided by M_i , A_i times M_i , and the summary of the last two factors are calculated. These calculated data are used to compute the molecular weight averages and distributions (Malawer and Senak, 2003).

$$\overline{M}_n = \frac{\sum_i A_i}{\sum_i A_i / M_i} \quad (1)$$

$$\overline{M}_w = \frac{\sum_i A_i M_i}{\sum_i A_i} \quad (2)$$

The polydispersity index is used as a measure of the broadness of a molecular weight distribution of a polymer, defined as:

$$\text{Polydispersity index} = \frac{M_w}{M_n}$$

The larger the polydispersity index, the broader the molecular weight.

The same measurement was carried out for xylans from birchwood, beechwood and oat spelts. The number average molecular weight and weight average molecular weight were converted to DP later by conversion factor of 132 g/mol monomer subunit for a xylan polymer for comparison with the results obtained by the reducing-end method.

3.5.3 DP measurement by reducing-end method

The reducing-end method provided the number average degree of polymerization of these

xylans, which was determined as the ratio of xylosyl monomer concentration divided by the reducing-end concentration. The xylosyl monomer concentration was determined by the same 4% sulfuric acid hydrolysis method discussed in the composition determination of extracted hemicellulosic samples. The reducing-end concentration was determined by a 2, 2'-bicinchoninate (BCA) method (Zhang and Lynd, 2005). This method featured incubation of the mixture of xylan solution and BCA working solution at 75 °C for 30 min. The BCA working solution was made by mixing equal volumes of two solutions. The first solution contained 0.971 g of disodium 2, 2'-bicinchoninate, 27.14 g of Na₂CO₃, and 12.1 g of NaHCO₃ dissolved in 500 mL of distilled water. The second solution contained 0.624 g of CuSO₄·5H₂O and 0.631 g of L-serine dissolved in 500 mL of water. Then absorbance was measured at 560 nm. Solutions of xylose with concentrations of 0, 5, 10, 20, 40 and 60 µM were run as standards. Since it is well known that the (4-O-Me)-GlcAp subunits are substituted onto the polymer backbone in xylans as an α-1, 2 glycosidic bond (Teleman et al, 2002) and the Araf subunits are linked to xylans with α-1, 2 linkage and/or α-1, 3 linkage (Ebringerová, 2005), there should only be one unique anomeric carbon or “reducing-end” per polymer chain in the xylans. Thus, the reducing-end concentration could be obtained. In combination with the xylosyl monomer concentration, the number average degree of polymerization of the xylans from different sources could be estimated.

3.5.4 Enzyme hydrolysis of hemicellulose

Hemicellulose (1 g) obtained from bleached hybrid poplar powder (HPPB) was put into a vial, and 10 g DI water added. Then the pH of the liquid was adjusted to 4.5-5.0 by sulfuric acid. A buffer solution (pH 5.5, 650 ml) was added to the liquid to maintain the pH during hydrolysis. Then DI water was added to make the liquid reach 13 g total.

Enzyme HTec 2 (Cellic, Novozymes, Bagsvaerd, Denmark) 61 μ l was added to this final liquid to reach a 1% concentration of enzyme (enzyme/hemicellulose, w/w). Then the vial was put in an incubator and shaken for 1 hour at a temperature of 50°C.

After hydrolysis, the vial was put in boiling water for 5 minutes to kill the enzyme. The solid was collected by centrifugation. Seventy percent ethanol (190 proof) solution was used to wash the solid for 4 times with repeated centrifugation. Then the solid was dried at room temperature for SEC measurement. Later, M_n and M_w obtained by SEC were converted to DPs by conversion factor of 132 g/mol monomer subunit for a xylan polymer for comparison.

3.5.5 FTIR analysis

Fourier transform infrared spectroscopy (FTIR) is a technique to identify the typical functional groups in a material and semi-quantification could be conducted based on the different absorption of infrared caused by the motion of the functional groups. It was used to identify lignin in both bleached and unbleached hemicellulose samples in this study. The samples from both bleached and unbleached HPP hemicellulose with the same weight were scanned by a Shimadzu IRPrestige-21 FTIR apparatus (Shimadzu, Japan) equipped with a Pike Technologies horizontal attenuated total reflectance (HATR) accessory. Infrared absorbance spectra within a wavenumber range of 2500-600 cm^{-1} were obtained with resolution number of 4 and scan number of 60. Two lignin samples, 42-7 bmwel lignin and AlcellTM organosolv lignin (Repap Inc., Valley Forge, PA, USA) were scanned as the lignin determination standards. Xylan from oat spelts (Sigma-Aldrich, USA) and hybrid poplar powder were also scanned as control samples. The experiment was conducted in triplicate.

3.5.6 UV-Vis analysis

Compounds containing double/triple bonds and nonbonding electrons can absorb ultraviolet radiation or visible radiation. So a Lambda 25 UV-Vis spectrometer (Perkin Elmer Instruments, Waltham, Massachusetts, USA) was used to record the UV-Vis spectra of HPP hemicellulose based films in the range of 200-800 nm to identify and determine lignin in the hemicellulose based films. Meanwhile, information about the transparency of these hemicellulose based films was obtained.

3.5.7 XRD analysis

X-ray diffraction (XRD) was employed to explore the crystal region of the hemicellulose based films if any formed during casting. It is a tool used for determining the atomic and molecular structures of crystal lattices in a sample without destruction. A crystal can diffract a beam of incident X-rays into many specific directions. By measuring the angles and intensities of these diffracted beams, the density of electrons within the crystal, as well as the mean positions of the atoms and their chemical bonds, their disorder etc., can be obtained.

In this study, X-ray diffraction was used to characterize the structure of the extracted hemicellulose powder as well as hemicellulose films with/without additives. The XRD instrument was a Bruker AXS D8 Advance X-ray diffractometer (Bruker Co., Billerica, MA, USA) equipped with a Cu K α radiation source (wavelength $\lambda = 0.154$ nm) setting at 40 kV and 40 mA. The sample was scanned over a 2 theta range of 10 ° to 45 ° at a step time of 0.5 s and a step size of 0.02 °. Sorbitol was also scanned as a control.

Xylan based films using xylans purchased from Sigma-Aldrich (S: G=4:1, 25% additives) were scanned in the same manner.

3.5.8 DSC analysis

Differential scanning calorimeters (DSC) measure the relationship between temperatures and heat flows, which can indicate the thermal transitions in a material, such as glass transition, “cold” crystallization, phase changes, and melting. By knowing this information, the structure and thermal stability of the material can be obtained.

In this study, a DSC Q 100 (TA Instruments, New Castle, DE, USA) was employed to record the spectra of HPP bleached and unbleached hemicelluloses and their films. These films were made from a series of recipes (hemicellulose with no additives; hemicellulose:sorbitol /1:0.2; hemicellulose:sorbitol:glutaraldehyde / 1:0.2:0.05). Before measurement, these hemicellulose samples were dried at a temperature of 50 °C for 4 hrs. These samples were all measured over a temperature range of 42°C to 280°C at a heating scan rate of 10 °C min⁻¹.

3.5.9 Tensile tests

For the mechanical properties analysis, an Instron electromechanical load frame (series 5565) was used to test the tensile properties. Based on the tested data, tensile strength (TS), elongation at break (El), modulus of elasticity (MOE), specific strength and flexural stiffness (S) were obtained.

Tensile tests are fundamental materials tests in which a sample is subjected to a controlled force until failure. A complete tensile profile can show how the tested sample reacted to the forces being applied. Information about properties such as tensile strength, elongation at break, tensile energy absorption (TEA), Young's modulus, tensile stiffness and yield strength can be obtained. Results are typically displayed in a schematic as shown below from Instron (Figure 11).

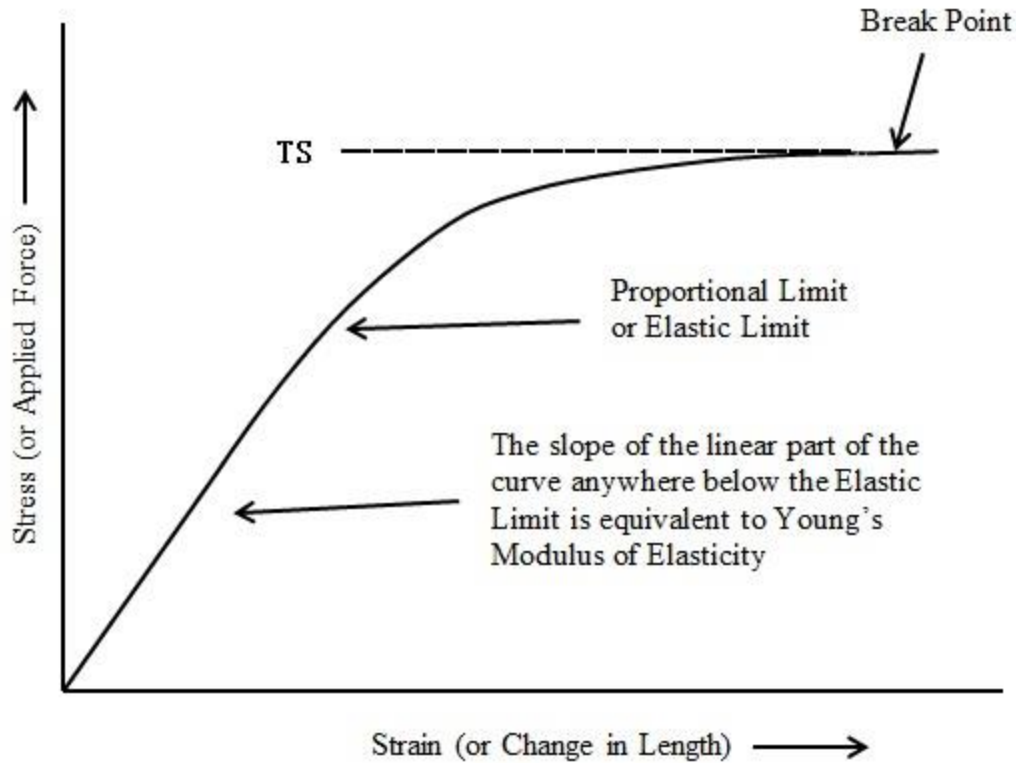


Figure 11 Tensile stress-strain diagram

For most tensile testing of materials, in the initial portion of the test, the curve of the profile is linear. In this linear region, the line obeys the relationship defined as "Hooke's Law" where the ratio of stress to strain is a constant, or $\frac{\sigma}{\epsilon} = E$. E is the slope of the line in this region where stress (σ) is proportional to strain (ϵ) and is called the "modulus of elasticity" or "Young's modulus". The modulus of elasticity is a measure of the stiffness of the material, but it only applies in the linear region of the curve. If a specimen is loaded within this linear region, the material will return to its exact same conditions if the load is removed.

The specific strength of a material is calculated by the material's strength divided by its density. This means not only the strength of a material is considered, but also at the same time, the material's weight is considered. It is an important way to remove the influence of the material's density. The material density is calculated by the mass divided by the volume. The

strength can be obtained from the tensile properties test. A high specific strength can mean a material has both lighter weight and higher strength.

As a packaging material, the bending stiffness of a film is an especially important quality parameter. It affects the appearance, machinability and functionality of the product (Koran and Kamdem, 1989; Wyser et al., 2001). The bending stiffness, also referred to flexural stiffness (S), is defined as the resistance of a sheet material to bending forces. Many different instruments have been designed to measure the flexural stiffness using different measurement schemes, such as the Taber tester, Lhomary tester, Gurley tester, Instron tester and Clark tester (Koran and Kamdem, 1989). The Instron tension method is a relatively simple approach to measure stiffness in theory:

$$S = \frac{EI}{b}$$

where E is the elastic modulus, b is the width of the material and I is the moment of inertia of the cross-section. For a uniform film, the equation above can be modified by applying the moment of inertia of a rectangular cross-section:

$$I = \frac{bt^3}{12}$$

where t is the thickness of the material. Hence:

$$S = \frac{Et^3}{12}$$

The flexural stiffness is finally proportional to the tensile modulus multiplied by the thickness to the third power. Thus, the flexural stiffness depends on both the intrinsic property of the material (E) and its thickness (t). For very thin films, the flexural stiffness will be very low. Even though the Instron tension method for measurement of the flexural stiffness is rather simple in theory, it

has too low sensitivity to permit accurate determination of this property for a film material (Wyser et al., 2001).

In this study, the samples from the six approaches were conditioned at about 23 °C and RH 50% until equilibrium before tensile properties testing. The moisture content was measured by the weight method, drying at 105 °C for 5 hours. Then samples were cut into rectangular strips of size 2"× 0.25". Thickness was measured before testing using a TMI digital micrometer at three points for each strip, and an average was calculated. Twenty four replicate specimens equally from six films were tested using an Instron universal testing machine (Instron 5565) with a load cell of 100 N. The samples were tested with an initial grip separation of 1 inch and stretched at a speed of 0.5 inch/min. A computer was used to record the force-extension curve. Tensile strength in psi and maximum load were output by the computer. Elongation in percentage was defined as the percentage change in the length of the specimen compared to the original testing length. The modulus of elasticity was defined as the ratio of stress to strain at the proportional limit.

The tensile tests for hemicellulose films with smaller thickness values and different additives from the HPP approach were conducted under the same conditions, except that 8 replicates were applied in these tests.

The same test was applied to the purchased xylan based films (S: G=4:1, 25% additives) and also the films (S: G=4:1, 25% additives) made of hemicellulose samples from HPPB with/without enzyme hydrolysis.

3.5.10 SEM analysis

Scanning electron microscopy (SEM) was used to display the surface morphology of the hemicellulose based films. SEM is a type of electron microscope that produces images by

scanning the sample with a focused beam of electrons. The electrons interact with atoms in the sample surface, and then the atoms emit secondary electrons which were excited by the electron beam. When they are captured and detected, they contain information about the sample's surface topography and composition which is displayed in image form. SEM can achieve resolution better than 1 nanometer.

In this study, bleached and unbleached hemicelluloses extracted from hybrid poplar powder based films were cut into small pieces and mounted on aluminum stubs using high vacuum carbon tabs (SPI Supplies, West Chester, PA). These pieces were then coated with osmium (≈ 10 nm thickness) in an NEOC-AT osmium coater (Meiwafosis Co., Ltd., Osaka, Japan). A JEOL JS-6610LV scanning electron microscope (JEOL Ltd., Tokyo, Japan) was used to examine these film samples.

3.5.11 Water vapor barrier property test

Mocon equipment was used to test water vapor barrier properties of the hemicellulose based films. It allowed samples to be exposed under controlled relative humidity and temperature. When transmission reached the steady state, the amount of the substance permeating the sample in a unit time was measured. In this study, a water vapor permeation analyzer (Permatran-W Model 3/33, MG module, Mocon) equipped with infrared sensor with parts-per-million sensitivity was used to test the water vapor transmission rate (WVTR) at 23°C , RH 100% for 24 hours with a nitrogen carrier. It was conducted according to the standard ASTM F-1249, and reported in units of $\text{g}/(\text{day}\cdot\text{m}^2)$. At least six replicate samples were tested at each condition. The permeability was calculated from the WVTR and the thickness measured separately, and reported in units of $\text{g}\cdot\text{mil}/[\text{d}\cdot\text{m}^2\cdot\text{mmHg}]$.

3.5.12 Oxygen barrier property test

Similar Mocon equipment was used to test oxygen barrier properties of the hemicellulose based films. An oxygen permeation analyzer (Ox-Tran Model 2/21, MH Module, Mocon) equipped with infrared sensor with parts-per-million sensitivity was used to test the oxygen transmission rate (OTR) at 23°C, RH 0% for one week with a nitrogen carrier. The test was conducted according to the standard ASTM F-3985, and reported in units of $\text{cm}^3/(\text{day}\cdot\text{m}^2)$. At least six replicate samples were tested at each condition. The permeability was calculated from the OTR and the thickness measured separately, and reported in units of $\text{cm}^3\cdot\text{mil}/[\text{d}\cdot\text{m}^2\cdot\text{mmHg}]$.

3.6 Statistical analysis

In order to analyze the difference between the six levels of treatment (CTMP aspen bleached/unbleached, CTMP spruce bleached/unbleached and hybrid poplar powder bleached/unbleached), and their effects on the tensile properties of hemicellulose films (tensile strength (TS), elongation (El) and modulus of elasticity (MOE)), multivariate analysis of variance (MANOVA) was conducted to analyze the collected data by different models; while one-way analysis of variance (ANOVA) was applied also to analyze the effect of the six levels of treatment on hemicellulose molecular weight, barrier properties and other experiments for determining significant differences. Post-hoc HSD (honestly significant difference) pairwise comparisons were conducted using the Tukey test with 95% level of confidence ($\alpha=0.05$) in both analyses (MANOVA and ANOVA). All analyses were conducted using SPSS (version 22, IBM Corporation, NY, US).

In the statistical analysis of MANOVA, T1 represents bleached CTMP aspen; T2 represents unbleached CTMP aspen; T3 represents bleached CTMP spruce; T4 represents unbleached

CTMP spruce; T5 represents bleached hybrid poplar powder; and T6 represents unbleached hybrid poplar powder.

4 PROPERTIES OF XYLAN BASED FILMS AND EXTRACTED HEMICELLULOSE BASED FILMS

4.1 Xylan based films

4.1.1 Function of additives

As is seen in Figure 25 (appendix), among these different ratios of sorbitol to GA (3:1, 2:1, 1:1, 1:0, 0:0, 0:1, 1:2, 1:3), only the film at the ratio of sorbitol to GA 1:0 could be peeled from the petri dish. It formed a big piece of self-standing film, but was very brittle. No continuous self-standing films were observed at the other ratios. At the ratios with higher sorbitol such as 2:1 and 3:1 (sorbitol: GA), the films were soft but at the same time, sticky. They could not be peeled from the petri dish as continuous big piece of films. The films at the ratios with higher GA (0:1, 1:2, 1:3) showed similar behaviors as the films at the ratios with higher sorbitol. They could not form continuous and self-standing films either. Comparable to the films with higher sorbitol, they were much stickier at the ratios of sorbitol to GA 1:2 and 1:3 (sorbitol: GA). The solutions with ratios of 1:1 and 0:0 (sorbitol: GA) formed self-standing films but non-continuous, in a form of very brittle small pieces. The film with a ratio of 0:0 formed much smaller brittle pieces compared to the film with a ratio of 1:1. This indicates that both of the additives promote xylan to form a continuous film. But a proper ratio of sorbitol to glutaraldehyde exists, too much or too little of either additive can lead to poor film formation properties, such as sticky or brittle.

4.1.2 Proper amount of additives

As is seen in Figure 26 (appendix), among these different additive amounts, the solutions with 0.125 g and 0.25 g additives showed better film forming ability than the other conditions.

They formed big piece of self-standing films, and could be peeled from the petri dish. But the film with 0.125 g additive was more brittle than the one with 0.25 g. No continuous self-standing film was observed under the other conditions. With higher additive addition, the xylan films tended to be soft and sticky. They could not be peeled from the petri dish as continuous big piece of films. The film with 0.25 g (Sorbitol: GA=4:1) additive displayed the best film properties, continuous and flexible, under the conditions tested in this study.

4.2 Extracted hemicellulose based films

4.2.1 UV-Vis spectra of hemicelluloses based films

The UV-Vis spectra of bleached and unbleached HPP hemicelluloses based films were shown in Figure 12. The absorption spectrum is to display from 260nm to 400nm (Figure 12 a), the transmittance spectrum is shown from 200nm to 800nm (Figure 12 b). As is seen from the absorption spectrum (Figure 12 a), unbleached HPP hemicellulose film shows higher absorbance than bleached HPP hemicellulose film in the whole range of 260nm-400nm. There is an obvious absorption peak at 275 nm on the curve of unbleached HPP hemicellulose film, which is the characteristic absorption maximum corresponding to the $\pi \rightarrow \pi^*$ electron transition in the aromatic ring of lignin. This has a good agreement with the research on bark lignin (Seca et al., 1998). This type of electron transition usually appears in lignin at 280 nm. The hypsochromic shift is due to the relatively higher content of syringyl unites in the lignin (Morohoshi, 1991; Seca et al., 1998). The absorption band above 300 nm indicates the presence of structures containing unsaturated moieties conjugated with the aromatic moieties in lignin (Oliveira et al., 2006; Singh et al., 2012).

The transparencies of both of the two samples increase from the UV radiation to visible radiation (Figure 12 b). This result has a good agreement with the study of hemicellulose film reported by Guan et al. (Guan et al., 2014). The HPP bleached hemicellulose based film increased more sharply compared to the unbleached sample. Moreover, the transparency of HPP bleached hemicellulose based film was higher than that of unbleached film in the range of UV to visible region (300-800 nm). It was reported that the absorbance in the visible region was due to the chromophoric groups contained in lignin (Singh et al., 2012). These results indicate that lignin plays an important role on the absorption of the UV and visible light in the hemicellulose based films. It reveals that unbleached HPP hemicellulose film contains higher lignin content than bleached HPP hemicellulose film. This result corresponds to the result of composition analysis; the lignin contents in the bleached samples were slightly smaller than that in the unbleached samples. Meanwhile, the unsaturated bonds and n electrons from atom O can be excited by UV and visible radiation (Robinson et al., 2005). Absorption then might come from the C=O bond contained in the additive compound, glutaraldehyde. However, when same amount of glutaraldehyde were added into both of the bleached and unbleached films, no difference could be considered between the two samples from this point of view. So it is confirmed that the changing of the absorbance and transmittance spectra results from the differences of lignin content in the two types of samples. The transmittance of the two types of films in the UV and visible ranges favors the packaging application, where the packed item is designed to be seen by the customers, especially the bleached sample, which was over 80%. The visual colors of the unbleached hemicellulose films in this study were all yellowish than the bleached films, which was in agreement with the UV-Vis analysis results.

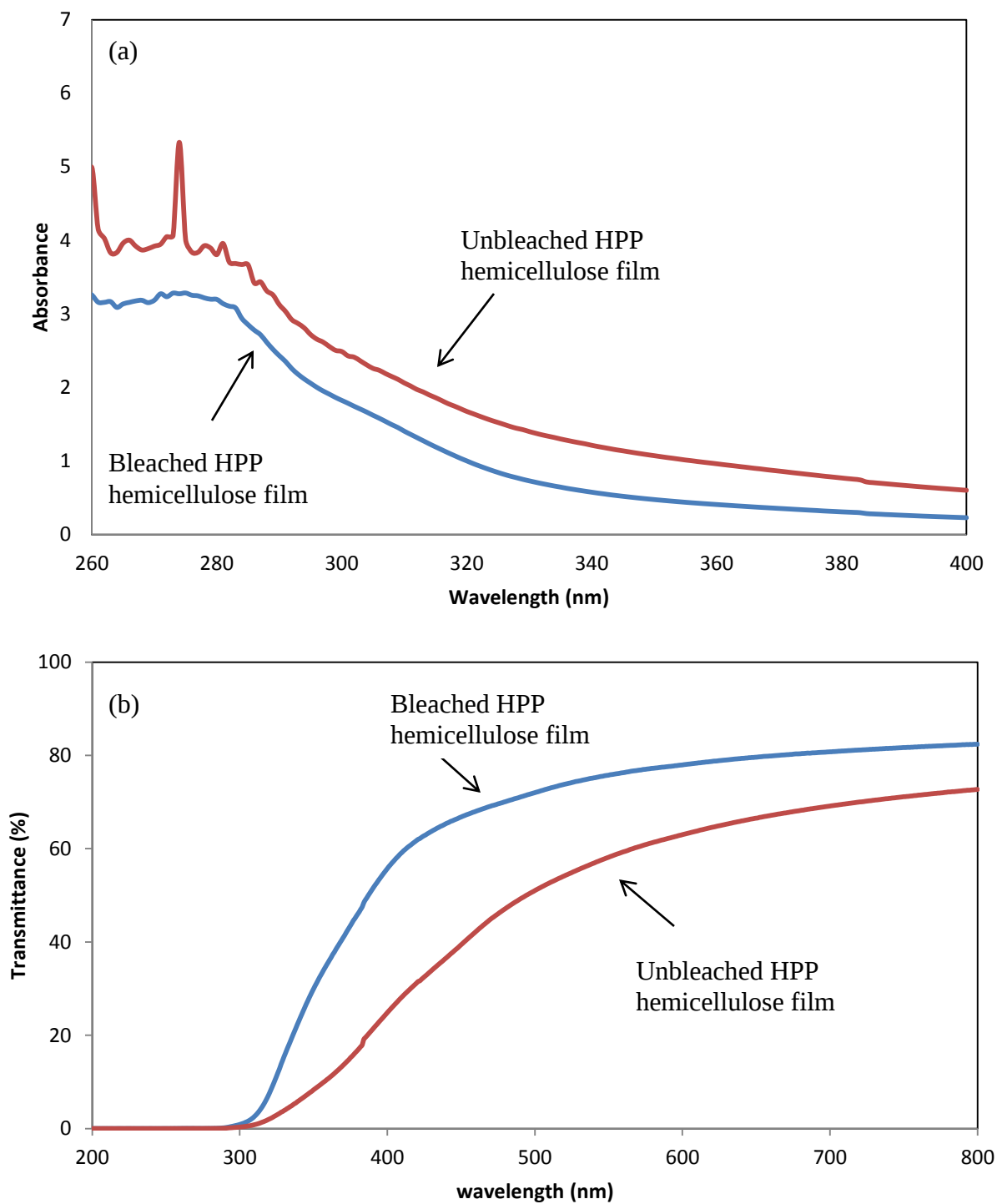


Figure 12 UV-Vis absorption spectrum (a) and transmittance spectrum (b) of bleached and unbleached HPP hemicelluloses based films

4.2.2 Thermal properties of hemicellulose based films

The DSC spectra of bleached & unbleached extracted hemicelluloses (BH & UH) and their films without additives (BHF & UHF), with sorbitol (BHSF & UHSF), with sorbitol and glutaraldehyde (BHSGF & UHSGF) are displayed in Figure 13. These spectra present two clear endothermic peaks for all of the bleached and unbleached HPP hemicellulose powder and their films. The first endothermic peak behavior is similar to the study of extracted hemicellulose from olive, chilli and pepper (Egüés et al., 2013). This endothermic peak for unbleached HPP hemicellulose is observed around 114 °C. After it formed film, it became more thermal stable than hemicellulose powder. The peak point increased from 114 °C to 140 °C for the unbleached hemicellulose film with no additives. However, the addition of the additives made the films less thermal stable. The temperature for this endothermic peak point decreased to around 126 °C for unbleached sorbitol-hemicellulose film and sorbitol-glutaraldehyde-hemicellulose film. The T_g values are observed to shift to a lower temperature (80-90 °C to 70-75 °C) with addition of the two additives. The plasticizer increased the chain mobility which reduced T_g , increasing the film flexibility (Georget et al., 1999; Matveev et al., 2000). The endothermic peak that appeared at around 240-250 °C for unbleached hemicellulose films without additives is suggested to be attributable to the melting of the crystallites. When the unbleached hemicellulose formed film, this peak changed to be sharper. This obvious change indicates a difference in the structure of the material. Combined with the results from XRD analysis, it is probably due to the crystalline melting. It is worthy to notice that two melting peaks are present in this endothermic event. Sato et al. suggested two types of crystalline formation from solvent induced crystallization (Sato et al., 2013). Since other research reported hemicellulose weight loss between 220 °C and 315 °C (Gao et al., 2013; Xiang et al., 2014), it may also be due to hemicellulose decomposition. It was

also reported that addition of plasticizer could increase the spacing between the crystal lattice planes (Gröndahl et al., 2004; Mikkonen et al. in 2009). Thus the structure of the crystallites changed. It is shown on the changing of the endothermic event at around 240 °C - 250 °C for unbleached sorbitol plasticized hemicellulose films compared with the unbleached hemicellulose film without sorbitol. It is worth noticing that the two endothermic peaks remain. Similar results are found in the bleached hemicellulose and its films, except that only one endothermic peak presents at around 240 °C - 250 °C after the addition of plasticizer. The exact reason for this phenomenon is not known. Bleaching treatment is a complex process.

