EFFECTS OF HEMICELLULOSE EXTRACTION AND EXTRUSION PARAMETERS ON THE PROPERTIES OF HEMICELLULOSE BASED POLYMERIC MATERIALS OBTAINED FROM DIFFERENT LIGNOCELLULOSIC BIOMASS

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ABSTRACT

EFFECTS OF HEMICELLULOSE EXTRACTION AND EXTRUSION PARAMETERS ON THE PROPERTIES OF HEMICELLULOSE BASED POLYMERIC MATERIALS OBTAINED FROM DIFFERENT LIGNOCELLULOSIC BIOMASS

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There is growing interest worldwide in utilization of renewable sources for fuels, materials and chemicals due to depletion of fossil sources and the environmental damages of synthetic products. Lignocellulosic biomass is the most promising material to become a substitute for fossil sources because of its abundancy in nature, low price and utilization area which does not compete with the food. Biodegradable films can be produced from hemicellulosic part of biomass and their main use can be especially food packaging due to their low oxygen permeability. In this study, hemicellulose is extracted from corn cobs and cotton stalk by alkaline extraction and extrusion process was utilized for the production of hemicellulose based materials. Within the context of this study, alkali extraction (particle size of the corncobs, extraction time, alkaline concentration and boron compound addition) and extrusion (extrusion temperature and screw speed) parameters were investigated and compared in terms of films mechanical, thermal and morphological properties. The best conditions in the range tested, were found as 1.19 - 0.6 mm particle size corn cobs, 1 h of extraction time with 15% KOH and no boron compound addition. The tensile strength of about 80 MPa and the elongation at break of 48% were obtained for the corn cob based extruded strips. The tensile strength of about 91 MPa was obtained for the solvent casted cotton stalk films. These mechanical properties suggest that the solvent casting was a suitable method for the cotton stalk hemicellulose while the extrusion was more convenient method for the corn cob hemicellulose.

Keywords: Hemicellulose based polymeric material, extrusion, lignocellulosic biomass, mechanical, extraction

ÖZ

HEMİSELÜLOZ EKSTRAKSİYON VE EKSTRÜZYON PARAMETRELERİNİN FARKLI LİGNOSELÜLOZİK BİYOKÜTLELERDEN ELDE EDİLEN HEMİSELÜLOZ TEMELLİ POLİMERİK MALZEMELERİN ÖZELLİKLERİNE ETKİSİ

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Fosil kaynakların tükenmesi ve onların bir ürünü olan sentetik polimerlerin doğaya verdikleri zararlardan ötürü, dünyada yenilenebilir kaynakların yakıt, malzeme ve kimyasal üretimindeki kullanımı konusuna artan bir ilgi vardır. Lignoselülozik biyokütle, doğada sıkça bulunması, düşük maliyeti ve gıdasal ürünlerle rekabet etmemesi nedeniyle, fosil kaynakların yerine geçebilecek en umut vadeden kaynaktır. Biyobozunur filmler, biyokütlenin hemiselülozik kısmından üretilebilir ve düşük oksijen geçirgenliklerinden ötürü, gıda paketlemesi bu filmlerin kullanım alanı olabilir. Bu çalışmada, hemiselüloz, mısır koçanı ve pamuk sapından alkali ekstraksiyonu ile ayrılmış ve hemiselüloz temelli malzeme üretimi için ekstrüzyon yöntemi kullanılmıştır. Bu çalışma kapsamında, alkali ekstraksiyon (mısır koçanı parçacık boyutu, alkali derişimi, ekstraksiyon süresi, bor bileşiği ilavesi) ve ekstrüzyon (ekstrüzyon sıcaklığı ve vida hızı) parametreleri incelenmiş ve bu parametreler elde edilen filmlerin mekanik, termal ve morfolojik özellikleri yönünden karşılaştırılmıştır. Çalışılan bölgedeki en iyi koşulların; parçacık boyutu 1.19- 0.6 mm olan mısır koçanı ile borik bileşik eklenmeden, 15% KOH çözeltisi kullanılarak 1 saatlik ekstraksiyon olduğu belirlenmiştir. Hemiselüloz temelli ekstrüde edilmiş şeritler ile yaklaşık 80 MPa dayanım ve 48% uzama elde edilmiştir. Sıvı dökme yöntemiyle elde edilen pamuk sapı temelli filmlerin ise dayanımı 91 MPa dır. Bu mekanik özellikler, sıvı dökme yönteminin pamuk sapı hemiselülozu için, ekstrüzyon yönteminin ise mısır koçanı hemiselülozu için daha uygun olduğunu göstermiştir.

