INVESTIGATION OF PROCESSING PARAMETERS ON PRODUCTION OF HEMICELLULOSE BASED FILMS FROM DIFFERENT AGRICULTURAL RESIDUES VIA EXTRUSION

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INVESTIGATION OF PROCESSING PARAMETERS ON PRODUCTION OF HEMICELLULOSE BASED FILMS FROM DIFFERENT AGRICULTURAL RESIDUES VIA EXTRUSION

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

INVESTIGATION OF PROCESSING PARAMETERS ON PRODUCTION OF HEMICELLULOSE BASED FILMS FROM DIFFERENT AGRICULTURAL RESIDUES VIA EXTRUSION

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Today, due to the environmental concerns about petroleum based polymers, the use of renewable polymers including polysaccharides in food packaging applications is increasing rapidly. In the present study, hemicellulose was extracted from corn cobs, wheat straw and sunflower stalks, and two different techniques, solvent casting and extrusion, were utilized for biodegradable film production. Films produced from different types of biomasses were compared in terms of their mechanical, thermal and morphological properties while studying the process parameters of extraction temperature, extrusion temperature and screw speed. Film formation was achieved by extrusion from all the hemicelluloses. Increasing the extrusion temperature had a slightly positive effect on the mechanical properties of films, whereas screw speed did not have a noticeable effect. Hemicellulose extraction at room temperature is determined a better temperature than 60°C in terms of mechanical properties of films. Among the films produced via extrusion, corn cob hemicellulose extracted at room temperature showed the best mechanical properties depending on Ara/Xyl ratio of hemicelluloses, with a toughness of 13MJ/m^3,while the toughness value of the sunflower stalk based films were relatively poor, which was 2MJ/m^3. On the other hand, homogenous and strong films with a tensile strength of 107 MPa were obtained from the same sunflower stalk hemicellulose when solvent casting technique was used. The onsets of thermal degradation temperature for solvent casted and extruded films were determined via TGA as 300°C for corn cob and wheat straw hemicellulose and 296°C for the films produced from sunflower stalk hemicellulose. The films were mostly homogenous and crack-free except for the sunflower stalk films extruded at 75°C as observed via SEM analysis.

Keywords: Hemicellulose, Xylan, Extrusion, Lignocellulosic biomass, Mechanical

ÖZ

FARKLI TARIMSAL ATIKLARDAN EKSTRÜZYON YÖNTEMİYLE HEMİSELÜLOZ TEMELLİ FİLM ÜRETİMİ İÇİN SÜREÇ KOŞULLARININ İNCELENMESİ

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Günümüzde, petrol temelli polimerler hakkında duyulan çevresel endişelerden dolayı, yenilenebilir polimerlerin gıda ürünlerinin paketlemesinde kullanımı gözle görülür bir şekilde artış göstermektedir. Bu çalışmada hemiselüloz, mısır koçanı, buğday samanı ve ayçiçek saplarından özütlenerek, sıvı dökme ve ekstrüzyon olmak üzere iki farklı teknikle biyobozunur filmlerin üretiminde kullanılmıştır. Özütleme sıcaklığı, ekstrüzyon sıcaklığı ve vida dönme hızını içeren işlem parametreleri çalışılarak farklı çeşitlerdeki biyokütlelerden üretilen filmler, mekanik, ısıl ve morfolojik özellikleri açısından karşılaştırılmıştır. Tüm hemiselüloz çeşitlerinden ekstrüzyon yöntemi ile film üretilmiştir. Vida dönme hızının mekanik özellikler üzerine önemli bir etkisi olmaz iken, ekstrüzyon sıcaklığının artması filmlerin mekanik özelliklerini olumlu etkilemiştir. Ekstrüzyon ile elde edilen filmlerin içerisinde, ayçiçek sapından özütlenen hemiselülozlardan elde edilen filmlerin dayanım değerleri çok az iken (2MJ/m^3), oda sıcaklığında özütlemesi yapılan mısır koçanı hemiselülozu, Ara/Xyl oranına bağlı olarak, 13MJ/m^{3}dayanım değeri ile en iyi mekanik özelliğe sahip film olarak gözlemlenmiştir. Diğer yandan, ayçiçek sapı hemiselülozundan sıvı dökme yöntemi kullanıldığında 107 MPa çekme gerilimine sahip homojen ve güçlü filmler elde edilmiştir. Sıvı dökme ve ekstrüzyonla elde edilen filmler için ısıl bozunmanın başladığı ilk sıcaklık TGA ile analiz edilerek mısır koçanı ve buğday samanı hemiselülozundan elde edilen filmler için 300°C, ayçiçek sapı hemiselülozundan elde edilen filmler için ise 296°C olarak bulunmuştur. Taramalı elektron mikroskobu yardımıyla, ayçiçek sapı hemiselülozundan 75°C'de ekstrüzyonla elde edilen filmler haricinde üretilen filmlerin genellikle homojen olduğu ve çatlak içermediği gözlemlenmiştir.

Anahtar Kelimeler: Hemiselüloz, Ksilen, Ekstrüzyon, Lignoselülozik Biyokütle, Mekanik

To my lovely family,

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NOMENCLATURE

PE: Polyethylene

LDPE: Low density polyethylene

HDPE: High density polyethylene

PP: Polypropylene

PVC: Polyvinyl chloride

CMC: Carboxymethyl cellulose

MC: Methylcellulose

HPC: Hydroxypropyl cellulose

HPMC: Hydroxypropyl methylcellulose

CAP: Cellulose acetate propionate

CA: Cellulose acetate

CAB: Cellulose acetate butyrate

PLA: Polylactic acid

PHA: Polyhydroxyalkanoates

PHB: Polyhydroxybutyrates

PVOH: Polyvinyl alcohol

EVOH: Ethylene vinyl alcohol

CNF: Cellulose nano fibers

TPS: Thermoplastic starch

AX: Arabinoxylan

AIL: Acid insoluble lignin

ASL: Acid soluble lignin

DF: Dilution factor

DP: Degree of polymerization

rpm: Revolutions per minute

wt %: Weight %

w/v: Weight/volume

w/w: Weight/weight

L: Liter

ml: Mililiter

g: Gram

mg: Miligram

cm: Centimeter

nm: Nanometer

µm: Micrometer

N: Newton

kN: Kilonewton

MPa: Megapascal

KOH: Potassium Hydroxide

$NaBH_4$: Sodium borohydride

NREL: National Renewable Energy Laboratory

E: Young’s modulus

eB : Elongation at break

TEB: Tensile energy to break

UTS: Ultimate tensile strength

HPLC: High Performance Liquid Chromatography

TGA: Thermogravimetric Analysis

SEM: Scanning Electron Microscopy

SEC: Size Exclusion Chromatography

CHAPTER 1

INTRODUCTION

In the past decades, the remarkable decrease in fossil based resources including petroleum, natural gas as well as coal and environmental concerns related to the utilization of these resources have led researchers to focus on renewable raw materials. It is recognized that plant based raw materials and particularly lignocellulosic biomass have the potential to replace a major part of fossil based resources for the industrial production of energy, chemicals and materials. The utilization of biofuels, biochemicals and biopolymers can decrease greenhouse gas emissions to prevent global warming, and reduce environmental pollution.

1.1. Lignocellulosic Biomass

Lignocellulosic biomass is the non-starch, fibrous part of plants with a complex matrix comprising different polysaccharides, phenolic polymers and proteins but the main constituents are cellulose, hemicellulose and lignin (Zafar, 2013). As depicted in Figure 1.1, lignocellulosic biomass can be converted into valuable chemical products such as alcohols, organic acids, vitamins, amino acids, enzymes and biodegradable polymers (Hansen and Plackett, 2008; Tamaru and Lopez, 2013). In the recent years, lignocellulosic biomass has become a promising feedstock for the biorefinery industry due to its abundance, low cost and carbon-neutral structure. Agricultural, forestry and industrial wastes are considered as various sources of lignocellulosic biomass.

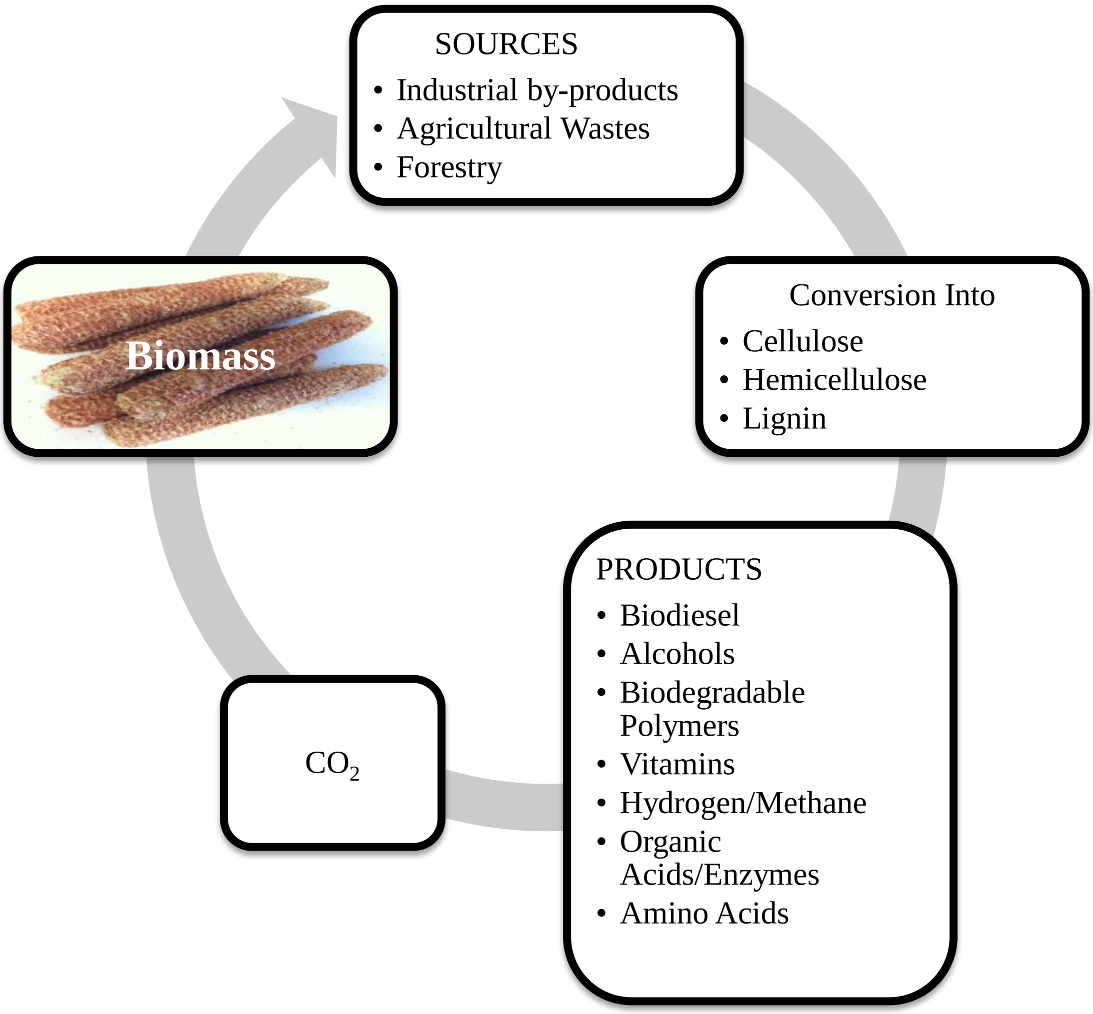


Figure 1.1 Schematic diagram of sources and products of lignocellulosic biomass.

1.2. Structure of Lignocellulosic Biomass

Lignocellulosic biomass mostly consists of three major components including cellulose, hemicellulose and lignin with different proportions, depending on the type of biomass. The compositions of various lignocellulosic biomasses are given in Table 1. In general, biomass consists of 40-50% cellulose, 25-30%

hemicellulose and 15-20% lignin with minor amounts of protein, ash, pectin and extractives (Knauf and Moniruzzaman, 2004).

Table 1.1 Composition of various lignocellulosic feed stocks. (Hon and David, 1995; Deng et al., 2009; Menon and Rao, 2012)

Source	**Composition (%)**			
	Cellulose	**Hemicellulose**	**Lignin**	**Extractives**
Hardwood	43 – 47	25 – 35	16 – 24	2 – 8
Softwood	40 – 44	25 – 29	25 – 31	1 – 5
Corn Cob	35 – 45	35 – 40	6 – 15	5
Corn Stover	35 – 40	20 – 25	11-19	5-9
Cotton Stalk	35 – 40	20 – 25	15 - 20	10 – 15
Wheat Straw	30-35	45-50	15	5
Switch Grass	35-45	25-35	15-20	5-15
Sunflower Stalk	32	41	17	10
Barley Hull	34	36	19	1

Cellulose and hemicellulose are polysaccharides of different carbohydrate monomers and lignin, being the third main component of the lignocellulosic biomass, consists of phenolic monomers. In the structure of lignocellulose, hemicellulose surrounds the cellulose fibers and link cellulose to lignin (Figure 1.2). As for the lignin, it provides a protective sheath and holds the fibers of polysaccharides together with high rigidity by concentrating between the outer layers of the fibers (Stöcker, 2008).

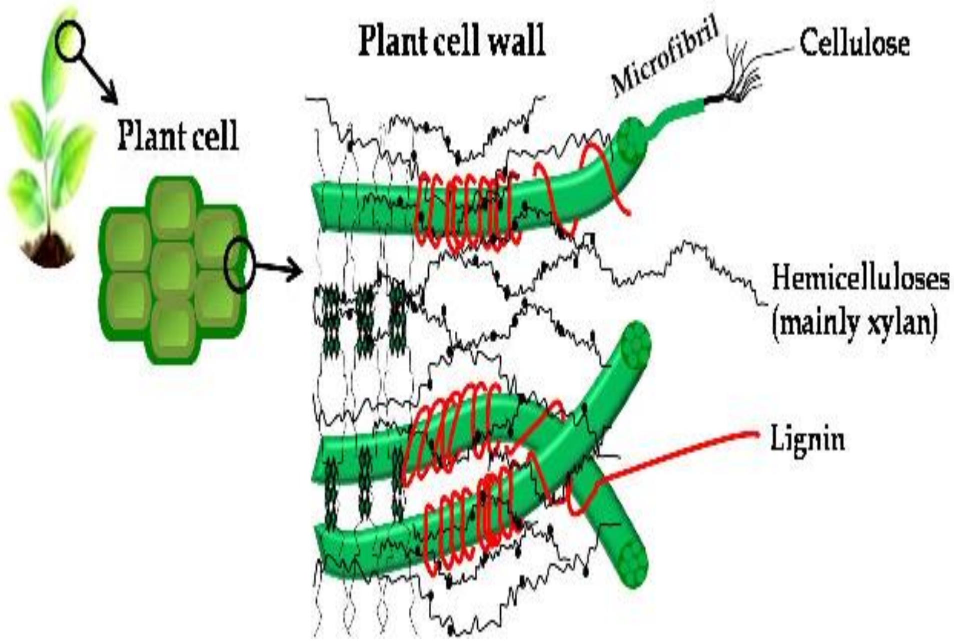


Figure 1.2 Structure of lignocellulosic plant biomass (Tomme et al., 1995).

1.2.1. Cellulose

Cellulose is the main component of lignocellulosic biomass, which consists of seven hundred to over ten thousand linearly β (1→4) linked D-glucose molecules (Figure 1.3) (Menon and Rao, 2012). It is a highly crystalline and low density polymer, and it is the most abundant natural organic compound (Stöcker, 2008).

Cellulose can be found in the woody fraction of plants such as stalks, cobs and stems (Lehninger et al., 2005). Moreover, cellulose can be obtained by the recycling of agro-fiber based products such as waste wood or paper (Marsh and Bugusu, 2007). Biosynthesis by green algae or some bacteria is another way to obtain cellulose (Jonas, 1998). Since cellulose chains contain multiple hydroxyl groups, many intra and inter-hydrogen bonds are present between the hydrogen and oxygen atoms holding the cellulose chains together while forming larger microfibrils with a very high tensile strength and modulus (Jarvis, 1984).

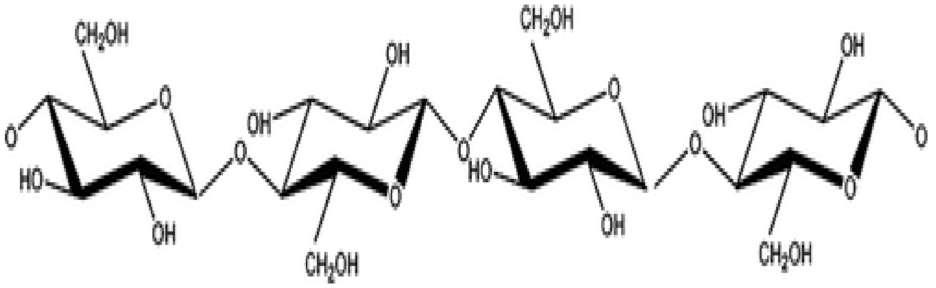


Figure 1.3 Structure of cellulose (Fincher et al., 2004)

The most important application of cellulose and its derivatives is the production of paper. Wood pulp is a major cellulose source for paper and paperboard production. After some chemical or mechanical modifications of wood pulp, lignin is removed by bleaching process and white pulp, pure cellulose, is used to produce paper (Figueiredo et al., 2010). Cellulose can also be utilized in the textile industry for the production of cotton, rayon and Lyocell. Rayon manufacture begins with cellulose, mostly from wood pulp. The utilization of caustic soda immersion and carbon disulfide reaction in the process creates environmental problems.

Lyocell, another artificial cellulose fiber, is generated in the recent years by directly dissolving wood pulp in a non-toxic chemical solvent followed by spinning. For this reason, Lyocell production is a less damaging process than rayon manufacturing (Miao and Hamad, 2012). Many derivatives of cellulose such as cellulose acetate, cellulose phthalate and hydroxymethyl cellulose phthalate have been used in pharmaceutical applications (Figueiredo et al., 2010).

Chemical or enzymatic hydrolysis of cellulose produces individual glucose monomers which are utilized as raw material in many industrial processes. Glucose molecules can be converted into various biochemicals including ethanol as biofuel, by using fermentation technologies. Physical, chemical or biological pretreatment of lignocellulosic biomass is always required to enhance the product yields prior to the enzymatic hydrolysis (Zheng et al., 2009). Production of bioethanol from biomass can reduce the depletion of crude oil reserves as well as preventing the environmental pollution.

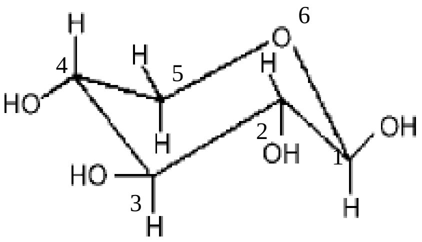
Bacterial cellulose, which is normally of crystalline structure have many applications such as stabilizer of cosmetics or food emulsions to maintain viscosity and improvement of binders for nonwoven fabric or paper restoration (Weyerhaeuser, 1989). Furthermore, bacterial cellulose can be applied for human therapy in the cases of skin burns, ulcers and dental implants (Biofill, 1986).

1.2.2. Hemicellulose

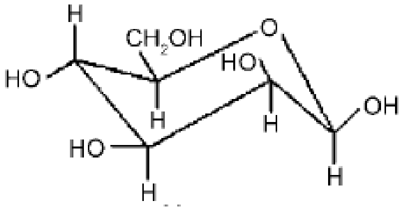
Hemicellulose is the second most abundant biopolymer in nature with the existence of 25-35% of lignocellulosic biomass. Xylans (xyloglycans), mannans (mannoglycans), β-glucans and xyloglucans are the main classes of hemicelluloses depending on the backbone-chain composition (Hansen and Plackett, 2008).

Among these, xylan presents as the most common hemicellulose type. Hardwood hemicelluloses usually include xylans, whereas softwood hemicelluloses include glucomannans (Saha, 2003). In most cases, hemicelluloses are smaller molecules than cellulose, having a degree of polymerization between 30 and 300 (Eremeeva, 1993). They present in non-crystalline structure as well as being in hydrophilic nature. In addition, hemicelluloses are alkali soluble and they can be easily isolated from biomass by alkaline hydrolysis. They can also be hydrolyzed into monomers with acids (Sun, 2008).

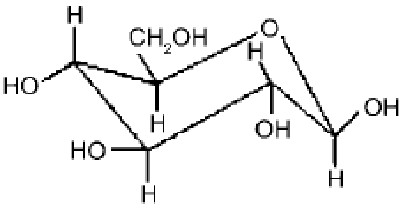
Hemicelluloses might also be classified as pentosans or hexosans with chemical formulas of $(C_5H_8O_4)_n$ and $(C_6H_{10}O_5)_n$, respectively (Sun, 2008). Differently from cellulose, hemicellulose has a heterogeneous structure consists of branched polysaccharides of pentose (xylose, arabinose) and hexose (mannose, glucose, galactose) groups and sugar acids (glucuronic acid) (Saha, 2003). The structures of hemicellulose monomers are given in Figure 1.4.



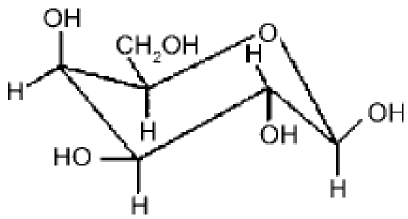
Xylose



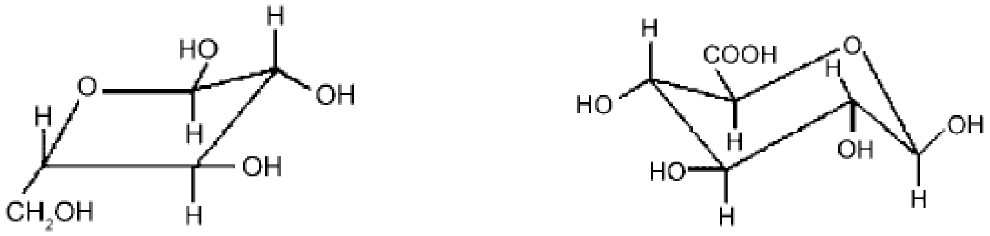
Mannose



Glucose



Galactose



Arabinose

Glucuronic Acid

Figure 1.4 Monomer components of hemicellulose (Stöcker, 2008).

The configurations of most abundant hemicelluloses are shown in Table 1.2. According to Table 1.2, while galactoglucomannan, arabinoglucuronoxylan and arabinoxylan occur in softwood hemicellulose and have a degree of polymerization as 100, glucuronoxylan and glucomannan are found in hardwood hemicellulose and have a DP as 200. In each hemicellulose monomer, three entries are presented in addition, the letter descriptions of D and L are referred to a standard configuration for two optical isomers of glyceraldehyde at each entry. The configuration of the hydroxyl group at the first carbon atom is referred by the letters of α and β (Hansen and Plackett, 2008). While the first entry is an abbreviated form of the sugar name, the second entry signifies the ring structure. Moreover, the third entry is a shortening usually used for the sugar residue in polysaccharides (Pettersen, 1984). Mannans usually exist in acetylated form. The arabinose residues in xylan, usually attached to C-3 atom of a xylose monomer.

Table 1.2 Major components of some hemicellulose types (Pettersen, 1984).

Hemicellulose Type	**Occurrence**	**Composition**			**DP$_n$**
		Units	**Molar Ratios**	**Linkage**	
Galactaglucomannan	Softwood	β-D-Man*p* β-D-Glu*p* α-D-Gal*p* Acetyl	3 1 1	1→4 1→4 1→6	100
Arabinoglucuronoxylan	Softwood	β-D-Xyl*p* 4-*O*-Me-α-D-Glu*p*A α-L-Ara*f*	10 2 1.3	1→4 1→2 1→3	100
Glucuronoxylan	Hardwood	β-D-Xyl*p* 4-*O*-Me-α-D-Glu*p*A Acetyl	10 1 7	1→4 1→2	200
Glucomannan	Hardwood	β-D-Man*p* β-D-Glu*p*	1 2	1→4 1→4	200
Arabinoxylan	Softwood	β-D-Xyl*p* 4-*O*-Me-α-D-Glu*p*A α-L-Ara*f*	3 3 2	1→4 1→4	100

DP$_n$: Degree of Polymerization

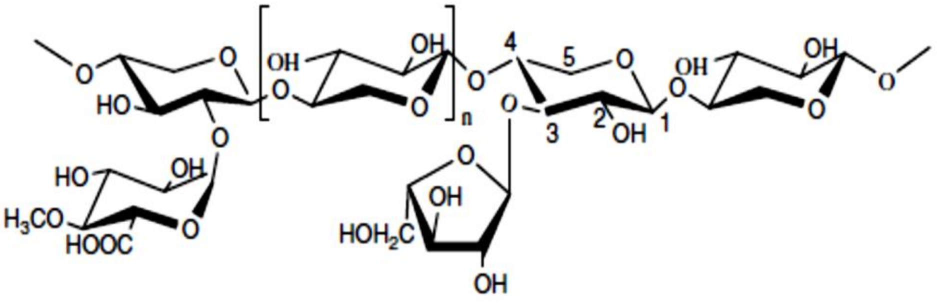
1.2.2.1. Xylans

Xylans are formed particularly by xylose monomers. All of xylan variations are formed by β (1→4) linked D-xylopyranose backbone, but can have different compositions depending on the biomass sources (Ebringerova et al., 2005).

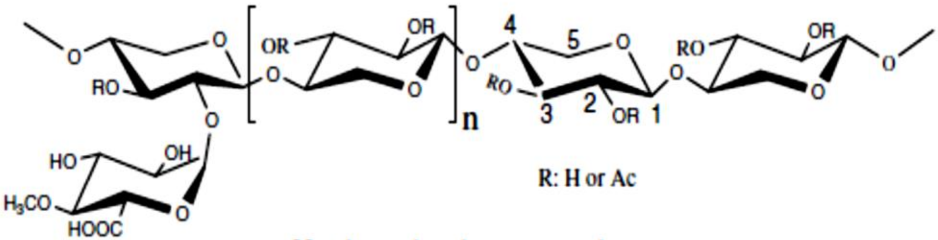
For example, wheat arabinoxylan contains 65.8% xylose, 33.5% arabinose, 0.1% mannose, 0.1% galactose and 0.3% glucose while corn fiber xylan contains 48–54% xylose, 33–35% arabinose, 5–11% galactose, and 3–6% glucuronic acid (Gruppen et al., 1992; Doner, et. al.1987).

Xylans can be obtained by the extraction of plant-based agricultural and forestry by-products or wastes such as straws, stalks, husks and hulls of various crops, wood chips and saw dust. Cereals (wheat, rye, barley, oat, rice, corn, sorghum) contain mostly arabinoxylans, whereas hardwoods contain mostly glucoronoxylans (Fincher and Stone, 1986). They can be isolated via different methods including alkaline, ammonia or dimethyl sulfoxide (DMSO) extraction, as well as steam or microwave treatment (Ebringerova et al., 1996; Lindblad and Albertsson, 2005; Rowley, 2013).