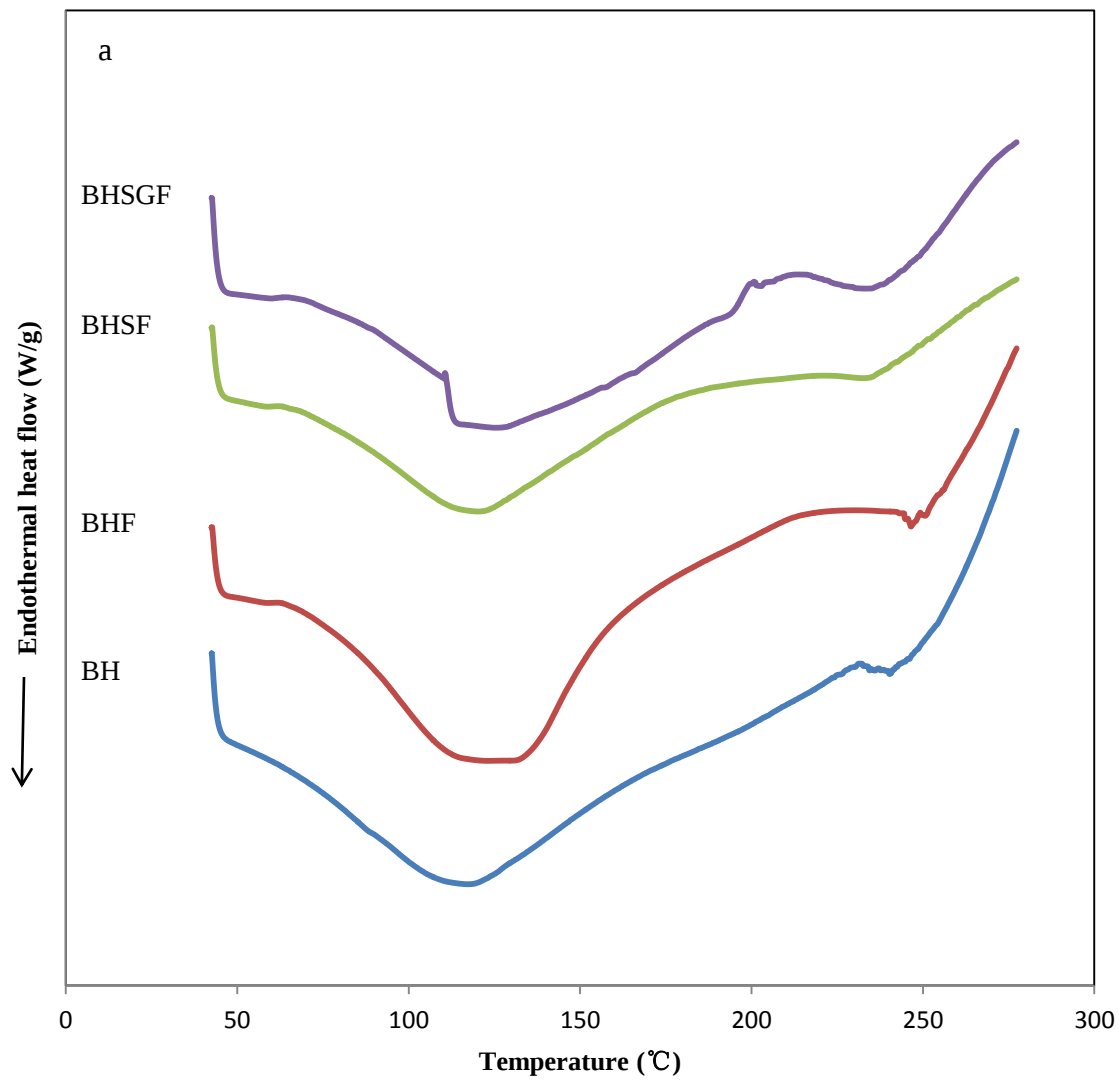
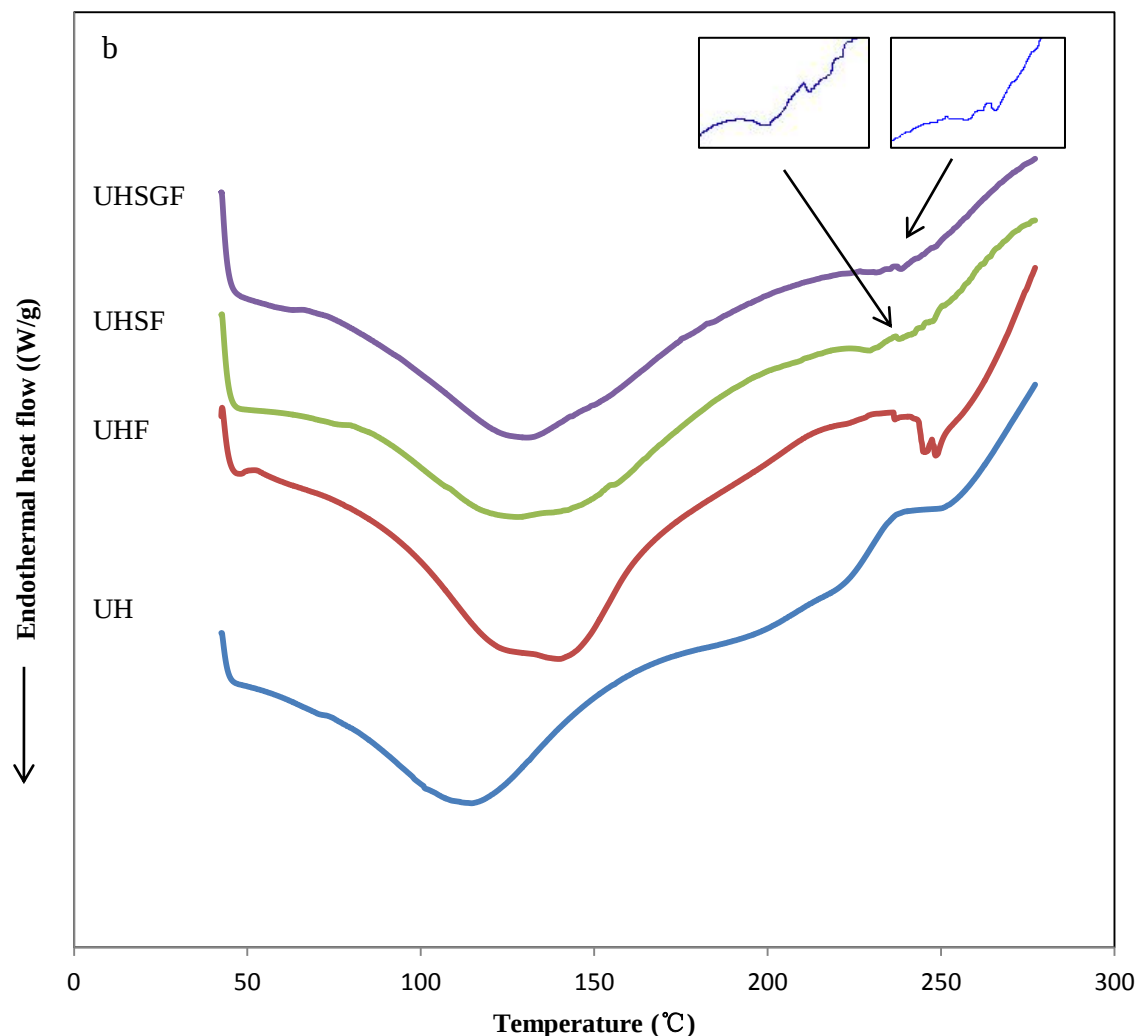


Figure 13 DSC thermograms of HPP hemicelluloses and their films with and without additives, (a) bleached; (b) unbleached.

Figure 13 (cont'd)



4.2.3 Mechanical properties of hemicellulose based films

Data for tensile strength (TS), modulus of elasticity (MOE), percent (%) elongation at break (El), and other physical and mechanical properties for different hemicellulose based films are listed in Table 2. And also, a typical tensile load-extension diagram obtained in this study is displayed in Figure 14.

The highest TS is from unbleached HPP hemicellulose based films, which is 76.5 MPa. This was about 60% higher than the TS of films made from arabinoxylan obtained from corn hull

plasticized with sorbitol (Zhang and Whistler, 2004), and even higher than the strength of sorbitol plasticized birch wood xylan films enhanced with nanofibrillated cellulose which was 66 MPa when plasticized with 20% sorbitol (Hansen et al., 2012). It was reported that the tensile strength of xylan films varied from less than 1 MPa with nearly 90% elongation to 50 MPa with 2.5% elongation (Mikkonen et al., 2009). These properties are highly related to hemicellulose source, concentration & type of plasticizer, molecular weight, and substitution (Gröndahl et al., 2004; Mikkonen et al. in 2009; Heikkinen et al., 2013; Heikkinen et al., 2014). For hardwood xylan film with 20% plasticizer, such as sorbitol and glycerol, elongation is below 2%; for oat spelt xylan film, it is above 5%. But oat spelt film tensile strength is lower than for hardwood xylan film (Gröndahl et al., 2004; Mikkonen et al. in 2009). In this study, the largest elongation comes from the films made from bleached HPP (7.4%), larger than the other hardwood xylan films with a similar amount of sorbitol (less than 2%) (Gröndahl et al., 2004). And unbleached HPP hemicellulose based films also provide the biggest MOE value (3.5 GPa), which is superior to herbaceous plant xylan film (0.5 GPa-1.0 GPa), similar to hardwood xylan film (close to 4.0 GPa) (Gröndahl et al., 2004; Mikkonen et al. in 2009; Heikkinen et al., 2013; Heikkinen et al., 2014). Compared with cellophane, a successful commercialized cellulose film, the TS of hemicellulose films obtained in this study is much lower (76.5 MPa in this study versus 101.6 MPa), but comparable elongation at break (7.4 % in this study versus 7.6%), and higher MOE (3.5 GPa in this study versus 1.3 GPa) (Bhat and Makwana, 1988). However, the tensile strength values of films in this study are much larger than the commonly used packaging petro-plastic, high density polyethylene (HDPE), which is 29.9 MPa. The highest MOE of these films is 2.3 times that of HDPE. But the elongation at break is one order of magnitude lower. For convenient comparison, the three main tensile properties of the current most-used plastics in packaging are

listed in Table 3. As is seen from this table, the TS of the commonly used plastics are typically below 50 MPa, much smaller than the highest TS of the films in this study.

The specific strength showed the same tendency as tensile strength, which removed the influence of the density on the tensile strength of the films. The flexural stiffness followed the direction of the sample thickness. The thickness of the film sample had a very strong effect on the flexural stiffness, since the MOEs of the six samples in this study were comparatively close. From this point of view, it is suggested that the bending stiffness of the hemicellulose based films in this study is comparable or better than that of common commercial packaging plastics.

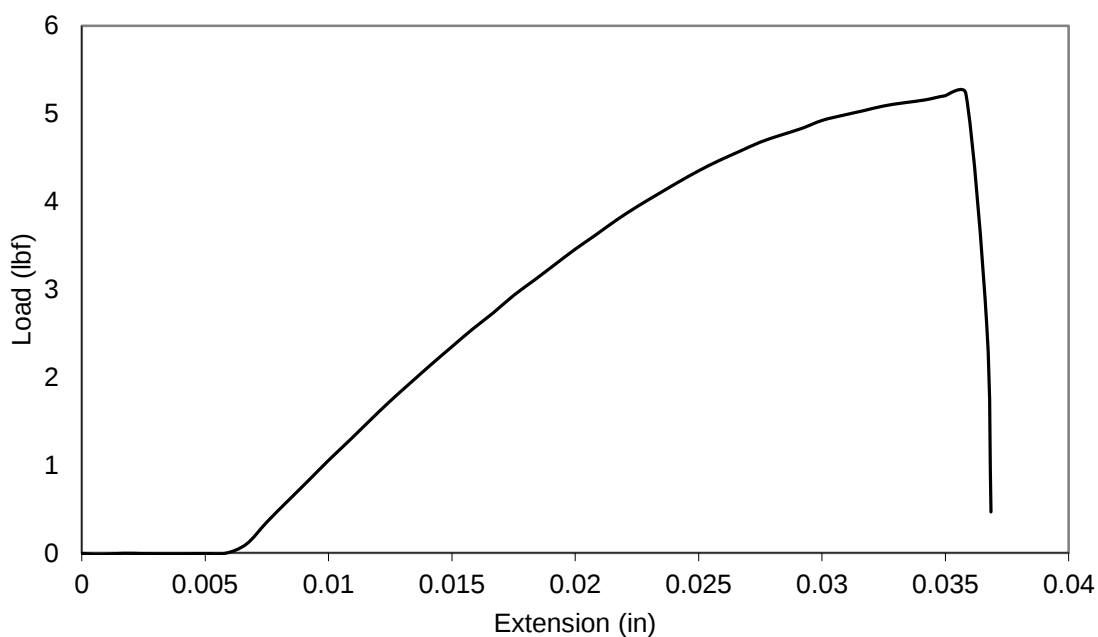


Figure 14 Tensile load-extension diagram

Table 2 Mechanical properties of hemicellulose films from different treatments

Properties	CTMP Aspen Bleached	CTMP Aspen Unbleached	CTMP Spruce Bleached	CTMP Spruce Unbleached	HPP Bleached	HPP Unbleached	HDPE
Tensile strength, MPa	47.0 (3.8)	51.8 (4.6)	59.6 (5.5)	71.0 (7.3)	66.8 (3.7)	76.5 (7.0)	29.9
Elongation, %	5.6 (1.5)	4.4 (0.6)	7.0 (1.3)	6.2 (1.4)	7.4 (1.1)	5.4 (0.9)	56.5
MOE, GPa	2.7 (0.3)	2.7 (0.2)	2.3 (0.3)	2.7 (0.3)	2.9 (0.2)	3.5 (0.4)	1.5
MC, %	14.5 (0.3)	14.4 (0.5)	13.0 (2.0)	14.5 (0.3)	15.9 (0.7)	17.0 (0.3)	
Thickness, μm	63.5 (7.6)	66.0 (10.2)	119.4 (20.3)	116.8 (12.7)	91.4 (10.2)	68.6 (5.1)	
Density, g/cm^3	1.4 (0.1)	1.3 (0.0)	1.4 (0.1)	1.4 (0.1)	1.2 (0.1)	1.3 (0.0)	
Specific strength, $\text{N}\cdot\text{m}/\text{kg}, 10^3$	33.6	39.8	42.6	50.7	55.7	58.8	
Flexural stiffness, $\text{N}\cdot\text{m}, 10^{-5}$	5.8	6.5	32.6	35.9	18.5	9.4	

Notes: The numbers in parentheses are STDEV.

All measurements were performed in 20 replicates.

HDPE: Tensile Tests of Various Plastic Materials (1). Available from:

<http://www.shimadzu.com/an/industry/petrochemicalchemical/i215.html>

Table 3 Tensile properties of several commercially used plastics in packaging

Polymer Type	Density (g/cm ³)	Tensile strength (MPa)	Elongation at break (%)	Modulus of Elasticity (MOE) (GPa)
High-density polyethylene (HDPE)	0.95-0.97	20-30	10-1000	1-1.5
Low-density polyethylene (LDPE)	0.92-0.93	8-30	100-650	0.25-0.35
Polypropylene (PP)	0.90-0.91	30-40	100-600	1.2-1.7
Polystyrene (PS)	1.0-1.1	35-50	1-2	2.6-3.4
Acrylonitrile-butadiene- styrene (ABS)	1.0-1.1	15-55	30-100	0.9-3.0
Polyvinyl chloride (PVC)	1.3-1.6	40-50	2-80	2.1-3.4

Notes: Properties and applications of commercially important plastics.

Available from: <http://www.britannica.com/EBchecked/topic/463684/plastic>.

Statistical analysis was then conducted on the tensile properties of hemicellulose based films. Three dependent variables (TS, El and MOE) were contained in this study. Thus, multivariate analysis of variance (MANOVA) is suitable to use for assessing the difference of the six levels of treatment (CTMP aspen bleached/unbleached, CTMP spruce bleached/unbleached and hybrid poplar powder bleached/unbleached) and their impacts on these three tensile properties.

1) One-way MANOVA

Before processing MANOVA analysis, normality of the collected data was checked by Q-Q Plot and correlations among the tensile properties were examined pairwise for feasibility of use of MANOVA.

A normal Q-Q Plot of tensile strength of hemicellulose films from bleached aspen CTMP pulp fiber was taken as an example (Figure 15). A nice match of observed value and expected normal value is displayed in (a). The distribution of observed data does not exhibit a systematical pattern (b). Similar results were observed in the other normal Q-Q Plot graphics (Figure 27,

appendix). The normality of the collected data is good enough to process multivariate ANOVA.

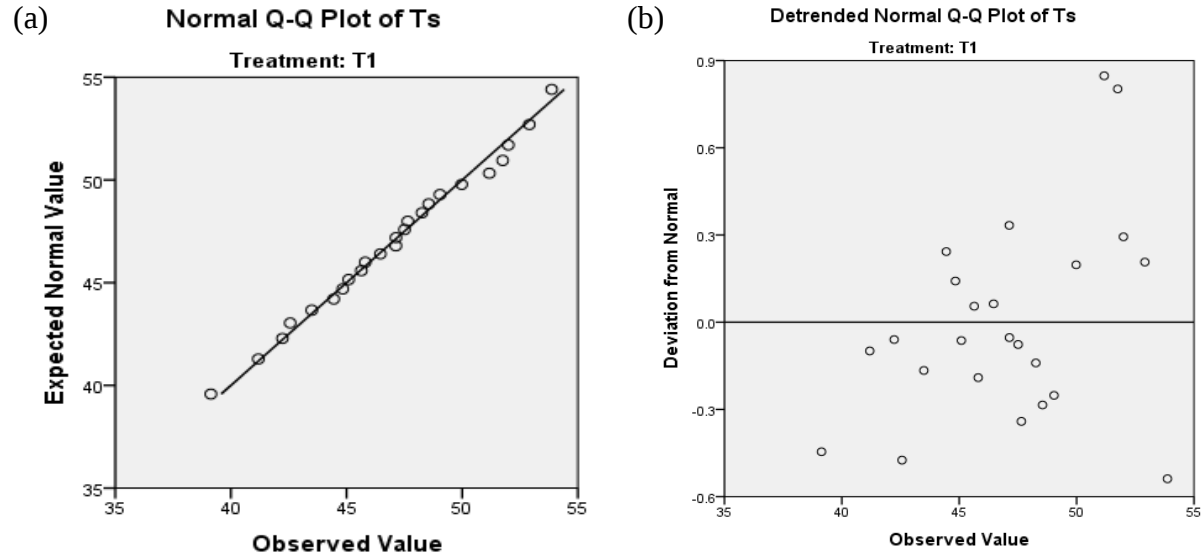


Figure 15 Normal Q-Q Plot of tensile strength of hemicellulose films from bleached aspen CTMP pulp fiber

The correlation analysis (Table 13, appendix) indicated that all of the three outcomes (tensile strength, elongation and MOE) were correlated pairwise with each other ($p < 0.05$). From Pearson analysis, the correlations between TS and El; TS and MOE are positive (0.187; 0.581), which means tensile strength behaves similarly to elongation and MOE. But the similarity between TS and EL (0.187) is much weaker than it between TS and MOE (0.581). Usually, only when the correlation coefficient is larger than 0.6, a strong positive correlation can be concluded. Yet the correlation between elongation and MOE is negative (-0.200), which means elongation behaves in an opposite way comparing with MOE, but not strong.

From the above analysis, the collected data are distributed randomly and the three tensile properties are significantly correlated pairwise with each other. MANOVA is approved to be suitable for use in this study.

1) One-way MANOVA

One-way MANOVA is used to analyze the effect of the six levels of treatment on the means of the three tensile properties. Pillai's Trace test was chosen to determine statistical difference across treatment levels because of its robust properties (Hair et al., 2009). The results indicate that the six levels of treatment have a significant effect on the tensile properties of hemicellulose films ($p=0.000$) (Table 14, appendix). To determine which of these three tensile properties contributed to the significant difference, a univariate test was further conducted to assess this effect. The outcome shows that the six levels of treatment significantly impact the three tensile properties individually, TS, El and MOE (All the three P value equal 0.000) (table 15, appendix).

To assess how the six levels of treatment impact the means of the three tensile properties individually, multiple pairwise comparisons among the six means for each property were conducted post-hoc using the Tukey HSD test (Table 16, appendix). The results revealed that nearly all of the tensile strengths were significantly different ($p<0.05$), except for that between T12 (unbleached CTMP spruce) and T13 (bleached hybrid poplar powder) ($p=0.133$). For the multiple pairwise comparisons of El and MOE, approximate half of the comparison groups showed significant differences ($p<0.05$). Among all the six levels of treatment, the groups of TS with the largest significant difference are T1 (bleached CTMP aspen) and T6 (unbleached hybrid poplar powder). The largest difference value is -29.5465 with 95% confidence interval located between lower bound -34.2487 and upper bound -24.8443. For elongation, the largest significant difference presents between T2 (unbleached CTMP aspen) and T5 (bleached hybrid poplar powder). The largest difference value is -3.0217 with the 95% confidence interval between lower bound -3.9428 and upper bound -2.1006. In comparisons of MOE, the largest significant difference exists between T3 (bleached CTMP spruce) and T6 (unbleached hybrid poplar powder)

with a difference value -1.1700, and 95% confidence interval in the range of -1.4364 to -0.9035. More information about other pairwise comparisons can be obtained from Table 16.

2) Two-way MANOVA

The analyses above state how the six levels of treatment affect the tensile properties. However, we are interested in the function of each of these factors, hardwood & softwood, bleached & unbleached and chemithermomechanical pulp & mechanically ground powder. For assessing the effect of each of the three factors on the tensile properties, further statistical analysis needs to be conducted. Three-way MANOVA would be the ideal analysis method to answer this question. However due to the scope of my research, collecting data from bleached/unbleached softwood powder was not feasible. Therefore, two-way MANOVA was applied to obtain the maximum information regarding the factors' impact.

Within hardwood

Within hardwood, the effect of pretreatments (chemithermomechanical pulp & mechanically ground powder; bleached & unbleached) on the tensile properties were assessed by two-way MANOVA. The results indicate that both of the pretreatments (chemithermomechanical pulp & mechanically ground powder; bleached & unbleached) had statistically significant influence on the tensile properties ($p < 0.05$) (Table 17, appendix), and on each of the properties (TS, El and MOE) ($p < 0.05$) (Table 18, appendix). They had significant interaction on the impact of the three properties ($p < 0.05$) (Table 17, appendix). The pretreatments did not show significant interaction on elongation ($p = 0.224$) but did on TS and MOE ($p = 0.013$; $p = 0.000$).

Within CTMP pulp

Within CTMP pulp, the impact of factors, hardwood & softwood and bleached & unbleached, on the tensile properties were assessed by two-way MANOVA. Similar results were

found in two-way ANOVA within hardwood test. Hardwood & softwood and bleaching & non-bleaching worked in the same manner (Table 19 and Table 20, appendix).

These statistical analyses results indicate that the combination of hemicellulose sources (hardwood & softwood; pulp & powder) and pretreatments (chemithermomechanical treatment & mechanically ground; bleached & unbleached) highly affected the hemicellulose film tensile properties. As is seen in the statistical analysis results, the three factors (hardwood & softwood; CTMP treatment & mechanically ground; bleached & unbleached) all have statistically significant impact on the three tensile properties (TS, El and MOE). Within hardwood, each of the other two factors significantly impacts the properties individually. All of the TS from unbleached samples were significantly bigger than that from the corresponded bleached ones; the TS from mechanically ground samples were significantly bigger than that from CTMP ones ($p < 0.05$). Within CTMP pulp, the same impact was found. All of the TS from unbleached samples were significantly larger than that from the corresponded bleached ones; the TS from softwood samples were significantly larger than that from hardwood ones ($p < 0.05$). Similar impacts were observed for El and MOE in the two further MANOVA tests, only in the opposite direction for El.

From Table 2, it can be seen that the hemicellulose based films from CTMP spruce and were thicker than the other samples. To remove the influence of thickness, thinner hemicellulose films obtained from three of the six approaches were made to compare with the thicker samples. The results are listed in Table 4. In general, the mechanical properties of the thinner film samples corresponded well to the thicker samples. No significant differences were observed between thinner and thicker samples. Therefore, thickness did not appear to impact the observed differences in mechanical properties between formulations.

Table 4 Comparison of mechanical properties of hemicellulose films with different thickness

	CTMP Spruce Bleached		CTMP Spruce Unbleached		HPP Bleached	
	Thin	Thick	Thin	Thick	Thin	Thick
Tensile strength, MPa	62.7 (1.3) ^a	59.6 (5.5) ^a	66.8 (3.6) ^b	71.0 (7.3) ^b	68.4 (3.1) ^c	66.8 (3.7) ^c
Elongation, %	6.5 (0.5) ^a	7.0 (1.3) ^a	5.6 (0.2) ^b	6.2 (1.4) ^b	6.6 (0.9) ^c	7.4 (1.1) ^c
MOE, GPa	2.5 (0.1) ^a	2.3 (0.3) ^a	2.6 (0.3) ^b	2.7 (0.3) ^b	2.9 (0.1) ^c	2.9 (0.2) ^c
MC, %	12.8 (0.8) ^a	13.0 (2.0) ^a	15.8 (3.6) ^b	14.5 (0.3) ^b	16.4 (0.3) ^c	15.9 (0.7) ^c
Thickness, μm	88.9 (2.5)	119.4 (20.3)	91.4 (7.6)	116.8 (12.7)	76.2 (5.1)	91.4 (10.2)

Note: The numbers in parentheses are STDEV.