Anahtar kelimeler: Hemiselüloz temelli polimerik malzeme, ekstrüzyon, lignoselülozik biyokütle, mekanik, ekstraksiyon

To my beloved family

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TABLE OF CONTENTS

CHAPTERS

APPENDICES

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

NOMENCLATURE

DP: Degree of polymerization

LCC: Lignin carbohydrate complex

GaM: d-galacto-d-mannan

GM: d-gluco-d-mannan

CMC: Carboxymethyl cellulose

PLA: Polylactic acid

PVA: Polyvinyl alcohol

EVOH: Ethylene vinyl alcohol

CNF: Cellulose nano fibers

AX: Arabinoxylan

AGX: Arabinoglucuranoxylan

XH: Xylan-rich hemicellulose

osAX: Oat spelt arabinoxylan

AcGGM: O-acetyl-galactoglucomannan

BnGGM: Benzylated AcGGM

PET: Polyethylene terephthalate

DF: Dilution factor

NREL: National Renewable Energy Laboratory

DMSO: Dimethyl sulfoxide

KOH: Potassium hydroxide

NaOH: Sodium hydroxide

H_2SO_4: Sulfuric acid

CH_3COOH: Acetic acid

H_3BO_3: Boric acid

NaBH4: Sodium borohydride

$CaCO_3$: Calcium carbonate

KAc: CH_3COOK: Potassium acetate

HCl: Hydrochloric acid

LiOH: Lithium hydroxide

NH_3/H_2O: Liquid ammonia
$Ca(OH)_2$: Calcium hydroxide
C16: Palmitic acid
C18: Stearic acid
OK35: Hydrogenated palm oil
rpm: Revolutions per minute
RH: Relative humidity
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
OP: Oxygen permeability
WVP: Water Vapor Permeability
WVTR: Water vapor transfer rate
NWVTR: Normalized water vapor transfer rate
E: Young’s modulus (Elastic modulus)
ƐB: Elongation at break
TEB: Tensile energy to break (toughness)
UTS: Ultimate tensile strength
HPLC: High Performance Liquid Chromatography
TGA: Thermogravimetric Analysis
SEM: Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

Petroleum has always been a vital resource as raw material for the production of multiple products such as oil, synthetic polymers and chemicals which have numerous application areas. While fossil sources are running out, price of petroleum and its products will increase extensively. This condition will affect the petroleum dependent industries and countries. Aside being a non-renewable raw material, petroleum has several damaging characteristics such as being an environment pollutant, not being biodegradable and increasing the greenhouse effect when burned.

Lignocellulosic biomass, which is a renewable composite biomaterial, is considered as an attractive replacement to fossil fuels in the last decades. The components of this biomass can be utilized in many applications as substitute to petroleum based products including chemicals, polymeric materials and fuels. It has low economic value since it is abundant all over the world. Besides being economically favorable, lignocellulosic biomass, its components and products are biodegradable so environmentally friendly. This indicates that from forestry and agricultural waste with no or low value, lignocellulosic biomass can be converted to value added products.

1.1. Lignocellulosic Biomass

Biomass can be described as biological material which is derived from living or recently living organisms. The term frequently indicates plants or plant-based materials. Because of the largest constituents of plants are cellulose, hemicellulose and lignin; plant based biomass is specifically known as lignocellulosic biomass (www.biomassenergycentre.org.uk).

Agricultural foods, particularly corn and sugar beet are the most widely utilized crops worldwide and produce millions of tons of waste. For instance, 48% of corn mass is unused (Çelebioğlu et al., 2012). This means, for corn nearly half of the weight of harvested corn is considered as waste. The same situation is valid for other crops. Until the last decades, these wastes had been used as animal feed or just disposed of. However, due to the recent intensive research efforts, scientists have developed novel methods to use the valuable components in agro-food industrial wastes (Çelebioğlu et al., 2012).