In general, xylans develop a structural pattern classified by a main backbone of β (1→4) linked xylopyranose residues, with side chains of D-glucuronic acid (or its 4-*O*-methyl derivative) and L-arabofuronase attached at the C-2 position (Hirst, 1959). The distribution of side chains in heteroxylans is reported as an important aspect affecting their solubility, interactions with other polymeric cell wall substances, solution behavior, enzyme degradability and other functional properties (Ebringerová et al., 2013). The most important xylans are categorized as *O*-acetyl-4-*O*-methyl-D-glucuronoxylans and L-arabino (4- *O*-methyl- D-glucurono) xylans (Sun, 2008) as given in Figure 1.5. Xylan structures of cereal straws and grasses are identical to structure of wood xylans (Saha, 2003).



Softwood - arabinoglucuronoxylan



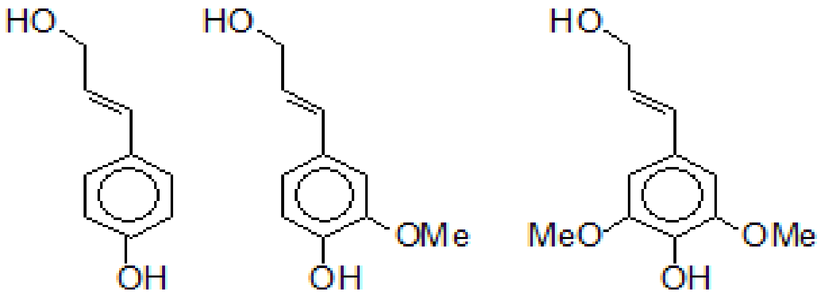
Hardwood - glucuronoxylan

Figure 1.5 Structure of softwood arabinoglucuronoxylan and hardwood glucuronoxylan (Pu et al., 2011)

Xylans have different applications in the industry, for instance xylooligosaccarides, which are generated by the autohydrolysis of xylan, can be utilized in the pharmaceutical, food and cosmetic sectors (Garrote et al., 2002). Xylan hydrolysate can be converted to xylitol, which is a sweetener alternative to sucrose (Kim et al., 1999). Xylans also have a role in bread making as additives due to their high water binding capacity (Sedlmeyer, 1984). In the recent years, biodegradable film and coating production from xylans receive significant interest, particularly due to the good oxygen barrier properties of xylan based polymeric materials, which makes them suitable for food packaging applications (Hansen and Plackett, 2008).

1.2.3. Lignin

Lignin represents the third largest fraction of plant based biomass, constituting around 15-25% of whole dry biomass (Sjöström, 1993). Among the plant cell wall polymers, lignin is the only polymer that does not contain carbohydrate monomers. Oxidative coupling of three major phenylpropane units, namely, coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol (Figure 1.6) create the lignin molecules (Sun, 2008). The frequency of functional groups such as methoxyl, phenolic hydroxyl, benzyl alcohol or carbonyl groups defines the conformation of lignin with the linkages of mostly ether or carbon-carbon bonds present between the subunits (Sjöström, 1993). A schematic representation of the lignin molecule is given in Figure 1.7.



Coumaryl Alcohol Coniferyl Alcohol Sinapyl Alcohol

Figure 1.6 Structure of three phenylpropane monomers in lignin (Boerjan et al., 2003).

Lignin plays an important role providing mechanical support to hold plant fibers together as well as constituting a three dimensional structure in plant cell walls. In the plant cell walls, the water absorption capacity of polysaccharides can

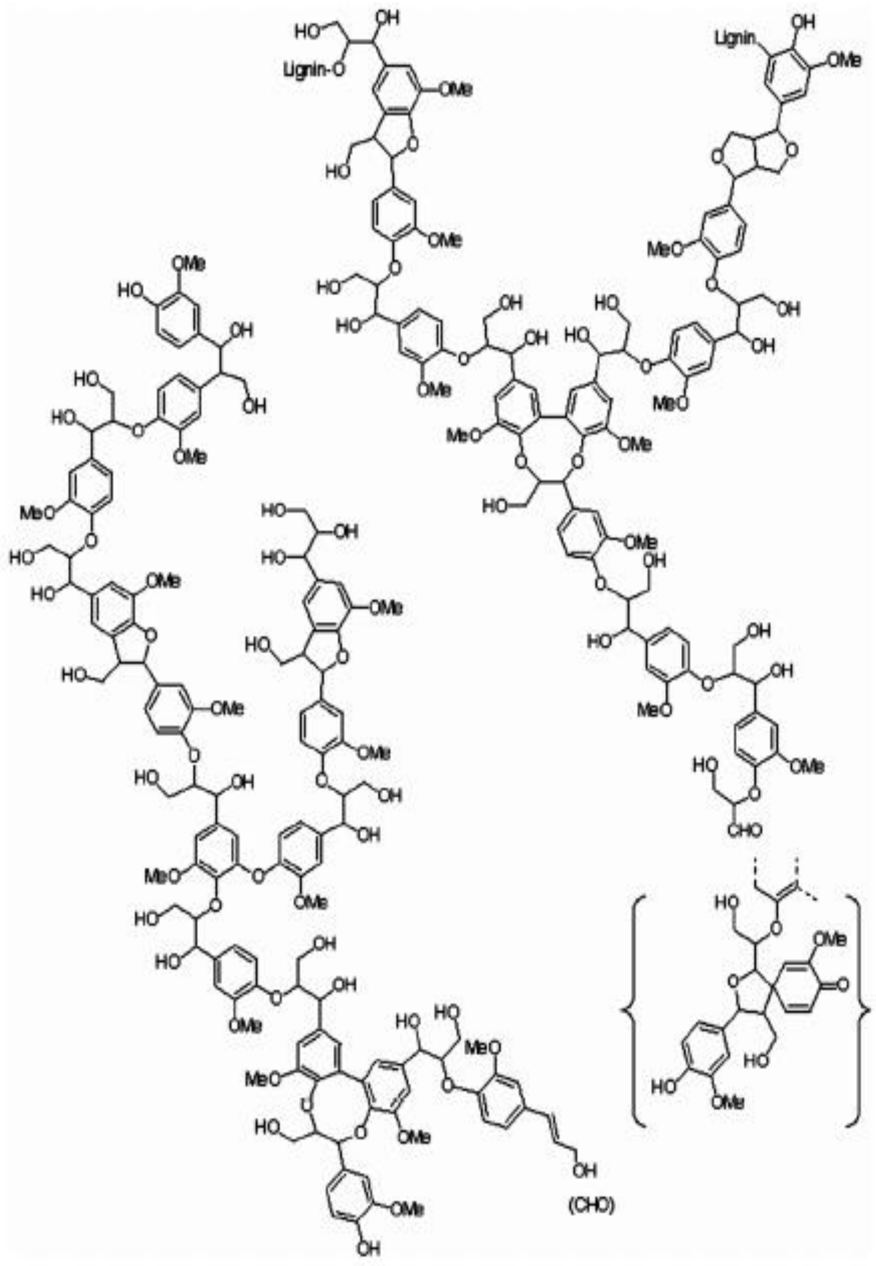


Figure 1.7 Schematic structure of softwood lignin (Adler, 1977 and later modified by Karhunen et al., 1995).

decrease by the presence of lignin, which is a good transporter of water and nutrients (Sarkanen et al., 1971).

Lignin is undesirable in most papermaking processes, and it is removed by pulping and bleaching processes. In the pulp and paper industry, lignin extracted from lignocellulosic materials is used to generate energy and some chemicals. These products include epoxy resins, phenolic resins for board production, and materials for automotive industry and biodispertants (Danielson and Simonson, 1998; Gargulak and Lebo, 2000, Lora and Glasser, 2002 and Gosselink et al., 2004).

Commercial lignin can be classified into two groups, sulfur-containing and sulfur-free lignins (Mansouri and Salvado, 2006). Sulfur-containing lignins, which are also called conventional lignins, include Kraft lignin and lignosulfonates. They are more accessible compared to sulfur-free lignins.

Sulfur-free lignins can be produced from many different processes including soda, steam explosion, hydrolysis, organosolv and oxygen delignification (Mansouri and Salvado, 2006). Lignosulfonates, the most important lignin derivatives, can be utilized in concrete and cement production, oil industry, dye and pigment production and metallic ore processing (Doherty et al., 2011; Kamoun et al., 2003). Moreover, kraft lignin can be used as a precursor for carbon fiber production (Brodin, 2009).

1.3. The Biomass Potential of Turkey

Turkey is a developing country with a critical geographical location between the continents of Asia, Europe and Africa and is one of the major agricultural countries of the world having 23.07 million ha agricultural arable land (Acaroglu et al., 1999). Of this arable land, 18.11 million ha is cultivated and the remaining part is left for cultivation in the following year (Kocar, 2013). Total amount of agricultural waste products in Turkey is recorded approximately as 40-53 million tones (Acaroglu et al., 1999). Major agricultural residues produced as biomass source in Turkey are shown in Table 1.3. Wheat straw is the leading agricultural residue produced in Turkey followed by barley, cotton and sunflower residues. In addition to various biochemical and energy production, these materials can be promising resources for biodegradable polymers.

Table 1.3 Production of agricultural residues in Turkey (Acaroglu, 1999).

Crop Residue	**Total Residues (Ton)**		**Utility Residue (ton)**	**Utility (%)**
	Theoretical	**Real**		
Wheat Straw	29,170,785	23,429,907	3,514,486	15
Barley Straw	9,992,948	8,963,012	1,344,452	15
Cotton Stalk	6,137,181	2,520,281	1,512,169	60
Sunflower Stalk	2,341,554	2,259,121	1,355,472	60
Corn Stover	596,592	1,907,307	1,144,384	60
Rice Straw	582,555	209,532	125,719	60
Cotton Ginning	481,527	732,220	585,776	80
Oat Straw	419,678	321,236	48,185	15
Rye Straw	405,188	358,040	53,706	15
Tobacco Stalk	362,763	410,778	246,467	60

Peanut Straw	127,054	-	-	-
Rice Hull	88,527	77,747	62,198	80
Soybean Straw	60,468	21,872	13,123	60
Peanut Hull	27,621	28,638	22,910	80

1.4. Food Packaging Materials

Today, the materials used for food packaging are produced from a variety of petroleum-derived polymers, paper and cardboard, metals, glass, or combinations of these with exploiting functional properties of each material (Weber et al., 2001). Unfortunately, most of these materials, especially polymers are non-renewable, not environment-friendly and accumulate in nature. Therefore, developments are necessary in the production of food packaging materials considering the environmental impact of this industry.

The food packaging materials are required to protect the food from environmental effects and to preserve the freshness of nutrients during the specified shelf life of a food product. The selection of packaging material and packaging technique is very important to prevent the product from external influences as well as to delay the deterioration of food by chemical, physical or biological effects (Marsh and Bugusu, 2007). In terms of chemical protection, food packaging provides a barrier against gases (O_2, CO_2, and N_2) and light. It also prevents moisture loss or gain of the product, its non-enzymatic browning and lipid oxidation (Petersen et al., 1999). Moreover, microbial growth or enzymatic changes inside the packaging material should be limited or prevented by biological protection (Marsh and Bugusu, 2007). Finally, physical packaging protects the food from mechanical destruction that might occur due to crash, vibrations or compression. Mechanical properties such as tensile strength, elastic modulus, puncture resistance and elongation of a material selected for food packaging should also be considered (Petersen et al., 1999).

Another issue that needs to be taken into consideration is the impact of food packaging materials on the environment. Considering the huge amount of food consumption in the world, enormous amounts of packaging wastes are accumulated and polluted the environment. Therefore, packaging materials should be degradable in the nature. Finally, production cost of packaging materials is another point that should be considered. At present, even if the cost of biobased packaging materials is more expensive than the conventional packaging materials, new processing technologies can be developed to reduce the production cost (Petersen et al., 1999).

1.4.1. Petroleum Based Synthetic Polymers

The largest part of materials utilized in packaging industry such as polyethylene, polypropylene or polyvinyl chloride are thermoplastic synthetic polymers produced based on petroleum. Synthetic polymers have been preferred as packaging materials due to their suitable processing and packaging properties and low cost. Moreover, they are recyclable since they can be easily melted and reused as raw materials for further products (Marsh, 2007).

Polyethylene (PE) is used widely in packaging industry due to its low cost, moderate gas and humidity barrier properties (Roy, 2011; Vasile, 2013). There are two different types of PE: low density and high density. Low density polyethylene (LDPE) is preferred in film applications due to its transparency and considerable flexibility (Marsh, 2007). It can also be used as an additive in biodegradable films, such as starch-based and chitosan-based films, to enhance their mechanical and thermal properties (Arvanitoyannis, 1998; Vasile, 2013). On the other hand, high density polyethylene (HDPE) is used for the production of bottles for drinks, food containers, grocery and trash bags since it is stronger and stiffer than LDPE.

Polypropylene (PP) is another thermoplastic polymer, which is widely used for food packaging. It has a moderate barrier to moisture, gases and odours. Oriented polypropylene has a clear glossy apperance with good optical properties and high mechanical properties (Bowditch, 1997).

Polyvinyl chloride (PVC) is used in the production of food packages including bottles and films, due to its poor permeability to chemicals, low density, easy processibility and high transparency (Leadbitter, 2003). It is stiff, ductile, medium strong, amorphous and transparent material. It can be transformed into flexible materials with the addition of plasticizers (Marsh, 2007). However, PVC causes problems related to public health as a result of its chlorine content during the processes of manufacturing, packaging, recycling and reproduction (Kao, 2012).

Despite being widely used, packaging materials derived from synthetic polymers cause serious global environmental problems. Biodegradable film production using bio-based packaging materials will lead to a decrease in the pollution of the environment. The future generation of packaging materials is expected to be produced based on renewable resources.

1.4.2. Biodegradable Polymers

Biodegradation is basically a process that decomposes organic substances by living organisms such as bacteria or other microorganisms found in the environment. The rate of biodegradation depends on temperature, humidity, type and abundance of microorganisms in the environment besides the nature of the material to be degraded (Siracusa et al., 2008). In the case of synthetic substances like synthetic polymers, degradation rate is affected by the nature of the functional groups and the polymer reactivity with water and catalysts (Siracusa et al., 2008). The increase in crystallinity, macromolecular weight, hydrophobic character of the polymer and presence of metal impurities, decreases the rate of biodegradability (Karlsson and Albertsson, 1998).

Biodegradable polymers can be categorized as nature-based or human-made (synthetic) polymers (Figure 1.8). The nature-based biodegradable polymers can be classified in three groups.

1. Polymers isolated from biomass; for instance, polysaccharides such as starch, cellulose or chitosan and proteins such as casein or gluten. These materials are hydrophilic and crystalline, which may cause processing and performance problems in packaging applications (Petersen et al., 1999). Among these polymers, the most important commercial materials are cellulose-based and starch-based materials (Weber et al., 2010).

2. Polymers produced by classical chemical synthesis using renewable monomers. Polylactic acid (PLA), a biopolyester polymerized from lactic acid monomers, has the highest application potential for this category (Petersen et al., 1999). The monomers of PLA are produced biotechnologically via fermentation of carbohydrate feedstocks (Hujanen et al., 1998).

3. Polymers produced by microorganisms or genetically modified bacteria. Polyhydroxyalkanoates (PHA), mainly polyhydroxybutyrates (PHB) are produced by many bacterial species, and they can be modified chemically in order to tune their properties (Anderson et al, 1990). Bacterial cellulose also has an increasing potential in the food packaging industry where it is not used extensively at present (Iguchi et al, 2000).

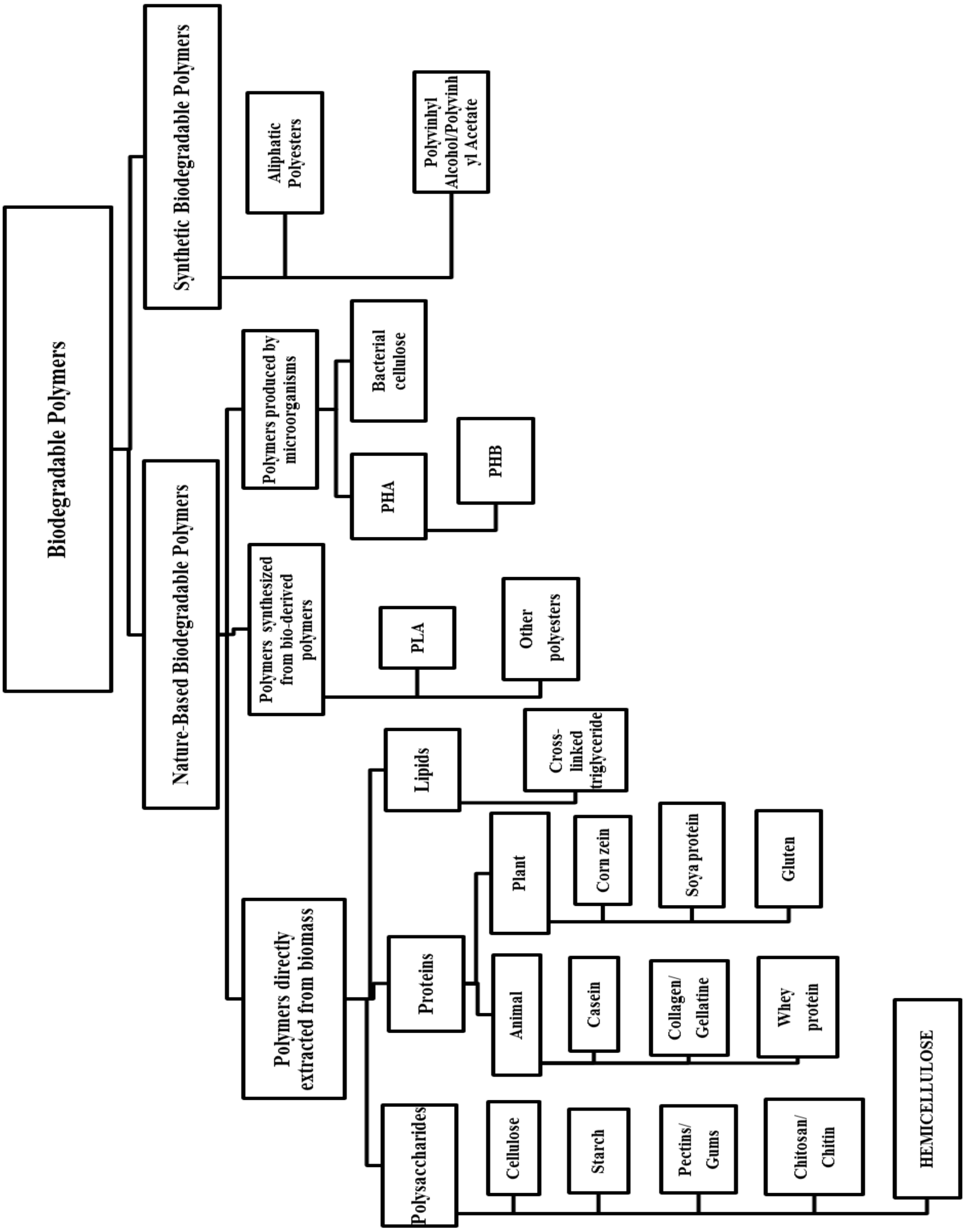


Figure 1.8 A schematic presentation of biodegradable polymers.

In a similar manner to conventional synthetic polymers, the production methods of biodegradable films can be classified into two categories as dry and wet processing (Rhim and Ng, 2007). The dry processes include extrusion, compression or injection molding of polymers. The wet processes rely on the preparation of a film forming solution followed by the evaporation of solvent in order to obtain the film where solvent casting is the most frequently utilized wet processing technique (Rhim and Ng, 2007). While, starch, PLA and protein films may be processed with dry processing, optical or medical films are generally processed by wet processing techniques (Zhang, et al., 2001; Rhim and Ng, 2007).

Among dry processes, extrusion is a method of processing the raw material into a product in the desired shape by forcing the polymer through a die under specified conditions (Breitenbach, 2002). Production rate and operation temperature can be fixed in an extruder. The feed (polymer) can have different shapes such as granules or powder. Basically, an extruder involves two parts: a die system for shaping the product and a conveying system that is capable of transporting the product to the die (Breitenbach, 2002). The extrusion channel consists of three sections including feed zone, transition zone and metering zone (Breitenbach, 2002). Following its transportation from the feed zone, the material is mixed, compressed and plasticized with melting at the transition zone (Johnson, 1982). Compression molding is advantageous to solvent casting method due to its simplicity and potential of producing films without polymer solubilization. Injection molding is a frequently utilized dry processing method where it is especially used for the production of objects rather than films.

Solvent casting method consists of three stages, including solubilization of a polymer in a solvent, casting of the film forming solution and evaporation of the solvent to create a film matrix on a flat surface (Rhim and Ng, 2007). Solvent casting is particularly suitable for the production of optical films and medical films in addition to sheet forming for electronic applications (Siemann, 2005). This method enables the production of high quality films with homogenous thickness, high optical purity and high transparency but at a high cost because of its energy-intensive and slow nature (Siemann, 2005; Rhim and Ng, 2007). Therefore, dry processing methods are preferred in large-scale applications.

1.4.2.1. Starch Based Biodegradable Polymers

Starch is an abundant and low-cost polysaccharide produced generally from corn, cereal grains and potatoes (Lourdin et al., 1995). Starch is composed of two macromolecules, amylose and amylopectin. Although the monomers of both amylose and amylopectin are glucose, amylose is a linear polymer whereas amylopectin is a branched polymer (Lörcks, 1997). In nature, starch exists in granular form. Melting process of dry granular starch without any treatment is difficult because of thermal degradation (Nafchi et al., 2012). Thermoplastic starch (TPS) can be produced by the disruption of starch granule structure by thermal and mechanical processing with low water content and in the presence of plasticizers (Bastioli, 2001). Starch is frequently processed by using extrusion, film blowing or foaming technologies, however, starch based films can also be produced by the utilization of solvent casting technique (Paes et al., 2008; Mensitieri et al., 2011).

The main disadvantage of starch is its hydrophilic nature, which limits its use in high moisture environments. Starch-based polymers also have poor mechanical properties compared to other thermoplastic materials (Carvalho et al. 2008). Water resistance and mechanical properties of starch can be improved by lamination with some synthetic polymers such as polyvinyl chloride or polyethylene (Shogren et al., 1993).

1.4.2.2. Cellulose Based Biodegradable Polymers

Cellulose, as a renewable and biodegradable biopolymer, has a high potential to be utilized as raw material for the production of packaging materials (Rhim and Ng, 2007). Mechanical properties of cellulose based films depend on the molecular weight of cellulose (Krochta et al., 1997). Many cellulose derivatives exist including the cellulose ethers, methylcellulose (MC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), and hydroxypropyl methylcellulose (HPMC), as well as the cellulose esters, cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB) (Rhim and Ng, 2007). Being water soluble and compatible with other biopolymers, CMC has excellent properties for film production (Tharanathan, 2003). CMC based films are efficient barriers to oxygen, carbon dioxide and lipids but it has poor resistance to water vapor transmission (Ghanbarzadeh, 2011). Currently, CA is added into films or to injection molded thermoplastics in fibrous form to obtain functional materials that have higher mechanical and thermal properties (Rhim and Ng, 2007). However, the gas and moisture barrier properties of CA films are not well enough for food packaging applications (Petersen et al., 1999). Because CA films allow gas permeability and reduce fogging, they are used for high-moisture products such as bakery products (Hanlon, 1992).

Cellophane, a regenerated cellulose film, is produced by dissolving cellulose in a toxic mixture of sodium hydroxide and carbon disulphide and recasting in acid solution (Petersen et al., 1999). Due to its poor moisture barrier properties, cellophane is usually coated with nitrocellulose wax or polyvinylidene chloride (Krochta et al., 1997).

1.4.2.3. Polylactic Acid Based Biodegradable Polymers

Polylactic acid (PLA) is one of the most promising biodegradable polymers, and it is produced by the polymerization of lactic acid, which is obtained via the fermentation of a sugar feedstock (Cabedo et al., 2006). It has desired properties such as high transparency, high molecular weight, high mechanical strength and low toxicity while it has low thermal stability (Siracusa et al., 2008; Jamshidian et al., 2010). PLA can be processed using different technologies such as solvent casting, extrusion, blow molding, thermoforming and injection molding (Jamshidian et al., 2010).

The major PLA applications existing are in the food packaging industry (70%) where these applications include the packaging of fresh products such as, fruits, vegetables and salads, as well as the production of beverage bottles, cereal bags and bakery containers (Vink et al., 2004). However, some developments are still required to enhance the properties of PLA in order to make PLA competitive with petroleum-based plastics in challenging applications. For instance, oxygen permeability of PLA should be reduced for the packaging of oxygen sensitive foods (Auras et al., 2003).

1.4.2.4. Polyhydroxyalkanoates Based Biodegradable Polymers

Polyhydroxyalkanoates (PHA) are produced by bacterial fermentation of various lipids and sugars. Depending on the monomer, they can be formed as thermoplastic or elastomeric polymers (Tharanathan, 2003). Blending PHA with starch results improvement in mechanical and thermal properties (Godbole et al., 2003). Polyhydroxybutyrate (PHB), the most frequent type of PHA, is formed via the polymerization of 3-hydroxybutyrate monomer. PHB has similar properties with PP but it is stiffer and more brittle (Siracusa et al., 2008). Various modifications are applied to PHB to improve its mechanical properties including the addition of nucleating agents, plasticizers or lubricants during the processing (El-Hadi et al., 2002). PHA and its derivatives have a very high cost due to their limited production (Siracusa et al., 2008). The use of food waste as an alternative way for the production of PHAs is under investigation (Siracusa et al., 2008).

1.5. Hemicellulose Based Biodegradable Films

Cellulose, starch, PLA and PHA are the biodegradable polymers that are available in market (Robertson, 2008). Various applications have been recognized for hemicelluloses including film products, food coatings and biomedical uses (Hansen and Plackett, 2008). Hemicellulose does not compete with food products unlike other biodegradable polymers such as starch, PLA and PHA (Mikkonen and Tenkanen, 2012). Moreover, it is a promising material for food packaging industry due to its low oxygen permeability values compared to amylopectin, chitosan, polyvinyl alcohol (PVOH) and ethylenevinyl alcohol (EVOH) based materials (Gröndahl et al., 2004).

In the nature, polysaccharides exist as hydrophilic polymers because of their high hydroxyl group content. The film structure and properties may vary with water content since water acts as a plasticizer for the films. The water sensitivity of hemicelluloses makes their use quite challenging in practical packaging applications. However, there are a number of studies that focused on the production of more hydrophobic films based on hemicellulose. With this purpose, some modifications such as esterification or acetylation were applied on hemicellulose films (Jain et al., 2000; Moine et al., 2004). It is also possible to reduce water sensitivities of xylan films by developing laminates with a hydrophobic structure (Peroval et al., 2002).