All measurements for thin samples were performed in 8 replicates; for thick samples, there were 20 replicates.

Values between thin and thick samples in the same row in the same formulation by the same letter are not significantly different ($p>0.05$).

4.2.4 Morphology of hemicellulose based films surface

Figure 16 shows the smooth evaporation surfaces of both HPP bleached and unbleached hemicellulose based films, which revealed homogeneous structures on the surfaces. The small white particles observed on the surface were probably attributable to the dust in the air or impurities in the films, such as salt crystals. No nanocellulose-like substance was found in either of the sample surfaces. This indicates that the mechanical property changes observed in the tensile tests were attributable to the addition of sorbitol and glutaraldehyde, not to the reinforcement by accidentally included nano particles, such as the nano cellulose fiber from the hemicellulose extraction process (e.g. hemicellulose alkaline solution centrifugation).

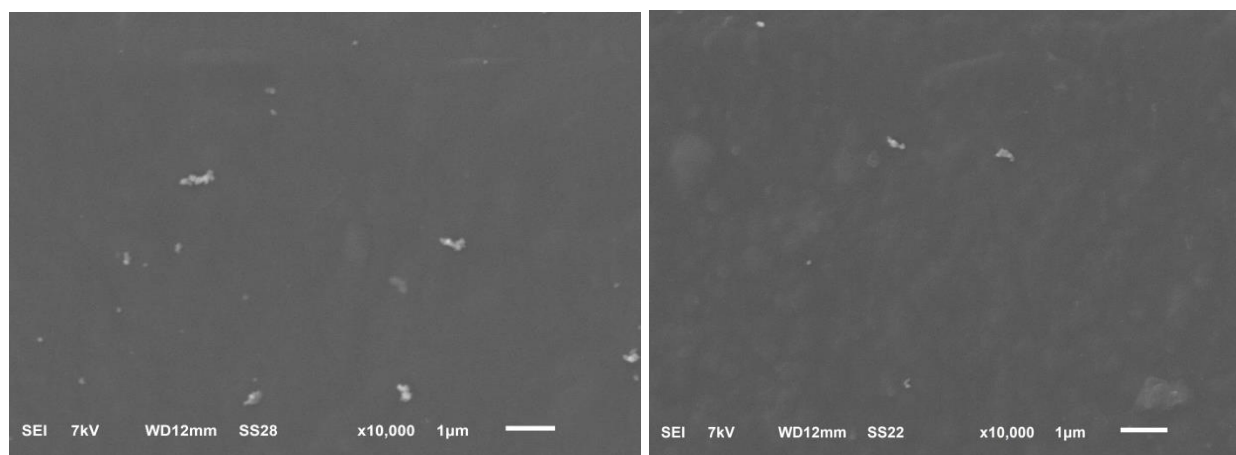


Figure 16 SEM morphology of HPP hemicellulose based films, a: bleached; b: unbleached

4.2.5 Water vapor barrier properties of hemicellulose based films

The WVTR values of hemicellulose based films from the six different approaches are listed in Table 5. WVP values were calculated based on the thicknesses measured separately. The WVTR values of these films varied from 4600 g/ d•m² to 5600 g/ d•m², which were higher by several orders of magnitude than those from current commercial packaging films (Table 6). Among these plastics, HDPE is known as a common moisture resistant petro-polymer used in

food packaging. The WVTR values in this study are larger by 2-3 orders of magnitude than that of HDPE. Furthermore, the WVP values obtained in this study are still two orders of magnitude larger than the WVP value (7.9×10^{-11} g Pa $\cdot$ m $\cdot$ s $^{-1}$) of CellophaneTM (Phan The et al., 2009). Hence, the water vapor barrier properties of the films in this study need to be improved to meet the requirements of commercial use in many food packaging areas.

As shown in Table 5, the WVTRs of unbleached hemicellulose based films were slightly lower than those of bleached hemicellulose based films. This is probably attributable to the higher crystallinity of unbleached hemicellulose based films, as shown in the XRD analysis for hemicellulose based films from hybrid poplar powder. In addition, this trend corresponded to the changes in tensile strength. In general, the higher was the tensile strength for the film, the lower the WVTR value. This behavior is possibly attributable to the increased intermolecular bonding in the films with higher tensile strength. The intermolecular bonding reduced the molecular mobility in the hemicellulose matrix, and thus decreased the WVTR value. The WVTR values obtained in this study were 2-3 times higher than the values (1800 g/ d $\cdot$ m 2 , 10% sorbitol; 2050 g/ d $\cdot$ m 2 , 40% sorbitol) from arabinoxylan based films from oat spelt (Mikkonen et al., 2009), which were reported to be comparable to the values from corn arabinoxylan films (P éroval et al., 2002; Zhang and Whistler, 2004), methyl cellulose films (Greener-Donhowe and Fennema, 1993; Phan The et al., 2002) and nanofibrillated cellulose reinforced birch wood xylan films (Hansen et al., 2012), but they were the same level of magnitude. The reason why the WVTR values of films in this study were higher than those from arabinoxylan based films from oat spelt may be attributable to the different humidity gradients (0/100% in this study versus 0/86%), measurement methods (Mocon method versus cup method) and also the different hemicellulose sources. It was reported that the humidity gradient significantly affected the WVTR values of

hydrophilic films (Hagenmaier and Shaw, 1990; McHugh et al., 1993; Mikkonen et al., 2009).

The WVTR values for hydrophilic films can increase greatly at very high RH.

Table 5 Water vapor permeability of hemicellulose based films from six different approaches

Properties	CTMP Aspen Bleached	CTMP Aspen Unbleached	CTMP Spruce Bleached	CTMP Spruce Unbleached	HPP Bleached	HPP Unbleached
Thickness, μm	63.5 (5.1)	58.4 (10.2)	137.2 (7.6)	124.5 (2.5)	88.9 (5.1)	66.0 (10.2)
WVTR, $\text{g}/(\text{d}\cdot\text{m}^2)$	5654 (180) ^a	5530 (246) ^a	4805 (363) ^b	4519 (356) ^b	4957 (281) ^b	4673 (151) ^b
Permeability, 10^{-3} $\text{g}\cdot\text{m}/(\text{d}\cdot\text{m}^2\cdot\text{KPa})$	122.3 (9.5) ^b	115.6 (15.2) ^{ab}	233.0 (12.6) ^e	200.0 (18.9) ^d	153.6 (4.8) ^c	107.5 (16.0) ^a

Notes: The numbers in parentheses are standard deviation.
All measurements were performed in 6 replicates.
Values in the same row with different superscripts are significantly different ($p < 0.05$).

Table 6 Water vapor transmission rates of common used plastic films

Polymer type	WVTR g/(d•m ²)
Ethylene Vinyl Alcohol (EVOH)	100 [*]
Polyethylene terephthalate (PET)	55 [*]
Linear low density polyethylene (LLDPE)	17 [*]
Low density polyethylene (LDPE)	18 ^{**}
High-density polyethylene (HDPE)	5-10 ^{**}
Polypropylene (PP)	19 ^{**}
Oriented polypropylene (BOPP)	9 ^{**}
Polyamide (PA)	300 ^{**}
Oriented polyamide (BOPA)	145 ^{**}
Polystyrene (PS)	110-160 ^{**}

Notes: ^{*}Flexible Packaging Solution. Available from:

<http://www.dura-pack.com/PDF/Bags-FilmRev1.pdf>.

^{**}The barrier performance of common plastic film. Available from:

<http://www.evergreen-packaging.com/en/ShowNews.asp?id=70>

4.2.6 Oxygen barrier properties of hemicellulose based films

The values of oxygen transmission rate (OTR) and oxygen permeability (OP) of hemicellulose based films from four different approaches are listed in Table 7, due to the lack of availability to collect the data from the films made from the other two approaches. These values were one to two orders of magnitude lower than those reported for hemicellulose based films (Hartman, 2006; Mikkonen et al., 2009; Mikkonen et al., 2012; Heikkinen et al., 2013; Heikkinen et al., 2014); also much lower than that of HDPE (600 cm³/(d•m²)), and slightly lower than that of PET (60 cm³/(d•m²)). Grubb in 2010 reported that a xylan-based barrier had a

similar OTR (cc/m²/day) as polyvinylidene chloride (PVdC). Compared with cellophane, a successful commercialized cellulose product, the hemicellulose films in this study also present superior oxygen barrier ($267.8 \times 10^{-9} \text{ cm}^3 \cdot \text{m} / \text{d} \cdot \text{m}^2 \cdot \text{KPa}$, 100% RH in this study versus $3.7 \times 10^{-14} \text{ cm}^3 \cdot \text{m} / \text{s} \cdot \text{m}^2 \cdot \text{Pa}$, 0% RH) (Tomé et al., 2011). Thus, the hemicellulose films in this study have superior oxygen barrier properties to most current commercialized packaging polymers. The previous studies about hemicellulose films mostly investigated the type and amount of plasticizer and crosslinking agent added to different types of hemicellulose films. Heikkinen et al. reported that sorbitol plasticized hemicellulose film (40%) showed a higher oxygen permeability coefficient than that in this study (Heikkinen et al., 2014). For hemicellulose film with increasing sorbitol amount added, slightly higher OP value was observed (Mikkonen et al., 2009). Study of the Ara/Xyl ratio of arabinoxyln film suggested that films with larger substitution had higher OP values as well (Heikkinen et al., 2013). In this study, no significant difference was found among the different types of hemicellulose films. There were no differences in the type or amount of the additives in the tested hemicellulose films, and all of the hemicelluloses were extracted from wood. These are probably the reason why no significant differences were observed in this study.

Table 7 Oxygen permeability of hemicellulose based films from different approaches

Properties	CTMP Aspen Bleached	CTMP Aspen Unbleached	CTMP Spruce Bleached	HPP Bleached	HDPE	PET
Thickness, μm	61.0 (7.6)	55.9 (7.6)	121.9 (10.2)	106.7 (20.3)		
OTR, $\text{cm}^3/(\text{d}\cdot\text{m}^2)$	20.7 (19.6) ^a	14.8 (11.2) ^a	15.5 (8.7) ^a	23.8 (16.4) ^a	600	60
Permeability, 10^{-9} $\text{cm}^3\cdot\text{m}/(\text{d}\cdot\text{m}^2\cdot\text{KPa})$	125.5 (117.7) ^a	85.0 (70.6) ^a	193.6 (93.1) ^a	267.8 (226.9) ^a		

Note: The numbers in parentheses are STDEV.

All measurements were performed in 6 replicates.

Values in the same row with the same superscripts are not significantly different ($p>0.05$).

HDPE/PET: The barrier performance of common plastic film. Available from:

<http://www.evergreen-packaging.com/en/ShowNews.asp?id=70>

5 FACTORS THAT INFLUENCE THE PROPERTIES OF EXTRACTED HEMICELLULOSE BASED FILMS

For better understanding the changes in the properties of the hemicellulose films from the six different approaches, further tests and analyses were conducted.

5.1 Composition of extracted hemicellulose samples

Table 8 shows the compositions of hemicellulose samples obtained from the six different approaches. The results show that xylan is the main hemicellulose type contained in these extracted hemicellulose samples, followed by mannan. Meanwhile, small amount of glucan, galactan and arabinan are contained in these hemicellulose samples, no more than 5% for each of them. They are attributed to the substitutes in xylan backbone chain. No statistically significant difference was observed in the amount of xylan obtained between hardwood and softwood. They are very close. But mannan amounts are somewhat higher in softwood hemicellulose samples compared with that in hardwood samples. This can be attributable to the difference in the main sugar unit of hemicelluloses between hardwood and softwood. Softwood hemicellulose is known to contain more mannan than hardwood hemicellulose (Sjöström, 1993). Klason lignin as impurity was found in these different hemicellulose samples in small amounts. The percentage of lignin in the unbleached hemicellulose samples was larger than that in the bleached hemicellulose samples. No ash or acetyl groups were observed in any of the six samples. The strong extraction condition (10% potassium hydroxide) was believed to be responsible for the elimination of acetyl groups (Teleman et al., 2000).

Table 8 Composition of hemicellulose samples

Hemicellulose	Glucan (%)	Xylan (%)	Mannan (%)	Galactan (%)	Arabinan (%)	Klason lignin (%)	Ash (%)	Acetyl (%)	Total (%)
CTMP Aspen Bleached	2.0 (0.5)	73.9 (1.4) ^a	5.1 (2.4) ^a	2.5 (0.9)	4.0 (1.6)	1.0 (0.1) ^{ab}	N/D	N/D	88.6 (1.5)
CTMP Aspen Unbleached	1.6 (0.7)	73.8 (0.8) ^a	4.2 (3.0) ^a	3.7 (0.8)	1.8 (1.0)	1.2 (0.3) ^{ab}	N/D	N/D	86.4 (1.5)
CTMP Spruce Bleached	1.9 (1.3)	74.0 (0.6) ^a	9.7 (2.2) ^a	2.8 (1.1)	2.1 (1.9)	0.6 (0.1) ^a	N/D	N/D	91.1 (1.5)
CTMP Spruce Unbleached	2.1 (0.2)	73.9 (1.7) ^a	9.5 (0.8) ^a	4.6 (0.2)	1.3 (0.7)	1.1 (0.2) ^{ab}	N/D	N/D	92.5 (0.9)
HPP Bleached	1.6 (0.1)	76.5 (0.6) ^a	5.6 (2.3) ^a	3.4 (1.0)	3.0 (0.7)	1.1 (0.3) ^{ab}	N/D	N/D	91.2 (1.2)
HPP Unbleached	1.4 (1.2)	75.8 (1.0) ^a	5.3 (1.8) ^a	2.8 (0.5)	1.3 (1.6)	1.6 (0.5) ^b	N/D	N/D	88.2 (1.3)

Notes: Values are reported as mean of two replicates, the numbers in parentheses are the standard deviation.
Values in the same column by the same letter are not significantly different (p>0.05).
N/D =not detected

5.2 Molecular weight information analysis of hemicellulose samples

A linear relationship with a R^2 of 0.99 was found between the logarithm of the molecular weight and the volume eluted of the dextrans with known molecular weight used as reference as illustrated in Figure 18. The linear relation between Log (MW) as Y and the elution volume (V) is expressed in the equation below:

$$Y = -0.38V + 10.3$$

Clearly indicates a negative slope (-0.38) suggesting a decrease of Log (MW) with an increase of V. The smaller the elution volume is, the larger the molecular weight.

The elution profile of hemicellulose extracted from bleached CTMP aspen is shown in Figure 19 as an example. The other elution profiles of hemicellulose samples are shown in Figure 28 in the appendix. There are mainly four elution peaks present in the elution profiles of the extracted hemicellulosic preparations. The peak with elution time from 17 min to 20 min (1st peak) was assumed to be from the aggregation of hemicellulose, which could be significantly reduced by using longer sonication time. Similar observations were reported by Stoklosa and Hodge (Stoklosa and Hodge, 2012) and Skaake et al. (Skaake et al., 2001) with hardwood glucuronoxyylan extracted with KOH. Some researchers also noted that arabinoxylan from rye bran aggregated to clusters as a function of solvent and time (Ebringerova et al., 1994). They noticed that these clusters could be partly broken either by exposing the solution to shear force during intense shaking or by heating. The molecular weight of the peak at elution time from 30 to 32.5 min (3rd peak) was lower than 3000 g/mol and assumed to be from oligosaccharides or oligomers.

A peak was shown from elution time about 33 min to 34 min, which was followed by a negative peak. It was believed that this peak was attributed to the encounter with the permeation

limit of the column system (Ultrahydrogel 250 1K-80K; Ultrahydrogel 500 10K-400K, Waters), which was not observed in the profile eluted using a single column (Ultrahydrogel 250). The figures are shown in Figure 29 in the appendix.

The peak around elution time 35 min (4th peak) is below the permeation limit for the column system and represents all the other contaminants with much lower molecular weight than 1K contained in these samples, e.g. salts.

The elution peak from elution time about 20 min to 30 min (elution volume 12 ml to 18 ml, 2nd peak) covered the range of molecular weights from 3K to 500K, which was taken as the peak standing for the primary extracted hemicellulose molecules, separately shown in Figure 20. The elution profiles of xylans from birchwood and oat spelts freshly made and after 5 days storage with longer sonication are shown in Figure 30 in the appendix. As is seen in the chromatograms, the 1st peak presented increased RI signals after 5 days storage compared to the freshly made samples, yet the 2nd peak kept the same response. This had a good agreement with aggregation phenomenon. Thus, the second peak was taken as the primary hemicellulose peak for calculation of molecular weight averages. The same behavior was observed in research by Saake et al. in 2001.

Therefore, the molecular weight information such as number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of the extracted hemicellulose samples, was calculated based on this peak (2nd peak).

The molecular weight averages and distributions are shown in Table 9. The molecular weight averages (M_n and M_w) from the hybrid poplar powder sample were larger than those from pulp samples in general. This agreed with research by Jacobs and Dahlman did in 2001. They found that in most cases, the hemicelluloses extracted from wood displayed higher molecular

weight than did the corresponding hemicelluloses from chemical pulps. It seemed that the type of raw materials played an important role on the extracted hemicellulose molecular weight averages. Bleaching made the hemicellulose molecules from hybrid poplar significantly smaller than the unbleached ones. For both M_n and M_w , the largest average molecular weight came from the HPP unbleached hemicellulose sample, 46.6 and 112.8 KDa, respectively. These values were somewhat higher than the molecular weight values reported for fast-growing poplar wood, maple, beechwood (Sun et al, 2001; Stoklosa and Hodge, 2012; Saake et al, 2001). This was probably attributed to the variance of the extraction method (Sun and Hughs, 1998; Peng et al, 2012), solvent quality (Sakke et al, 2001; Izydorczyk and Biliaderis, 1995) and eluted peak ranges for calculation (Sun et al, 2001). The polydispersity index (PDI) had similar results to the molecular weight averages, in the opposite way. Hemicellulose from CTMP aspen bleached treatment displayed the largest PDI. Polymers with lower PDI usually display better mechanical properties than those with larger PDI.

The relationship between hemicellulose film properties (TS and MOE, obtained in chapter 4) and molecular weight / distribution obtained by using SEC two columns system demonstrate a linear relationship that larger molecular weight favoring larger TS and MOE; the PDI versus for TS, no significant linear relationship was found between MOE and PDI (Figure 17). This relationship could not be observed from the analysis by the SEC one column system. Two columns separated the hemicellulose molecules with different molecular weight more clearly, which improved the accuracy of calculation of the hemicellulose molecular weight.

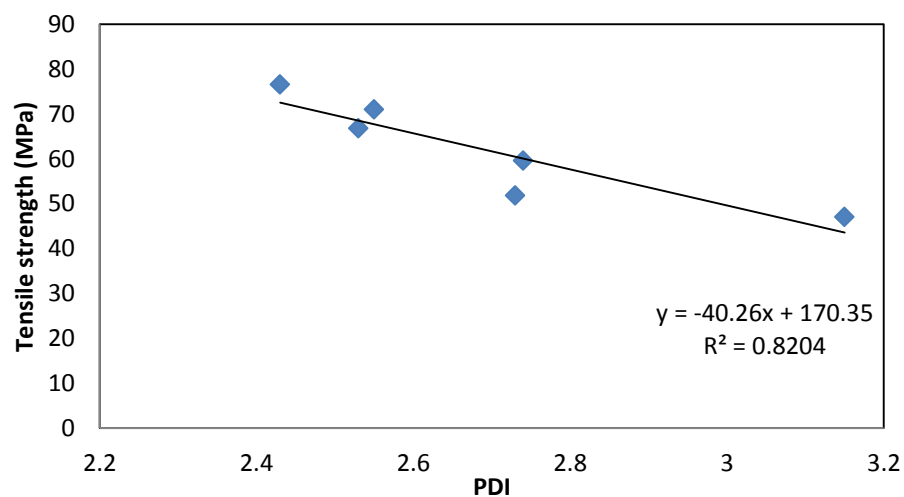
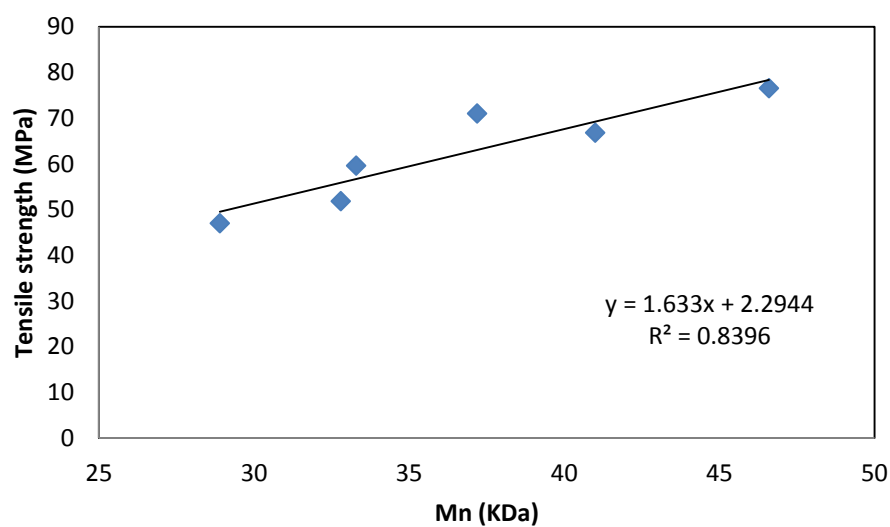
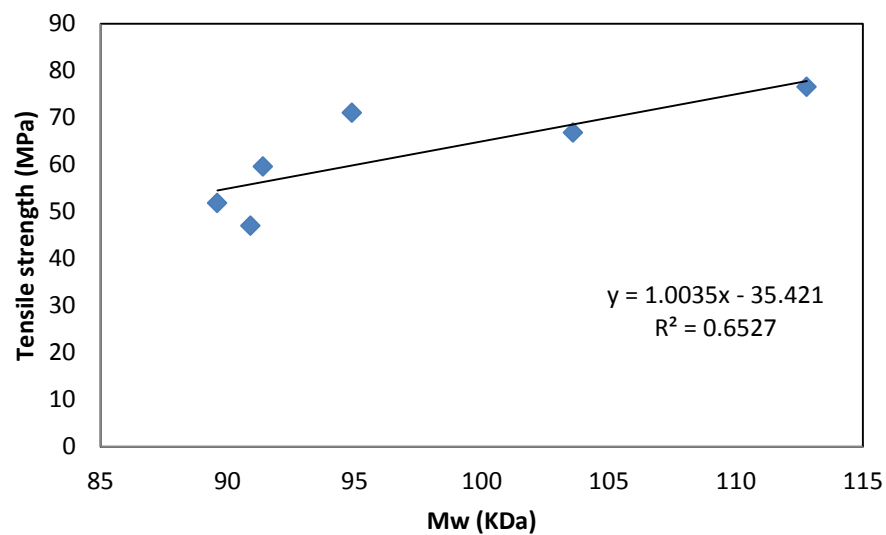
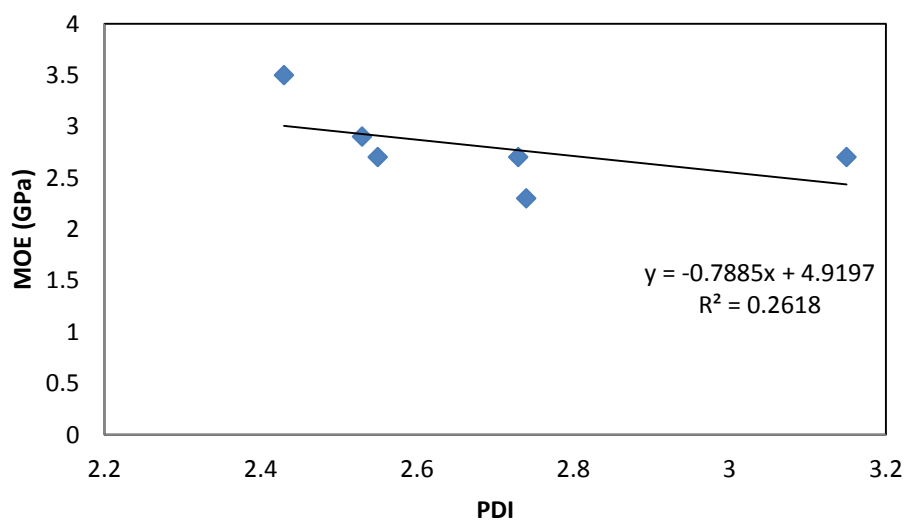
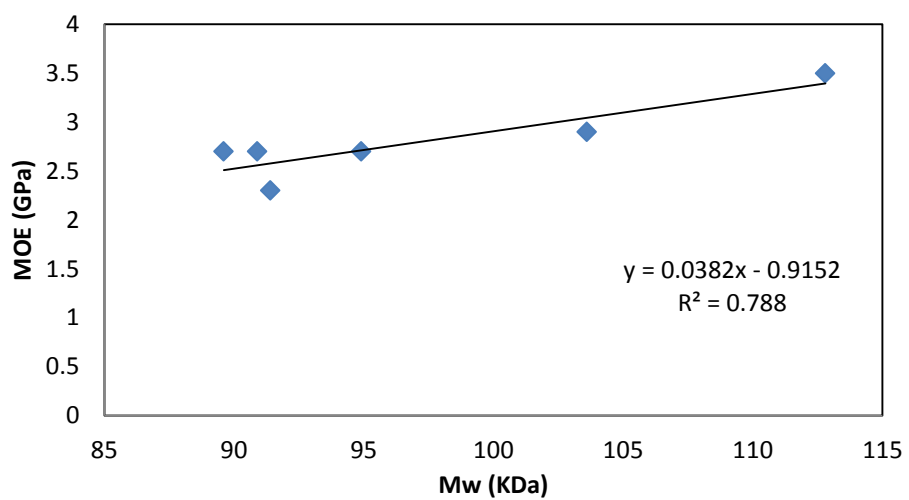
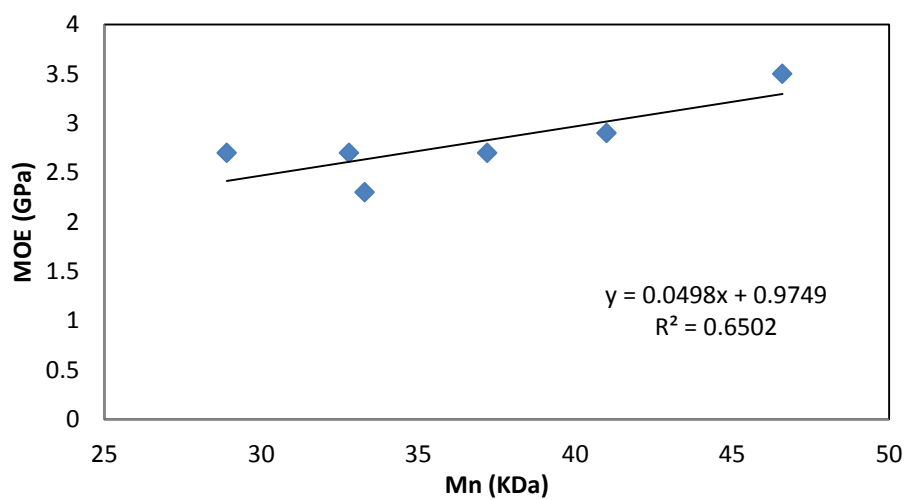


Figure 17 Relationship between films TS/ MOE and molecular weight/ distribution

Figure 17 (cont'd)



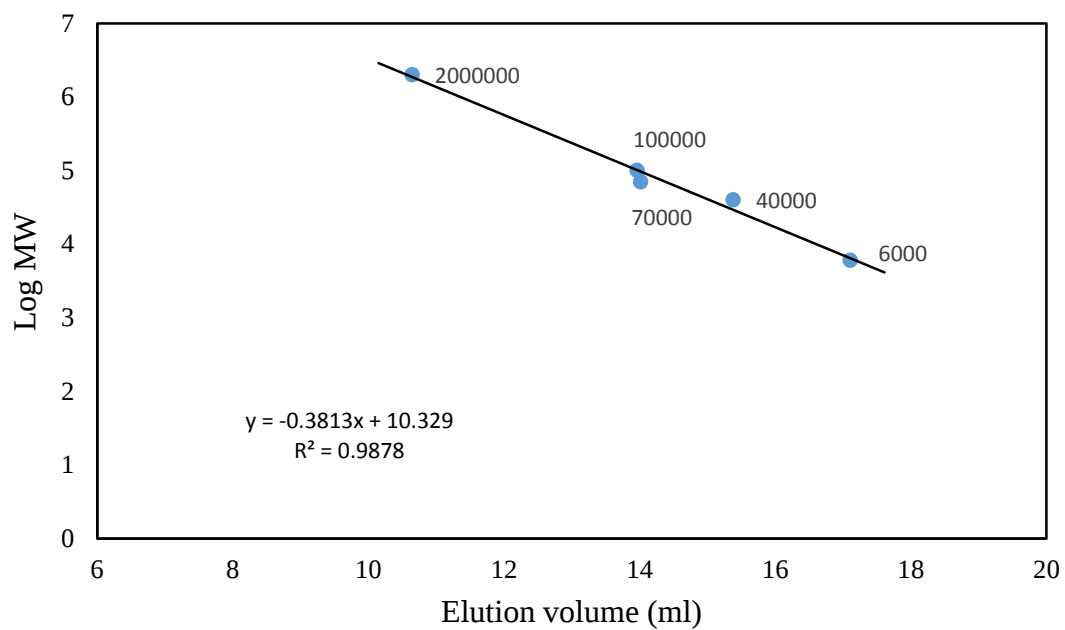


Figure 18 Calibration curve of dextrans with known molecular weights

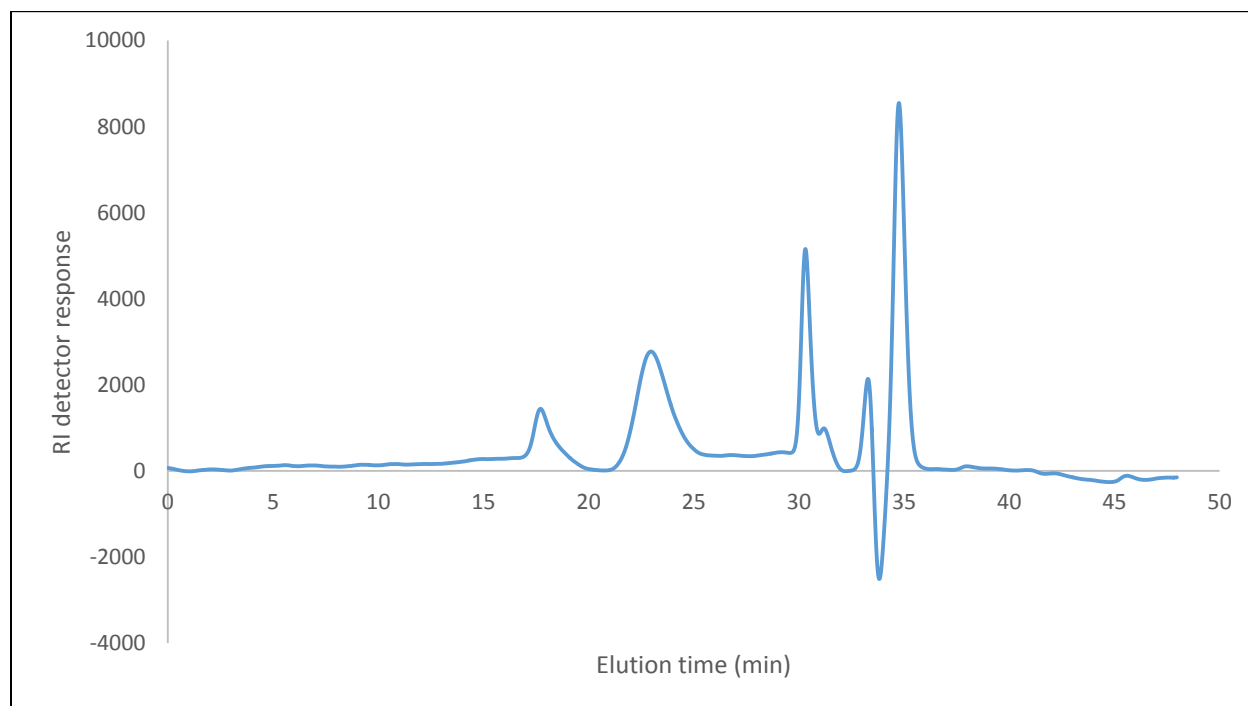


Figure 19 SEC elution profile of hemicellulose extracted from bleached CTMP aspen

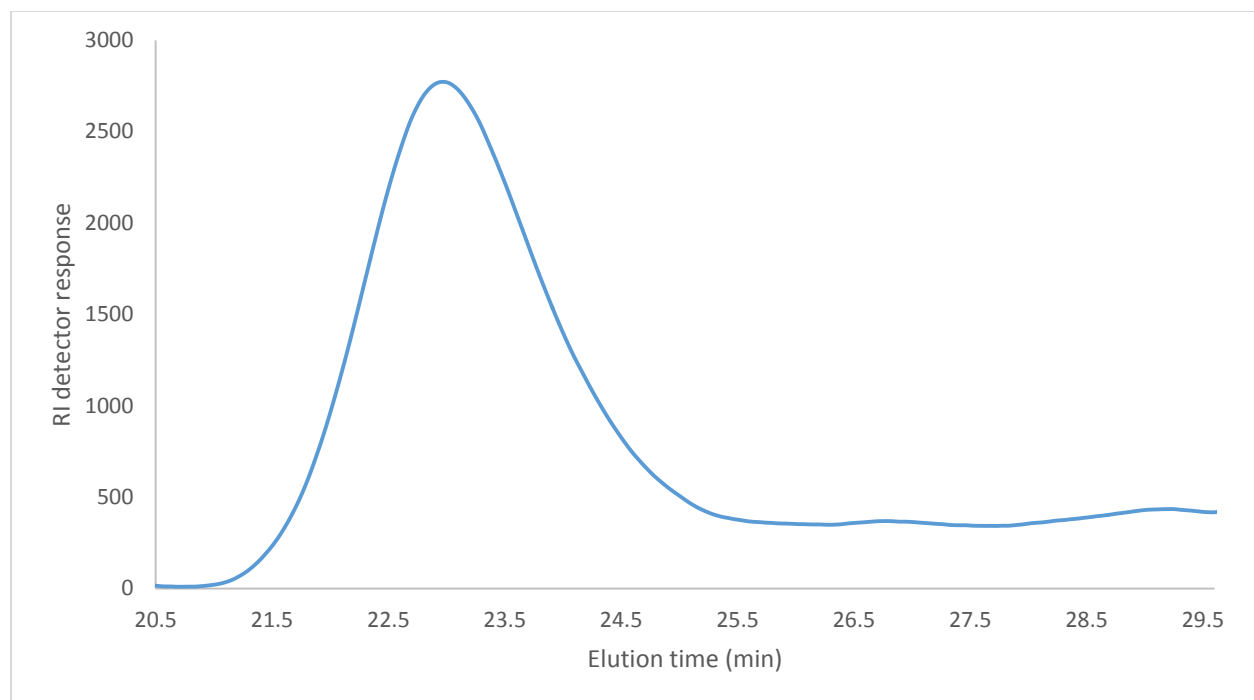


Figure 20 SEC expanded elution profile of hemicellulose from bleached CTMP aspen

Table 9 Molecular weight averages of extracted hemicelluloses specimens and their distributions

	CTMP A B	CTMP A UB	CTMP S B	CTMP S UB	HPP B	HPP UB
M _n , KDa	28.9 (1.7) ^a	32.8 (1.2) ^{ab}	33.3 (0.8) ^{ab}	37.2 (0.8) ^{bc}	41.0 (1.7) ^{cd}	46.6 (4.5) ^d
M _w , KDa	90.9 (1.2) ^a	89.6 (3.5) ^a	91.4 (2.3) ^a	94.9 (3.2) ^a	103.6 (1.6) ^b	112.8 (2.4) ^c
PDI	3.15 (0.17) ^a	2.73 (0.02) ^{bc}	2.74 (0.12) ^b	2.55 (0.03) ^{bc}	2.53 (0.07) ^{bc}	2.43 (0.17) ^c

Note: Values are reported as mean of three replicates, the numbers in parentheses are the standard deviation.
Values in the same row by the same letter are not significantly different (p>0.05).
A aspen, B bleached; S spruce, UB unbleached.

5.3 Molecular weight information of purchased xylans & HPPB hemicellulose samples and the tensile properties of their films

The values of degree of polymerization (DP) for the purchased xylans & bleached extracted hemicellulose samples from HPP before / after enzymatic hydrolysis and the tensile properties of their films are summarized in Table 10. The DPs were obtained by two methods, the reducing-end method (Red. End) and SEC method. For xylan from oat spelts, its $\overline{DP}_n$ from reducing-end method (130) is much smaller than it is from the SEC method (459), which suggests xylan from oat spelts has large substitutes in its backbone chain. It is a highly branched polymer. This leads to its relatively great water solubility, which makes it easier to build networks among hemicellulose molecules and thus to form film (Mikkonen et al., 2012). The number average DPs of the three types of xylans estimated from the reducing-end method are very close. They are also close to the DPs of xylans from beechwood and birchwood obtained by the SEC method. The hemicellulose sample from HPPB after enzymatic hydrolysis was smaller than that of the sample without enzymatic hydrolysis. The DPs of xylans obtained by the SEC method were smaller than the values for HPPB except for the xylan from oat spelts. The PDI results of xylans from beechwood and birchwood were close to each other and smaller than that from oat spelts. And also, the enzymatic hydrolysis slightly increased the PDI for the hemicellulose sample from HPPB.

The TS of xylan film from oat spelts was significantly smaller than that of the xylan films from birchwood and beechwood ($p < 0.05$). Yet, the elongation was much larger than for those films. MOE values among the three samples show significant differences from each other.

After enzymatic hydrolysis of bleached HPP hemicellulose sample, the degree of polymerization, PDI, TS and Elongation all decreased (Table 10). The enzyme cut the

hemicellulose molecules shorter, which led to the reducing of TS. This corresponds to the analysis about the relationship between TS and molecular weight. The result confirms that molecular weight is an important factor for the tensile properties of hemicellulose film, which is also suggested by Gröndahl et al (Gröndahl et al., 2004; Heikkinen et al., 2013). Heikkinen et al also suggested the substitution was a considerable factor for attention.

In addition, the DPs (Red. End) for purchased xylans and DPs (SEC) for extracted HPPB hemicellulose samples before and after enzymatic hydrolysis present a good linear relationship with their corresponding tensile strength (Figure 21). This is in good agreement with the study on the relationship between TS / MOE and molecular weight earlier in this section (Figure 17).

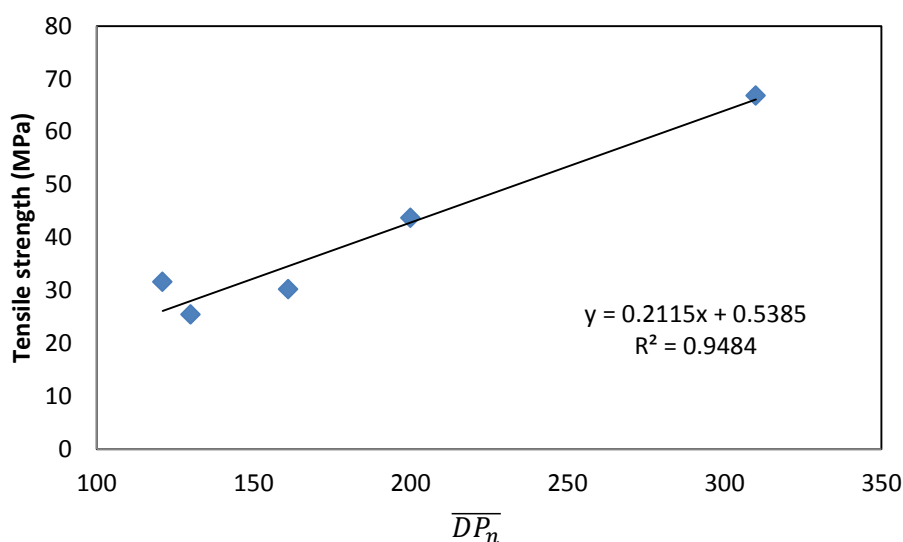


Figure 21 Relationship between the TS of hemicellulose films and hemicellulose DPs

Therefore, molecular weight (for hemicellulose with fewer substitutions, molecular weight corresponds to its degree of polymerization) is believed to have a significant effect on the tensile properties of hemicellulose film.

Table 10 Comparison of purchased xylans and hemicellulose sample from HPPB and their films

Xylan sources	$\overline{DP}_n$ (Red. End)	$\overline{DP}_n$ SEC	$\overline{DP}_w$ SEC	PDI	Tensile strength (MPa)	Elongation (%)	MOE (GPa)
Oat spelts	130	459 (13) ^a	1514 (91) ^a	3.30 (0.16) ^a	25.4 (2.7) ^d	10.5 (1.5) ^a	1.3 (0.1) ^d
Beechwood	121	145 (1) ^d	301 (4) ^d	2.08 (0.04) ^d	31.6 (3.1) ^c	1.9 (0.4) ^d	2.4 (0.3) ^b
Birchwood	161	130 (1) ^d	289 (7) ^d	2.22 (0.05) ^{cd}	30.2 (2.8) ^c	2.7 (0.5) ^{cd}	1.8 (0.2) ^c
HPP B	—	310 (24) ^b	768 (59) ^b	2.48 (0.20) ^{bc}	66.8 (3.7) ^a	7.4 (1.1) ^b	2.9 (0.2) ^a
HPP B (hydrolysis)	—	200 (19) ^c	534 (30) ^c	2.63 (0.07) ^b	43.7 (3.6) ^b	4.1 (0.6) ^c	2.9 (0.3) ^a

Note: Values are reported as mean of 3 replicates for SEC analysis, 8 replicates for mechanical analysis except that HPP B is 20 replicates.

The numbers in parentheses are the standard deviation.

Values in the same column by the same letter are not significantly different ($p > 0.05$).

5.4 Lignin identification and semi-quantification

Fourier transform infrared spectra of all samples are shown in Figure 22. Two different sources of lignin displayed coincident characteristic peaks, which were in good agreement with the AlcellTM organosolv lignin study done in 2004 (Boeriu et al., 2004). The occurrence of obvious bands at 1597, 1514 and 1425 cm^{-1} involving aromatic skeleton vibrations and the peak at 1460 cm^{-1} due to the combination of C-H deformation and aromatic ring vibration can be observed for all samples, except for xylan from oat spelts. These peaks are the typical characteristic peaks for lignin (Seca et al., 1998; Boeriu et al., 2004; Peng et al., 2012; Egüés et al., 2013; Rodríguez-Gutiérrez et al., 2014). Their presence confirmed the existence of lignin in those samples. The xylan from oat spelts were purchased from Sigma-Aldrich had a high concentration of hemicellulose, and the typical peaks for lignin were absent from its FTIR spectrum. The unbleached HPP hemicellulose sample exhibited more obvious peaks than other samples. The absorption bands below 1400 cm^{-1} are complicated, which can be attributed to various vibration modes. This makes it difficult to analyze the monolignol units vibrations in this region. The peak at 1269 cm^{-1} shows the vibration for the guaiacyl unit (guaiacyl ring and C=O stretching) and a vibration at 1213 cm^{-1} can be attributed to the C-C plus C-O plus C=O stretching. The most obvious peak at 1043 cm^{-1} is a complex vibration attributed to the aromatic C-H deformation associated with the C-O, C-C stretching and C-OH bending in polysaccharides (Boeriu et al., 2004). The unbleached HPP hemicellulose sample displayed more obvious peaks on these region compared with the other samples. All of the above indicate that the unbleached HPP hemicellulose sample contains a relatively higher content of lignin than the bleached HPP hemicellulose sample. Bleaching is an effective approach for delignification of the alkaline extracted hemicellulose sample. The peak at 1043 cm^{-1} is assigned to the C-O, C-C stretching

and C-OH bending in xylans and the small band at 896 cm^{-1} to the characteristic β -glycosidic bonds between sugar units (Peng et al., 2012). And the shoulder peaks (1160 cm^{-1} and 990 cm^{-1}) near the most obvious peak indicate the presence of arabinosyl side chains (Buranov and Mazza, 2010; Peng et al., 2012; Egüés et al., 2013). These results indicate that xylan is the dominant hemicellulose in the bleached and unbleached HPP samples; arabinosyl units are attached to the xylan backbone chain. All of the results obtained by this FTIR analysis corresponded to the data obtained in the HPLC composition analysis (Table 16).

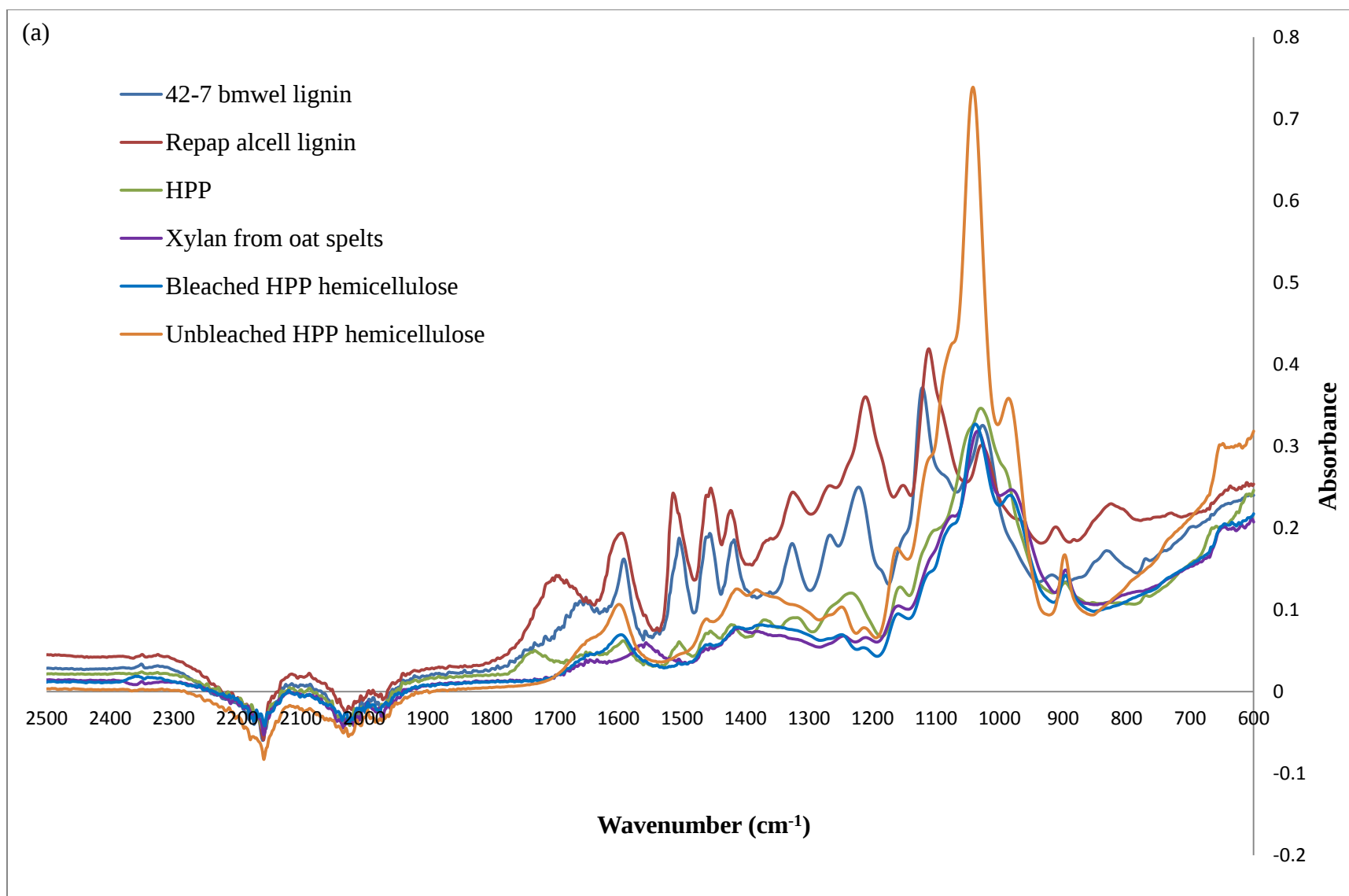
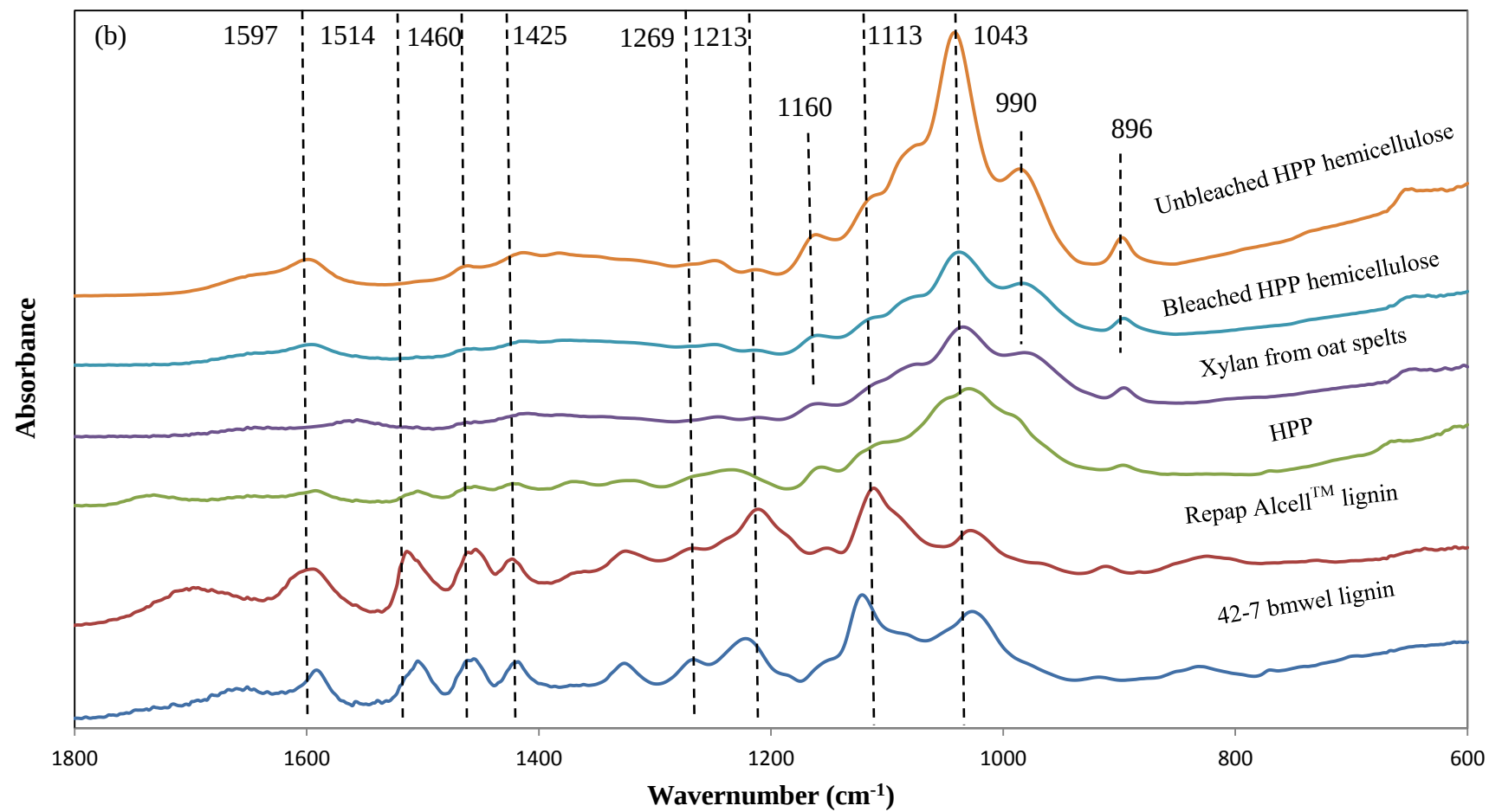


Figure 22 FTIR spectra of HPP hemicellulose samples, HPP, xylan and lignin (a) and its expanded spectra (b)

Figure 22 (cont'd)



5.5 Crystallinity of hemicellulose based films

Hemicellulose is an amorphous polymer in its native status; but it can form crystalline structure under some conditions, such as decreasing side group substitution (Höje et al., 2008). Xylan and sorbitol bought from Sigma-Aldrich, bleached & unbleached extracted hemicelluloses (BH & UH), and their films without additives (BHF & UHF), with sorbitol (BHSF & UHSF), and with sorbitol and glutaraldehyde (BHSGF & UHSGF) were scanned by X-ray for structure analysis with results shown in Figure 23. The additive, sorbitol, presents sharp distinct peaks in the scanned range 2θ from 10° to 45° . No obvious crystalline peak could be observed from the X-ray diffraction patterns of purchased xylan and both of the bleached & unbleached extracted hemicelluloses in the scanned range (Figure 23 a and b). The slight fluctuation observed in both of the extracted hemicellulose diffractograms was likely due to the scattering from the amorphous structure. However, the extracted hemicellulose based films BHF / UHF & BHSF / UHSF & BHSGF / UHSGF (without additives & with sorbitol & with sorbitol and glutaraldehyde) all exhibited broad but obvious peaks (corresponding to reflections 100, 101 and 011, 110, 202 and 022) (Heikkinen et al., 2013), even though BHF & UHF films do not contain the crystalline sorbitol. Within this test condition, no sorbitol characteristic peaks were observed in the diffractograms of these films. These results suggest that hemicellulose possesses some crystalline structures in the formed film. This result is in agreement with the other studies on different types of hemicelluloses (different types of xylans and mannan) (Gröndahl et al., 2004; Peura et al., 2008; Mikkonen et al. in 2009; Zhang et al., 2011; Heikkinen et al., 2013; Heikkinen et al., 2014). Similar crystallization behavior was also found in the study of starch (amylopectin) films (Anglès and Dufresne, 2000). It was reported by Peura et al that during film forming (water evaporation), glycerol plasticized oat spelts xylan formed new crystallite nucleations resulting in

increasing crystallinity, but the average size of the crystallites remained constant (Peura et al., 2008). Gröndahl et al. also stated that sorbitol and xylitol plasticized aspen glucuronoxylan films displayed a crystalline structure, and the increasing amount of plasticizer added in those films did not increase its crystallinity, but increased the distance between the lattice planes making the peak positions move to lower angles under the tested condition that the amount of plasticizer added was no more than 50% (Gröndahl et al., 2004). Similar to aspen xylan, this study displays the same shift direction following the addition of the additives. Gröndahl et al. also suggested that sorbitol could interact and even cocrystallize with xylan leading to the increasing of the spacing between the crystal lattice planes, but Mikkonen et al. believed that it was caused by different degrees of hydration (Mikkonen et al. in 2009). But both studies suggested that plasticizer may increase the mobility of the polymer chains, therefore promoting crystallization of the xylan molecules. Substitution was suggested to prevent crystallization. Lower Ara/Xyl ratio (0.14, 0.23, 0.27 compared with 0.34, 0.56) and lower β -glucan/AX (2%, 6% compared with 13%, 18%) were reported to enable the crystallization of xylan molecules; no crystal structure was detected in the films with higher substitution ratios (Mikkonen et al., 2009; Zhang et al., 2011; Mikkonen et al. in 2012; Heikkinen et al., 2013). Unsubstituted regions along the xylan chain were reported to promote crystallization (Dervilly-pinel et al., 2004). From the results of the composition analysis portion of this study, no acetyl groups were detected in the extracted hemicellulose samples in this study. This may be the reason for extracted hemicellulose films possessing such high crystallinity. The average crystallinity of bleached hemicellulose films with sorbitol and glutaraldehyde was computed as 52.3% (± 0.7); and 63.4% (± 1.1) for the unbleached hemicellulose film with both additives by the XRD analysis.