1.6. Aim of the Study

Environment-friendly biodegradable polymers and materials produced from agricultural residues have become one of the most widely studied research subjects in recent years mostly due to the undesired properties of the petroleum based synthetic polymers. There are lots of studies about biodegradable films produced from renewable materials such as polysaccharides, lipids, proteins or derivatives of sugar monomers. Hemicellulose, the second most abundant polymer among plants after cellulose, has limited applications in industry compared to cellulose. Hence, the research on hemicellulose based biodegradable films may extend the utilization areas of hemicellulose.

Lignocellulosic agricultural residues are by-products of cultivation industry and they cause disposal problems related to their under-utilization. Utilizing agricultural residues as a raw material for hemicellulose based biodegradable film production has many benefits due to the abundance, low cost and easy accessibility of these agricultural wastes.

The study focuses on the production of hemicellulose based films from different lignocellulosic biomass resources including corn cob, wheat straw and sunflower stalk. For this purpose, hemicellulose was isolated from these agricultural wastes via alkaline extraction at two different temperatures followed by the conversion of the isolated hemicelluloses into films, which was accomplished via two different techniques: extrusion and solvent casting. The extrusion conditions in terms of temperature and screw speed were evaluated. Finally, the effect of the film production techniques was compared in terms of the mechanical, thermal and morphological properties of the films.

CHAPTER 2

LITERATURE SURVEY

Hemicellulose Based Films

Gabrielii et al. studied (1999) hemicellulose isolation, characterization and utilization for hydrogel production. The hemicellulose was separated from aspen wood via alkali extraction with hydrogen peroxide treatment. The weight and number average molar masses were calculated as 73,100 g/mol and 48,000 g/mol respectively. Xylan and chitosan were mixed in different ratios to analyze their effect on film forming properties. On account of lower molar mass of xylan, more brittle films were produced when the components were mixed in higher xylan/chitosan ratio. No film formation was observed from pure xylan. However, films were produced with the addition of 5% chitosan and above. Moreover, the crystallinity of films was reduced with the addition of chitosan, which was verified by the analysis of X-ray spectroscopy. The film and hydrogel forming properties were attributed to crystalline domains of xylan connected to the chitosan chains and to electrostatic interactions between the amino groups of chitosan and the acidic groups of hemicellulose.

Kayserilioglu and coworkers (2002) have investigated the effect of xylan addition on wheat gluten based biodegradable film production. Films were produced by solvent casting method with 2% (w/w) glycerol addition and drying at two different conditions, 80°C and 35% relative humidity and uncontrolled conditions.

The film forming solutions were prepared at acidic or basic pH. At pH 4, a uniform solution could not be achieved without xylan addition. In this case, film formation was observed with the addition of xylan up to 20%. On the other hand, at pH 11, the film formation was observed for all xylan concentrations lower than 40%. According to mechanical test results, drying under controlled conditions would not be necessary, since no improvements were observed. Films prepared at pH 11 showed better mechanical properties compared to the films prepared at pH 4. Use of corn cob or grass xylan reduced the tensile strength and elastic modulus of films, however elasticity of gluten films increased 3-fold by adding corn cob xylan. No significant difference in water vapor transfer rates was observed with xylan addition.

Whistler et al. (2004) studied the water vapor permeability of solvent casted corn hull arabinoxylan films. Composition of AX was determined as 31% L-arabinose, 49% D-xylose, 6% D-galactose, 11% D-glucose and glucuronic acid in mole percentages. The molecular weight of AX was reported as 50,600 g/mol. Glycerol, sorbitol or propylene glycol were added to the film forming solutions as plasticizers in the range of 0-20%. The plasticizer use reduced water vapor permeabilities of AX films. All of the films were smooth, homogenous, stable and transparent. The best mechanical properties were observed in 0.163 (wt/wt) propylene glycol added films, 60.7 MPa tensile strength and 7.9% elongation. Sorbitol plasticized films showed good moisture barrier properties.

Höije et al. studied (2005) the characterization of barley husk arabinoxylan isolated by different methods including enzyme or hydrochloric acid pretreatment, organosolv or chlorite delignification as well as alkali extraction and film formation. The highest content of AX was obtained with a yield of 83% in the chlorite- delignified sample. The average molecular weights were determined as

35,000 - 45,000 g/mol by size exclusion chromatography (SEC). Strong, stiff and mildly brittle films were obtained by casting. Films showed approximately a tensile strength of 60 MPa and 2.5% strain at 23^{o}C and 50% relative humidity conditions.

Plasticized glucuronoxylan films were prepared from aspen wood by Gröndahl and coworkers (2004). The plasticizers, sorbitol or xylitol, were added in the ratios of 20, 35 and 50% of dry weight to reduce the glass transition temperature. Semicrystalline films were obtained with approximately 40 MPa UTS and 2% elongation by the addition of 20% of sorbitol or xylitol. The addition of more xylitol or sorbitol resulted in reduction in tensile strength and Young's modulus, but increase in elongation. Polyvinyl alcohol films, which are commercially used synthetic polymeric materials, were also prepared to compare the oxygen permeability properties of glucuronoxylan films. The films with 35 wt. % sorbitol exhibited excellent oxygen barrier properties at 50% RH which is lower than plasticized starch and ethylene vinyl alcohol (EVOH).

Hartman and coworkers (2005) worked on the oxygen barrier properties of hemicellulose based films. A mannan type hemicellulose, O-acetyl-galactoglucomannan (AcGGM), was obtained from industrial process water in thermomechanical pulping process. The average molecular weight of AcGGM was determined as 10,000 g/mol by size exclusion chromatography. Films were formed by dissolving the polymer in water at 95^{o}C for 20 minutes and then solvent casting. Xylitol, glycerol or sorbitol were used as plasticizers to cure brittleness of the films. Two-component films were also prepared with the addition of alginate or carboxymethylcellulose (CMC) to increase stability against moisture. By using glycerol and alginate together, favorable results were obtained in terms of oxygen permeability and handling of films as well as the mechanical and moisture resistance properties.

The effect of lignin content on xylan films was investigated by Goksu et al. (2007). With the addition of lignin in different concentrations (8-14%), film forming solutions were prepared by dissolving cotton stalk or birchwood xylan in water. Cotton stalk xylan was obtained by alkali extraction and some of lignin was removed with cold ethanol-acetic acid solution. Approximately 1% lignin (w/w) in birchwood xylan was determined to be convenient for film production. While keeping the lignin concentration constant, increasing the xylan composition from 8% to 14% improved mechanical properties in terms of tensile strength, elastic modulus and strain at break values. The most dramatic increase was observed in strain at break values that were altered from 45 to 57%. The addition of glycerol as a plasticizer increased the elongation, as well as the water vapor transmission rate; however decreased the water solubility of the films.

Edlund et al. (2010) developed barrier films and coatings from wood hydrolysate generated from pulping process of hydrothermal treatment of wood chips. They separated polysaccharides and some of lignin in the composition of 89% polysaccharides and 9% lignin through wood hydrolysate by membrane filtration. CMC or chitosan was used as co-components in the ratio of 1:1. While smooth and transparent free-standing films were obtained by using 50% (w/w) of CMC, the 50% (w/w) chitosan containing films did not appear homogenous. Afterwards, mixtures of hemicellulose and co-component (CMC or chitosan) coatings were applied on PET surfaces. Compared to uncoated PET films, tensile strength of coated films decreased from 202 MPa to 181 and 136 MPa, respectively for chitosan and CMC containing coatings. Coatings reduced the oxygen permeabilities of the films with no significant deviations in mechanical properties. Oxygen permeabilities of the films decreased to 0.8-6.2 cm^3 $\mu m m^{-2}$ day^{-1} kPa^{-1} from 14.6 cm^3 $\mu m m^{-2}$ day^{-1} kPa^{-1} by coating. Besides, coatings reduced water vapor transmission of the films.

Zhang et al. (2011) investigated the properties of arabinoxylan (AX) from wheat bran, and its potential usage in film packaging. Hemicellulose was obtained using different methods and three fractions of hemicellulose were obtained. The molecular weight of AX was in the range of 152,000 - 218,000 g/mol. The crystalline morphology and the water sorption properties of AX films were affected by the substitution degree of arabinose groups. Decrease in substitution degrees resulted in less hydrophilic and high crystalline AX.

Bahcegul et al. (2011) have studied the effect of alkaline pretreatment temperature on the co-production of glucose and hemicellulose films by solvent casting. Hemicellulose was extracted from cotton stalks with or without heat treatment at 25, 60 or 90^{o}C. Increasing the pretreatment temperature increased the hemicellulose yield whereas no significant change was observed in the glucose production yield. However, increasing temperature resulted in darker and cracked films. The best mechanical properties, 52 MPa of tensile strength and 3% elongation were obtained for the films having pretreatment temperature of 25^{o}C.

Egüés and coworkers (2013) have studied the effects of biomass type and lignin separation on film formation using 6 different agricultural wastes including corn cob, cotton waste, apple tree pruning, olive, pepper and chilli wastes. The films were produced via solvent casting. The film forming properties were enhanced by using hemicelluloses having high arabinose/xylose ratio and in the presence of lignin. Presence of lignin resulted in films having lower water solubility. In the case of corn cob based films, solubility increased from 56% to 98% by removal of lignin. Lignin contained hemicelluloses gave the value of molecular weight about 92,000-37,000 g/mol. The molecular weights of lignin free samples were varied between 20,000 and 17,000 g/mol.

Saxena et al. (2009a) produced nanocomposite films from oat spelt xylan and cellulose whiskers. Suspensions of sulfonated and hydrochloride cellulose whiskers were prepared and used for reinforcing material. Mechanical properties of oat spelt xylan films containing cellulose whisker (0-10%) and plasticizer (20-50%) were investigated. The sufficient plasticizer content was determined to be at least 50% (w/w) otherwise brittle and weak films were formed. Even though the tensile strength of the films increased by the addition of sulfonated and hydrochloride whiskers, hydrochloride whisker addition more than 5% caused a considerable reduction in mechanical strength.

The water vapor transmission properties of xylan films were investigated by Saxena and coworkers (2009b). Commercial oat spelt xylan having the composition of 81% xylose, 10% arabinose and 8% glucose was used to produce films with the addition of cellulose whiskers (0-50% wt.) as reinforcing material. Cellulose whiskers were prepared by hydrolysis of aqueous solution from softwood kraft pulping process. The incorporation of sulfonated cellulose whiskers decreased the water vapor transmission rate of films due to the formation of rigid hydrogen-bonded network of cellulose whiskers. In the case of 10% addition of cellulose whiskers, water vapor transmission rate decreased from 304 g/h.m^2 to 174 g/h.m^2.

In the another study of Saxena et al. (2011), moisture barrier properties of oat spelt xylan films reinforced with several celluloses including nanocrystalline cellulose, acacia bleached kraft pulp fibers and softwood kraft fibers were investigated. Solvent casted films having thickness of 0.09 mm were obtained. Xylan films reinforced with 10% acacia fiber and 10% hydrochloric nanocrystalline cellulose exhibited virtually no improvement in specific water vapor transmission rate in comparison to control. The highest specific water transmission rate was obtained as 807 g/h.m^2 for the xylan films containing 10%

softwood fiber and the lowest one was obtained as 174 g/h.m^2 xylan films contained 10% sulfuric nanocrystalline cellulose, while the control xylan exhibited water transmission rate was as 304 g/h.m^2. The high crystallinity of nanocellulosic composite film structure ensured to a reduction in moisture transmission.

In the study of Peng et al. (2011), mechanical improvement of xylan films was investigated by reinforcing with cellulose nano fibers (CNF). Xylan rich hemicellulose was separated from holocellulose of bamboo. CNF were synthesized from bleached sisal pulp fibers. Films were obtained by dissolving xylan in water with the addition of CNF (0-20% wt. based on the dry xylan) and sorbitol (25%), followed by drying for 10 days at 23^{o}C and 50% relative humidity. Poor mechanical properties were obtained for the films prepared from pure xylan. The addition of sorbitol did not prevent the crack formation on film surfaces, but it provided the films to be flexible and free-standing. A great improvement in film formation, thermal stability and mechanical properties were observed by the addition of 5% CNF into xylan matrix. . Young’s Modulus and tensile strength of the films increased from 735 and 11.9 MPa to 3404 and 39.5 MPa, respectively with the addition of 20% CNF indicating a strong interaction between cellulose and xylan molecules.

Bahcegul et al. (2013) studied the use of extrusion for the production of corn cob xylan based films. Xylans were conditioned at different relative humidities to determine the water content necessary for extrusion and then fed to the mini extruder at constant temperature (60, 90 or 120^{o}C). The results showed the importance of water content and extrusion temperature for being extrudable since only the xylans having 27% water could be extruded at 90^{o}C. Extruded strips had homogeneous interior structure and its mechanical properties were shown better than polylactic acid strips which used as control.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Corn cobs were provided from Hatay whereas wheat straw and sunflower stalks were obtained from Trakya Region (Malkara, Tekirdağ) in Turkey. Corn cobs were milled to pass a 10 mesh (2 mm) screen, then, the particles between sizes of 16 to 100 mesh (0.15 mm to 1.19 mm) were selected and used in this study. Wheat straw and sunflower stalks were grained to pass a 16 mesh (1.19 mm) sieve and used.

Potassium hydroxide, acetic acid, sulfuric acid, sodium hydroxide and sodium borohydride were purchased from Merck (Darmstad, Germany). Ethanol was obtained from Colony Sugar Mills Ltd. (Lahore, Pakistan).

3.2. Experimental Methods

3.2.1. Compositional Analysis of Biomass

The composition of biomass was analyzed according to the National Renewable Energy Laboratory (NREL, Golden, CO) analytical methods for biomass (NREL, 1996; 2011) procedure. Two-step acid hydrolysis was applied to examine the structural carbohydrates (cellulose and hemicellulose) and lignin (acid soluble or acid insoluble) of biomass. While the acid soluble lignin was measured with UV-Visible spectroscopy (Nicolet Evolution 100, Thermo Fisher Scientific Inc., USA), acid insoluble lignin was measured gravimetrically together with the ash content. In order to hydrolyze the biomass, 0.3 g of biomass and 3 ml of 72% (w/w) sulfuric acid were mixed in a long test tube by using a glass rod. The tube was placed in a water bath where it was incubated at 30°C for an hour. During the incubation, mixing was provided with glass rod in every ten minutes. After the incubation in water bath, 84 ml of deionized water was added into the tube to dilute 72% (w/w) sulfuric acid solution to 4% (w/w) which is autoclaved at 121°C for 1 hour. Following the hydrolysis in autoclave, the hydrolysate was vacuum filtered through the crucible, which was previously kept in a furnace at 105°C and weighed prior to the filtration. The filtrate was used to determine the amount of structural carbohydrates and acid soluble lignin (ASL). The crucible and acid insoluble lignin washed with deionized water and held at furnace at 105°C for 24 hours and then weighted for the calculation of % acid insoluble lignin (AIL) content of the biomass.

$$\text{AIL}(\%) = ((m_f - m_{crucible})/m_{biomass}) \times 100$$

Where, $m_{biomass}$ is the dry weight of initial biomass, $m_{crucible}$ is the dry weight of crucible and m_f is the final dry weight of crucible and acid insoluble lignin. The UV-visible spectrophotometer was used to determine acid soluble lignin (ASL). 4% (w/w) of sulfuric acid was utilized as a reference blank for the dilution of the hydrolysate. The measurement was conducted at 205 nm in a quartz cuvette having 1-cm light path. Acid soluble lignin content was calculated from the equation below;

$$\text{ASL}(\%) = \frac{A}{a \times b} \times DF \times \frac{V}{m_{biomass}} \times 29 \times 100$$

where, A is the absorbance at 205 nm, a is the absorptivity, 110 L/g.cm, b is the cell path length (1 cm), DF is the dilution factor, V is the initial volume of 72% (w/w) sulfuric acid solution (L), $m_{biomass}$ is the initial dry biomass (Haykir, 2013).

Hemicellulose and cellulose content of biomass was determined by calculating monosaccharide composition via high performance liquid chromatography (HPLC) analysis (Shimadzu LC-20AD Series Kyoto, Japan) which is equipped with a column "Transgenomic-CarboSep Coregel-87P" using 0.6 ml/min flow rate of filtered and degassed ultra-pure water as a mobile phase where D-glucose, D-xylose and D-arabinose and D-galactose were used as standards. Before the HPLC analysis, pH of the hydrolysate was adjusted to pH 5-6 with calcium carbonate. After adjusting pH of samples, the liquid part was filtered through a 0.2 μm filter before being injected to the HPLC. Glucose, xylose, galactose and arabinose concentrations were calculated with a calibration curve of standard solutions prepared in the range of 0-2 mg/ml. Additionally the areas under the peaks obtained by HPLC were analyzed by the help of software program (PeakFit v4.12). The concentrations of cellulose and hemicellulose were calculated by using the formulas given below (Haykir, 2013):

$$\%\ \text{Cellulose Content} = \frac{C_{\text{glucose}} \times V}{1.11 \times m_{\text{biomass}}}$$

$$\%\ \text{Hemicellulose Content} = \frac{C_{\text{xylose}} \times V}{1.14 \times m_{\text{biomass}}}$$

where, $C_{glucose}$ and C_{xylose} are glucose and xylose concentrations, V is the initial volume of sulfuric acid solution (L), $m_{biomass}$ is the dry weight of initial biomass (g).

3.2.2. Hemicellulose Isolation from Different Agricultural Residues

3.2.2.1. Hemicellulose Extraction from Corn Cobs

Hemicellulose was isolated from milled corn cobs according to the method given in the study of Zilliox and Debeire (1998) as shown in Figure 3.1. First, 100 grams of corn cobs were swollen in 2 L of water by using a magnetic stirrer for 15 minutes at room temperature. Swollen corn cobs were added to 850 ml of %24 KOH (w/v) containing alkaline solution and the suspension was left to mix on a magnetic stirrer for 2 hours at room temperature and 60^{o}C. After mixing, the solid particles that are insoluble in the alkaline solution, cellulosic portion, were removed by filtration. Liquid part was centrifuged (5000×g) for 5 minutes to completely remove smaller solid particles. Subsequently, hemicellulose was obtained by precipitation of the solution with 2500 ml of refrigerated acetic acid-ethanol mixture in 1:10 volumetric ratio. Following precipitation, hemicellulose was collected by filtration; the collected portion was immediately washed with 200 ml of de-ionized water and 600 ml of ethanol 3 times for desalting. Then, desalted xylan was left to dry at room conditions.

3.2.2.2. Hemicellulose Extraction from Wheat Straw

Ground wheat straw hemicellulose was extracted using the same method applied to corn cobs. The only difference was the extraction time which was increased to 3 hours from 2 hours, to increase the lower yield of xylan. Schematic diagram of extraction of wheat straw is shown in Figure 3.2.

3.2.2.3. Hemicellulose Extraction from Sunflower Stalks

Some modifications in extraction steps were performed to isolate hemicellulose from sunflower stalks in order to increase the yield. Differently from other two feed stocks, ground sunflower stalk particles were swollen in water at 60^{o}C for 16 hours. To the alkaline solution, 1% (w/v) $NaBH_4$ was added and 24 hours of extraction was performed. The other steps were kept the same as previously (Figure 3.3).