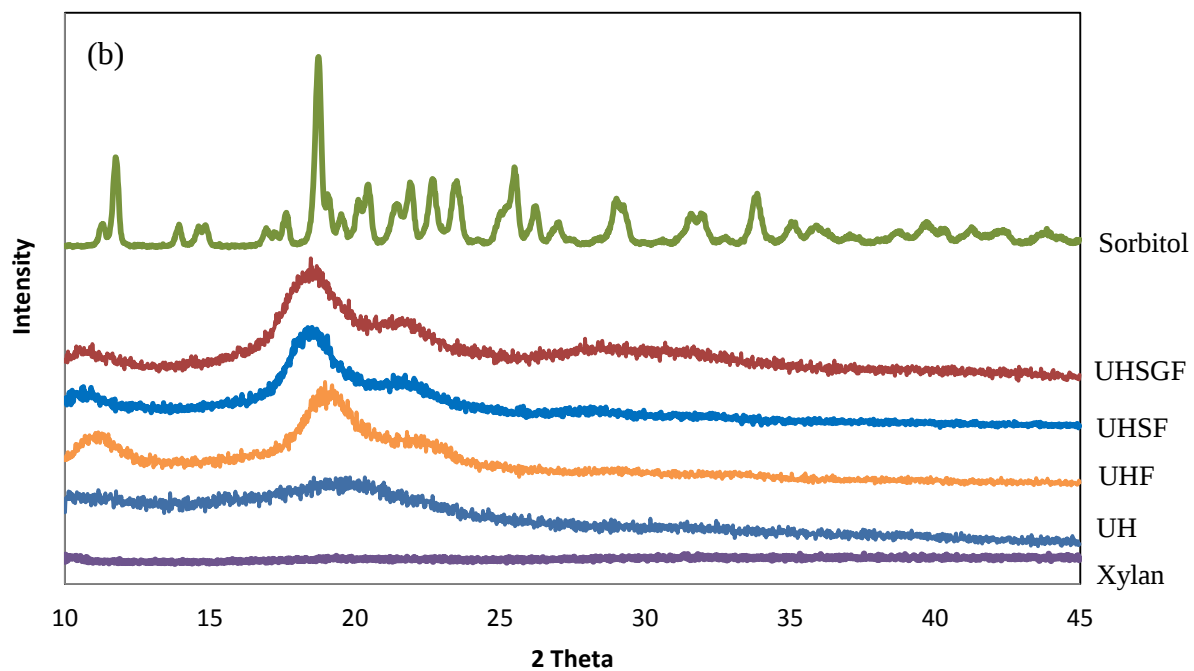
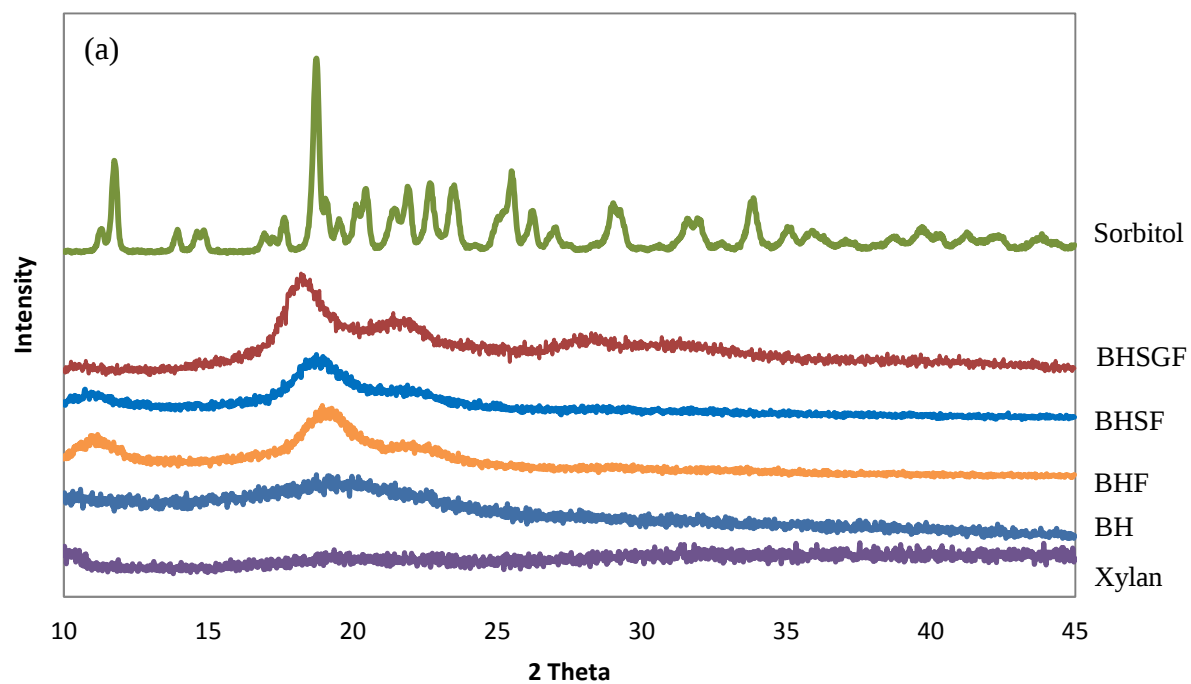


Figure 23 X-ray diffraction patterns of hemicelluloses and hemicellulose films, (a) bleached; (b) unbleached (The signal of sorbitol is reduced by a factor of 2.5 times).

The X-ray diffraction spectra of xylan films from beechwood, birchwood and oat spelts are displayed in Figure 24. The crystallinity for xylan films from beechwood, birchwood and oat spelts are 69.0% ($\pm 1.6\%$), 69.7% ($\pm 0.8\%$) and 62.4% ($\pm 1.2\%$), respectively. The crystallinity of xylan films from hardwood are significantly larger than that of xylan film from oat spelts ($p < 0.05$). The presence of the large substitutions of xylan from oat spelts is unfavorable for hemicellulose molecule to arrange in order for formation of crystalline. They can increase the spacing between hemicellulose molecules and thus decrease the interaction between them. Therefore the hemicellulose molecules can relatively move more easily. It is reasonable that the TS of xylan film from oat spelts is smaller than that from birchwood and beechwood. But considering the similarity of $\overline{DP}_n$ (Red. End) between xylan from oat spelts and xylan from hardwood, the difference of TS for xylan films from both of them is not remarkable, but still significant ($p < 0.05$).

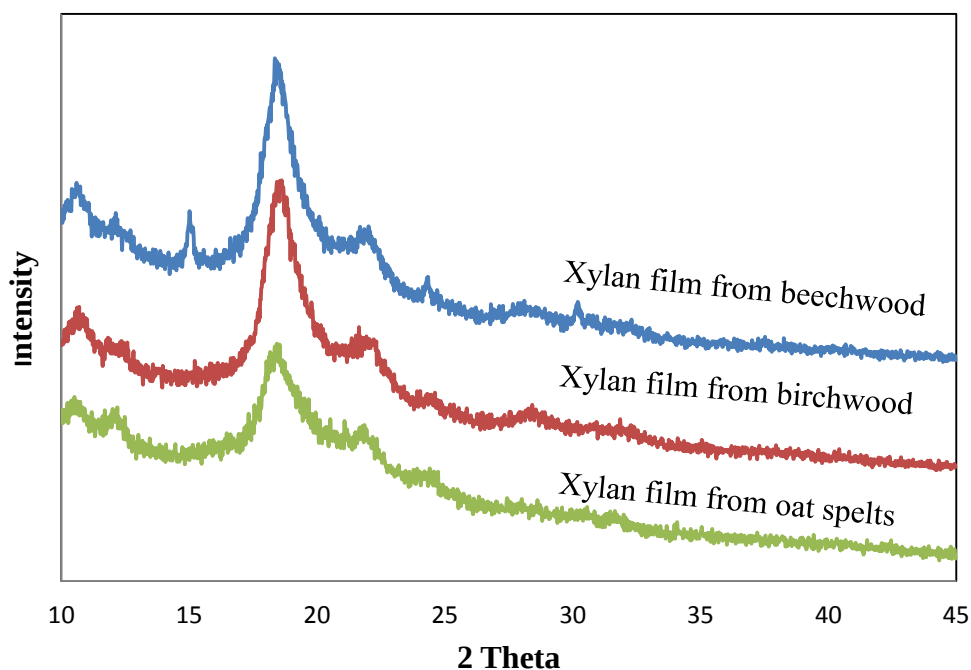


Figure 24 X-ray diffraction patterns of xylan films, from beechwood, birchwood and oat spelts.

5.6 Influence of additives on the tensile properties of hemicellulose films

The tensile properties of both bleached and unbleached HPP hemicellulose made films (HPPB & HPPU) and with sorbitol (HPPBS & HPPUS), with sorbitol and glutaraldehyde (HPPBSG & HPPUSG) are listed in Table 11 and Table 12. The functions of sorbitol and glutaraldehyde were confirmed by this test. As is seen in Table 11, the addition of sorbitol significantly decreased the film tensile strength (from 89.6 MPa to 53.1 MPa) and MOE (from 4.9 GPa to 3.0 GPa), but increased the elongation at break (from 3.1% to 4.7%). It can promote the hemicellulose molecule chain mobility, thus make the film more flexible. This benefits its application as packaging material. Similar results were observed in the unbleached HPP hemicellulose samples (Table 12). The addition of glutaraldehyde to the plasticized hemicellulose film significantly increased the film tensile strength (from 53.1 MPa to 66.8 MPa) and elongation (from 4.7% to 7.4%), while MOE was not significantly affected (from 3.0 GPa to 2.9 GPa). But the MOE value for the unbleached sample significantly increased after adding glutaraldehyde (from 3.0 GPa to 3.5 GPa). This corresponded to the results from sorbitol-glyoxal-galactoglucomannan film in general (Mikkonen et al., 2012). It was suggested that glyoxal could interact with the hydroxyl groups on the hemicellulose molecule chains to form hemiacetal bonds resulting in a network of crosslinked hemicellulose, besides hydrogen bonding of hemicellulose molecules (Zhao and Deng, 2006; Mikkonen et al., 2012). This is probably the reason why the tensile strength of unbleached HPP hemicellulose film in this study was superior to those for similar hemicellulose based films.

Table 11 Mechanical properties of HPP bleached hemicellulose films

	HPPB	HPPBS	HPPBSG
Tensile strength, MPa	89.6 (4.9) ^a	53.1 (4.3) ^c	66.8 (3.7) ^b
Elongation, %	3.1 (0.4) ^c	4.7 (1.0) ^b	7.4 (1.1) ^a
MOE, GPa	4.9 (0.4) ^a	3.0 (0.2) ^b	2.9 (0.2) ^b
MC, %	14.5 (0.3)	15.3 (0.3)	15.9 (0.7)
Thickness, μm	27.9 (5.1)	33.0 (2.5)	91.4 (10.2)
Breaking length, km	7.6	4.2	5.7

Note: HPP: hybrid poplar powder.

HPPB: HPP bleached hemicellulose made film without additives.

HPPBS: HPP bleached hemicellulose made film with sorbitol.

HPPBSG: HPP bleached hemicellulose made film with sorbitol and glutaraldehyde.

The numbers in parentheses are STDEV.

All measurements were performed in 6 replicates, except for BHPPSG, 20 replicates.

Values in the same row by the same letter are not significantly different ($p>0.05$).

Table 12 Mechanical properties of HPP unbleached hemicellulose films

	HPPU	HPPUS	HPPUSG
Tensile strength, MPa	98.8 (8.1) ^a	61.0 (7.1) ^c	76.5 (7.0) ^b
Elongation, %	2.6 (0.5) ^c	4.0 (0.7) ^b	5.4 (0.9) ^a
MOE, GPa	5.1 (0.5) ^a	3.0 (0.3) ^c	3.5 (0.4) ^b
MC, %	14.9 (0.5)	15.5 (0.2)	17.0 (0.3)
Thickness, μm	30.5 (5.1)	38.1 (5.1)	68.6 (5.1)
Breaking length, km	8.4	4.8	6.0

Note: HPP: hybrid poplar powder.

HPPU: HPP unbleached hemicellulose made film without additives.

HPPUS: HPP unbleached hemicellulose made film with sorbitol.

HPPUSG: HPP unbleached hemicellulose made film with sorbitol and glutaraldehyde.

The numbers in parentheses are STDEV.

All measurements were performed in 6 replicates, except for HHPPSG, 20 replicates.

Values in the same row by the same letter are not significantly different ($p>0.05$).

5.7 Discussion

From the results of the statistical analysis, bleaching was an effective treatment in this study, responsible for the changing of tensile properties of hemicellulose films from those six approaches. It could cause the difference of hemicellulose samples, such as hemicellulose molecular weight, its distribution, structure (side groups and side chain) and also the sample composition. From the analyses results earlier in this section, it is confirmed that bleaching caused a reduction in the hemicellulose molecular weight, decreased lignin content and crystallinity of hemicellulose films, and changed the composition of hemicellulose sample. From molecular weight analysis, it was shown that the unbleached samples had larger molecular weights in general, which contributed to the higher tensile properties (TS and MOE). Furthermore, XRD analysis showed that the unbleached HPP sample had higher crystallinity. In general, the higher crystallinity a film possesses, the higher tensile strength it exhibits. As is known, hydrogen bonding between hydroxyl groups in the hemicellulose molecular chains is the primary interaction in the hemicellulose films. The different hemicellulose molecular weight and structure could lead to different hydrogen bonding intensity and thus result in differences in the final tensile strength.

Bleaching was not the only important influence on the tensile properties of the hemicellulose based films. The sources, like hardwood and softwood; processes (fiber obtained through the chemical, mechanical or thermal processes or by grinding) also influenced the tensile properties. Films made from hemicellulose obtained from hardwood CTMP fibers had less strength than those made from hemicellulose obtained from softwood CTMP fibers, but higher elongation. As seen from the result of composition analysis, hardwood contains less mannan. The monosaccharide composition is different. Mannan is composed of hexose sugars, while

xylan is composed of pentose sugars. The number of hydroxyl groups will be higher in mannan than in xylan. It is possible this leads to more hydrogen bonding between mannan molecules and additives, resulting in a more compact film structure. This corresponds to the results of the study on glycerol and sorbitol plasticized oat spelt arabinoxylan (OsAX) and spruce galactoglucomannan (GGM) (Heikkinen et al., 2014). It might be also because hardwood fiber is more sensitive to the chemical, mechanical and thermal treatment during the pulping process. If raw materials are processed too much, this can have a great impact on the tensile properties of the films made from it. This could significantly reduce nearly all the tensile properties of the hemicellulose based films, including tensile strength, elongation and MOE, regardless of the bleaching procedure, as is shown for films from aspen CTMP fiber and hybrid poplar powder. This is suggested to be due to the relatively high degradation of hemicellulose molecules during those chemithermomechanical pulping procedures, which resulted in a lower molecular weight in general.

And also, the presence of lignin may contribute to the promotion of the tensile strength, since it could be involved in the interaction with different molecules in the hemicellulose based films by forming chemical bonds or other physical bonds. In plant cell walls, lignin crosslinks hemicellulose by covalent bonds (mainly R-benzyl ether linkages). This is believed to promote hemicellulose film formation (Hansen et al., 2012). It was also reported that without sufficient lignin addition, birchwood xylan could not form a continuous film alone (Goksu et al., 2007; Hansen et al., 2012). Therefore, it is suggested that lignin helps enhance the interaction among the hemicellulose molecules in the films, decrease the potential relative slippage between hemicellulose molecules, and then improve the tensile strength of these films, thus reducing the

percentage elongation at break. This corresponds to the results of earlier analyses about lignin content and tensile properties of hemicellulose films.

In all of above, the mechanical properties obtained in this study were probably attributed to the hemicellulose source and isolation method with proper plasticizer and crosslinking agent addition. The better performance of the HPP unbleached sample is likely attributable to the larger average molecular weight, higher lignin content and higher crystallinity. These characteristics had a good agreement with the mechanical and barrier properties in general.

The tensile strength and modulus of elasticity of hemicellulose films in this study are higher than those of the commonly used packaging plastics. But the values of elongation at break are much smaller, except for some types of polystyrene (PS) and polyvinyl chloride (PVC). The hemicellulose films also present superior oxygen barrier property, even better than PET. However, they still present poor water vapor barrier compared with the commonly used packaging petro-plastics. These features lead hemicellulose products to packaging applications with relatively high tensile strength and oxygen barrier requirements but a low humidity environment. But actually, in reality it is relatively hard to avoid the impact of moisture in the environment. One solution is to coat on or to laminate with plastics / paper; the composite can provide sufficient barrier and mechanical properties for those food packaging applications. Thus, it will be suitable to be used in food packaging applications such as chip bags, instant coffee boxes, beverage boxes, and nut bags. Another solution is just to design these as water soluble packages, such as the water soluble seasoning sachet in an instant noodle bag or certain candy inner layers in packages. A hemicellulose based barrier application has been already been successfully used as a large spice bag, waiting to be dispersed in industrial scale cooking operations (Grubb, 2010).

6 CONCLUSION

Hemicellulose obtained through alkaline extraction and ethanol precipitation procedures in this study were mainly composed of xylan, slightly contaminated by lignin. Slightly higher levels of lignin were present in the unbleached samples compared with the bleached ones. No O-acetyl groups were detected in the hemicellulose samples. With the approaches used in this study, a free-standing hemicellulose based film could be obtained with good transparency, a smooth surface, and a relatively uniform structure.

Powdered hemicellulose samples possessed higher molecular weight than the pulp samples; Molecular weights of unbleached samples were higher than the bleached samples, in general. The polydispersity index behaved in the opposite manner. The FTIR analysis confirmed that the unbleached hemicellulose samples contained more lignin. XRD analysis and DSC analysis proved that crystal regions were formed in the hemicellulose films, which benefited their properties.

These hemicellulose based films possessed superior strength. Among these six different approaches, hemicellulose from unbleached HPP had the highest tensile strength at 76.5 MPa, with specific strength 58.8×10^3 N m/kg and MOE 3.5 GPa. This is superior to the tensile strength from other hemicellulose based films and common commercial plastics, which are usually below 50 MPa; and comparable or higher MOE (from 0.25 GPa to 3.4 GPa). Glutaraldehyde appeared to enhance the film properties significantly and made the tensile strength in this study superior to the other hemicellulose films. All the unbleached samples displayed larger strength than the bleached samples. These differences were statistically significant. MOE was slightly larger for the unbleached samples compared with the bleached ones, except for aspen CTMP. The elongation at break was affected oppositely. Molecular

weight and lignin content were suggested to have significant effects on the tensile properties. Combined with crystallinity, this resulted in the differences in the tensile properties for the hemicellulose films from different approaches.

Comparable water vapor and oxygen barrier property to results from similar hemicellulose studies were obtained in this study. Better water vapor barrier properties were obtained for the unbleached hemicellulose based films, but they were still several orders magnitude lower than for the polymers currently used in packaging.

In all of above, the source of hemicellulose and its pretreatment had a great influence on the physical and mechanical properties of hemicellulose based films. These influences could provide useful information for guidance in the utilization of hemicellulose on an industrial scale.

7 FUTURE WORK

The hemicellulose source is suggested to be an important role on its film properties in this study. However, the reasons for the effects on properties are not well known. Molecular weight of the hemicellulose is proposed in this study to have a linear relationship with the tensile strength of the film. The hemicellulose type was not thoroughly investigated for its influence on the film properties. Most of the research focused on the properties of one type of hemicellulose (e.g. xylan) film, even though this type of hemicellulose may be from different sources. Few studies could be found in the open literature comparing film properties from different types of hemicelluloses. Only assumptions for the different behavior were suggested in the study of plasticized OsAX and GGM films (Heikkinen et al., 2014). Thus, more investigation needs to be conducted to determine the impact of hemicellulose type on the film properties, which would benefit the potential utilization of hemicellulose film as a packaging material on an industrial scale.

Another rising problem for hemicellulose film for applications in packaging is its long-term stability. Every packed item has a shelf life. During the shelf life, the physical stability of the hemicellulose film is crucial in determining if enough protection will be provided for the item, especially if small molecules (such as plasticizers and cross-linking agents) are added to the hemicellulose films. A study of the migration of plasticizers and crosslinking agents would give significant guidance in determining the stability of hemicellulose films. Some differences in film properties were observed for glycerol and sorbitol plasticized OsAX and GGM films after storage for 4 months (Heikkinen et al., 2014).

As a bio-renewable and biodegradable polymer, hemicellulose film is counted on as a good sustainable film for packaging applications. However, most of the research was conducted

on the biodegradation of PLA, PHA, starch, cellulose, chitosan and protein products (Rudnik, 2013 b). The biodegradability of hemicellulose products is seldom investigated, especially after plasticizers and cross-linking agents are added. Testing the biodegradability of hemicellulose products would be very helpful for the guidance of hemicellulose application as sustainable packaging materials.

Besides its biodegradability, hemicellulose has another well known feature, hygroscopicity, because it is very rich in hydroxyl groups. This feature makes the properties of hemicellulose products particularly sensitive to the presence of moisture in its surrounding environment. Many studies reported that the humidity gradient could significantly impact the permeability of water vapor for hydrophilic films. The higher the relative humidity is, the larger the WVTR value (Hagenmaier and Shaw, 1990; McHugh et al., 1993; Mikkonen et al., 2009). And also, it was reported that the strength of flax fiber increased first and then decreased following an increase in the relative humidity from 21% to 85% (Thuault et al., 2015). However, few reports of the impact of relative humidity on the mechanical properties of hemicellulose products could be found in the open literatures. This information would be very useful for guidance on hemicellulose used as a packaging material in different environments.

In addition, the solvent casting method in this study limits hemicellulose film potential for manufacturing on an industrial scale. Exploration of fabrication by extrusion or injection molding is recommended; as such traditional polymer processing techniques would fit the requirements for industrial manufacture. So far, starch, cellulose, PLA and PHA based products are widely investigated and even commercially produced (Plackett, 2011; Ebnesajjad, 2013).

APPENDIX

Table 13 Correlations of tensile strength, elongation and MOE

		TS	El	MOE
TS	Pearson Correlation	1	.187*	.581**
	Sig. (2-tailed)		.034	.000
	N	129	129	129
El	Pearson Correlation	.187*	1	-.200*
	Sig. (2-tailed)	.034		.023
	N	129	129	129
MOE	Pearson Correlation	.581**	-.200*	1
	Sig. (2-tailed)	.000	.023	
	N	129	129	129

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 14 Multivariate Tests for assessing the impact of treatment on tensile properties

Effect		Value	F	Hypothesis df	Error df	Sig.
Intercept	Pillai's Trace	.985	2661.502 ^b	3.000	120.000	.000
	Wilks' Lambda	.015	2661.502 ^b	3.000	120.000	.000
	Hotelling's Trace	66.538	2661.502 ^b	3.000	120.000	.000
	Roy's Largest Root	66.538	2661.502 ^b	3.000	120.000	.000
Treatment	Pillai's Trace	1.782	29.730	18.000	366.000	.000
	Wilks' Lambda	.044	38.144	18.000	339.897	.000
	Hotelling's Trace	7.061	46.553	18.000	356.000	.000
	Roy's Largest Root	5.149	104.690 ^c	6.000	122.000	.000

a. Design: Intercept + Treatment

b. Exact statistic

c. The statistic is an upper bound on F that yields a lower bound on the significance level.