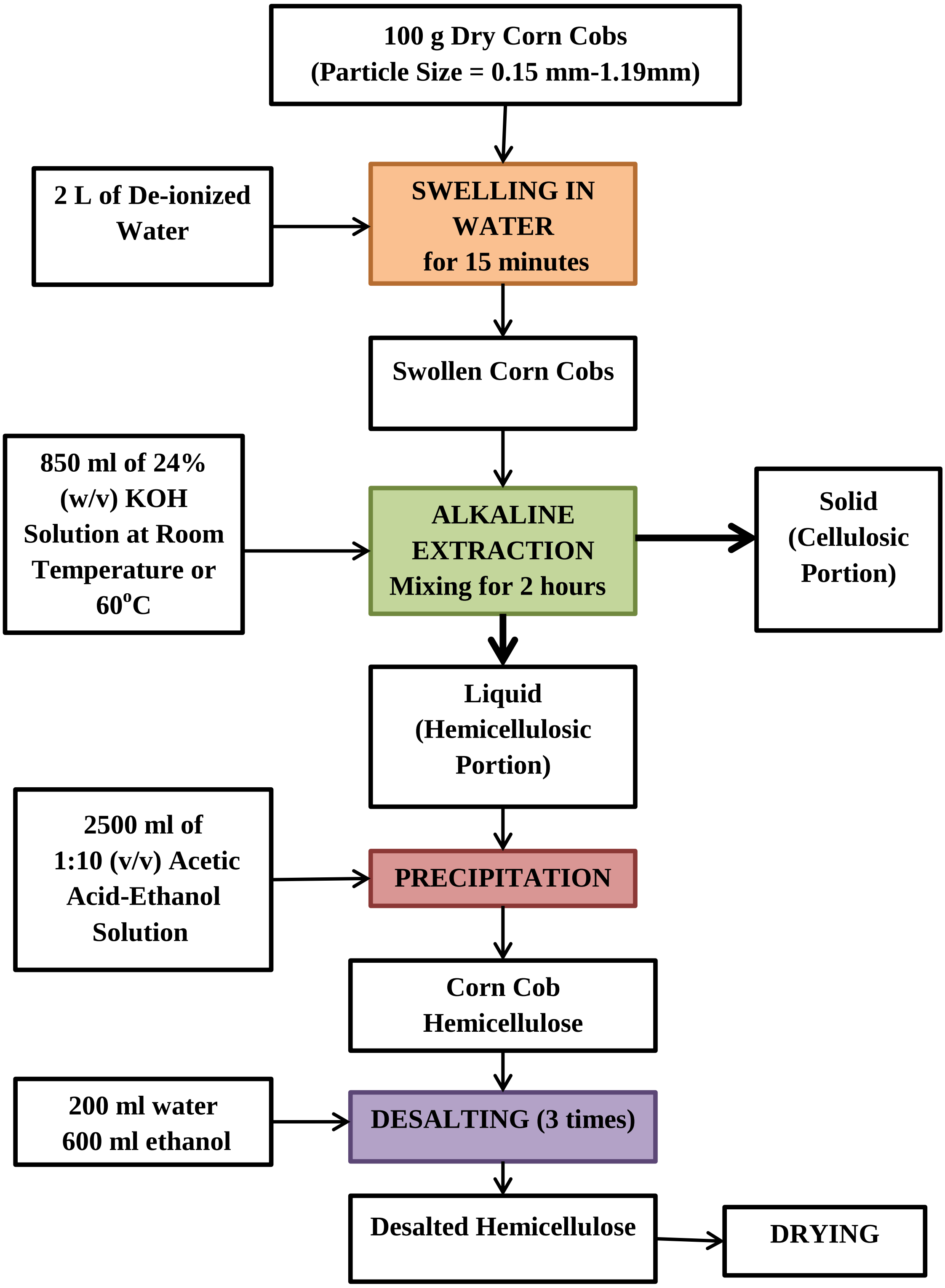


Figure 3.1 Schematic presentation of extraction of corn cob hemicellulose

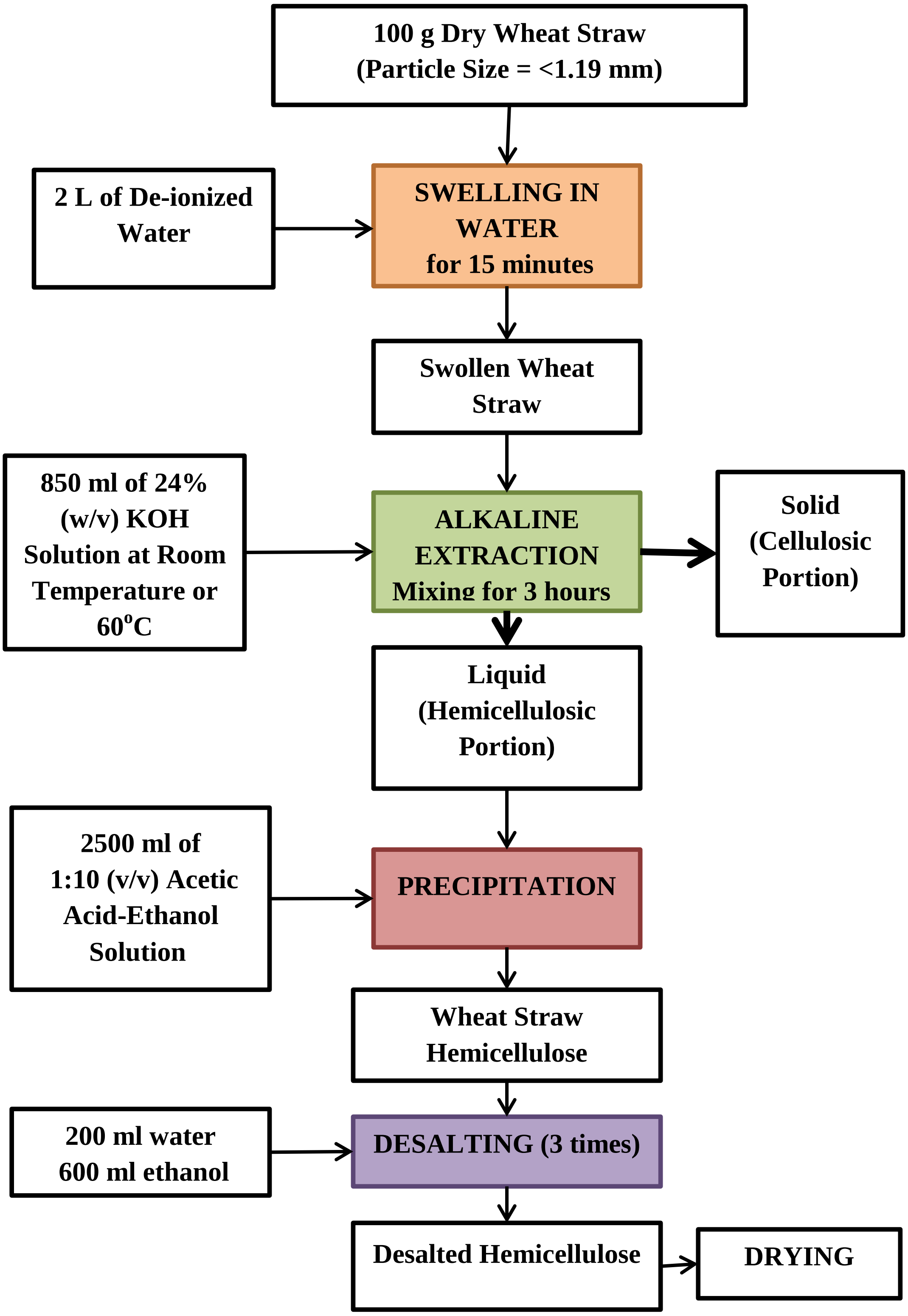


Figure 3.2 Schematic presentation of extraction of wheat straw hemicellulose

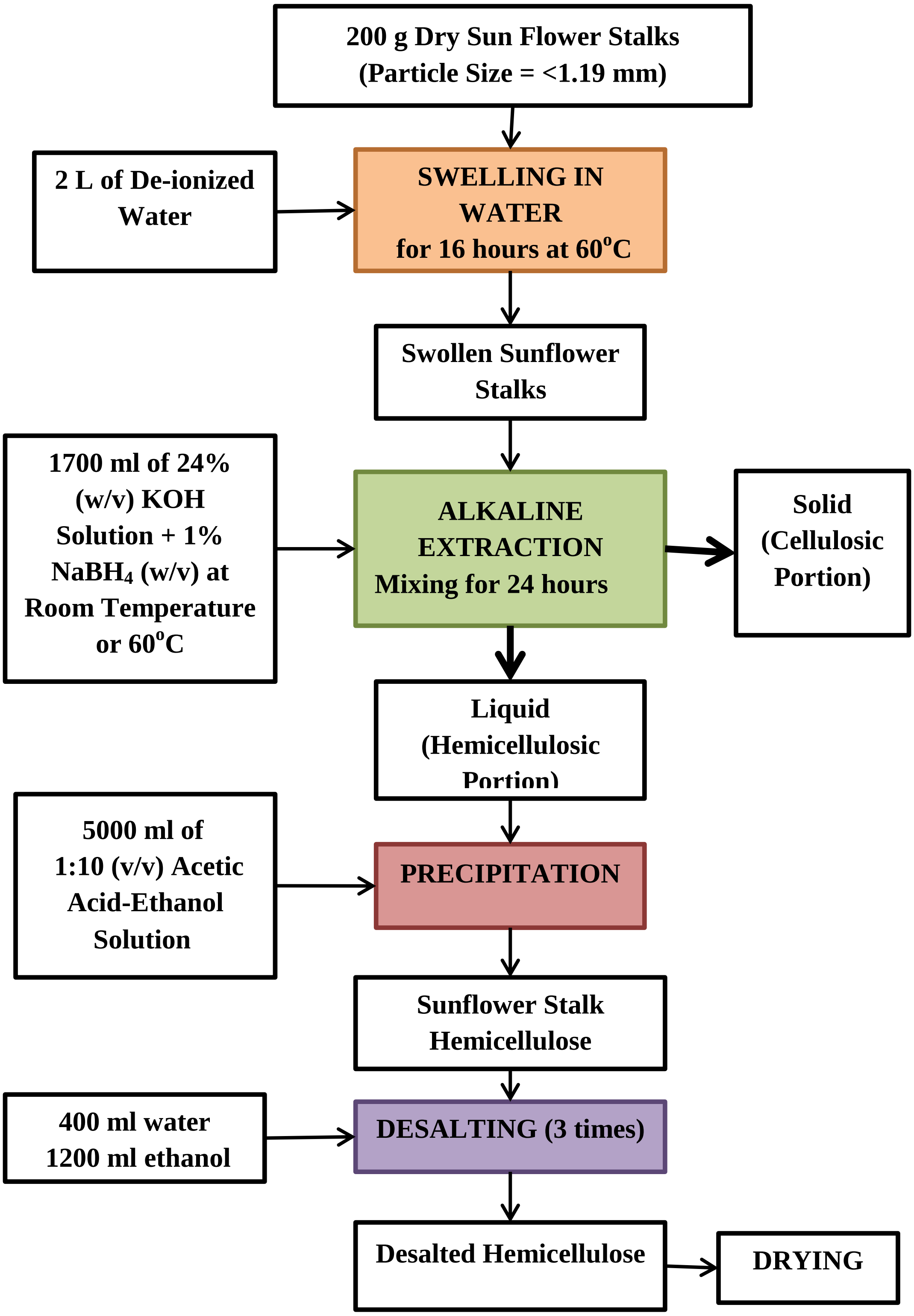


Figure 3.3 Schematic presentation of extraction of sunflower stalk hemicellulose

However, for the comparison of the physical properties of solvent casted films that were produced from different lignocellulosic biomass, another set of experiment having 3 hours extraction step was prepared.

Yield of hemicellulose production was calculated based on initial dry biomass weight by using the formula given below;

$$\% \text{ Yield} = \left(\frac{\text{weight of extracted hemicellulose}}{\text{weight of initial dry weight of biomass}}\right) \times 100$$

3.2.3. Film Production from Hemicellulose

3.2.3.1. Film Production via Solvent Casting

0.5 gram of extracted hemicellulose was dissolved in 15 ml of de-ionized water and left for stirring on a magnetic stirrer for 24 hours at room temperature. Following this step, the suspension was ultrasonificated at 40% amplitude for 8 minutes to maintain better dispersion of solid particles. After that, the solution was poured into a polystyrene petri dish with a diameter of 9 cm. In this case, films were left to dry in a conditioning cabinet (Medcenter 111 Climacell, MMM Group, Munich, Germany) at 23^{o}C and 50% relative humidity for 2 days. In order to obtain thicker films double amount of hemicellulose was dissolved in 15 ml of water.

3.2.3.2. Film Production via Extrusion

A co-rotating, conical twin-screw (Diameter: 4-15 mm; Length: 109.4 mm) extruder (Thermo HAAKE Mini CTW) with two heating zones was used for the extrusion of hemicellulose polymers (Figure 3.4). A plate in ribbon die with a rectangular opening (5 mm width and 0.5 mm thickness) that connected to extruder, ensures to obtain materials in strip form.

A speed-controllable moving belt exists to collect the strip that coming out from the extruder. Extrusion temperature and speed of screws are controlled digitally. Only 5 grams of polymer feeding would be enough to produce nearly 1.5 meter of strip. After each extrusion the extruder was cleaned carefully to remove everything since minor quantities of residues left might affect the following experiment.

From the previous studies, the importance of moisture content which hemicellulose required for being extrudable were observed and the minimum water content was determined as about 27% to provide extrusion process (Bahcegul et al., 2013). For this reason, hemicellulose was kept in 90% moisture contained desiccators for 24 hours prior to extrusion.

One of the main objectives of this study is to analyze and compare the properties of the films produced by two different methods, extrusion and solvent casting. An experimental set was designed and carried out to observe the effect of thickness on the mechanical properties of films. For this purpose, thickness of extruded strips was rendered similar to the solvent casted films by rolling through a roller (Yilmaz Machine Industry, Turkey). Before rolling, strips were held in 90% relative humidity containing desiccators for 1 day. The images of extruded strips before and after rolling are given in Figure 3.5

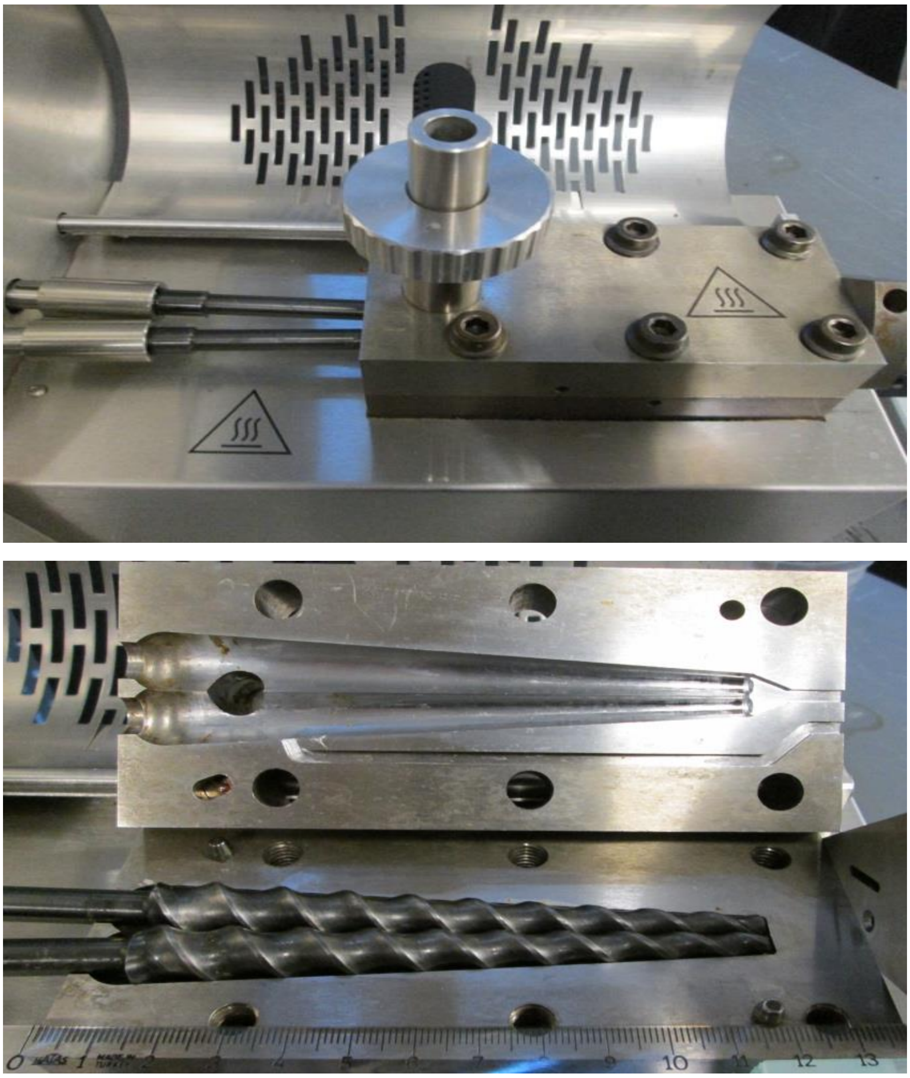


Figure 3.4 Images of the twin screw mini-extruder

Figure 3.5 Visual appearances of extruded strips before rolling and after rolling

3.2.4. The Characterization of Hemicellulose

3.2.4.1. Monosaccharide Analysis

Monosaccharide analysis of hemicelluloses was performed with HPLC (Shimadzu LC-20AD Series Kyoto, Japan) by the procedure of according to the National Renewable Energy Laboratory (NREL, Golden, CO) analytical methods (NREL, 1996; 2011) in the same way completed for the compositional analysis of biomass.

3.2.4.2. Lignin Content Determination of Hemicelluloses

The lignin content of isolated hemicellulose was analyzed by using UV spectrophotometer (Thermoscientific, Nicolet). Hemicellulose was dissolved in 4% or 8% NaOH (w/v) solution depending on the solubilities of hemicelluloses. Following that, according to the method that reported by Westbye et al. (2007), absorbance values at 280 nm were measured. Alkali lignin solutions at different concentrations were used as reference.

3.2.4.3. Moisture Content Determination

The moisture content of hemicelluloses prior to extrusion and extruded strips was determined by keeping the polymers in a furnace at 105°C for 24 hours. The moisture content was determined by using the formula given below;

$$\%\ \text{Moisture Content} = \left(\frac{w_0 - w_1}{w_0}\right) \times 100$$

Where w_o is the initial weight of the polymer or strip, and w_1 is the weight of the dried samples.

3.2.5. The Characterization of Films

3.2.5.1. Tensile Testing

Mechanical properties of films were analyzed by using the tensile testing equipment in the METU Central Laboratory. Prior to tensile testing, films were cut as dog bone shape by using a cutting press (ZCP 020, ZwickGmbH&Co., Ulm, Germany). The thickness and width of films or strips were measured by a digital micrometer (40 EXL, Mahr GmbH, Esslingen, Germany) with a sensitivity of 1 μm. Samples were conditioned at 23°C and 50% relative humidity containing cabinet for 24 hours before testing. The tests were performed in the controlled environment at a temperature of 23°C±2 and a relative humidity of 50±5%.

Specimens were analyzed using a tensile testing machine (Zwick/Roell Z250, ZwickGmbH&Co., Ulm, Germany) with a 100 N/10 kN load cell and pneumatic grips. While thicker strips were analyzed with 10 kN load cell, the load cell was replaced with 100 N for the thinner strips. Mechanical tests were carried out at 5 mm/min of crosshead speed and 10 mm grip separation. For each parameter, at least 5 samples were tested. Elastic modulus, ultimate tensile strength, elongation at break and tensile energy to break values were determined by a software program (testXpert 2) which is connected to the testing machine. Toughness of films was calculated from TEB values.

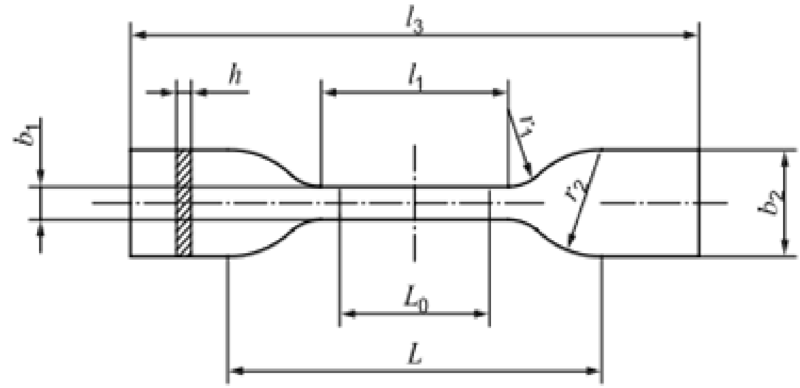


Figure 3.6 Shape of a Typical Tensile Specimen, b_1: Width of narrow section, b_2: Width of overall, L_o: Length of narrow section, I_1: Length of narrow parallel-sided portion, I_3: Length of overall, T: Thickness of specimen, r_1: Small radius, r_2: Large radius, h: Thickness, L: Initial distance between grips (Adapted from ISO: 527-2:2012).

Elastic modulus was defined as the resistance that specimen showed to elastic deformation.

Ultimate tensile strength (UTS) which is the maximum stress value of specimen was calculated by dividing the peak load by the initial cross-sectional area of the specimen. Elongation at break was expressed as percentage of the change of the original length of a specimen between grips at fracture. Tensile energy to break value was signified as the area under the stress-strain curve.

3.2.5.2. Thermogravimetric Analysis (TGA)

Thermal characterizations of the films were investigated using thermogravimetric analysis equipment (Pyris 1, Perkin Elmer). Film samples were heated from room temperature to 950^{o}C, at a heating rate of 10^{o}C/min with nitrogen flushing to obtain thermogravimetric curves. Then, nitrogen was changed with dry air. After holding the samples at 950^{o}C for 30 minutes, the analysis was ended.

3.2.5.3. Scanning Electron Microscopy (SEM)

A scanning electron microscopy (QUANTA 400F Field Emission SEM) was used to investigate cross sectional and surface images of the films. The films were broken in liquid nitrogen before the cross sectional image analysis. All samples were coated with gold-palladium prior to examination. SEM images were taken at 1500X magnification for cross sectional and 1000X for surface investigations.

3.2.5.4. Color Measurements

Color of the films was measured using a Minolta color reader (CR-10, Japan) using the L*, a*, and b* color scale. The color of the films was measured using white paper as the reference color. Readings were carried out at room temperature on four different locations of each sample, and the mean value was recorded. The L* value represents ‘lightness’, from zero (black) to 100 (white). The a* value represents, ’redness’ or ’greenness’ ranging from +60 to –60 while b* value represents ‘yellowness’ or ‘blueness’ ranging from +60 to –60. ΔE is the total color change, and it was calculated from the following equation in which white color was used as the reference point, which was denoted by L_0, a_0 and b_0.

$$\Delta E= [(L^*-L_0)^2+(a^*-a_0)^2+(b^*-b_0)^2]^{1/2}$$

3.2.5.5. Statistical Analysis

Statistical analysis was performed using Excel Software Program. T-test was applied for the comparisons and p values were calculated. For the values $p<0.05$, the difference was statistically significant.

CHAPTER 4

RESULTS AND DISCUSSION

In this study, biodegradable film production from hemicelluloses isolated from three different agricultural feedstocks including corn cob, wheat straw and sunflower stalk, was investigated. Studies on hemicellulose based film production started in 2002 in our laboratory, considering the negative impact of comparatively limited use of hemicellulose on the efficient utilization of lignocellulose and its great barrier property against oxygen (Table 4.1). In the previous studies, the possibility of using xylan has been studied firstly by Kayserilioglu and coworkers (2003) for biodegradable composite film production. Birchwood, corn cob and grass xylan were added as additives, as much as 40% (w/w), in wheat gluten films which corresponds to G:X ratios of (10:0, 9:1, 8:2, 7:3, 6:4). Composite films containing birchwood xylan gave the highest tensile strength; however, films containing corncob xylan gave the lowest tensile strength. Addition of corncob xylan resulted in increase in the elongation at break value. No continuous and self-supporting film formation was observed from pure xylan. Then, continuous film production from extracted cotton stalk xylan have been achieved but with very low mechanical strength by Goksu et al. (2007). Films were formed within the concentration range of 8-14%. Below 8%, film forming solutions did not produce films, whereas xylan concentration above 14% was not used because of high viscosity problems. Bahcegul and coworkers (2011) used cotton stalk xylan, and they obtained films with superior mechanical properties.

In all these studies, solvent casting method was used which had to be converted to extrusion considering industrial production. In 2011, extrusion method was started to be used for hemicellulose-based film production in our laboratory which has not been reported in the literature up to 2013 when our first report was published (Bahcegul et al., 2013).

Table 4.1 Mechanical properties of hemicellulose films produced in previous studies.

Method	**Component**	**Mechanical Properties**			**Reference**
		Tensile Strength (MPa)	**Elongation at Break (%)**	**Elastic Modulus (MPa)**	
Solvent Casting 10% (w/w) Gluten and Xylan 2% (w/w) Glycerol	Pure xylan	No film formation			Kayserilioglu et al., 2003
	Composite films (8:2) Wheat gluten: Birchwood xylan	7.6	50	140	
	Wheat gluten: Corn cob xylan	1.3	600	10	
	Wheat gluten: Grass xylan	2.0	50	25	
Solvent Casting 8-14% (w/w) Xylan 2% (w/w) Glycerol	Cotton waste xylan	1.1-1.4	46-57	0.1-0.5	Goksu et al., 2007
Solvent Casting 3% (w/w) Xylan	Cotton stalk xylan	52	3.1	3100	Bahcegul et al., 2011
Extrusion	Corn cob xylan	76	35	1073	Bahcegul et al., 2013

In this study the extrusion technique was used as the main film production method and the properties of extruded films were compared with those of the films obtained via solvent casting, which is a more common method used for the production of biodegradable films. In the first stage of this study, the hemicelluloses were isolated from agricultural feedstocks by alkaline extraction, and the effect of extraction conditions on the film qualities was studied. Although it was planned to keep all the extraction parameters constant except the extraction temperature, the extraction period was increased from 2 hours to 3 and 24 hours for the cases of wheat straw and sunflower stalk, in order to increase the low hemicellulose yields for the extrusion studies. Therefore, only within the same biomass, the effect of extraction temperature on film formation was observed whereas the effect of overall extraction conditions was observed in the comparisons between biomasses. In the second stage, the effect of extrusion conditions on hemicellulose based film properties was studied as a function of extrusion temperature and extrusion speed.

The moisture content of hemicellulose is very important for being extrudable and a successful extrusion was not achieved at high temperatures where high moisture losses were observed such as 120^{o}C. An extrusion temperature of 90^{o}C has already been determined as a convenient temperature since no strip formation was observed through extrusion at neither 60^{o}C nor 120^{o}C (Bahcegul et al., 2013). So, 90^{o}C together with 75^{o}C were chosen as extrusion temperatures. The reason for selecting a lower temperature is to prevent the excessive loss of moisture present in the hemicellulose. Two different extruder screw speeds, 50 and 100 rpm, were selected as the other extrusion parameters. The effects of extrusion parameters and extraction conditions on the mechanical, thermal, rheological and morphological properties were investigated.

4.1. Compositional Analysis

4.1.1. Compositional Analysis of Biomass

Compositional analysis of the corn cob, wheat straw and sunflower stalk was determined using high-performance liquid chromatography (HPLC) according to the laboratory analytical procedure (LAP) provided by National Renewable Energy Laboratory (NREL). The compositions of biomasses (corn cob, wheat straw and sunflower stalk) are given in Table 4.2. As shown in Table 4.2, the composition of the corn cob was determined to be about 24% cellulose, 38% hemicellulose, and 19% lignin including ash based on dry weight. In the literature, the corn cob composition was reported as 35-45% cellulose, 35-40% hemicellulose, 6-15% lignin and 5% of extractives by dry weight (Hon, 1995; Menon, 2012). The composition of wheat straw was found as 22% cellulose, 37% hemicellulose, and 24% lignin including ash. In the literature, the composition of wheat straw was given as 30-35% cellulose, 45-50% hemicellulose, 15% lignin and 5% others (Hon, 1995; Menon, 2012). Finally, for the sunflower stalk the amount of constituents was found as 29% cellulose, 17% hemicellulose, and 15% lignin including ash. However, in the literature, sunflower stalk composition was reported to be 34% cellulose, 20% hemicellulose, 17% lignin and 10% ash and 20% others (Ruiz et al., 2006). There are differences between the measured values of this study and the literature and the main difference was observed in the cellulose content of all the biomasses. Several reasons might be responsible for these differences. First of all, the compositional analysis was performed only once so the experimental error possibility is high. Secondly, biomasses were hydrolyzed in different particle sizes than specified in the procedure. Thirdly, the composition of biomass may change depending not only on its source but also on its age.

Table 4.2 Biomass compositions

Components	**Content (g dry weight/ 100 g dry biomass)**		
	Corn cob	**Wheat straw**	**Sunflower stalk**
Cellulose	24.2	21.7	28.9
Hemicellulose	37.8	37.1	16.9
Acid soluble lignin	3.1	1.8	1.5
Acid insoluble lignin + ash	16.0	22.0	13.3
Others (Protein, uronic acid etc.)	18.9	17.4	39.4

4.1.2. Compositional Analysis of Hemicellulosic Fraction

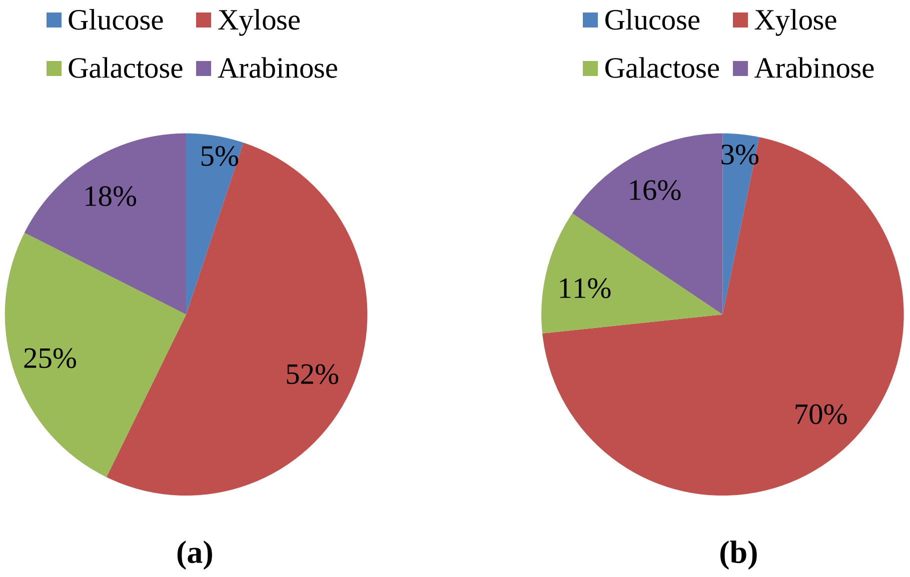
Monosaccharide content of hemicelluloses was determined by acidic hydrolysis following HPLC. Lignin quantity in the hemicelluloses was determined using UV-Vis spectroscopy. Since the compositions of the hemicelluloses may change with the extraction conditions, the monosaccharide and lignin analysis were performed for the hemicelluloses extracted both at room temperature and 60°C. The hemicellulose yield, lignin content and Ara/Xyl ratios of the hemicelluloses are given in Table 4.3. Although in the isolated hemicellulosic fraction, there might be other hemicelluloses in minor quantities, the hemicellulosic fraction is called as xylan in this study considering the large percentage of xylose in the hemicellulose hydrolylates.

Table 4.3 Xylan yield, lignin content and Arabinose/Xylose (Ara/Xyl) values of the xylans.

Xylan source	**Extraction temperature**	**Xylan yield (g dry xylan/ 100 g dry biomass)**	**Lignin content (g dry weight/ 100 g dry xylan)**	**Ara/ Xyl**
Corn cob xylan	Room temperature	30	10.4	0.34
	60°C	28	10.5	0.22
Wheat straw xylan	Room temperature	24	11.4	0.26
	60°C	15	10.5	0.23
Sunflower stalk xylan	Room temperature	10	1.8	0.12
	60°C	7.5	1.0	0.11

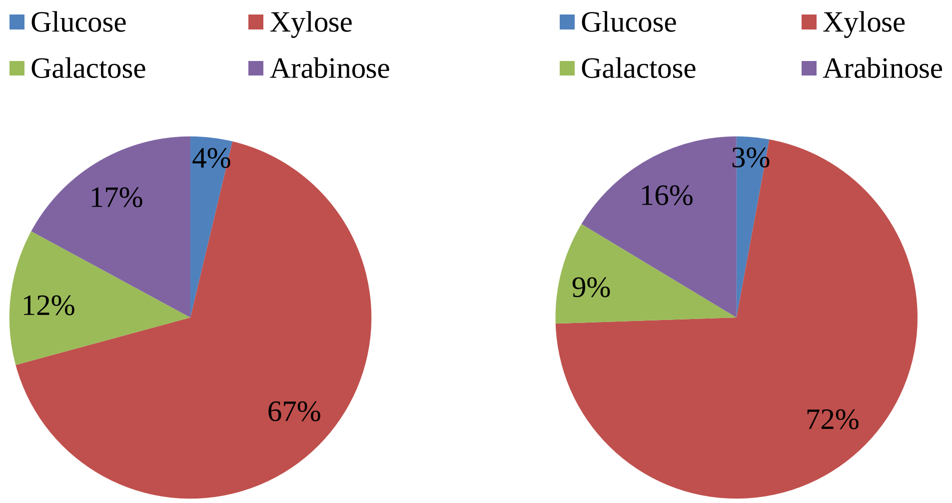
The lignin content did not change much with extraction temperature. Although the lignin content of corn cobs and wheat straw are similar to each other, the sunflower stalk xylan contains significantly lower lignin levels than the others, which is probably because of better separation of lignin from xylan resulted by much higher extraction period used to increase the low xylan yield. The influences of extraction temperature on the monosaccharide compositions for corn cob, wheat straw and sunflower stalk xylans are illustrated in Figures 4.1, 4.2, and 4.3, respectively. Xylose is the backbone monomer while galactose, arabinose and glucose are the side chains of xylans. When the extraction temperature was increased, the concentration of xylose increased for the corn cob and wheat straw xylans.