Table 15 Univariate tests for assessing the impact of treatment on tensile properties

Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	TS	13164.705 ^a	5	2632.941	100.301	.000
	El	143.388 ^b	5	28.678	21.172	.000
	MOE	13.602 ^c	5	2.720	34.955	.000
Intercept	TS	459782.477	1	459782.477	17515.282	.000
	El	4342.949	1	4342.949	3206.351	.000
	MOE	937.204	1	937.204	12042.074	.000
Treatment	TS	13164.705	5	2632.941	100.301	.000
	El	143.388	5	28.678	21.172	.000
	MOE	13.602	5	2.720	34.955	.000
Error	TS	3228.794	123	26.250		
	El	166.601	123	1.354		
	MOE	9.573	123	.078		
Total	TS	496845.019	129			
	El	5157.422	129			
	MOE	1033.759	129			
Corrected Total	TS	16393.500	128			
	El	309.990	128			
	MOE	23.175	128			

a. R Squared = .803 (Adjusted R Squared = .795)

b. R Squared = .463 (Adjusted R Squared = .441)

c. R Squared = .587 (Adjusted R Squared = .570)

Table 16 Multiple Comparisons among different treatment levels by Tukey test

Dependent Variable	(I) Treatment	(J) Treatment	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
TS	T1	T2	-4.8188 ⁺	1.49502	.020	-9.1471	-.4904
		T3	-12.5991 ⁺	1.55122	.000	-17.0901	-8.1080
		T4	-24.0019 ⁺	1.76438	.000	-29.1100	-18.8938
		T5	-19.7920 ⁺	1.38351	.000	-23.7975	-15.7865
		T6	-29.5465 ⁺	1.62416	.000	-34.2487	-24.8443
	T2	T1	4.8188 ⁺	1.49502	.020	.4904	9.1471
		T3	-7.7803 ⁺	1.56647	.000	-12.3155	-3.2451
		T4	-19.1832 ⁺	1.77780	.000	-24.3302	-14.0361
		T5	-14.9732 ⁺	1.40059	.000	-19.0282	-10.9183
		T6	-24.7278 ⁺	1.63874	.000	-29.4722	-19.9834
	T3	T1	12.5991 ⁺	1.55122	.000	8.1080	17.0901
		T2	7.7803 ⁺	1.56647	.000	3.2451	12.3155
		T4	-11.4028 ⁺	1.82532	.000	-16.6874	-6.1183
		T5	-7.1929 ⁺	1.46043	.000	-11.4211	-2.9648
		T6	-16.9475 ⁺	1.69016	.000	-21.8408	-12.0542
	T4	T1	24.0019 ⁺	1.76438	.000	18.8938	29.1100
		T2	19.1832 ⁺	1.77780	.000	14.0361	24.3302
		T3	11.4028 ⁺	1.82532	.000	6.1183	16.6874
		T5	4.2099	1.68511	.133	-.6687	9.0885
		T6	-5.5446 ⁺	1.88770	.045	-11.0098	-.0795
	T5	T1	19.7920 ⁺	1.38351	.000	15.7865	23.7975
		T2	14.9732 ⁺	1.40059	.000	10.9183	19.0282
		T3	7.1929 ⁺	1.46043	.000	2.9648	11.4211
		T4	-4.2099	1.68511	.133	-9.0885	.6687
		T6	-9.7545 ⁺	1.53768	.000	-14.2064	-5.3027
	T6	T1	29.5465 ⁺	1.62416	.000	24.8443	34.2487
		T2	24.7278 ⁺	1.63874	.000	19.9834	29.4722
		T3	16.9475 ⁺	1.69016	.000	12.0542	21.8408
		T4	5.5446 ⁺	1.88770	.045	.0795	11.0098
		T5	9.7545 ⁺	1.53768	.000	5.3027	14.2064

Table 16 (cont'd)

EI	T1	T2	1.4348 [*]	.33960	.001	.4516	2.4180
		T3	-1.0162	.35236	.052	-2.0363	.0040
		T4	-.3439	.40078	.956	-1.5042	.8164
		T5	-1.5869 [*]	.31427	.000	-2.4967	-.6770
		T6	.4200	.36893	.864	-.6481	1.4882
	T2	T1	-1.4348 [*]	.33960	.001	-2.4180	-.4516
		T3	-2.4510 [*]	.35583	.000	-3.4812	-1.4208
		T4	-1.7787 [*]	.40383	.000	-2.9479	-.6095
		T5	-3.0217 [*]	.31815	.000	-3.9428	-2.1006
		T6	-1.0148	.37224	.077	-2.0925	.0629
	T3	T1	1.0162	.35236	.052	-.0040	2.0363
		T2	2.4510 [*]	.35583	.000	1.4208	3.4812
		T4	.6723	.41463	.586	-.5281	1.8727
		T5	-.5707	.33174	.521	-1.5312	.3897
		T6	1.4362 [*]	.38393	.004	.3247	2.5477
	T4	T1	.3439	.40078	.956	-.8164	1.5042
		T2	1.7787 [*]	.40383	.000	.6095	2.9479
		T3	-.6723	.41463	.586	-1.8727	.5281
		T5	-1.2430 [*]	.38278	.018	-2.3512	-.1348
		T6	.7639	.42880	.481	-.4775	2.0054
	T5	T1	1.5869 [*]	.31427	.000	.6770	2.4967
		T2	3.0217 [*]	.31815	.000	2.1006	3.9428
		T3	.5707	.33174	.521	-.3897	1.5312
		T4	1.2430 [*]	.38278	.018	.1348	2.3512
		T6	2.0069 [*]	.34929	.000	.9957	3.0182
	T6	T1	-.4200	.36893	.864	-1.4882	.6481
		T2	1.0148	.37224	.077	-.0629	2.0925
		T3	-1.4362 [*]	.38393	.004	-2.5477	-.3247
		T4	-.7639	.42880	.481	-2.0054	.4775
		T5	-2.0069 [*]	.34929	.000	-3.0182	-.9957

Table 16 (cont'd)

MOE	T1	T2	.0467	.08140	.993	-.1889	.2824
		T3	.4091 [*]	.08446	.000	.1646	.6536
		T4	.0501	.09607	.995	-.2281	.3282
		T5	-.1641	.07533	.256	-.3822	.0540
		T6	-.7609 [*]	.08844	.000	-1.0169	-.5048
	T2	T1	-.0467	.08140	.993	-.2824	.1889
		T3	.3624 [*]	.08529	.001	.1154	.6093
		T4	.0033	.09680	1.000	-.2769	.2836
		T5	-.2108	.07626	.070	-.4316	.0100
		T6	-.8076 [*]	.08923	.000	-1.0660	-.5493
	T3	T1	-.4091 [*]	.08446	.000	-.6536	-.1646
		T2	-.3624 [*]	.08529	.001	-.6093	-.1154
		T4	-.3591 [*]	.09939	.006	-.6468	-.0713
		T5	-.5732 [*]	.07952	.000	-.8034	-.3430
		T6	-1.1700 [*]	.09203	.000	-1.4364	-.9035
	T4	T1	-.0501	.09607	.995	-.3282	.2281
		T2	-.0033	.09680	1.000	-.2836	.2769
		T3	.3591 [*]	.09939	.006	.0713	.6468
		T5	-.2141	.09175	.189	-.4798	.0515
		T6	-.8109 [*]	.10279	.000	-1.1085	-.5133
	T5	T1	.1641	.07533	.256	-.0540	.3822
		T2	.2108	.07626	.070	-.0100	.4316
		T3	.5732 [*]	.07952	.000	.3430	.8034
		T4	.2141	.09175	.189	-.0515	.4798
		T6	-.5968 [*]	.08373	.000	-.8392	-.3544
	T6	T1	.7609 [*]	.08844	.000	.5048	1.0169
		T2	.8076 [*]	.08923	.000	.5493	1.0660
		T3	1.1700 [*]	.09203	.000	.9035	1.4364
		T4	.8109 [*]	.10279	.000	.5133	1.1085
		T5	.5968 [*]	.08373	.000	.3544	.8392

Based on observed means.

The error term is Mean Square(Error) = .078.

*. The mean difference is significant at the .05 level.

Table 17 Multivariate Tests

Effect		Value	F	Hypothesis df	Error df	Sig.
Intercept	Pillai's Trace	.996	7164.266 ^c	3.000	90.000	.000
	Wilks' Lambda	.004	7164.266 ^c	3.000	90.000	.000
	Hotelling's Trace	238.809	7164.266 ^c	3.000	90.000	.000
	Roy's Largest Root	238.809	7164.266 ^c	3.000	90.000	.000
BI	Pillai's Trace	.535	34.528 ^c	3.000	90.000	.000
	Wilks' Lambda	.465	34.528 ^c	3.000	90.000	.000
	Hotelling's Trace	1.151	34.528 ^c	3.000	90.000	.000
	Roy's Largest Root	1.151	34.528 ^c	3.000	90.000	.000
PP	Pillai's Trace	.872	203.659 ^c	3.000	90.000	.000
	Wilks' Lambda	.128	203.659 ^c	3.000	90.000	.000
	Hotelling's Trace	6.789	203.659 ^c	3.000	90.000	.000
	Roy's Largest Root	6.789	203.659 ^c	3.000	90.000	.000
BI * PP	Pillai's Trace	.292	12.343 ^c	3.000	90.000	.000
	Wilks' Lambda	.708	12.343 ^c	3.000	90.000	.000
	Hotelling's Trace	.411	12.343 ^c	3.000	90.000	.000
	Roy's Largest Root	.411	12.343 ^c	3.000	90.000	.000

a. Wood = Hardwood

b. Design: Intercept + BI + PP + BI * PP

c. Exact statistic

Table 18 Tests of Between-Subjects Effects

Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	TS	11726.021 ^b	3	3908.674	179.388	.000
	EI	129.753 ^c	3	43.251	34.629	.000
	MOE	7.704 ^d	3	2.568	36.619	.000
Intercept	TS	334596.300	1	334596.300	15356.232	.000
	EI	3059.486	1	3059.486	2449.619	.000
	MOE	796.990	1	796.990	11364.851	.000
BI	TS	1212.092	1	1212.092	55.629	.000
	EI	67.604	1	67.604	54.128	.000
	MOE	1.727	1	1.727	24.623	.000
PP	TS	11311.654	1	11311.654	519.146	.000
	EI	38.630	1	38.630	30.929	.000
	MOE	5.389	1	5.389	76.840	.000
BI * PP	TS	139.038	1	139.038	6.381	.013
	EI	1.868	1	1.868	1.496	.224
	MOE	2.364	1	2.364	33.705	.000
Error	TS	2004.584	92	21.789		
	EI	114.905	92	1.249		
	MOE	6.452	92	.070		
Total	TS	359071.065	96			
	EI	3661.779	96			
	MOE	828.765	96			
Corrected Total	TS	13730.605	95			
	EI	244.657	95			
	MOE	14.156	95			

a. Wood = Hardwood

b. R Squared = .854 (Adjusted R Squared = .849)

c. R Squared = .530 (Adjusted R Squared = .515)

d. R Squared = .544 (Adjusted R Squared = .529)

Table 19 Multivariate Tests

Effect		Value	F	Hypothesis df	Error df	Sig.
Intercept	Pillai's Trace	.995	4489.992 ^c	3.000	74.000	.000
	Wilks' Lambda	.005	4489.992 ^c	3.000	74.000	.000
	Hotelling's Trace	182.027	4489.992 ^c	3.000	74.000	.000
	Roy's Largest Root	182.027	4489.992 ^c	3.000	74.000	.000
BI	Pillai's Trace	.457	20.720 ^c	3.000	74.000	.000
	Wilks' Lambda	.543	20.720 ^c	3.000	74.000	.000
	Hotelling's Trace	.840	20.720 ^c	3.000	74.000	.000
	Roy's Largest Root	.840	20.720 ^c	3.000	74.000	.000
Wood	Pillai's Trace	.829	119.532 ^c	3.000	74.000	.000
	Wilks' Lambda	.171	119.532 ^c	3.000	74.000	.000
	Hotelling's Trace	4.846	119.532 ^c	3.000	74.000	.000
	Roy's Largest Root	4.846	119.532 ^c	3.000	74.000	.000
BI * Wood	Pillai's Trace	.169	5.016 ^c	3.000	74.000	.003
	Wilks' Lambda	.831	5.016 ^c	3.000	74.000	.003
	Hotelling's Trace	.203	5.016 ^c	3.000	74.000	.003
	Roy's Largest Root	.203	5.016 ^c	3.000	74.000	.003

a. Raw material format= CTMP

b. Design: Intercept + BI + Wood + BI * Wood

c. Exact statistic

Table 20 Tests of Between-Subjects Effects

Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	TS	5505.417 ^b	3	1835.139	68.758	.000
	EI	68.697 ^c	3	22.899	14.784	.000
	MOE	2.203 ^d	3	.734	8.247	.000
Intercept	TS	248134.431	1	248134.431	9297.032	.000
	EI	2570.228	1	2570.228	1659.358	.000
	MOE	513.280	1	513.280	5763.902	.000
BI	TS	1240.829	1	1240.829	46.491	.000
	EI	20.936	1	20.936	13.516	.000
	MOE	.460	1	.460	5.165	.026
Wood	TS	4763.138	1	4763.138	178.464	.000
	EI	36.834	1	36.834	23.780	.000
	MOE	.802	1	.802	9.006	.004
BI * Wood	TS	204.416	1	204.416	7.659	.007
	EI	2.742	1	2.742	1.770	.187
	MOE	.777	1	.777	8.720	.004
Error	TS	2028.413	76	26.690		
	EI	117.719	76	1.549		
	MOE	6.768	76	.089		
Total	TS	253322.949	80			
	EI	2833.946	80			
	MOE	554.320	80			
Corrected Total	TS	7533.829	79			
	EI	186.416	79			
	MOE	8.971	79			

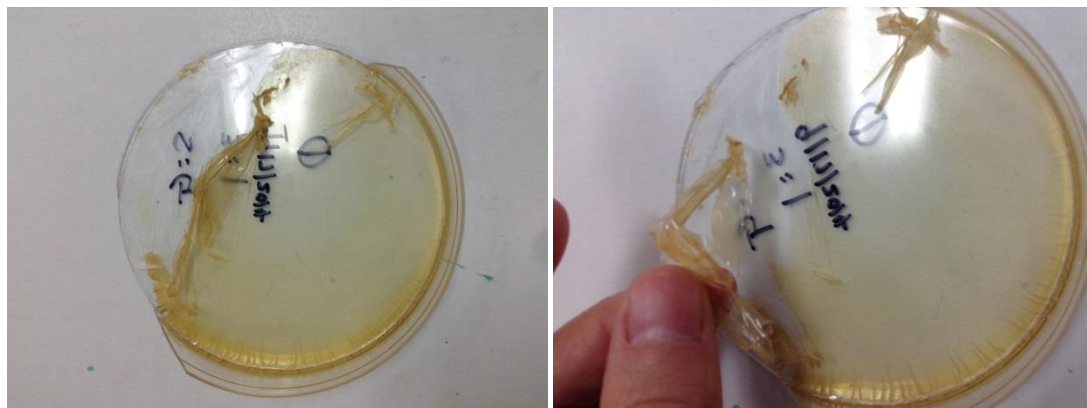
a. Raw material format= CTMP

b. R Squared = .731 (Adjusted R Squared = .720)

c. R Squared = .369 (Adjusted R Squared = .344)

d. R Squared = .246 (Adjusted R Squared = .216)

S: G 3:1



S: G 2:1



S: G 1:0

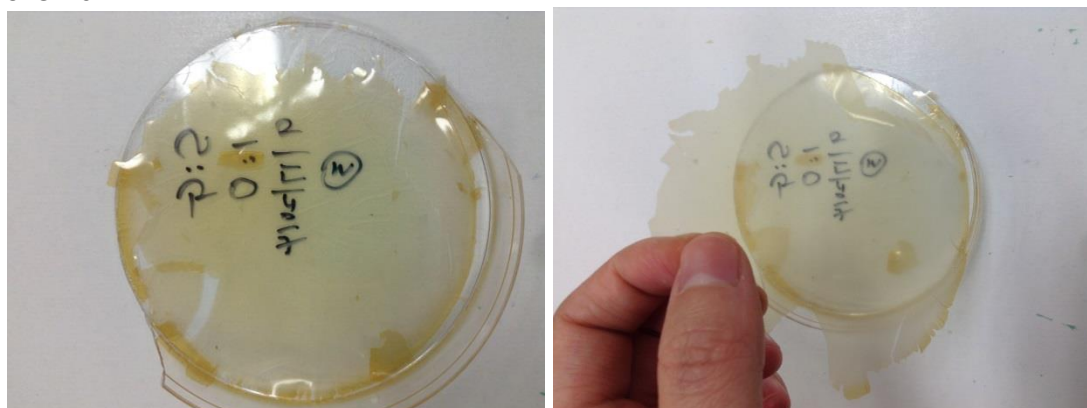
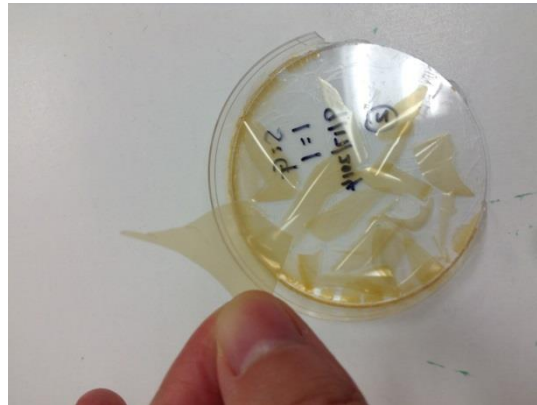
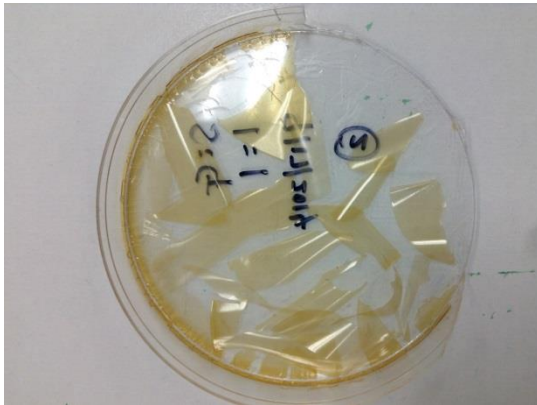


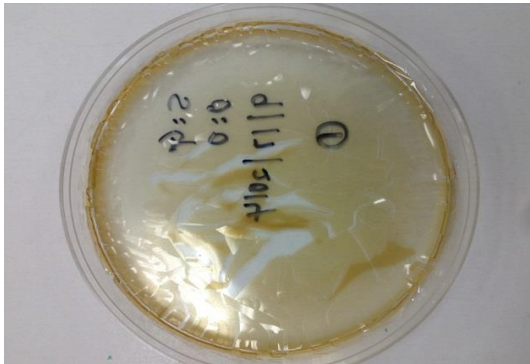
Figure 25 Xylan film from beechwood with different ratios of sorbitol and glutaraldehyde

Figure 25 (cont'd)

S: G 1:1



S: G 0:0



S: G 0:1

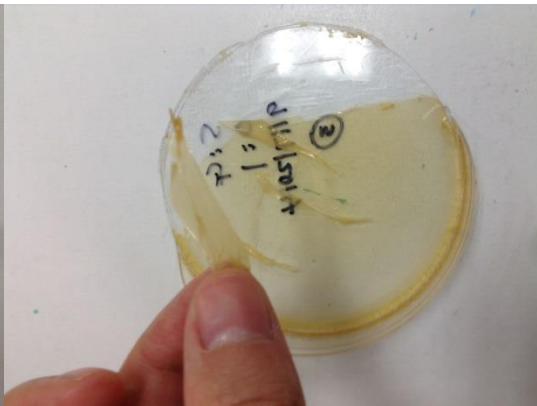
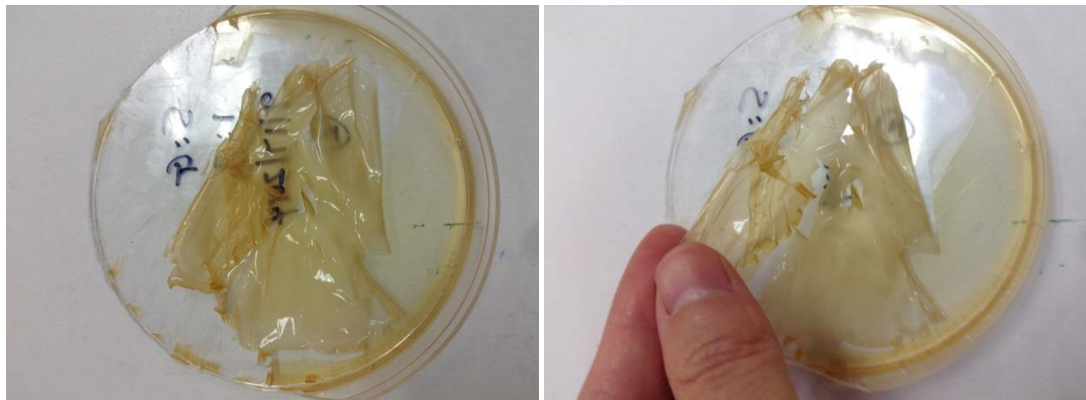
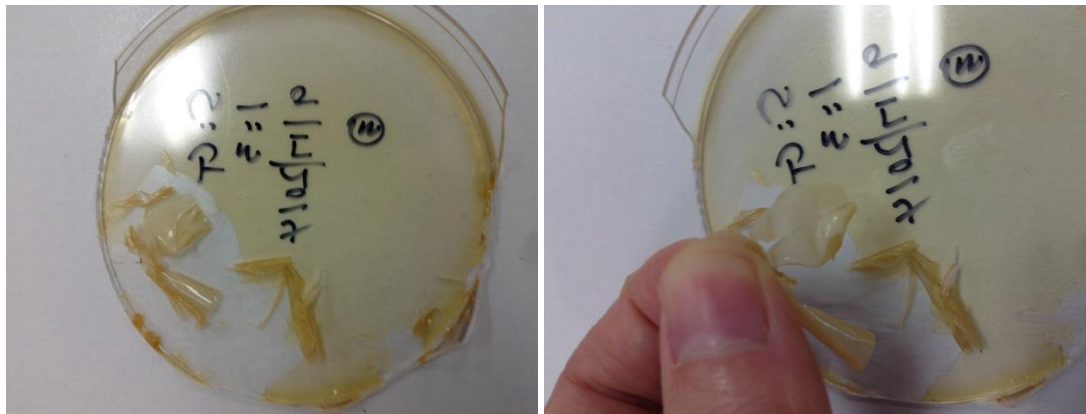


Figure 25 (cont'd)

S: G 1:2



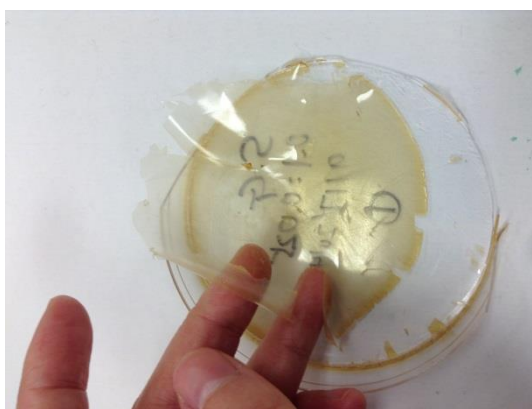
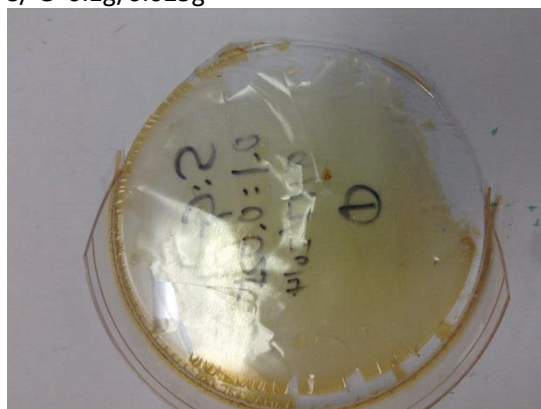
S: G 1:3



S/G 0g/0g



S/ G 0.1g/0.025g



S/ G 0.2g/ 0.05g

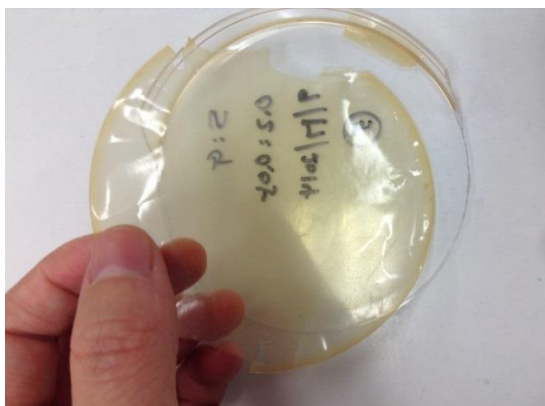
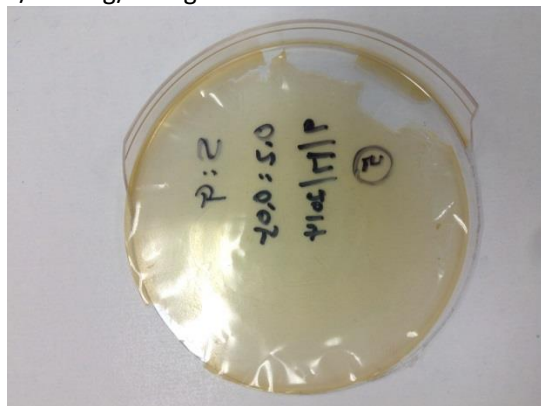
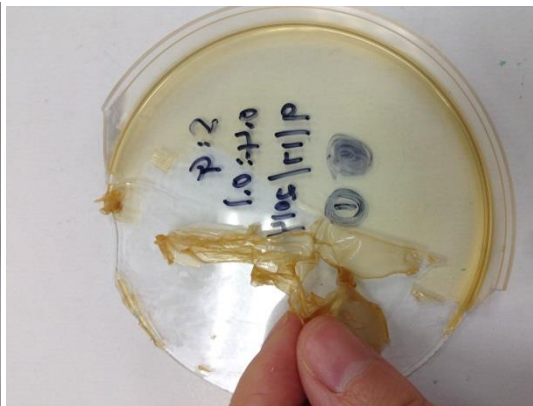
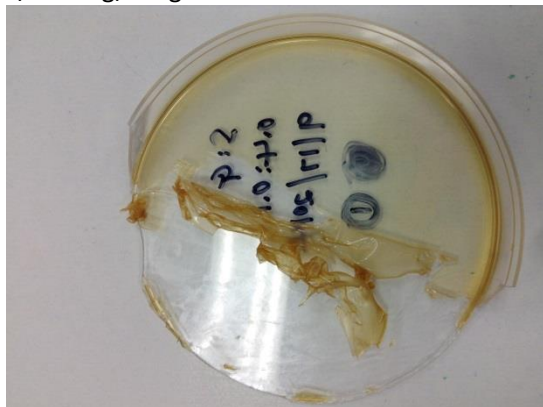


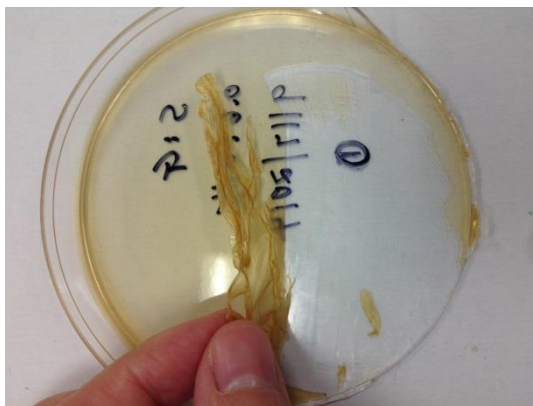
Figure 26 xylan film from beechwood with different amount of additives