However, the xylose concentration of sunflower stalks xylan decreased by increasing the extraction temperature. This result might be resulted from the longer extraction period of sunflower stalk xylan which can introduce xylan degradation. Additionally, when the extraction temperature was increased, Ara/Xyl ratio of corn cob xylan decreased from 0.34 to 0.22 and a smaller decrease in the Ara/Xyl ratio from 0.26 to 0.23 was observed for the wheat straw xylan which may show the hydrolysis of side chain arabinose groups from the xylan structures at high temperatures. However, the extraction temperature had very small effect on the Ara/Xyl ratio for the sunflower stalk xylan which may be again because of very long extraction periods. Galactose contents of the corn cob and sunflower stalk xylans extracted at room temperature and 60°C, respectively, are much greater than the other xylans.



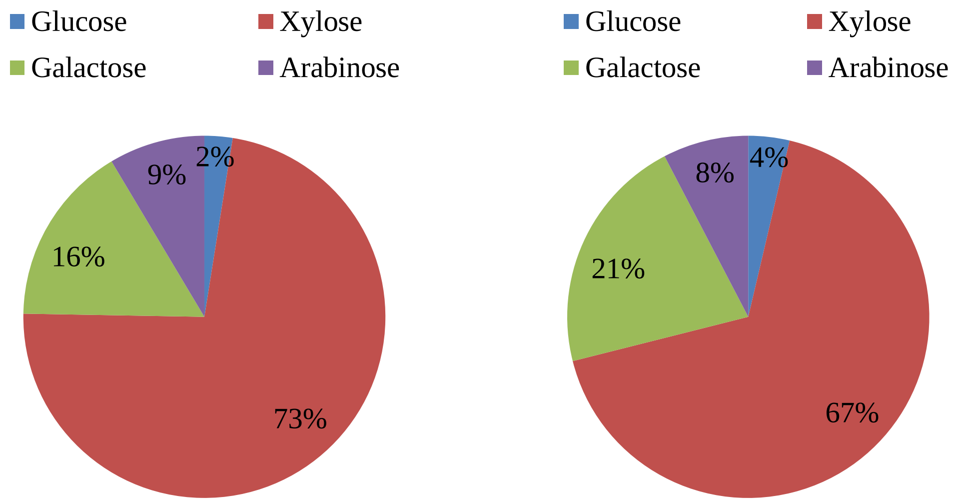
(a) **(b)**

Figure 4.1 Monosaccharide concentrations (%) of corn cob xylan (a) extracted at room temperature, (b) extracted at 60°C based on total amount of monosaccharides.



(a) **(b)**

Figure 4.2 Monosaccharide concentrations (%) of wheat straw xylan (a) extracted at room temperature, (b) extracted at 60°C based on total amount of monosaccharides.



(a) **(b)**

Figure 4.3 Monosaccharide concentrations (%) of sunflower stalk xylan (a) extracted at room temperature, (b) extracted at 60°C based on total amount of monosaccharides.

4.2. Effect of Extraction Temperature on Film Forming Properties of Xylans Isolated from Different Agricultural Feedstocks

Films were produced using solvent casting method from xylans which were extracted from different types of biomasses at the same conditions. The extractions of corn cob, wheat straw and sunflower stalk were conducted at room temperature and 60°C for the same period of 3 hours in this set of experiments. The solvent casted films produced from the corn cob, wheat straw and sunflower stalk xylans are shown in Figures 4.4, 4.5 and 4.6, respectively. It was noticed that the crack formation in the solvent casted films reduced when the extraction temperature was increased. For all three types of the xylans, the thicknesses of films were approximately 50 μm. Although crack-free continuous films were obtained, the films were mechanically so weak that their mechanical properties could not even be measured.

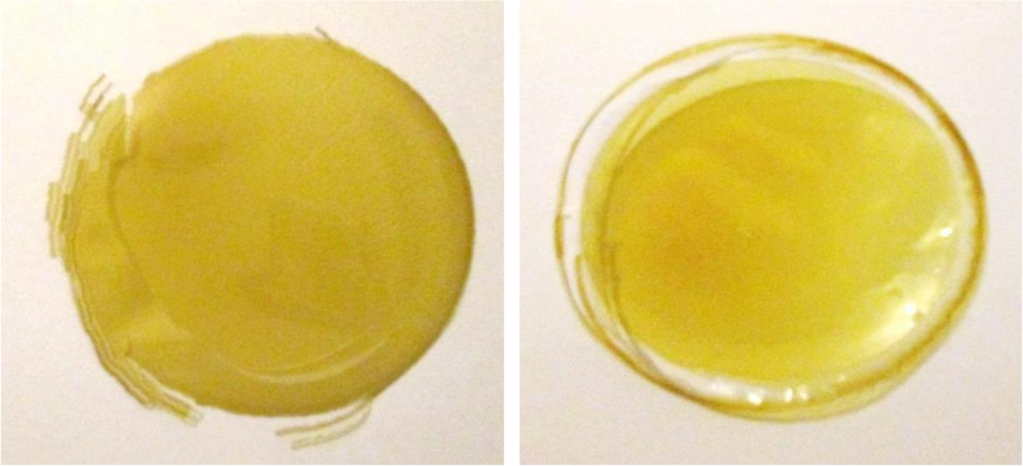


Figure 4.4 Effect of extraction temperature on the appearances of corn cob xylan based solvent casted films: Films were obtained from the xylan extracted at room temperature (left) and 60°C (right).

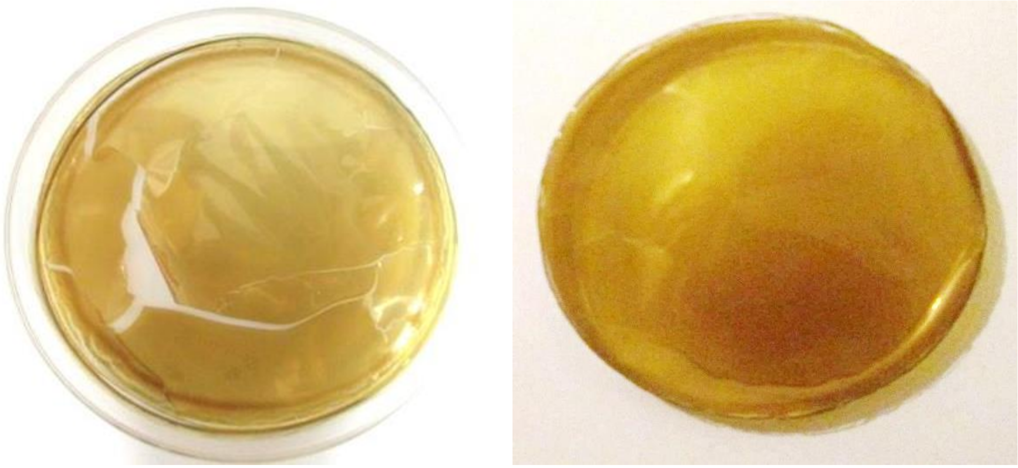


Figure 4.5 Effect of extraction temperature on the appearances of wheat straw xylan based solvent casted films: Films were obtained from the xylans extracted at room temperature (left) and 60°C (right).

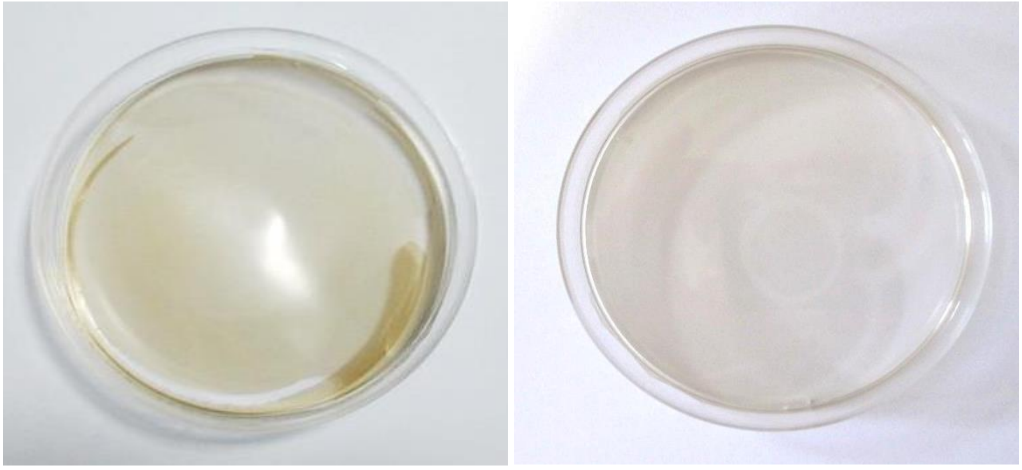


Figure 4.6 Effect of extraction temperature on the appearances of sunflower stalk xylan based solvent casted films: Films were obtained from the xylans extracted at room temperature (left) and 60°C (right).

The color of the films was measured by using color test. Total color change in comparison to white, ΔE, was calculated and given in Table 4.4. The darkest films were obtained from the wheat straw xylan and the lightest ones were obtained from the sunflower stalk xylan. The films produced from the sunflower stalk xylan were most transparent compared to other films. There was no significant difference between the color of xylan films that were produced using the same biomass source at different extraction temperatures ($p>0.05$). Also, similar color was seen for the corn cob and wheat straw xylan based films. However, the color of films formed by sunflower stalk xylan was different than other types of xylan films ($p<0.05$). Lighter color of sunflower stalk xylan films may be a result of lower lignin concentration of sunflower stalk xylan than other xylan types.

Table 4.4 Total color change values of solvent casted films

Xylan Source-Extraction Temperature	ΔE
Corn Cob- RT	49.8±1.7
Corn Cob- 60°C	49.4±1.9
Wheat Straw- RT	50.7±1.5
Wheat Straw- 60°C	51.0±1.7
Sunflower Stalk- RT	47.0±0.9
Sunflower Stalk- 60°C	47.8±2.0

RT: Room Temperature

4.3. Factors Affecting Mechanical Properties of Extruded Films

The most important aspect about this study is to illustrate the applicability of the production of films from xylans using extrusion technique and compare the mechanical properties of the extruded films with those of solvent casted films.

Mechanical properties (modulus, ultimate tensile strength, elongation at break and toughness) of the extruded films were analyzed using the tensile testing. The influences of operating temperature and speed of extrusion process on the mechanical properties of the films produced from different xylans were investigated. The speed of extrusion was controlled through adjusting the rotational speed (rpm) of the screws during the extrusion process.

4.3.1. Effect of Extrusion Conditions on the Mechanical Properties of Xylan Films

4.3.1.1. Effects of Extrusion Temperature and Speed on the Mechanical Properties of Corn Cob Xylan Based Films

Mechanical properties of the extruded films produced from the corn cob xylans extracted at room temperature and 60^{o}C are shown in Figures 4.7 and 4.8, respectively. As can be seen from Figure 4.7, the influences of the extrusion temperature or extrusion speed (rpm) on the Young’s modulus (E) and ultimate tensile strength (UTS) of the films obtained from the corn cob xylans extracted at room temperature were insignificant ($p>0.05$). Approximate E and UTS values of these films were 1120 MPa and 52 MPa, respectively. A significant difference was observed between flexibilities and toughness of films that are extruded at different temperatures ($p<005$). During extrusion, the xylans were molten and shaped under heat and shear. When the extrusion temperature was increased, more heat was supplied to xylan granules. Thus, the strips extruded at 90°C became more uniform than the strips extruded at 75°C. Also, defects formed on strip surfaces decreased when more heat was supplied. For this reason, films in higher elongation at break were produced using higher extrusion temperature for both the extrusion screw speeds of 50 and 100 rpm. As a result, the toughness of the films extruded at 90^{o}C (approximately 13 MJ/m^3) was higher than the films which were extruded at 75^{o}C (approximately 9.6 MJ/m^3).

Considering the original form of strips, mechanical properties decreased when rolling was applied. While original form of strips produced from corn cobs had a tensile strength and elongation at break of approximately 76 MPa and 35% respectively with a thickness of 400±50 µm, the rolled films showed lower mechanical properties as seen in Figure 4.7. Obviously, mechanical properties of films were affected by thickness of films or this might be resulted from the defects on film surfaces that were formed during rolling process.

Figure 4.8 shows the mechanical properties of the extruded films produced from the corn cob xylans extracted at 60^{o}C. The extrusion temperature and extrusion speed did not influence the mechanical properties of these films considerably ($p>0.05$). The modulus, tensile strength, elongation at break, toughness of these films were approximately 1100 MPa, 54 MPa, 13.5%, and 6.0 MJ/m^{3}.

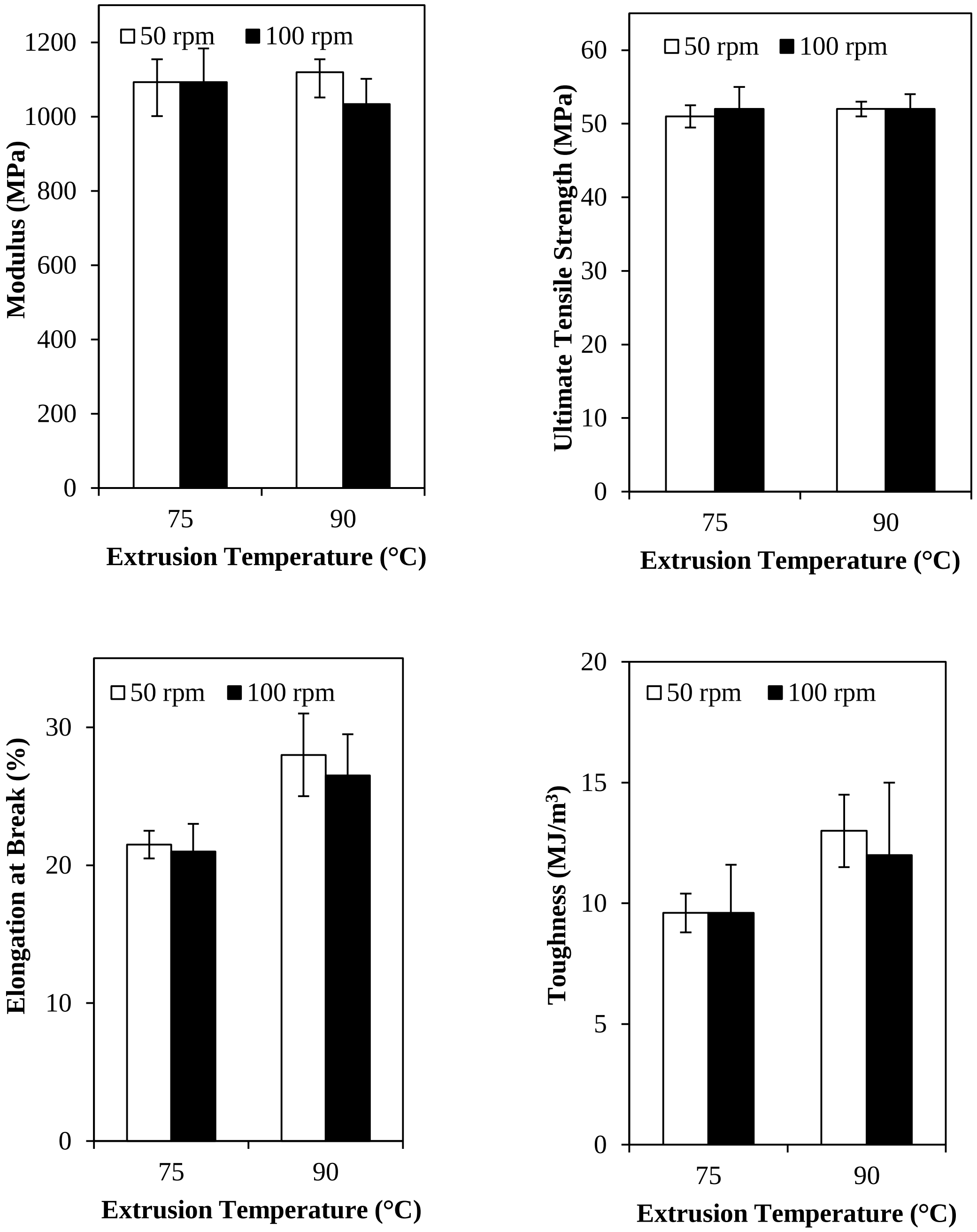


Figure 4.7 Mechanical properties of the extruded films produced from the corn cob xylan extracted at room temperature.

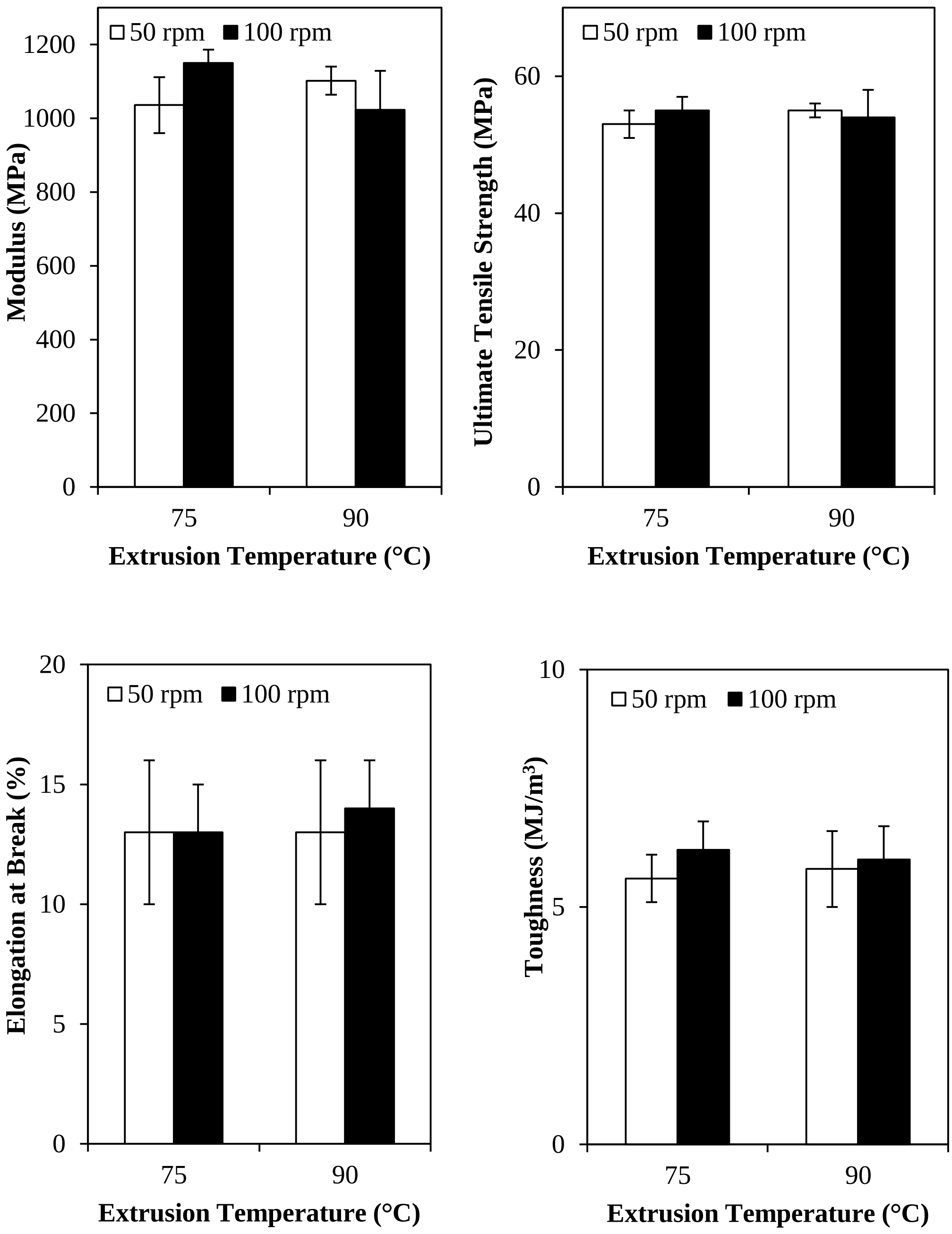


Figure 4.8 Mechanical properties of the extruded films produced from the corn cob xylan extracted at 60°C.

In xylan extrusion, the loss of the water content of xylans plays a major role since water acts as a plasticizer. Therefore moisture contents of the xylan feed and products of extruder were measured and are given in Table 4.5. As observed, the moisture loss of the extruded strips was about 2-3% within the extruder and not affected by the varying parameters of the experimental set.

Table 4.5 Water contents of the corn cob xylan feed and the extruded strips for the corn cob xylan extracted at room temperature and at 60^{o}C.

Extraction Condition	**Extrusion Conditions, T=Temp, S=Speed**	**% Water Content of Xylan Feed**	**% Water Content of Extruded Strips**
Room Temperature	T=90°C, S=50 rpm	27.3	24.6
	T=90°C, S=100 rpm	28.5	23.9
	T=75°C, S=50 rpm	29.8	26.1
	T=75°C, S=100 rpm	26.7	24.6
60^{o}C	T=90°C, S=50 rpm	26.7	24.6
	T=90°C, S=100 rpm	24.6	22.5
	T=75°C, S=50 rpm	25.1	22.6
	T=75°C, S=100 rpm	26.9	23.4

4.3.1.2. Effects of Extrusion Temperature and Speed on the Mechanical Properties of Wheat Straw Xylan Based Films

Mechanical properties of the extruded films produced from the wheat straw xylans extracted at room temperature and 60^{o}C are shown in Figures 4.9 and 4.10, respectively. The elastic modulus and ultimate tensile strength values of the films produced from wheat straw xylans extracted at room temperature were almost independent of extrusion speed (rpm). The difference between the mechanical properties in terms of UTS, elongation at break and toughness were significant between the films extruded at 75^{o}C and 90^{o}C and at 50 rpm ($p<0.05$). The films extruded at 75^{o}C were more brittle than the films extruded at 90^{o}C at the same extrusion speed. While the lowest toughness was obtained for the films extruded at 75^{o}C and the extrusion speed of 50 rpm with a value of 3.9 MJ/m^3, the highest toughness was obtained for the ones at 90^{o}C and the extrusion speed of 50 rpm with a value of 6 MJ/m^3 as shown in Figure 4.9, suggesting that the increasing the extrusion temperature affected positively the toughness of films. For the corn cob xylans, a possible explanation might be the positive effect of heat on uniformity.

The Young's modulus and the ultimate tensile strength of the films produced using wheat straw xylans extracted at 60^{o}C were nearly independent of both the extrusion temperature and speed ($p>0.05$). The Young's modulus and the ultimate tensile strength of these films were approximately 1130 MPa and 52 MPa, respectively. However, the elongation at break values and toughness of these films increased with increasing the extrusion temperature for the films extruded at 50 rpm. But, no significant difference was noticed between the toughness of films extruded at different temperatures for 100 rpm ($p>0.05$). As a result, the maximum toughness (5.1 MJ/m^3) was obtained for the films extruded at 90^{o}C and 100 rpm.

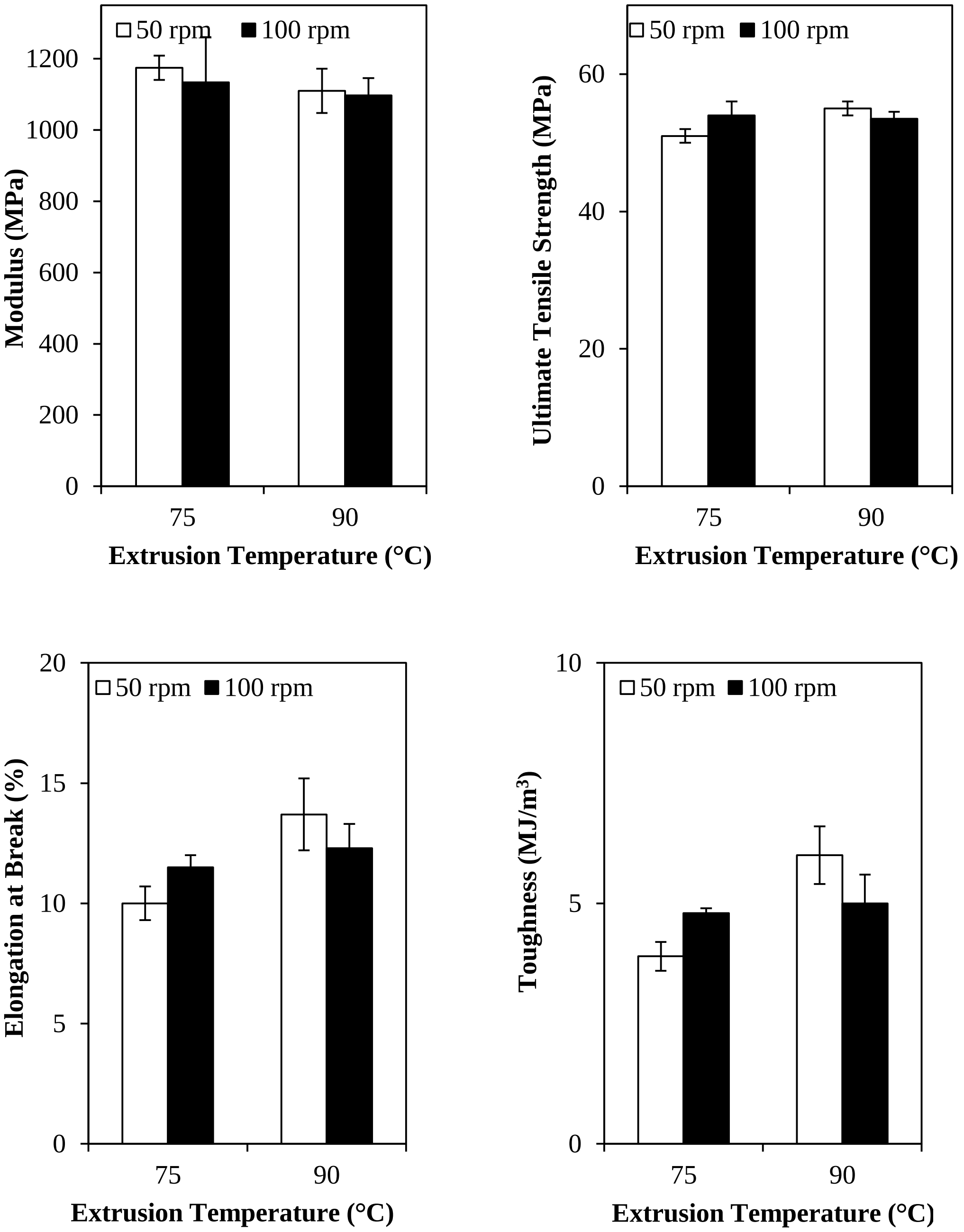


Figure 4.9 Mechanical properties of the extruded films produced from the wheat straw xylans extracted at room temperature.

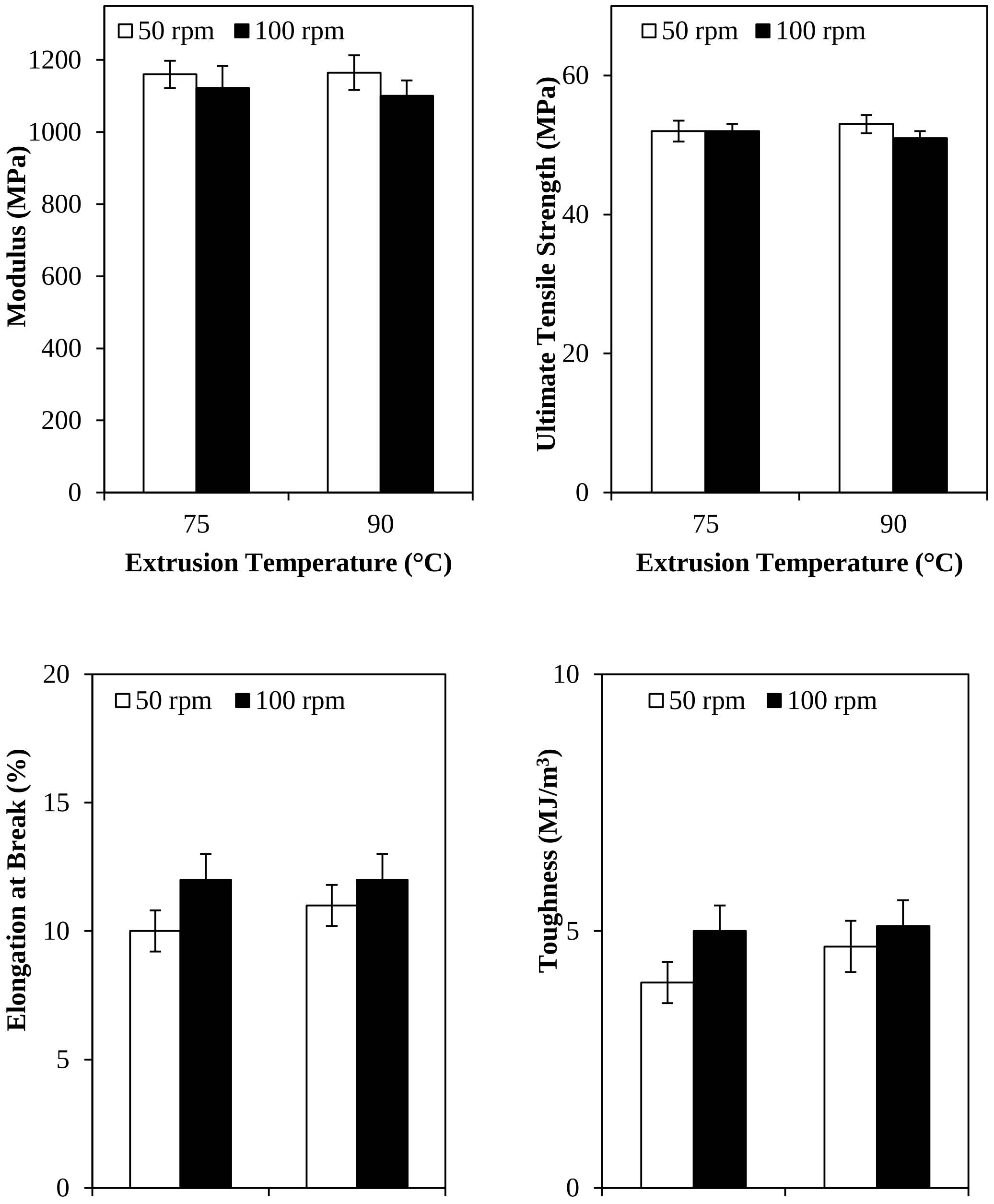


Figure 4.10 Mechanical properties of the extruded films produced from the wheat straw xylans extracted at 60^{o}C.

The water contents of wheat straw xylans prior to and just after the extrusion process, which are given in Table 4.6, showed no significant water loss during the extrusion process.

Table 4.6 Water contents of the wheat straw xylan feed and the extruded strips for the wheat straw xylan extracted at room temperature and at 60^{o}C.

Extraction Temperature	**Extrusion Conditions, T=Temp, S=Speed**	**% Water Content of Xylan**	**% Water Content of Strip**
Room Temperature	T=90°C, S=50 rpm	27.8	27.1
	T=90°C, S=100 rpm	28.9	27.9
	T=75°C, S=50 rpm	30.5	27.8
	T=75°C, S=100 rpm	28.0	26.9
60^{o}C	T=90°C, S=50 rpm	29.3	26.9
	T=90°C, S=100 rpm	28.1	26.9
	T=75°C, S=50 rpm	29.2	27.5
	T=75°C, S=100 rpm	27.6	27.3

4.3.1.3. Effect of Extrusion Temperature and Speed on the Mechanical Properties of Sunflower Stalk Xylan Based Films

Mechanical properties of the extruded films produced from the sunflower stalk xylans extracted at room temperature and 60^{o}C are shown in Figures 4.11 and 4.12, respectively.

As can be seen from Figure 4.11, there was no apparent influence of the extrusion parameters (temperature and speed) on the mechanical properties of the films produced from the sunflower stalk xylans extracted at room temperature ($p>0.05$). The maximum ultimate tensile strength and Young’s modulus values of the films extruded at 90^{o}C and 50 rpm were approximately 50 MPa and 1130 MPa. The flexibility of films decreased slightly with the increasing of extrusion speed at the extrusion temperature of 75^{o}C, however, the opposite behavior was observed for the films extruded at 90^{o}C.

A significant difference between the flexibilities and toughness of films was observed with the increase at extrusion temperature at the same extrusion screw speed for the sunflower stalk xylan that extracted at 60^{o}C ($p<0.05$). The ultimate tensile strength of the films produced from the sunflower stalk xylans extracted at 60^{o}C was approximately 46 MPa as seen in Figure 4.12. The water contents of the sunflower stalk xylans for both extracted at room temperature and 60^{o}C are given in Table 4.7.

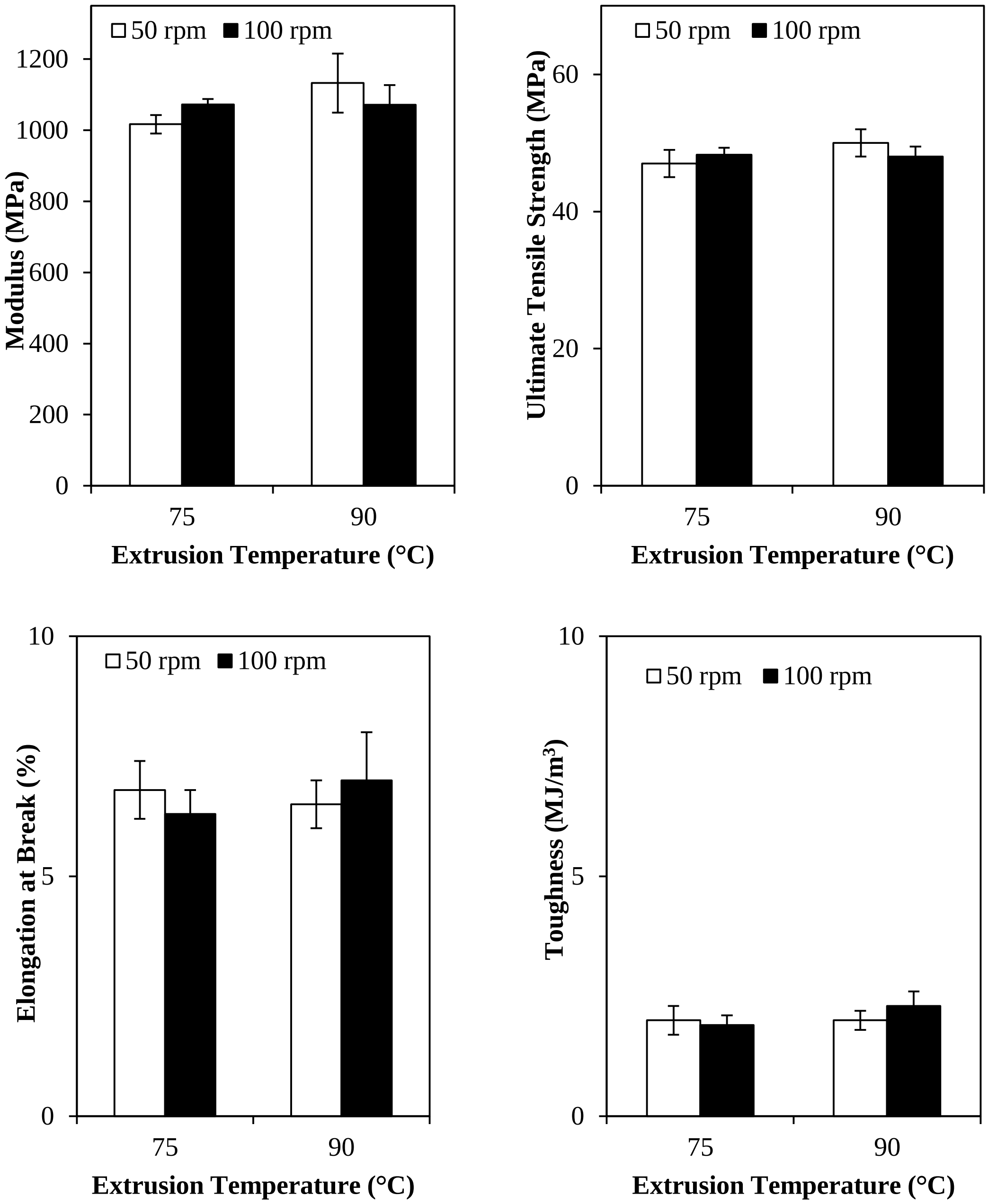


Figure 4.11 Mechanical properties of the extruded films produced from the sunflower stalk xylan extracted at room temperature.

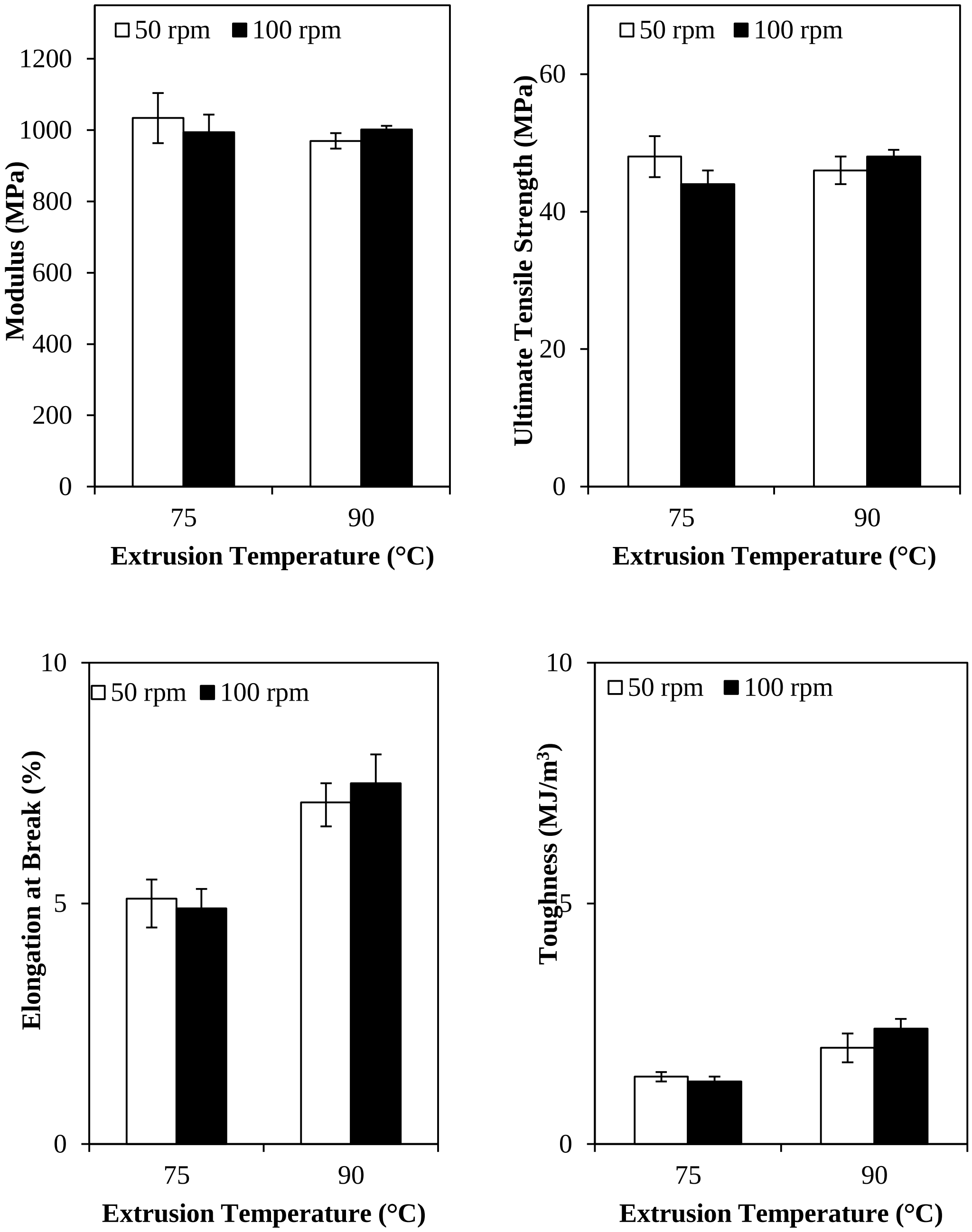


Figure 4.12 Mechanical properties of the films produced from sunflower stalk xylan extracted at 60°C.

Table 4.7 Water contents of the sunflower stalk xylan feed and the extruded strips for the sunflower stalk xylan extracted at room temperature and at 60^{o}C.

Extraction Temperature	Extrusion Conditions, T=Temp, S=Speed	% Water Content of Xylan	% Water Content of Strip
Room Temperature	T=90°C, S=50 rpm	29.0	25.5
	T=90°C, S=100 rpm	29.5	26.7
	T=75°C, S=50 rpm	30.1	27.8
	T=75°C, S=100 rpm	29.5	26.3
60^{o}C	T=90°C, S=50 rpm	32.0	28.0
	T=90°C, S=100 rpm	29.5	27.1
	T=75°C, S=50 rpm	28.2	25.5
	T=75°C, S=100 rpm	29.4	24.2

4.3.2. Effect of Different Types of Lignocellulosic Feedstocks on Mechanical Properties of Xylan Based Films Obtained via Extrusion

The mechanical properties of films produced by different lignocellulosic feedstocks are given in Figure 4.13. While the modulus of films produced by all three types of biomasses was similar to each other, the ultimate tensile strength, flexibility and toughness values were quite different ($p<0.05$) for room temperature extracted xylans. However, all the mechanical properties were significantly different from each other for the films produced by xylans extracted at 60^{o}C including elastic modulus ($p<0.05$). Corn cob xylan based films showed the best mechanical properties, whereas sunflower xylan based films had shown serious flexibility problems for both xylans extracted at room temperature and 60^{o}C.

Increase at extraction temperature affected negatively on mechanical properties of corn cob and wheat straw xylan films except modulus. On the other hand, no significant effect of extraction temperature was observed on the toughness of sunflower stalk xylan films ($p>0.05$).

In general, xylan type and extraction temperature had marked influences on the flexibilities of films. Films in higher flexibility and toughness were obtained from corn cob xylan extracted at room temperature where xylans had higher Ara/Xyl ratio than those of extracted at 60^{o}C. Previously, it was reported that Ara/Xyl ratio enhanced the film formation capacity of xylans that were extracted from different biomasses in the literature (Egüés et al., 2013). Also in another study, an increase in the Ara/Xyl of the samples showed a clear plasticizing effect on the films (Sternemalm et al., 2008). However, the extraction temperature did not have a strong influence on mechanical properties of films based on wheat straw or sunflower stalk xylan. This situation is most probably observed because of compositional difference of corn cob than other biomass types. All the extrusions were conducted at the same conditions, 90°C and 50 rpm. The reduction in water contents of xylans during extrusion are around 2-3% as given in Table 4.8.

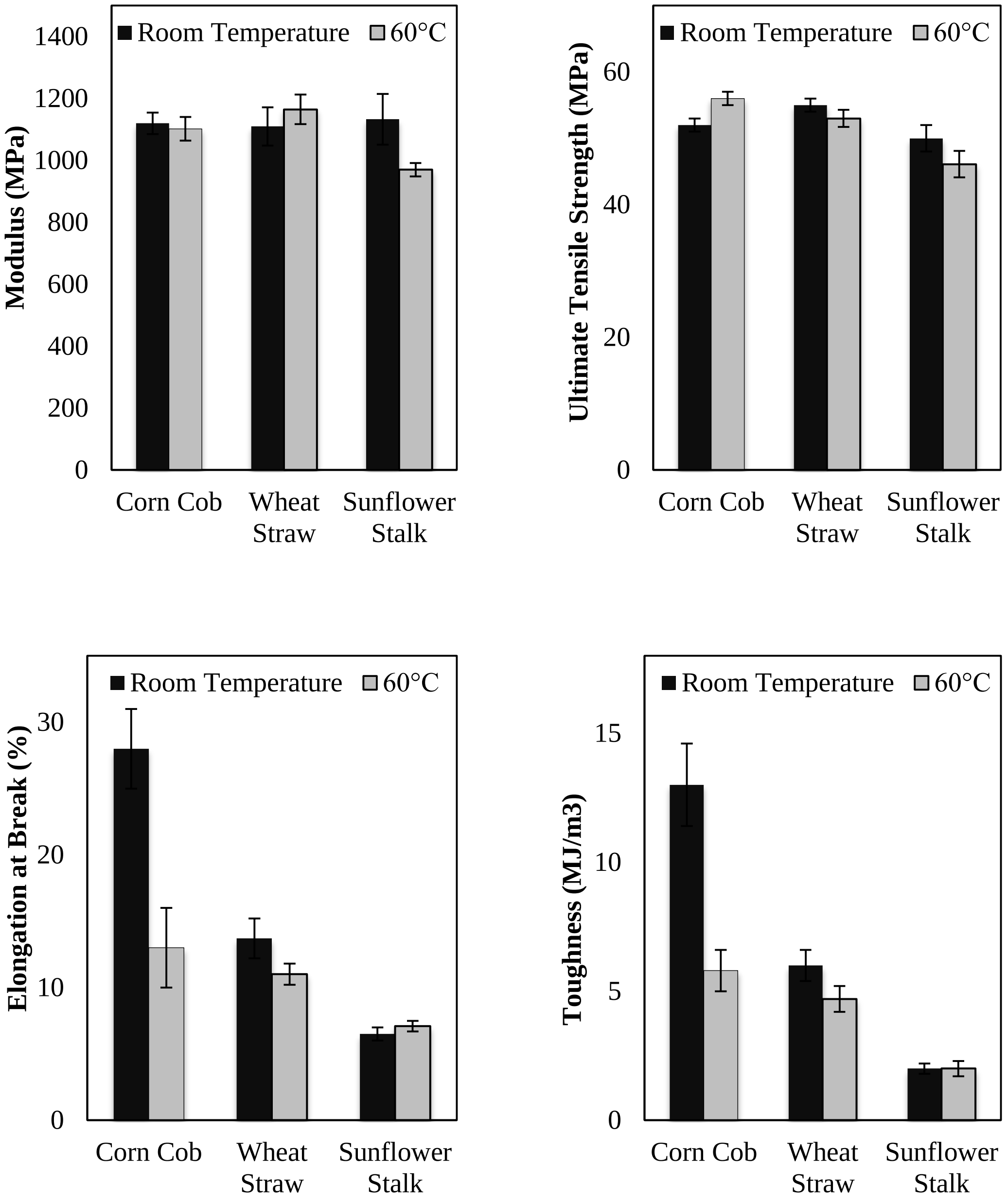


Figure 4.13 The effect of xylan extraction temperature on the mechanical properties of the films obtained via the extrusion.

Table 4.8 Water contents of xylan feeds and the extruded strips for different types of xylan extracted at both room temperature and 60^{o}C.

Extraction Temperature	**Biomass**	**% Water Content of Xylan**	**% Water Content of Strip**
Room Temperature	Corn Cob	27.3	24.6
	Wheat Straw	27.8	27.1
	Sunflower Stalk	29.5	26.7
60^{o}C	Corn Cob	26.9	23.4
	Wheat Straw	28.1	26.9
	Sunflower Stalk	29.5	27.1

4.4. Effect of Extraction Temperature on Thermal Properties of Extruded Films

The thermal gravimetric analysis (TGA) results for the extruded films produced using the room temperature extracted corn cob, wheat straw, and sunflower stalk xylans are given in Figures 4.14, 4.16, 4.18, also the TGA results of films produced using the xylans extracted at 60°C are given in Figures 4.15, 4.17 and 4.19, respectively. As can be seen in the TGA curves of the extruded films, the extraction temperature of xylans did not influence the degradation behavior of these films. The degradation onset temperatures of the extruded films produced using the corn cob, wheat straw, and sunflower stalk xylans were determined as approximately 301°C, 302°C, and 296 °C, respectively. These values were quite similar to each other which might be a result of using xylan as raw material to produce all films. Obviously, the differences on the compositions did not affect thermal properties of films.

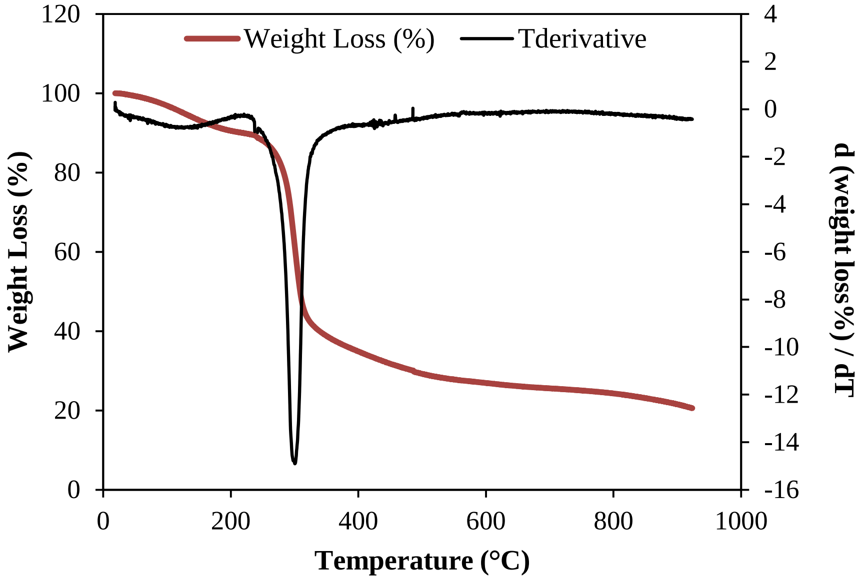


Figure 4.14 TGA curves of the extruded films produced using the corn cob xylans extracted at room temperature.

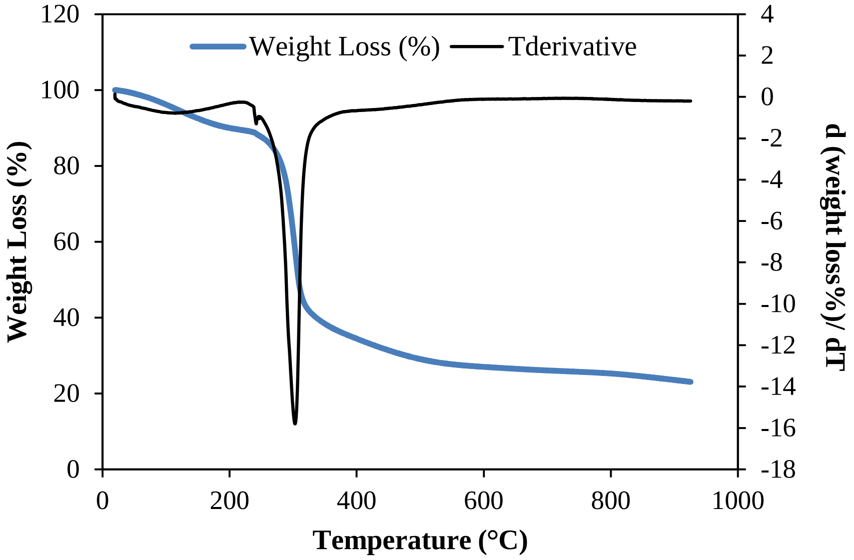


Figure 4.15 TGA curves of the extruded films produced using the corn cob xylans extracted at 60°C.

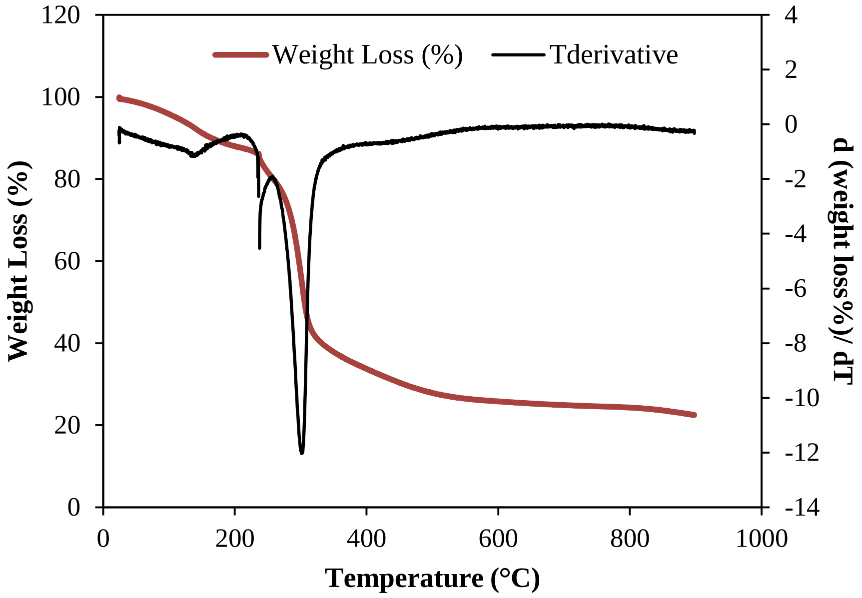


Figure 4.16 TGA curves of the extruded films produced using the wheat straw xylans extracted at room temperature.