Figure 26 (cont'd)

S/ G 0.4g/ 0.1g



S/ G 0.6g/ 0.15g



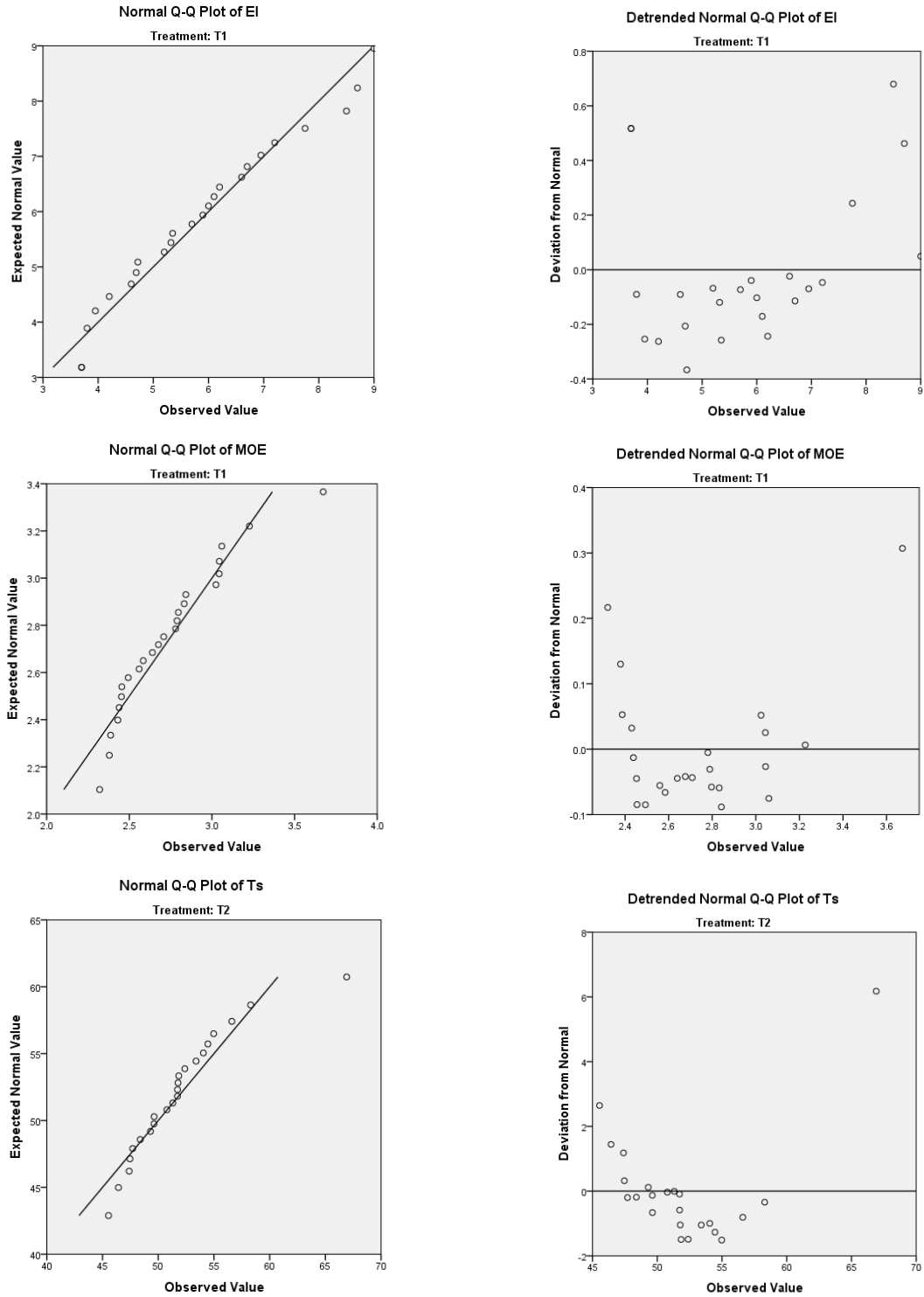


Figure 27 QQ Plots of TS, MOE and EI from different treatments

Figure 27 (cont'd)

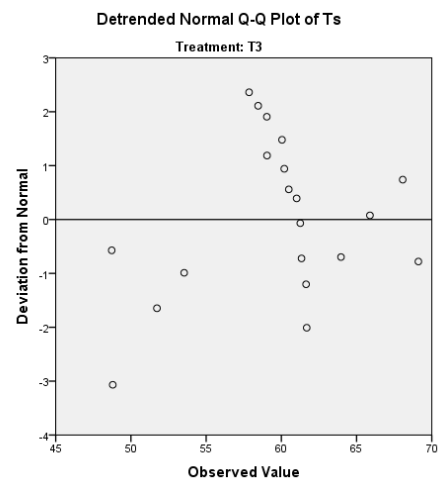
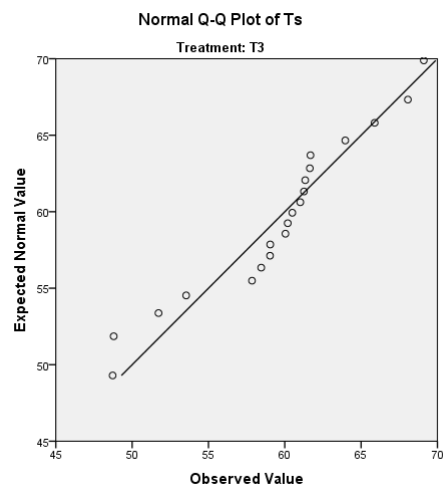
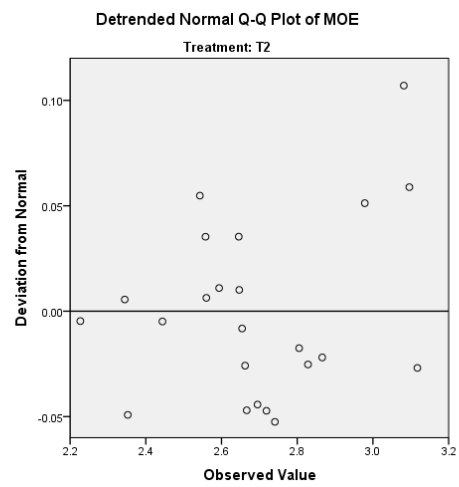
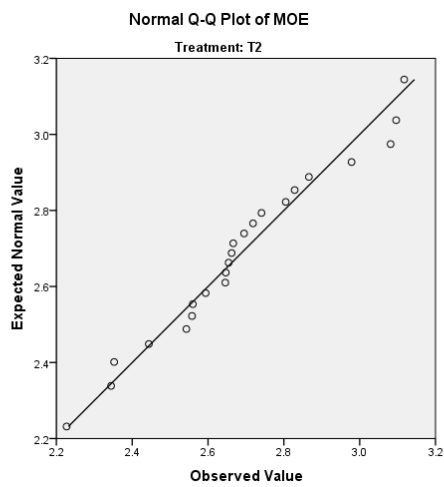
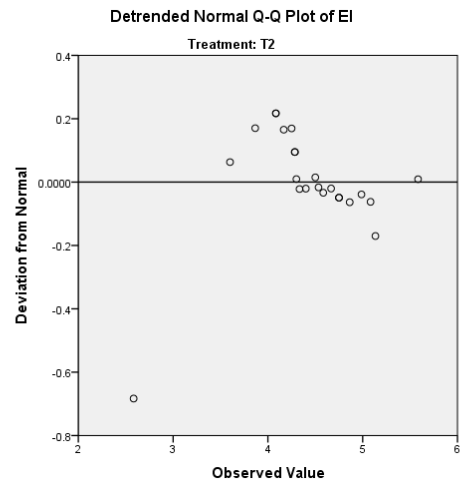
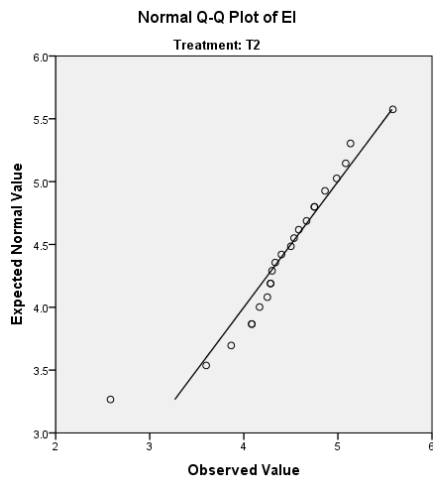


Figure 27 (cont'd)

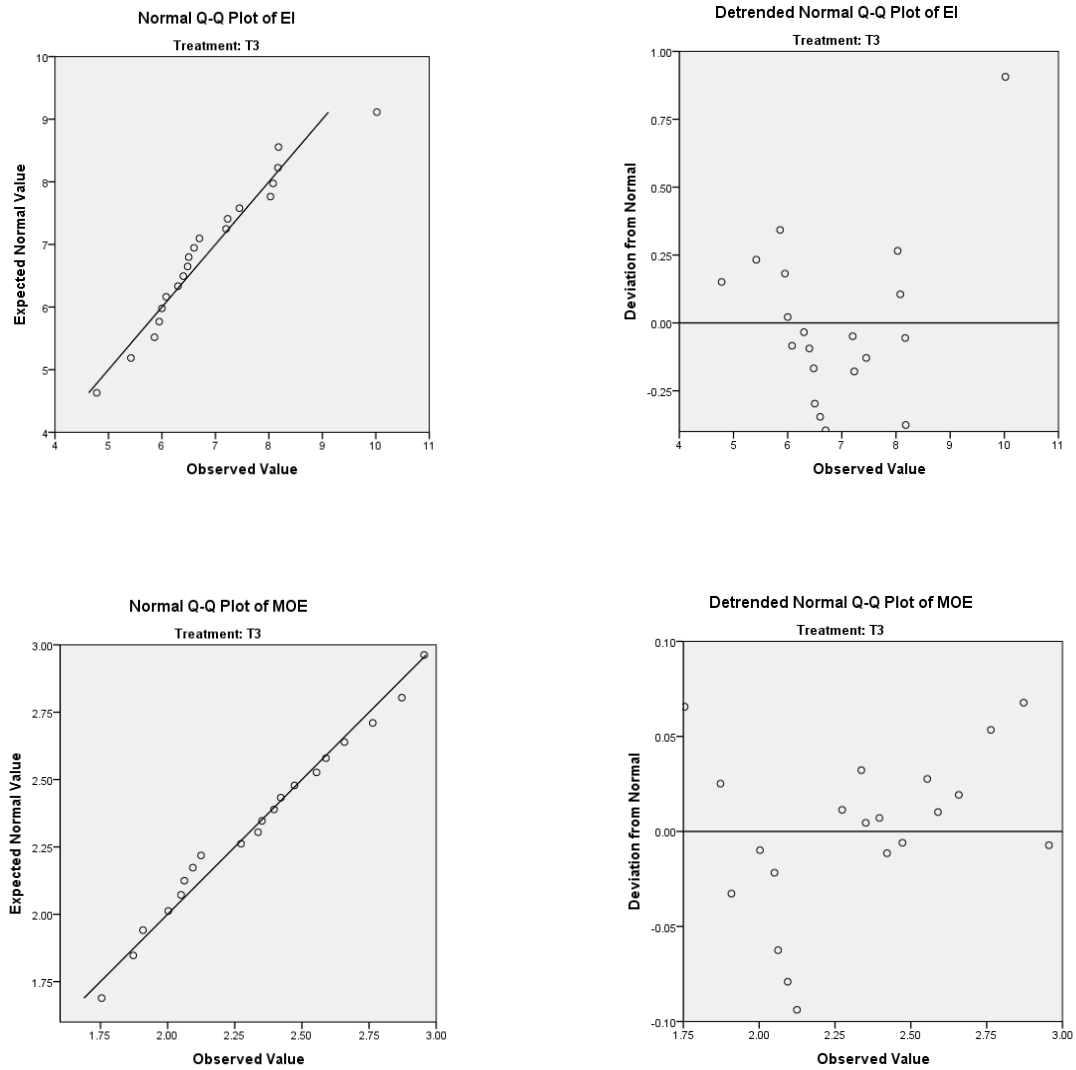


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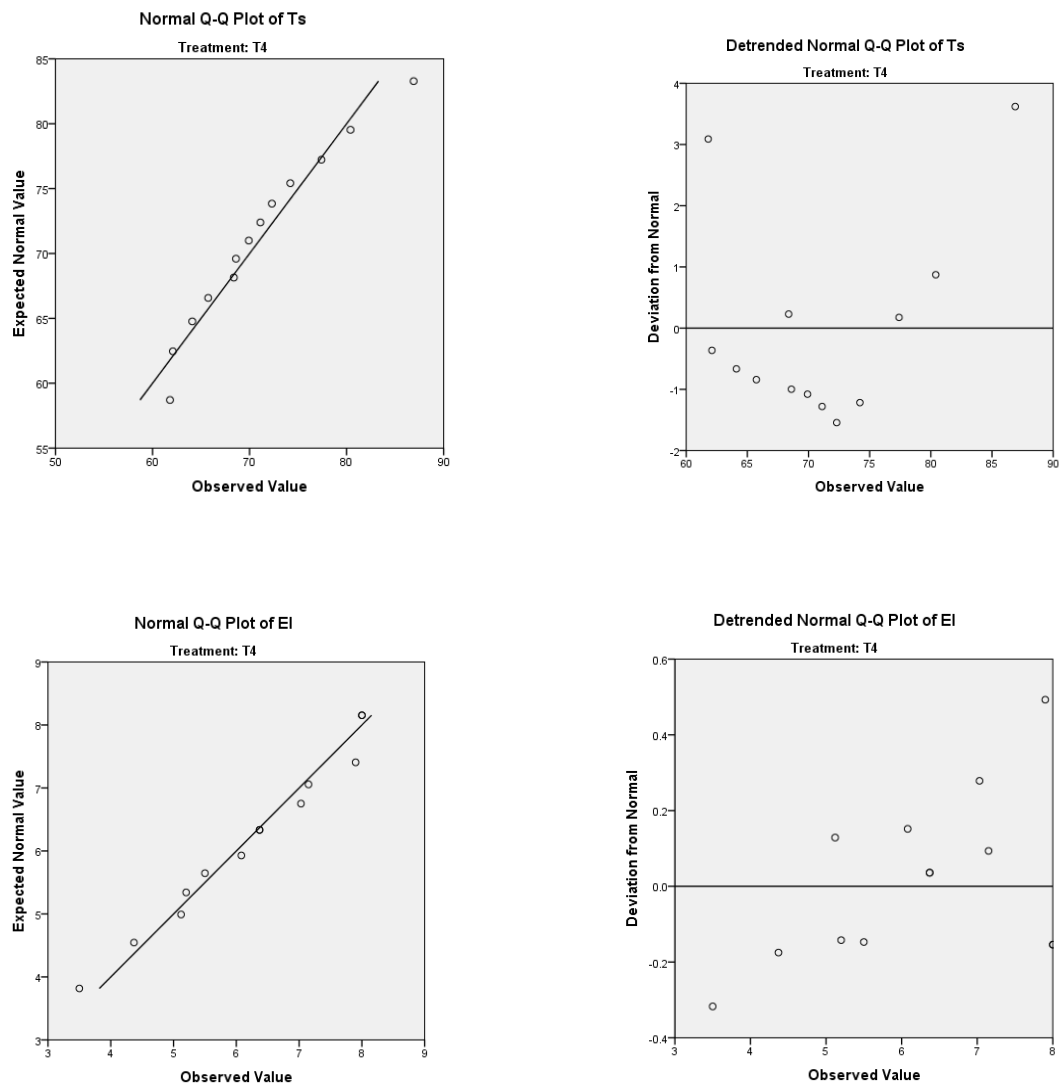


Figure 27 (cont'd)

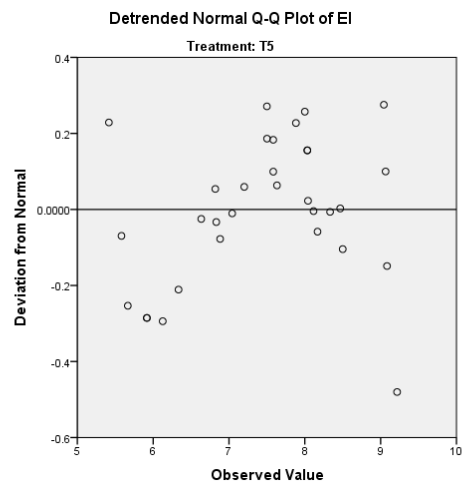
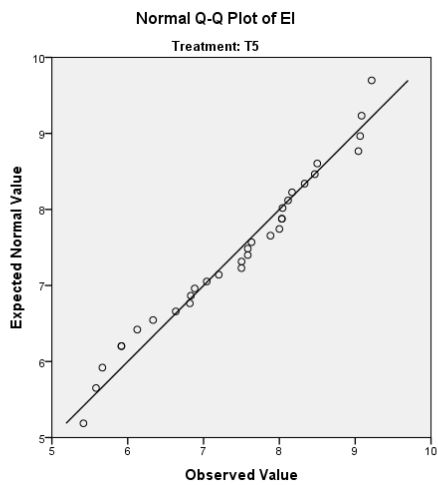
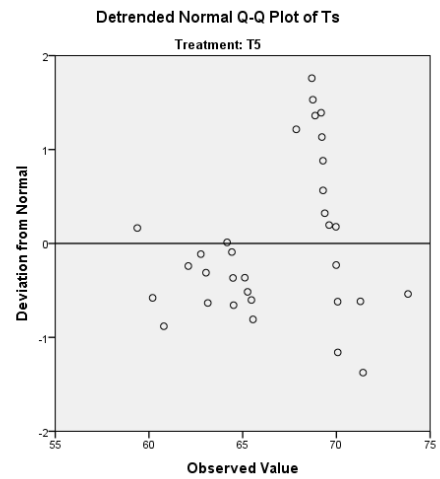
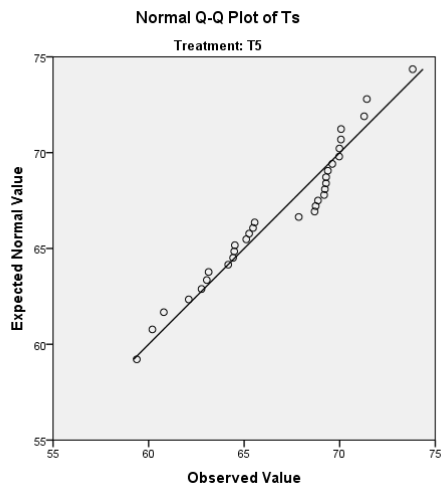
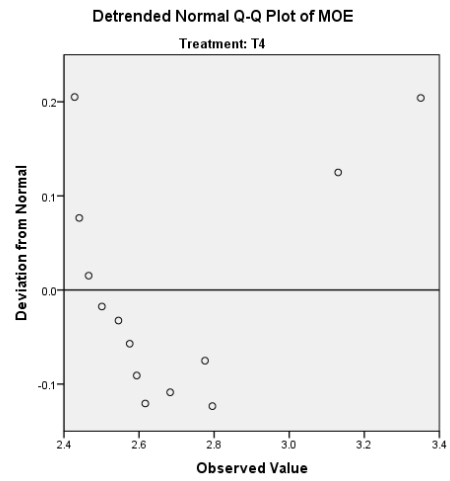
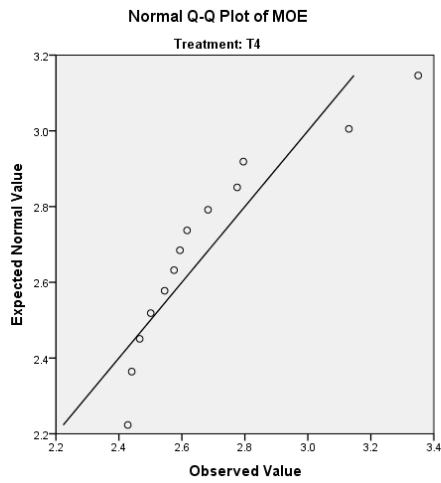


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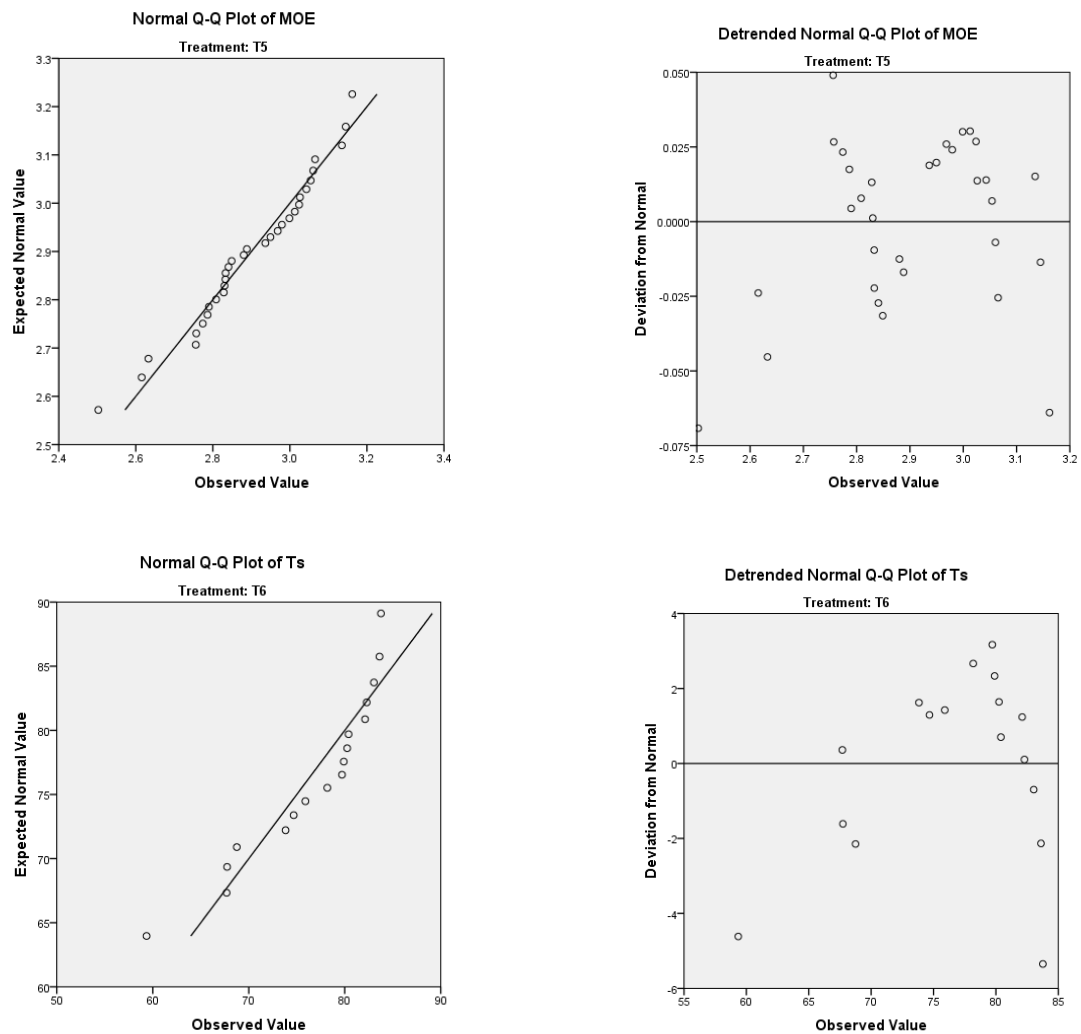
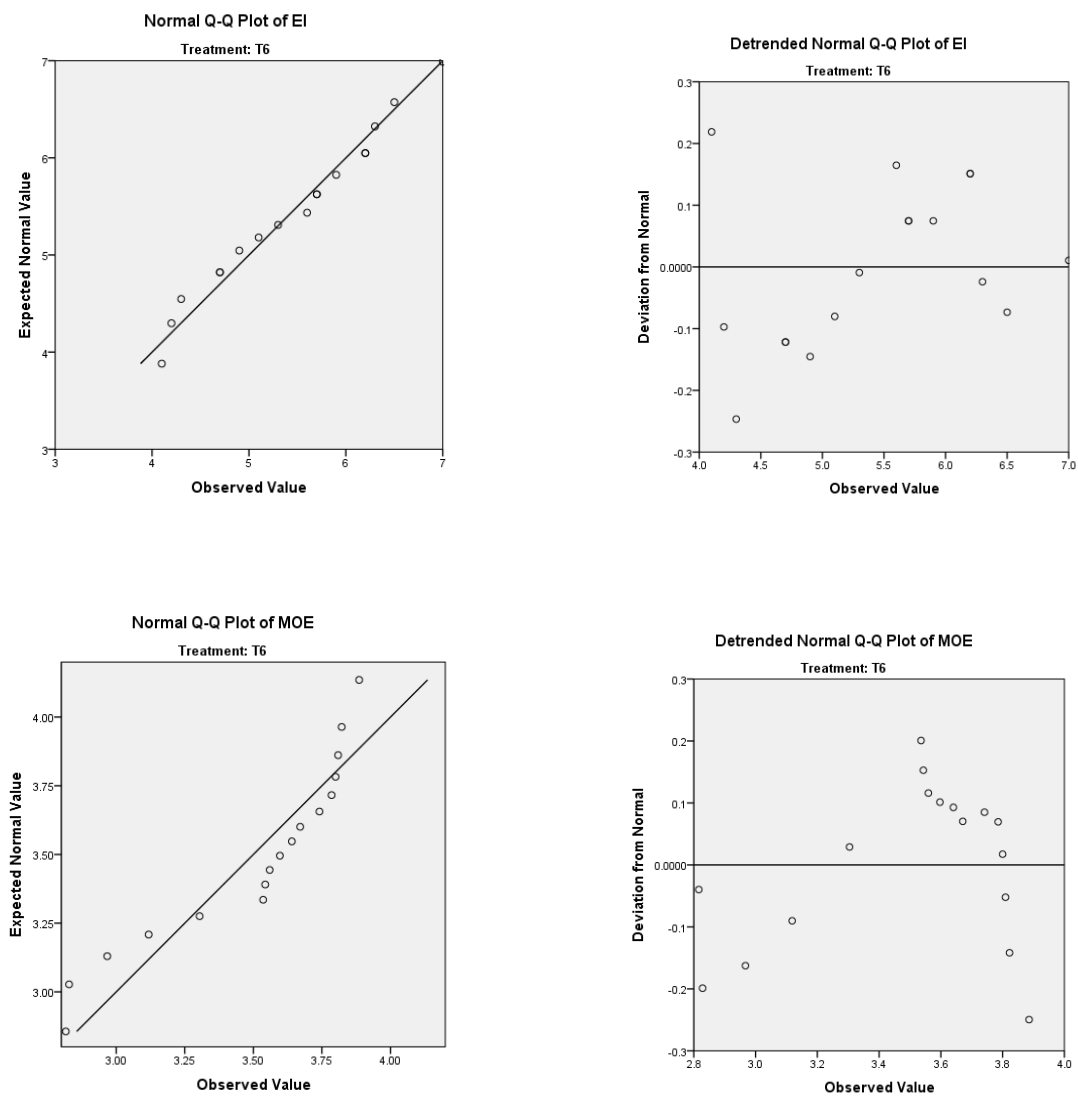
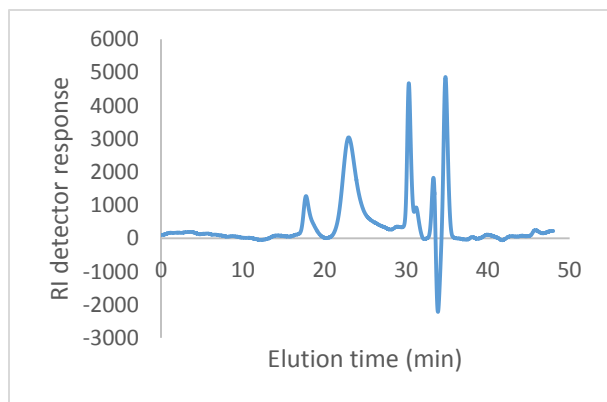