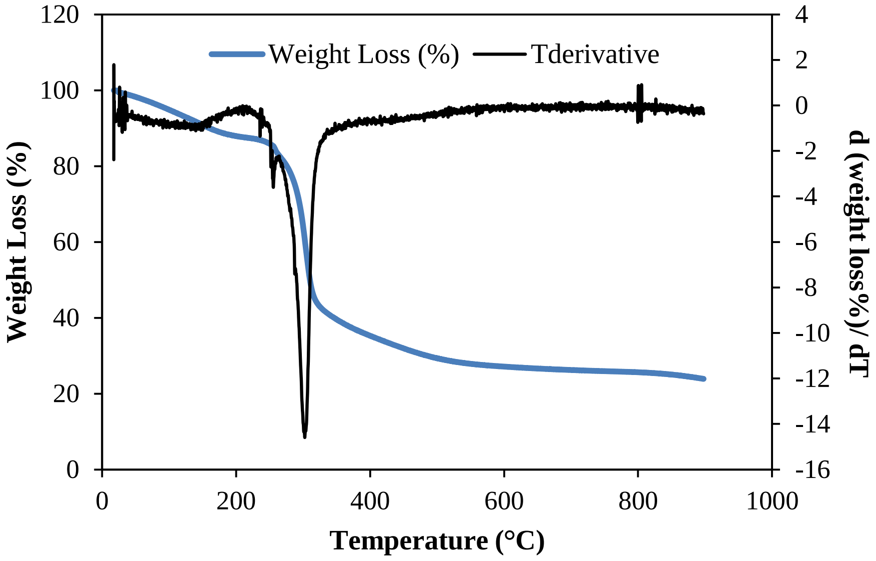


Figure 4.17 TGA curves of the extruded films produced using the wheat straw xylans extracted at 60^{o}C.

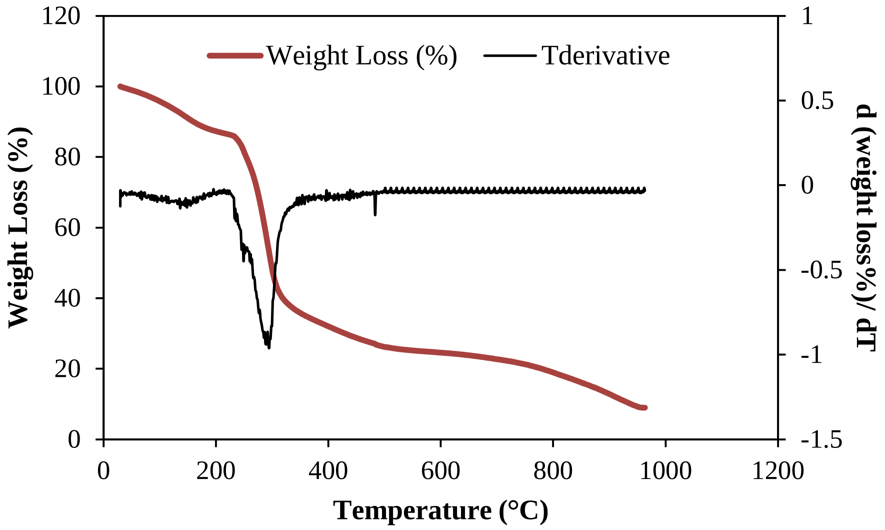


Figure 4.18 TGA curves of the extruded films produced using the sunflower stalk xylans extracted at room temperature.

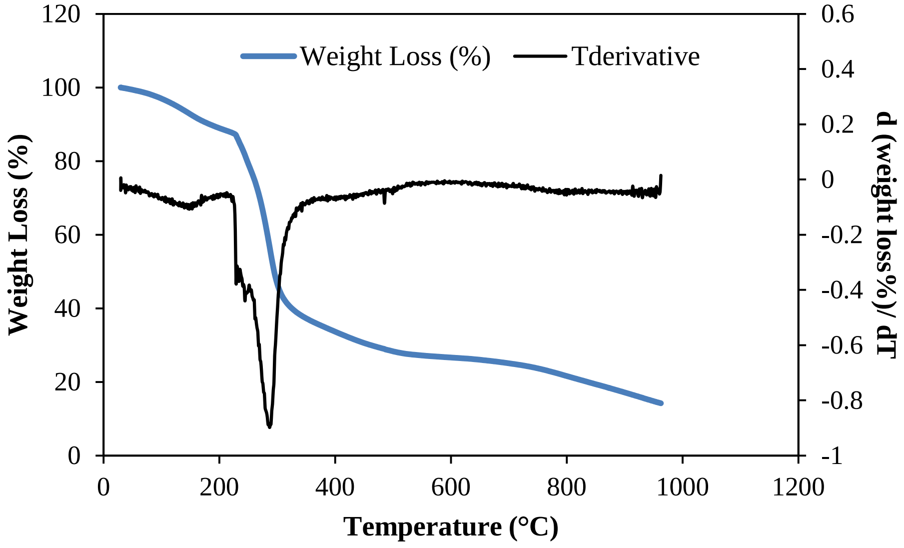


Figure 4.19 TGA curves of the extruded films produced using the sunflower stalk xylans extracted at 60°C.

4.5. Surface and Cross Sectional Morphology of the Extruded Films

Morphological properties of the extruded films were investigated by SEM analysis. The SEM images of the cross-sectional areas of the xylan films are given in Figures 4.20, 4.21 and 4.22. The cross sectional areas of the corn cob xylan films exhibited a relatively homogenous, smooth and compact structure. The microscopic characterization showed that the wheat straw xylan films also have homogenous structure. The SEM images showed that the cross section of the sunflower xylan based films were not as uniform as those of the films produced from the wheat straw and corn cob xylans. Some defects (cracks and voids) were observed on the cross sectional images of the sunflower stalk xylan based films. Mechanical properties of films should be related to these defects that were observed by SEM analysis.

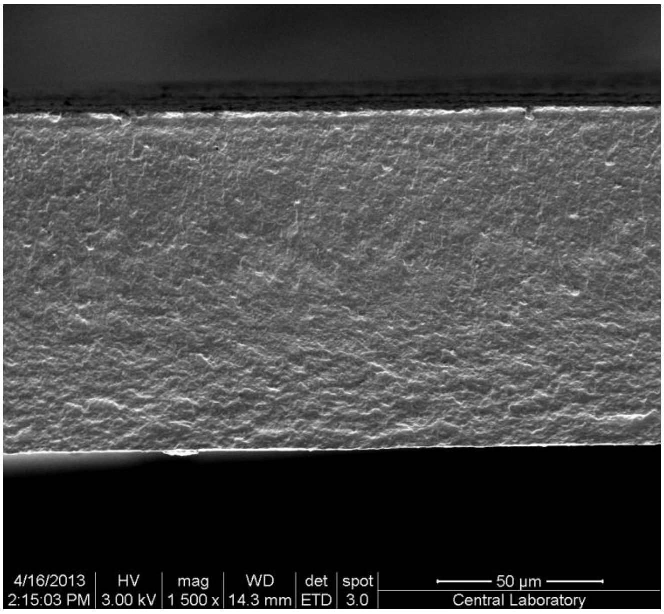


Figure 4.20 Cross section SEM images of the corn cob xylan based films extruded at 75^{o}C and 50 rpm.

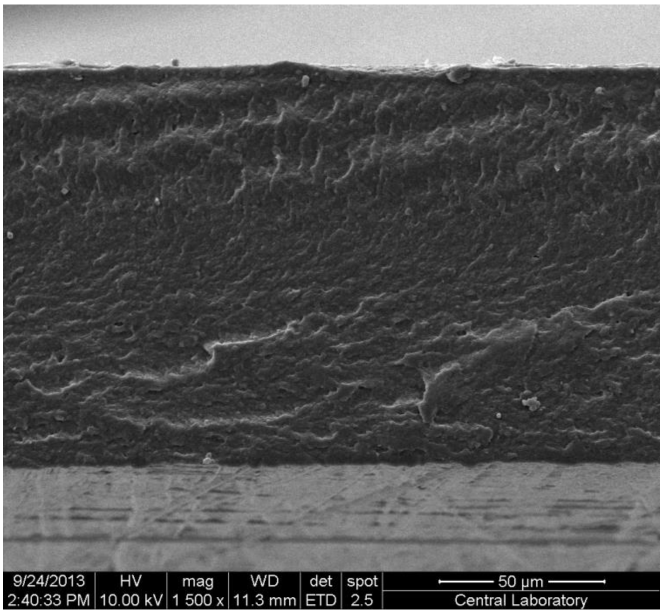


Figure 4.21 Cross section SEM images of the wheat straw xylan based films extruded at 75°C and 50 rpm.

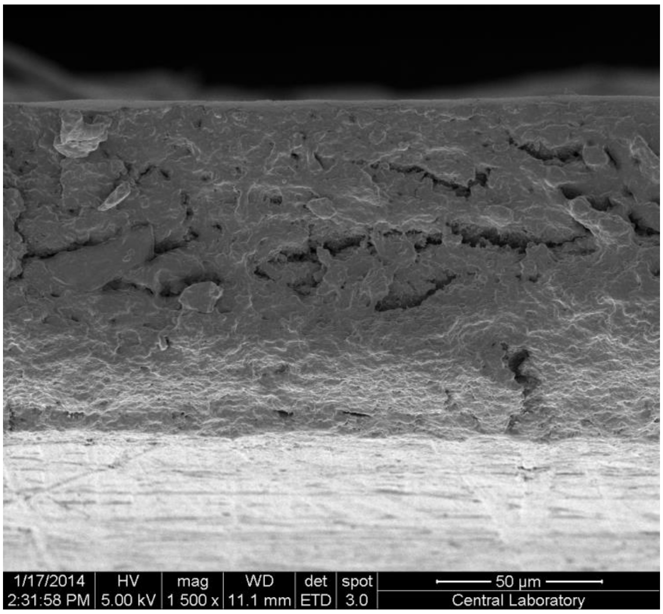


Figure 4.22 Cross section SEM images of the sunflower stalk xylan based films extruded at 75°C and 50 rpm.

Surface SEM pictures of the xylan films are given in Figure 4.23, 4.24, and 4.25. The surfaces of all xylan based films appear homogenous. Parallel and crossing lines on the surfaces of the extruded films were observed which should be related with the rolling process as a result of the rough surface of the roller. While parallel lines occurred on the surfaces of corn cob based films, crossing lines appeared on the surfaces of wheat straw and sunflower stalk films. The reason of this was rolling was applied more than one time in order to have thicker strips from the extrusion of wheat straw and sunflower stalk.

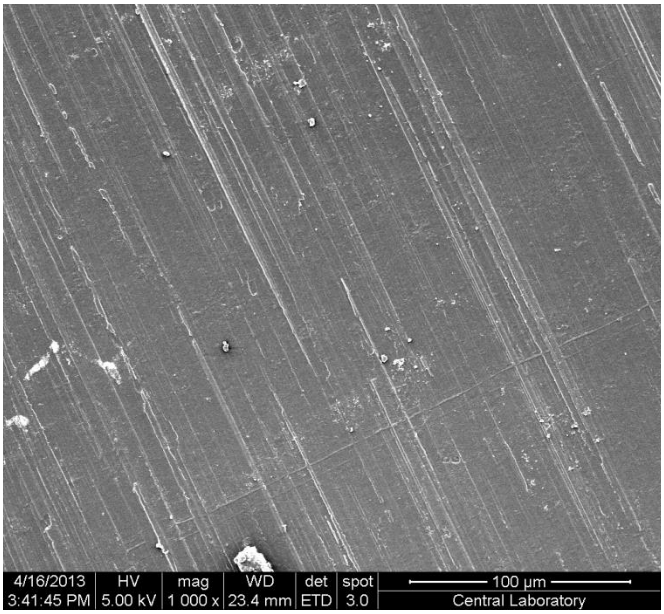


Figure 4.23 Surface SEM images of the corn cob xylan based films extruded at 90^{o}C and 50 rpm.

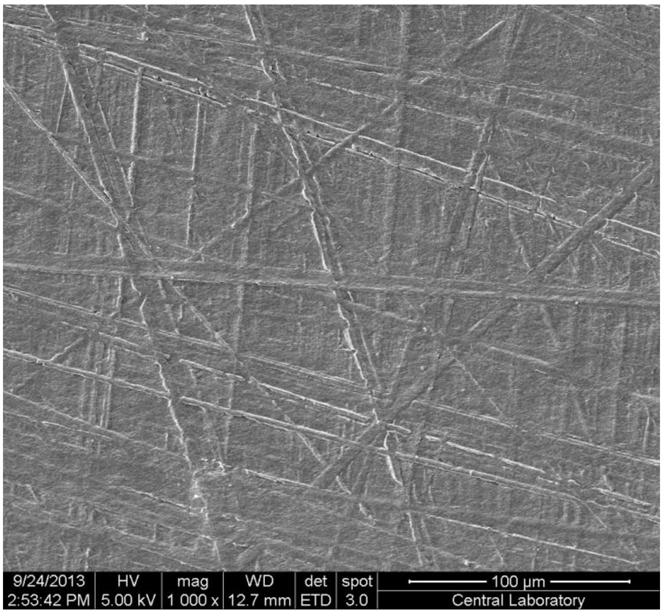


Figure 4.24 Surface SEM images of the wheat straw xylan based films extruded at 90°C and 50 rpm.

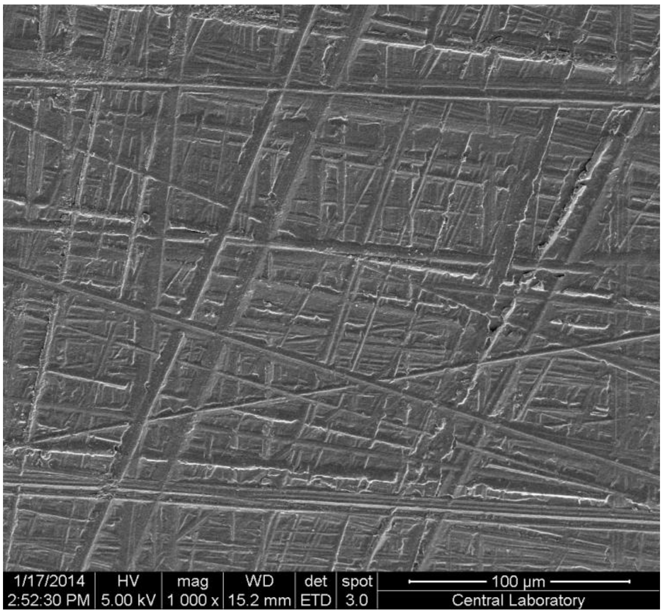


Figure 4.25 Surface SEM images of the sunflower stalk xylan based films extruded at 90°C and 50 rpm.

4.6. Comparison of Mechanical, Morphological and Thermal Properties of the Films Produced using Solvent Casting and Extrusion Techniques

4.6.1. The Films Based on Corn Cob Xylan

In this part of the study, the properties of the films produced using the corn cob xylans via the extrusion and solvent casting techniques were investigated. The extruded strips with a thickness of approximately 450±20 μm were rolled, and the rolled films with a thickness of about 160±20 μm were obtained. To compare the properties of the films produced using the extrusion and solvent casting techniques, the thickness of the films should be similar. Thus, the amount of xylans in the film forming solutions was increased to obtain similar thicknesses with that of the rolled films. However as the thicknesses of the solvent casted films are increased, more cracks are formed so the continuity of the films decreased. So, production of solvent casted films at the same thickness with the extruded and rolled films could not be performed. Some large cracks were observed in the solvent casted films produced using the corn cob xylans extracted at room temperature and the film formation was not possible via the solvent casting method when the corn cob xylans extracted at 60^{o}C were used (Figure 4.26). Even though some large cracks were observed in the solvent casted films produced using the corn cob xylans extracted at room temperature, it was possible to get small dog bone samples from the fractions in order to conduct mechanical tests.

The mechanical properties of the extruded and solvent casted films produced using the corn cob xylans extracted at room temperature and 60^{o}C are summarized in Table 4.9. Films were extruded at 90°C and 50 rpm. The extraction temperature of the corn cob xylans had a strong influence on the mechanical properties of extruded films. The elongation at break and toughness values of the extruded films produced from the xylan extracted at room temperature were higher compared to the ones extracted at 60^{o}C. Concerning the xylans extracted at room temperature, the elongation at break and toughness values of the extruded films were more than two times higher than those of the solvent casted films. However, by increasing the thicknesses of the solvent casted films from 50 to about 100 μm, the mechanical properties have been increased abruptly, since the thinner solvent casted films could not even be placed into the instrument for the mechanical measurements. While the extruded films had a toughness of 13 MJ/m^3, the solvent casted films only had 5 MJ/m^3. There was no difference on the degradation onset temperatures of the films produced by the two methods, which corresponds to approximately 300°C.

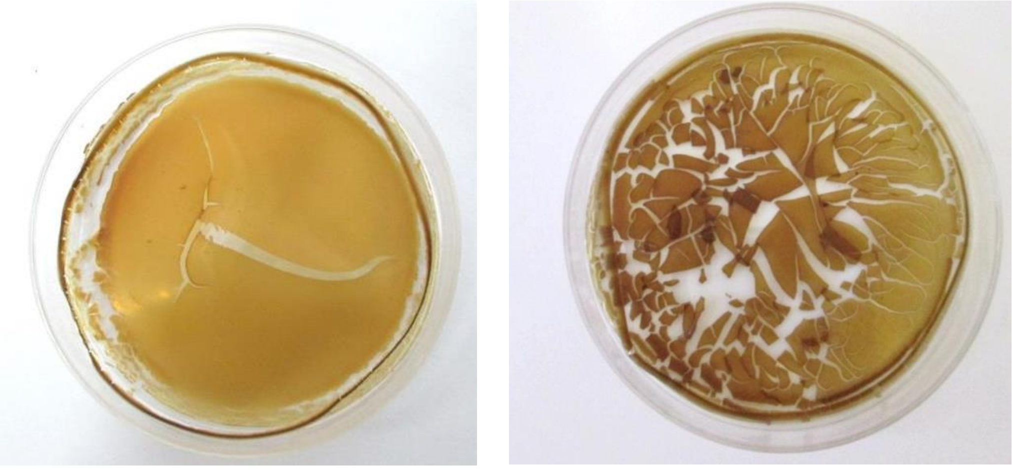


Figure 4.26 The films produced using the corn cob xylans extracted at room temperature (left) and 60°C (right) via solvent casting method.

Table 4.9 Mechanical properties and thicknesses of the corn cob xylan based films produced by the solvent casting and extrusion techniques.

Production Method	**Extraction Temperature**	**Modulus (MPa)**	**UTS (MPa)**	**Elongation at Break (%)**	**Toughness (MJ/m^3)**	**Thickness (µm)**
Solvent Casting	Room Temperature	1306±300	60±9	11±2	5±0.45	107±18
	60°C	-	-	-	-	-
Extrusion	Room Temperature	1120±35	52±1	28±3	13±1.6	154±12
	60°C	1102±38	56±1	13±3	5.8±0.8	162±26

Both the extruded and solvent casted films display a homogeneous structure on the surface and cross sections. The surfaces of solvent casted films were smoother than those of the extruded films (Figure 4.27, 4.28 and 4.29).

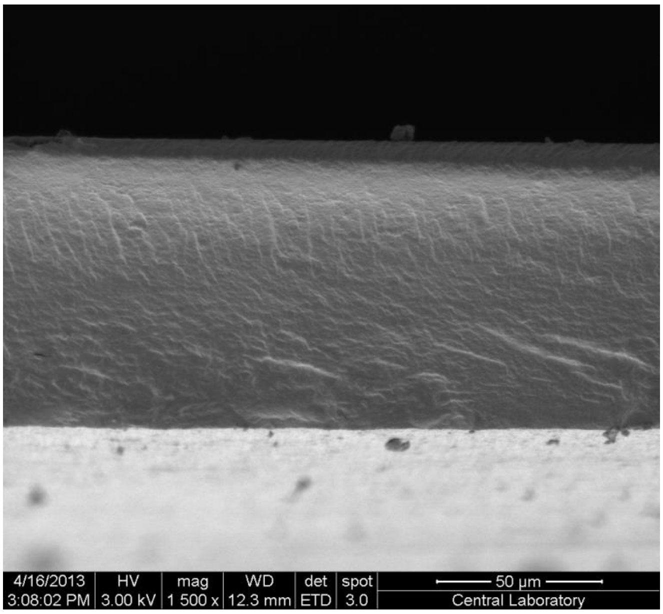


Figure 4.27 Cross section SEM images of the corn cob xylan based films produced via solvent casting.

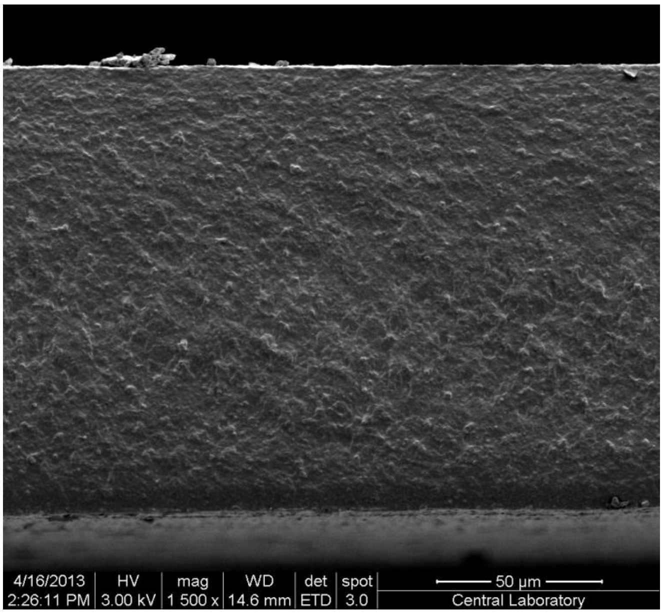


Figure 4.28 Cross section SEM images of the corn cob xylan based films produced via extrusion at 90^{o}C and 50 rpm.

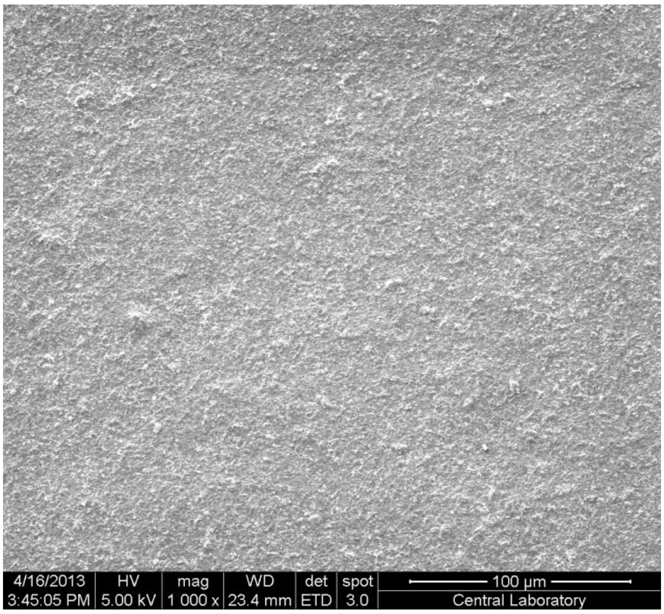


Figure 4.29 SEM images of corn cob xylan film surface produced via solvent casting.

4.6.2. The Films Based on Wheat Straw Xylan

As observed for the corn cob xylan based solvent casted films, no film formation was observed for the solvent casted films based on the wheat straw xylan when thicker films were attempted to produce. The fragments of the wheat straw xylan based films were smaller compared to those of the corn cob xylan based films; therefore, the mechanical testing could not be performed for these films. Extrusions were conducted at 90°C and 50 rpm similarly corn cob xylan. Moreover, the toughness of the extruded films was slightly decreased when the extraction temperature was increased as seen in Table 4.10. No significant difference was observed on the degradation temperature of the films produced by the two methods which was determined as approximately 300^{o}C.

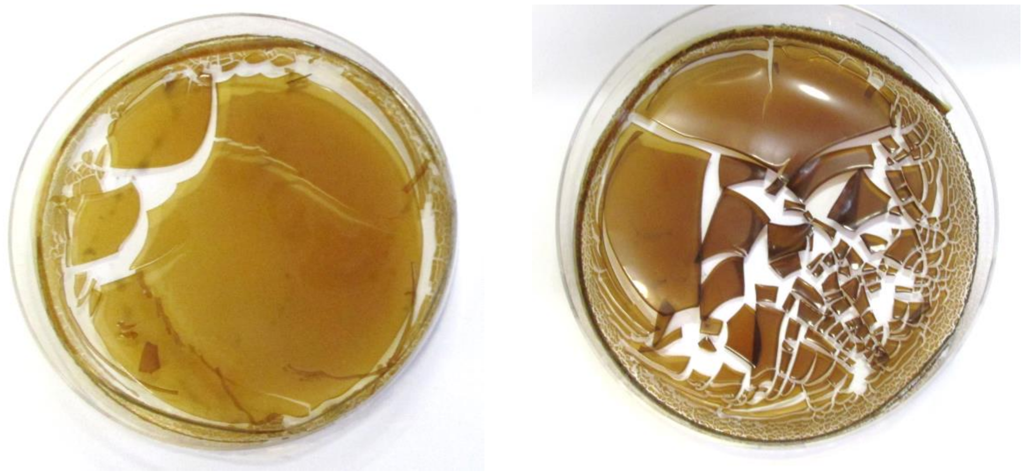


Figure 4.30 The solvent casted films produced using the wheat straw xylans extracted at room temperature (left) and 60°C (right).

Table 4.10 The mechanical properties and thickness of the wheat straw xylan based films produced by the solvent casting and extrusion methods.

Production Method	**Extraction Temperature**	**Modulus (MPa)**	**UTS (MPa)**	**Elongation at Break (%)**	**Toughness (MJ/m^3)**	**Thickness (µm)**
Solvent Casting	Room Temperature	-	-	-	-	-
	60°C	-	-	-	-	-
Extrusion	Room Temperature	1110±62	55±1	14±1,5	6±0.6	128±8
	60°C	1165±48	53±1	11±1	5±0.5	129±9

The surfaces and cross sections of the wheat straw xylan based films produced using the solvent casting and extrusion methods had homogenous and smooth appearances as seen in Figures 4.31, 4.32 and 4.33.

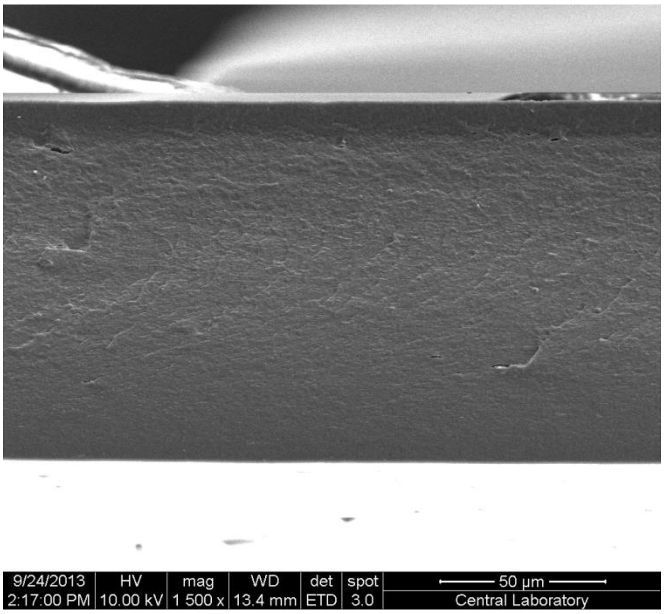


Figure 4.31 The cross sectional SEM images of the wheat straw xylan based films produced via the solvent casting method.

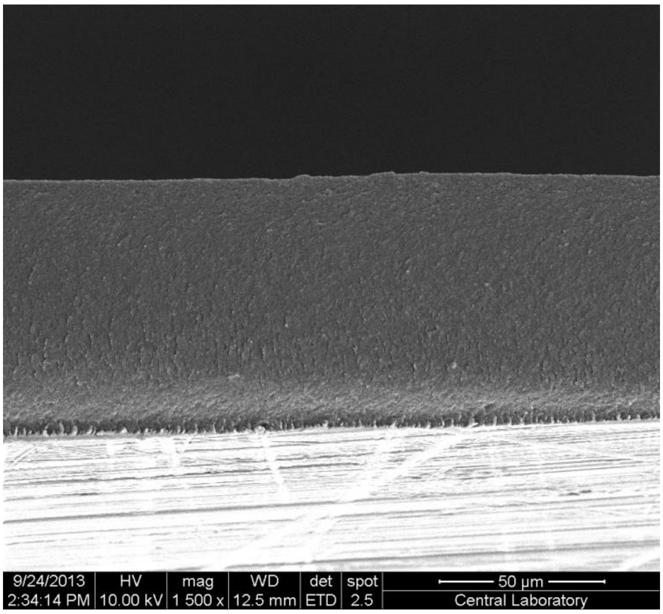


Figure 4.32 The cross sectional SEM images of the wheat straw xylan based films produced via the extrusion method at 90°C and 50 rpm.

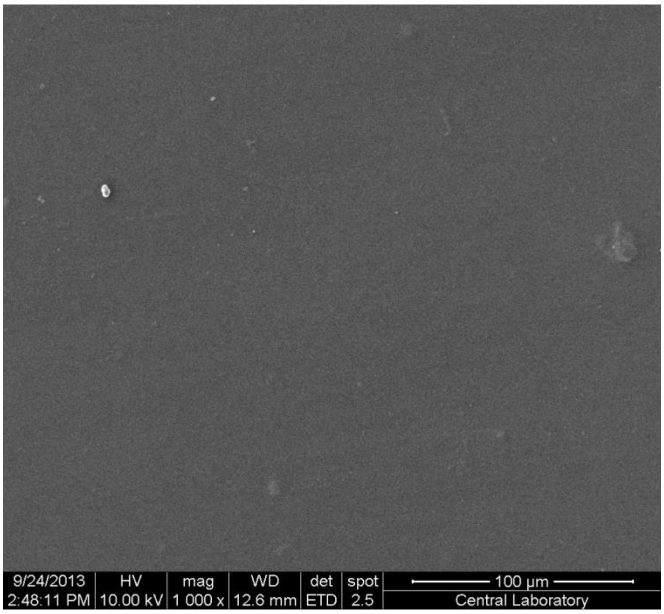


Figure 4.33 The SEM images of the wheat straw xylan based film surface produced via the solvent casting.

4.6.3. The Films Based on Sunflower Stalk Xylans

The images of the solvent casted films obtained using the sunflower stalk xylan is shown in Figure 4.34. As can be seen from Figure 4.34, crack free and homogenous solvent casted films obtained when the sunflower stalk xylan was used. Compared to other biomasses, more continuous films were formed as a result of better solubility of sunflower stalk xylan in water, the solvent in the film forming solution, than other types of biomass. Solubilities of xylans were identified by measuring the turbidities in water which corresponded to absorbance values at 600 nm (Brown, 1991) (Table 4.11). Sunflower stalk xylan showed the lowest turbidity in water as expected.

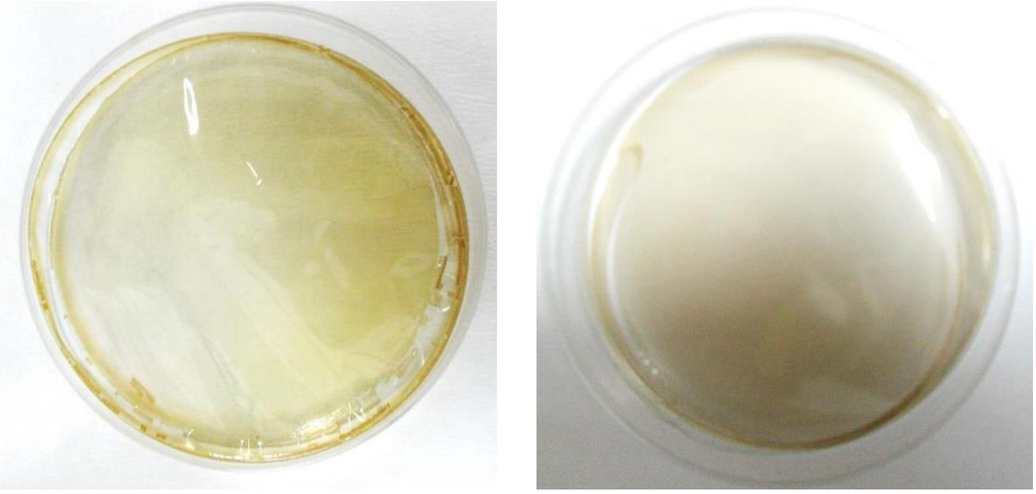


Figure 4.34 The solvent casted films produced using the sunflower stalk xylans extracted at room temperature (left) and 60^{o}C (right).

Table 4.11 Absorbance values of xylans at 600 nm.

Source of xylan	**Absorbance at 600 nm (A)**
Corn cob	2.164
Wheat straw	2.127
Sunflower stalk	1.583

Moreover, the extruded and subsequently rolled films were much weaker than the solvent casted films for the case of sunflower stalk xylan (Table 4.12). This may be resulted from $NaBH_4$ content that was added (1%) during the extraction of sunflower stalk xylan. The reason for using $NaBH_4$ is that, increasing the yield of xylans obtained from the extraction followed by precipitation. With the addition $NaBH_4$, xylan degradation was prevented which resulted in xylan molecules having higher molecular weight and higher yield. As compared to the films produced from xylans extracted without addition of $NaBH_4$, 1% $NaBH_4$ addition in corn cob hemicellulose extraction increased UTS and modulus of films from 10 MPa to 39 MPa and from 364 to 1743 MPa for solvent casted films in the previous studies (Toraman, 2012). In this study, the UTS and modulus of the solvent casted films were around 105 MPa and 2020 MPa. However, extruded films did not show any improvement in mechanically which might be because of presence of boron particles as impurities. The UTS and toughness of the extruded films were around 48 MPa and 2 MJ/m^3, which also were lower than other extruded films.

Table 4.12 The mechanical properties and thickness of the sunflower stalk xylan based films produced by the solvent casting and extrusion methods.

Production Method	**Extraction Temperature**	**Modulus (MPa)**	**UTS (MPa)**	**Elongation at Break (%)**	**Toughness (MJ/m^3)**	**Thickness (μm)**
Solvent Casting	Room Temperature	2021± 107	107± 3	9.5±0.5	7.3±0.5	99±12
	60°C	2062± 33	103± 10	7.6±1	5.5±1	90±3
Extrusion	Room Temperature	1133± 82	50±2	6.5±0.5	2±0.2	160±26
	60°C	970±22	46±2	7.1±0.5	2±0.3	188±15

All the films produced using both techniques showed similar thermal properties. The onset of degradation temperatures of the solvent casted films and the extruded films were around 290°C and 296±2°C, respectively. The cross sectional and surface SEM images of the sunflower stalk xylan based films via solvent casting were homogenous and smooth, but there were some cracks in the cross sectional of extruded films (see Figures 4.35, 4.36 and 4.37).

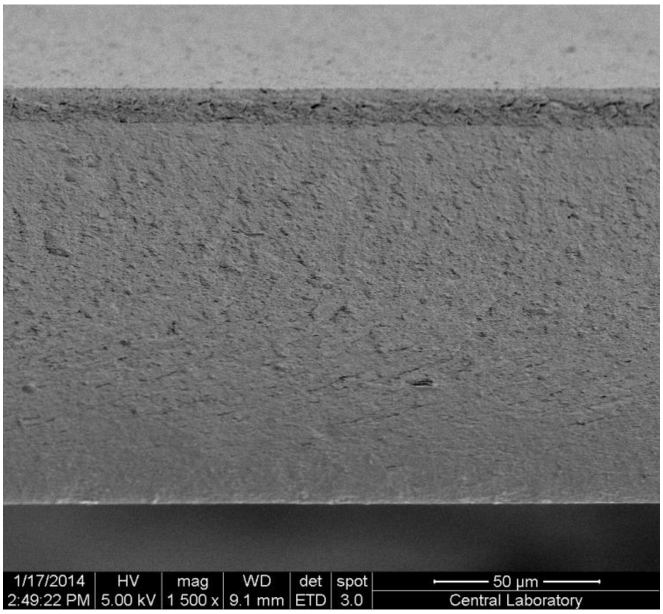


Figure 4.35 The cross sectional SEM picture of the sunflower stalk xylan based film produced via the solvent casting.

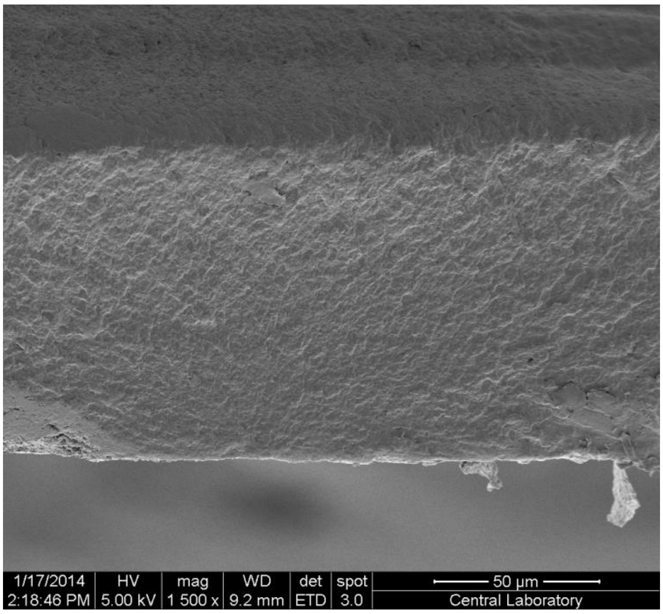


Figure 4.36 The cross sectional SEM picture of the sunflower stalk xylan based film produced via the extrusion at 90^{o}C and 50 rpm.

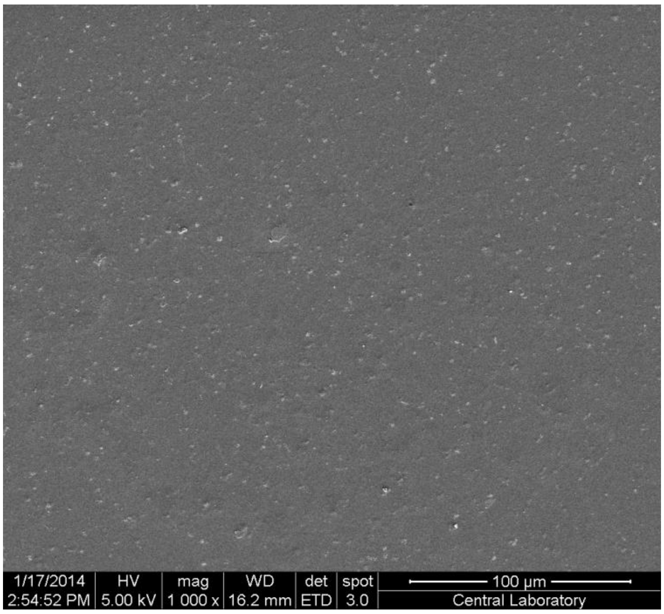


Figure 4.37 The surface SEM picture of the sunflower stalk xylan based film produced via the solvent casting.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The xylans were isolated from corn cob, wheat straw and sunflower stalk, and xylan based films were produced via extrusion and solvent casting. Films can be produced via extrusion of each type of xylans, and they were rolled to obtain films with a thickness of approximately 100 µm. First of all, film formation from three different xylans was achieved by extrusion. From a variety of experiments carried out, 90^oC was determined as a slightly better extrusion temperature considering the mechanical properties on films for all xylans, whereas no significant effect of extrusion screw speed was observed. Influence of extraction temperature on elongation at break and toughness of the films was noticeable only for corn cob xylans, which can be explained to result from differences in Ara/Xyl ratios of xylans. However there was no considerable effect on wheat straw and sunflower stalk xylans. So, film production from the films obtained by extraction at room temperature is better than the extraction at 60°C. As a result of comparing two production methods, extrusion could be determined as a better production method than solvent casting, because no continuous film forming was observed via solvent casting for the xylans extracted from corn cobs and wheat straw. Moreover, films were produced by corn cob xylan films with a 28% elongation at break and a 52 MPa tensile strength, which are quite satisfactory. Corn cob was determined the most consistent biomass due to having high hemicellulose content and showing favorable mechanical properties among three biomass. Stronger and stiffer films were produced from sunflower stalk xylan via solvent casting with a tensile strength of 107 MPa and a modulus of 2021MPa, since solubility of sunflower stalk xylan in water was better than other xylans. The onsets of thermal degradation temperature for solvent casted and extruded films were determined via TGA as 300°C for corn cob and wheat straw xylan and 296°C for the films produced from sunflower stalk xylan.

For further studies, it should be focused on enhancing the yield of xylans by changing the extraction parameters including particle sizes of biomass, temperature or period. Moreover, a better rolling system should be considered to decrease the defects that were formed by the roller used. Additional characterization of films can be performed including biodegradability, oxygen permeability or water vapor transmissions.

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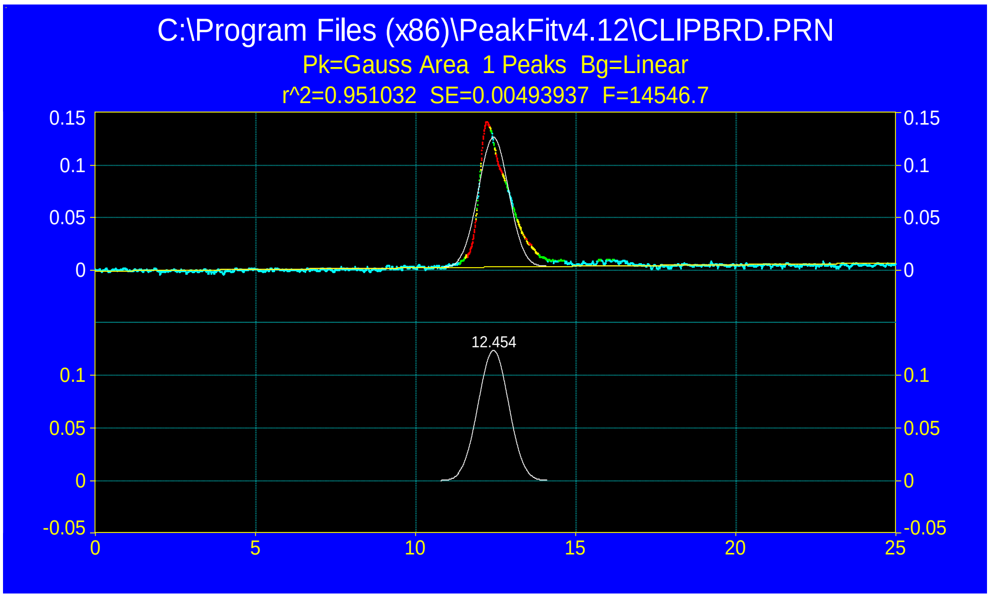
APPENDIX A

A Sample of HPLC Peak Details

Glucose at 2 mg/ml concentration



Description: C:\Program Files (x86)\PeakFitv4.12\CLIPBRD.PRN
File Source: C:\Program Files (x86)\PeakFitv4.12\CLIPBRD.PRN

Fitted Parameters

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.95103200	0.95095025	0.00493937	14546.7031

Peak	Type	a_0	a_1	a_2
1	Gauss Area	0.14346241	12.4540013	0.46317360
B	Linear Bg	-0.0007807	0.00030591	

Measured Values

Peak	Type	Amplitude	Center	FWHM	Asym50	FW Base	Asym10
1	Gauss Area	0.12356754	12.4540013	1.09069048	1.00000000	2.18324410	1.00000000

Peak	Type	Anlytc Area	% Area	Int Area	% Area	Centroid	Moment2
1	Gauss Area	0.14346241	100.000000	0.14346241	100.000000	12.4540013	0.21452978
	Total	0.14346241	100.000000	0.14346241	100.000000		

Parameter Statistics

Peak 1 Gauss Area

Parm	Value	Std Error	t-value	95

```
 Area     0.14346241      0.00074527      192.496847      0.14200112      0.14492371
  Ctr     12.4540013      0.00263872      4719.71352      12.4488274      12.4591752
  Wid     0.46317360      0.00268561      172.465053      0.45790778      0.46843942

Baseline  Linear Bg
 Parm     Value           Std Error       t-value         95
   a0     -0.0007807      0.00018282      -4.2702513      -0.0011392      -0.0004222
   a1     0.00030591      1.2493e-05      24.4865774      0.00028141      0.00033040
```

Analysis of Variance

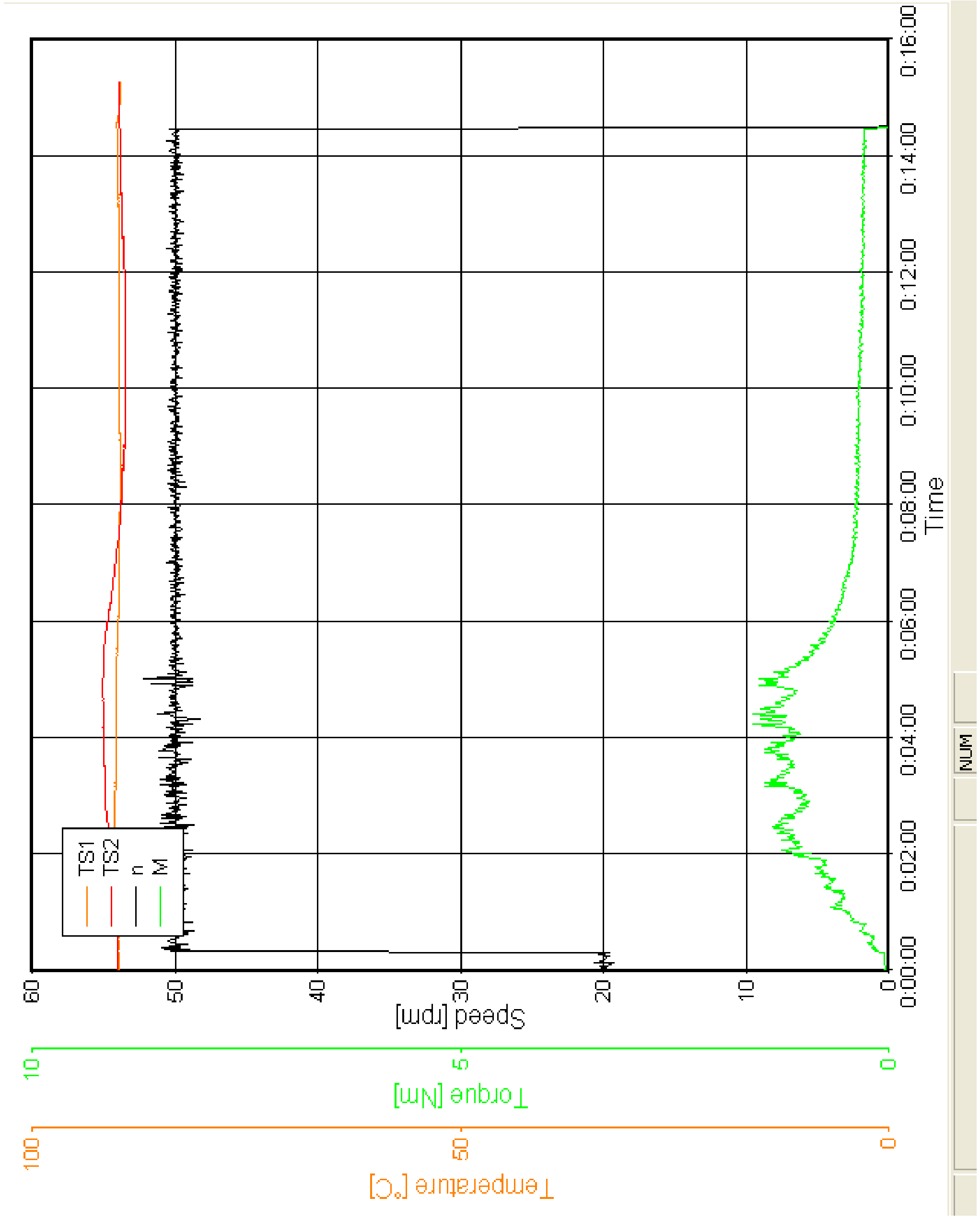
```
r^2 Coef Det      DF Adj r^2      Fit Std Err
0.95103200        0.95095025      0.00493937
Source      Sum of Squares       DF        Mean Square             F
Regr        1.4196049            4         0.35490123              14546.703
Error       0.073094506          2996      2.4397365e-05
Total       1.4926994            3000
```

Details of Fit

```
Set Convergence       State          Iterations        Minimization        Extent
   1E-6             Converged            13            Least Squares         1/1
Curvature Matrix                  Constraints                                  Violated
   Sparse-Roots         25.0000-5.00000-50.0000- None  - None                     0
```

APPENDIX B

A Sample of Extrusion Data for Room Temperature Extracted Corn Cob Hemicellulose Extruded at 90°C and 50 RPM



APPENDIX C

Statistical Analysis (p values) Between the Mechanical Properties of Films Produced Using Different Extrusion Parameters

Corn Cob Xylan Extracted at Room Temperature

Mechanical Properties	T=90°C, 50-100 rpm	T=75°C, 50-100 rpm	RPM=50, 75-90°C	RPM=100, 75-90°C
Modulus (MPa)	0.8101	0.7651	0.5302	0.2285
UTS (MPa)	0.9342	0.044	0.0786	0.7944
Elongation at Break (%)	0.1609	0.6787	0.0358	0.006
Toughness (MJ/m^3)	0.199	0.4686	0.04	0.010

Corn Cob Xylan Extracted at 60°C

Mechanical Properties	T=90°C, 50-100 rpm	T=75°C, 50-100 rpm	RPM=50, 75-90°C	RPM=100, 75-90°C
Modulus (MPa)	0.1006	0.8497	0.4179	0.0402
UTS (MPa)	0.1689	0.5193	0.9500	0.7271
Elongation at Break (%)	0.7444	0.6496	0.3818	0.2169
Toughness (MJ/m^3)	0.4777	0.4594	0.6400	0.9122

Wheat Straw Xylan Extracted at Room Temperature

Mechanical Properties	T=90°C, 50-100 rpm	T=75°C, 50-100 rpm	RPM=50, 75-90°C	RPM=100, 75-90°C
Modulus (MPa)	0.4875	0.5969	0.8174	0.3260
UTS (MPa)	0.4028	0.0560	0.0021	0.0855
Elongation at Break (%)	0.5815	0.0073	0.0106	0.5947
Toughness (MJ/m^3)	0.2019	0.0002	0.0009	0.0972

Wheat Straw Xylan Extracted at 60°C

Mechanical Properties	T=90°C, 50-100 rpm	T=75°C, 50-100 rpm	RPM=50, 75-90°C	RPM=100, 75-90°C
Modulus (MPa)	0.0734	0.1275	0.5457	0.5950
UTS (MPa)	0.0574	0.4327	0.7280	0.5401
Elongation at Break (%)	0.0598	0.0067	0.0211	0.7237
Toughness (MJ/m^3)	0.1269	0.0041	0.0100	0.7100

Sunflower Stalk Xylan Extracted at Room Temperature

Mechanical Properties	T=90°C, 50-100 rpm	T=75°C, 50-100 rpm	RPM=50, 75-90°C	RPM=100, 75-90°C
Modulus (MPa)	0.3779	0.0712	0.0710	0.7443
UTS (MPa)	0.9447	0.6978	0.4476	0.9950
Elongation at Break (%)	0.1909	0.5505	0.2602	0.3820
Toughness (MJ/m^3)	0.3047	0.8414	0.9400	0.4100

Sunflower Stalk Xylan Extracted at 60°C

Mechanical Properties	T=90°C, 50-100 rpm	T=75°C, 50-100 rpm	RPM=50, 75-90°C	RPM=100, 75-90°C
Modulus (MPa)	0.0558	0.3775	0.1104	0.8042
UTS (MPa)	0.0821	0.0264	0.2564	0.0073
Elongation at Break (%)	0.3306	0.5082	0.0001	0.0015
Toughness (MJ/m^3)	0.0707	0.0601	0.0100	0.0006

Statistical Analysis (p values) Between the Mechanical Properties of Films Produced from Different Xylan Sources

Xylans Extracted at Room Temperature

Mechanical Properties	Corn Cob- Wheat Straw	Corn Cob-Sunflower Stalk	Wheat Straw-Sunflower Stalk
Modulus (MPa)	0.1195	0.4043	0.4487
UTS (MPa)	0.0175	0.0262	0.0027
Elongation at Break (%)	2.5×10^{-6}	8.6×10^{-8}	2.6×10^{-5}
Toughness (MJ/m^3)	1.1×10^{-5}	1.9×10^{-7}	8.5×10^{-6}

Xylans Extracted at 60°C

Mechanical Properties	Corn Cob- Wheat Straw	Corn Cob-Sunflower Stalk	Wheat Straw-Sunflower Stalk
Modulus (MPa)	0.0439	0.0003	6.12×10^{-6}
UTS (MPa)	0.0002	0.0006	0.0024
Elongation at Break (%)	0.0456	0.0014	8.08×10^{-8}
Toughness (MJ/m^3)	0.0347	0.0006	7.7×10^{-8}

Statistical Analysis (p values) Between the Mechanical Properties of Films Produced from the Same Xylan Source Extracted at Different Temperatures

Corn Cob Xylan

Mechanical Properties	Room Temperature- 60°C
Modulus (MPa)	0.4171
UTS (MPa)	0.0002
Elongation at Break (%)	2.4×10^{-5}
Toughness (MJ/m^3)	0.0001

Wheat Straw Xylan

Mechanical Properties	Room Temperature- 60°C
Modulus (MPa)	0.8409
UTS (MPa)	0.0268
Elongation at Break (%)	0.1252
Toughness (MJ/m^3)	0.0759

Sunflower Stalk Xylan

Mechanical Properties	Room Temperature- 60°C
Modulus (MPa)	0.0033
UTS (MPa)	0.1756
Elongation at Break (%)	0.0459
Toughness (MJ/m^3)	0.9800