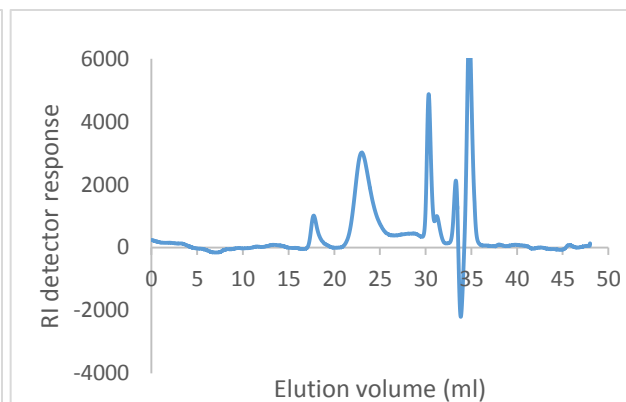
Figure 27 (cont'd)



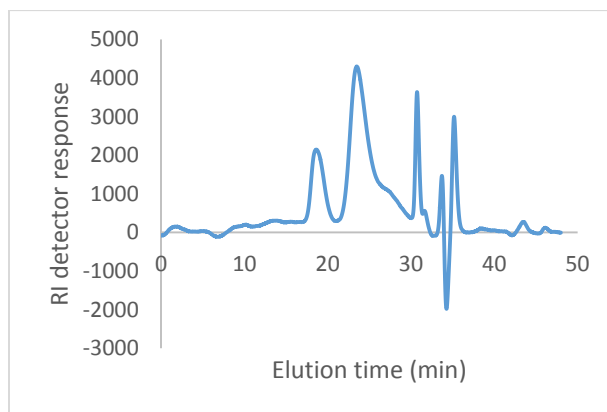
CTMP A B 2



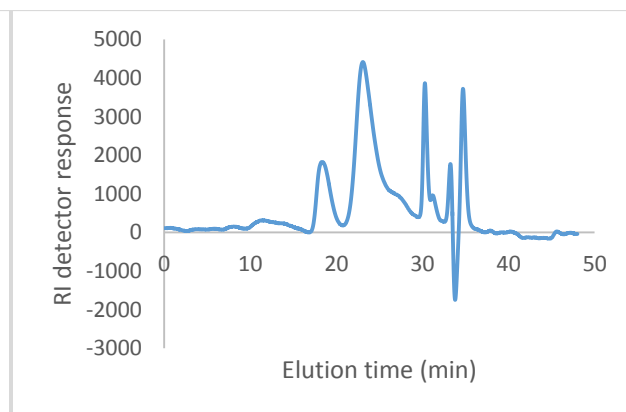
CTMP A B 3



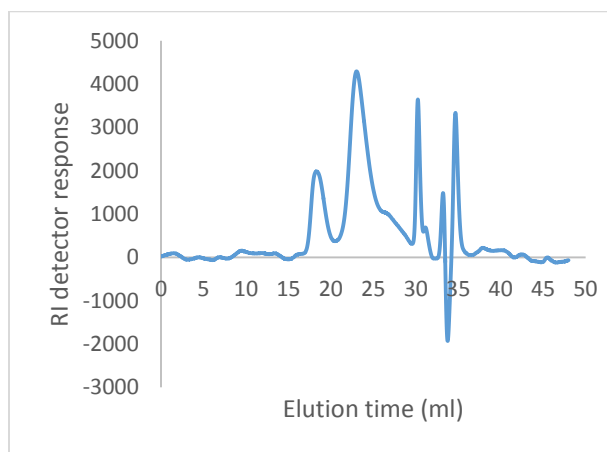
CTMP A UB 1



CTMP A UB 2



CTMP A UB 3



CTMP S B 1

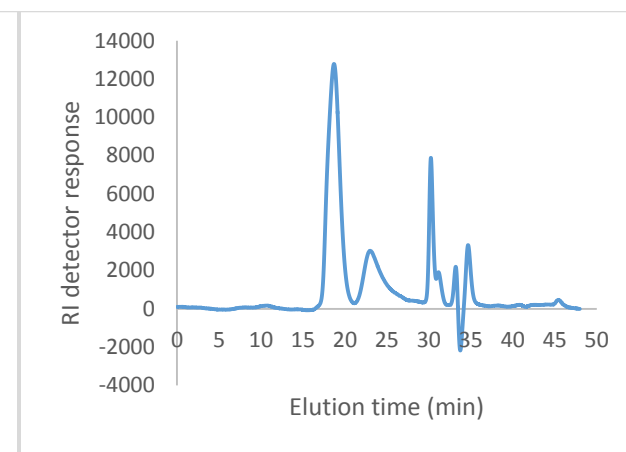
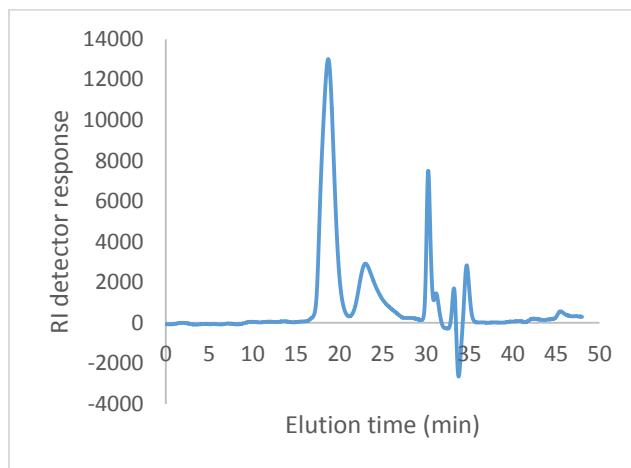


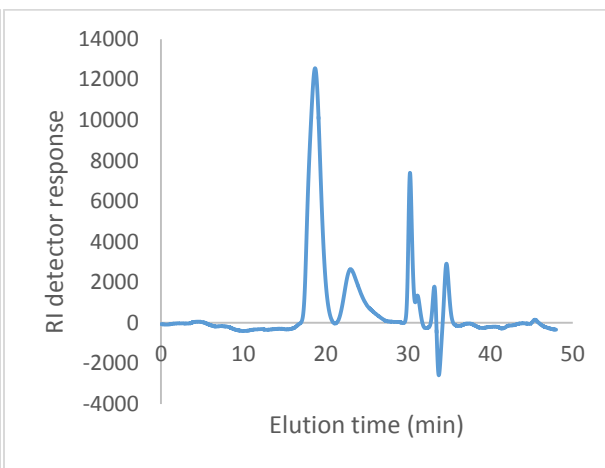
Figure 28 Size exclusion chromatography whole elution profiles from two columns system of hemicelluloses from different approaches, (A: aspen; B: bleached; S: spruce; UB: unbleached).

Figure 28 (cont'd)

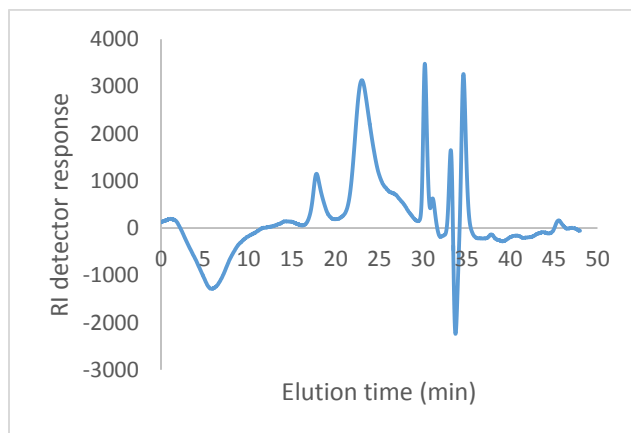
CTMP S B 2



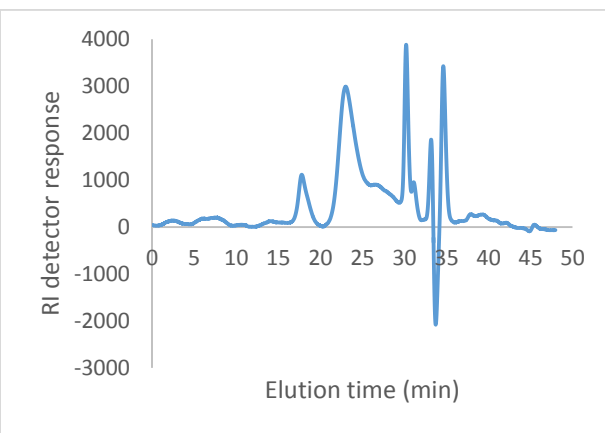
CTMP S B 3



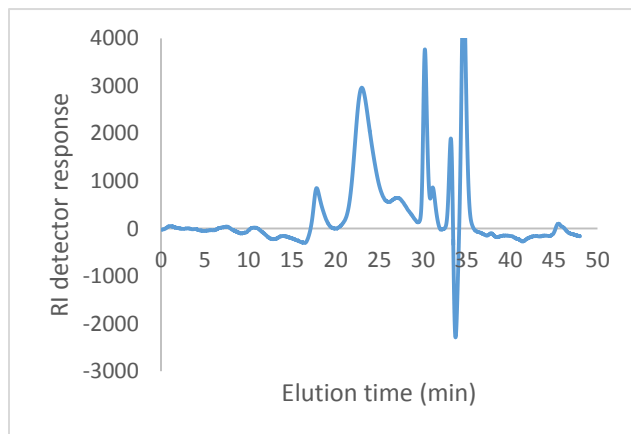
CTMP S UB 1



CTMP S UB 2



CTMP S UB 3



HPP B 1

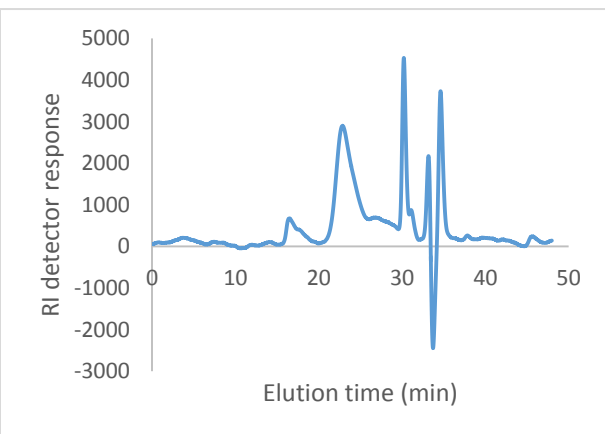
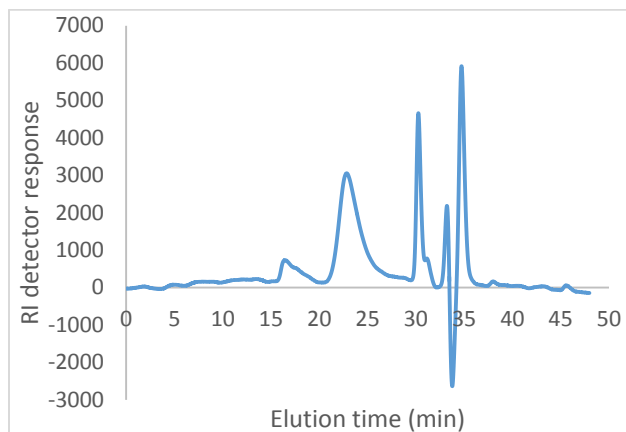
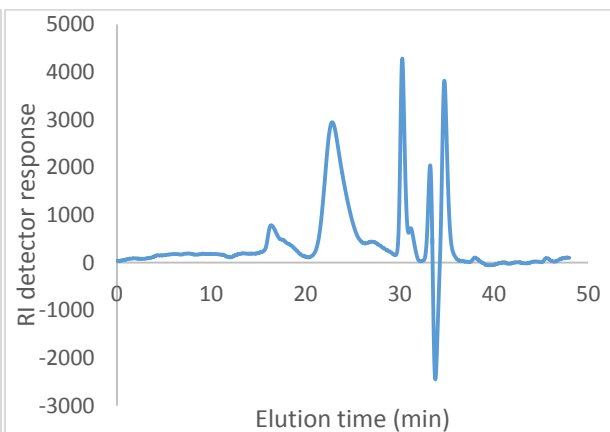


Figure 28 (cont'd)

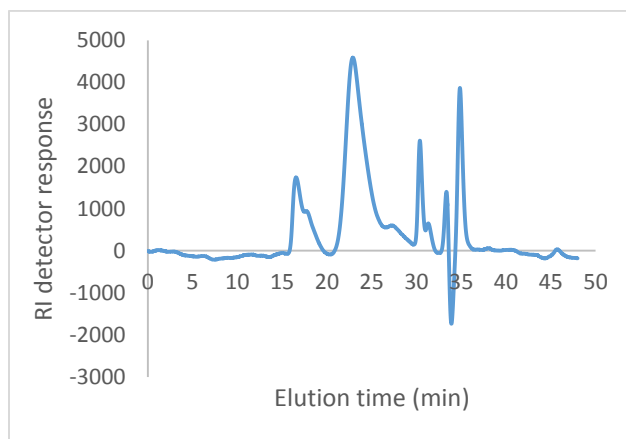
HPP B 2



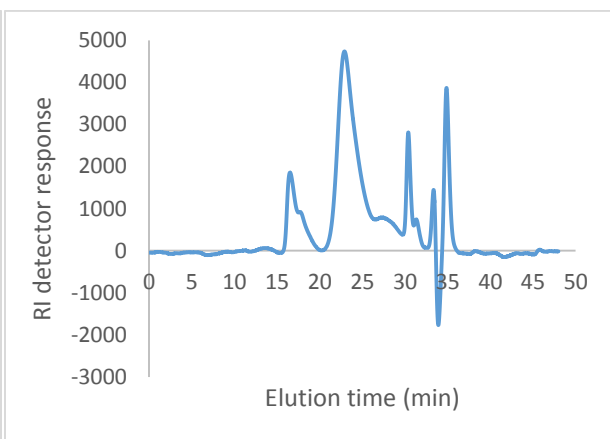
HPP B 3



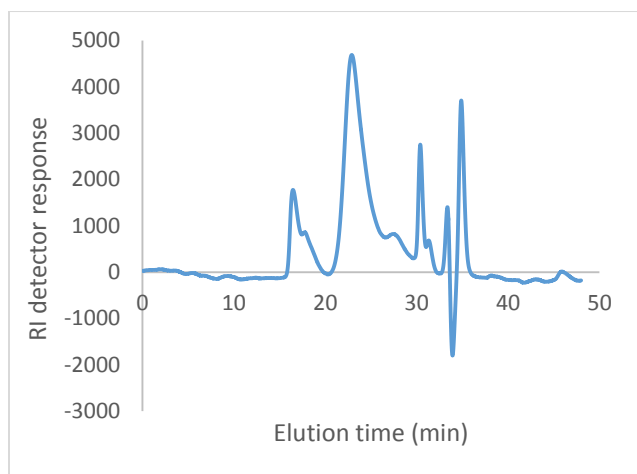
HPP UB 1



HPP UB 2



HPP UB 3



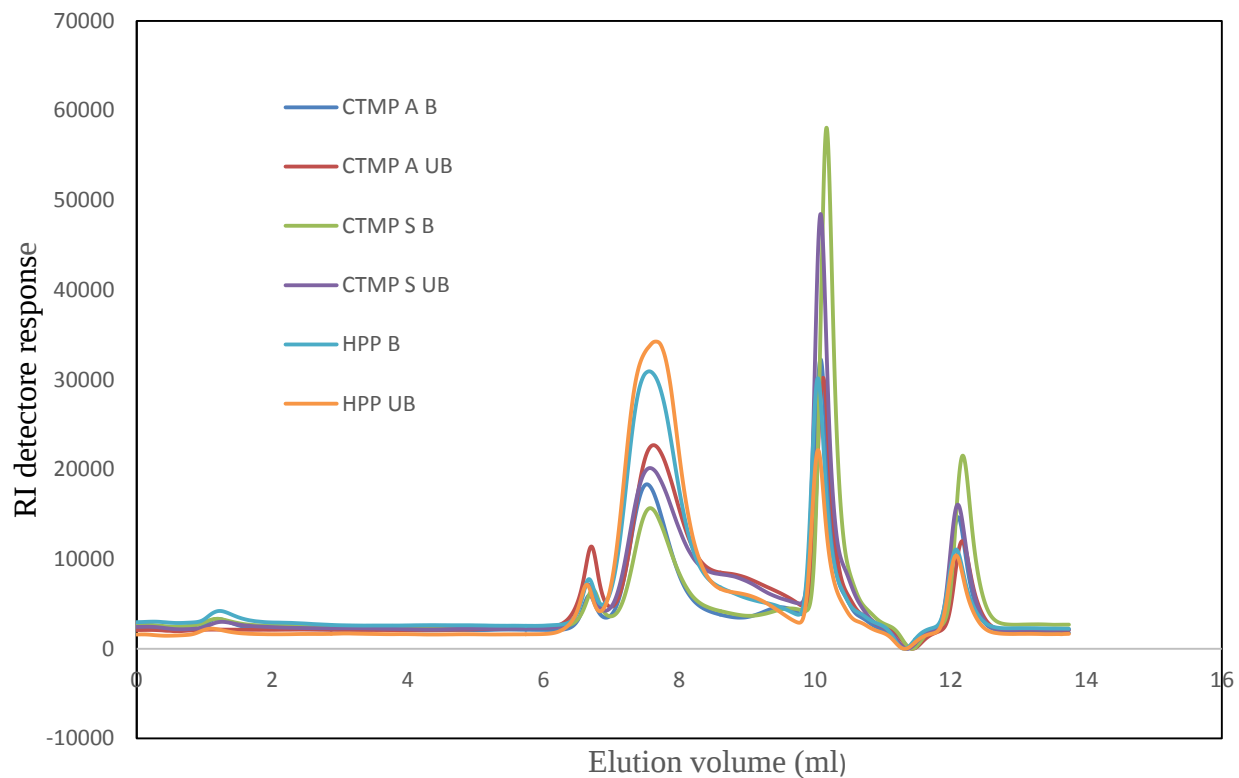


Figure 29 Size exclusion chromatography whole elution profiles from single column system of hemicellulose from different approaches, (A: aspen; B: bleached; S: spruce; UB: unbleached).

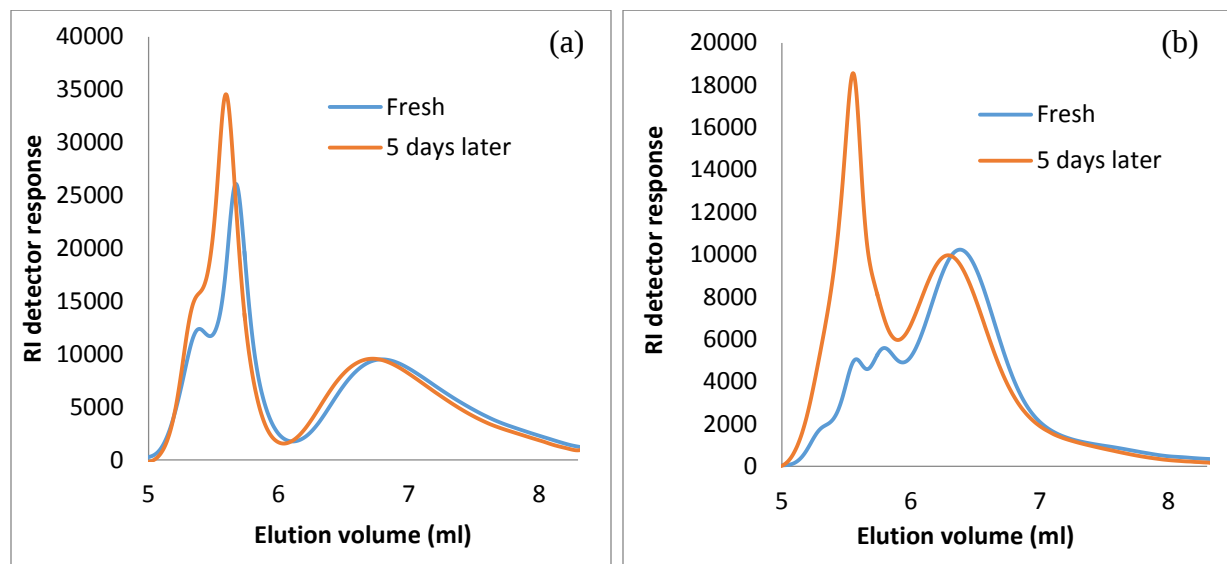


Figure 30 Size exclusion chromatography elution profiles of xylans, freshly made solution and after 5 days storage, (a) xylan from birchwood; (b) xylan from oat spelts.

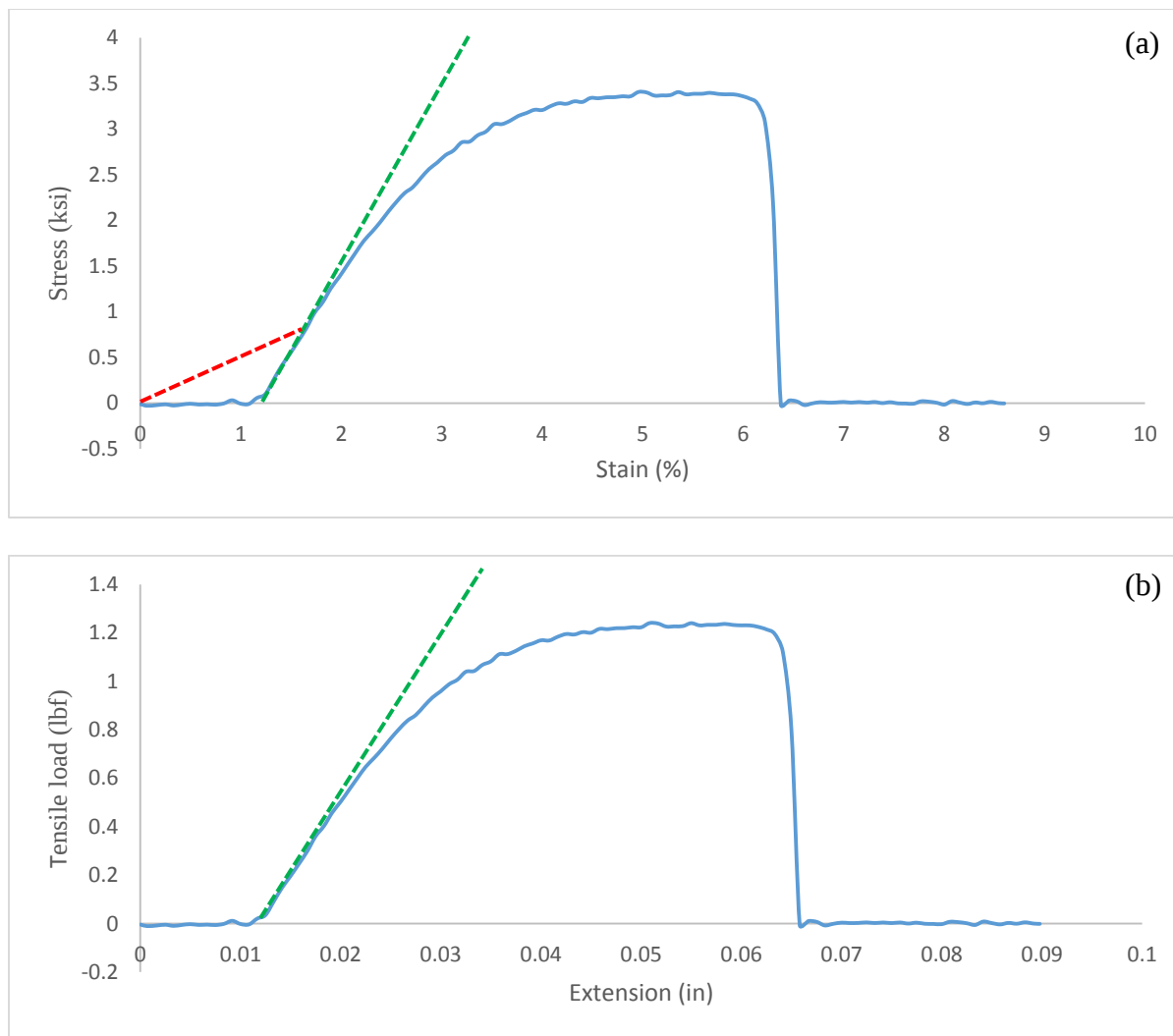


Figure 31 Schematic diagrams of MOE calculation, (a) stress-strain method; (b) tensile load-extension method.

$$MOE = \frac{Stress}{Strain} = \frac{\frac{Load}{area}}{\frac{\Delta L}{L_0}} = \frac{\frac{Load}{width \times thickness}}{\frac{\Delta L}{L_0}} = \frac{L_0}{width \times thickness} \cdot \frac{Load}{\Delta L}$$

Table 21 MOE calculation by three different approaches

Computed maximum slope (lbf/in)	MOE (Gpa)	Load/extension slope (lbf/in)	MOE (Gpa)	Stress/strain slope (ksi)	MOE (Gpa)
63.47	1.20	63.52	1.20	177.30	1.22
77.97	1.30	74.71	1.25	184.91	1.27
91.62	1.31	94.88	1.36	199.87	1.38
	1.27		1.27		1.29
	0.06		0.08		0.08

Note: Numbers in red frame are the average values of the 3 times calculation of MOE above.
Numbers in green frame are the STDEV values of the 3 times calculation of MOE above.

REFERENCES

REFERENCES

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3. Agoda-Tandjawa G., Durand S., Berot S., Blassel C., Gaillard C., Garnier C. and J.L. Doublier. 2010. Rheological characterization of microfibrillated cellulose suspensions after freezing. *Carbohydrate Polymers*, 80: 677–686.
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