Nowadays, the need for a better resource that replaces fossil fuels is more than ever due to several reasons. Depletion of fossil resources (Lal et al., 2004), increasing energy request especially for transportation fuels (HoVert et al., 2002), accumulation of atmospheric CO_2 from the burning of fossil fuels (Whitesides et al., 2007) are the main motives for the search for sustainable sources of energy and renewable materials (Zhang et al., 2008). At this point, bioresources emerge as the best choice that can replace fossil based non-renewable resources.

Lignocellulosic biomass can be separated to its components mainly cellulose, hemicellulose and lignin after various physical and chemical steps. These components can be converted into valuable products that substitute fossil based fuels, polymers and other various chemicals. After enzymatic hydrolysis, cellulose transformed to its monomers, glucose, which can then be fermented to the ethanol and other bio-based chemicals such as lactic acid, succinic acid etc. The other constituent that every lignocellulosic biomass contains, hemicellulose, is a vital source for important materials such as thickeners, adhesives and coatings etc. (Zhang et al., 2008). Similar to cellulose, hemicellulose degrades into simple sugars and with fermentation xylitol, ethanol and organic acids can be obtained. On the other hand, the third component lignin can be used as a raw material for the production of polymer, glue, binders and carbon fiber (Zhang et al., 2008).

1.1.1. Abundance of Lignocellulosic Biomass in Turkey and in the World

While there are lots of options to utilize lignocellulosic biomass as biofuels and bio-based products, it is a major subject if these wastes are sufficient to respond to the need for fuels, materials and other bio-based chemicals.

The sources of these agricultural and forest wastes are wide across the world. U.S.A., one of the most important agricultural countries in the world has millions of acres field to grow crops. Among them, corn has the largest planted area with 90 million acres; the second one is wheat which has more areas (56 million acres) than the rest. Cotton, sun flower, sugar beet and barley are the other main agricultural sources. (USDA, NASS, 2014)

Table 1. Planted areas of the crops in U.S.A.

Crops	Corn	Cotton	Wheat	Sun Flower	Sugar beet	Barley
Planted Area In 2014 (million acres)	90.885	11.010	56.822	1.573	1.162	2.975

Turkey has a unique location and geographical formations which create multiple climates. The country has fertile soil and receives rain for the production of different type of grains, which makes it one of the major agricultural countries of the world having 38.4 million hectare of total utilized agricultural land. The planted area for the cereals and other crop products are 15.6 million hectare (TUIK, 2014).

Table 2. Production quantities of the grain and other crops in a year in Turkey

Production quantities of grain and other crops in Turkey in a year (2012-2013) (million tons)					
Wheat	Barley	Corn	Sunflower	Cotton	Sugar Beets
22.05	7.9	5.9	1.52	2.25	16.49

The production quantities of the crops in Turkey is provided in Table 2. As seen in the table, wheat production is in the first place with 22 million tons a year, sugar beets follow it with 16.5 million tons. Other significant crops are barley, corn, cotton and sunflower with the production amounts approximately 7.9, 5.9, 2.25 and 1.52 million tons a year respectively (TUIK, 2014). USA, on the other hand produced extensive amounts of crops such as wheat, barley and corn with amounts approximately 2187, 220 and 10780 million tons.

Total amount of agricultural residue in Turkey is about 40-53 million tons (Acaroğlu et al. 2012). Main agricultural residues and their production amounts in Turkey are shown in Table 3. Wheat straw is the foremost agricultural waste in Turkey followed by barley straw, corn stalk, cotton stalk and sunflower stalk. These residues could be a resource for both biochemical and energy production and also use for the biodegradable polymer manufacturing.

Table 3. Agricultural residue quantities in Turkey (Acaroğlu, 1999; Başçetinçelik 2005)

Crops	Residue	Total Residue (million ton)		Utility Residue (million ton)	Utility (%)
		Theoretical	Real		
Wheat	Straw	29.17	23.42	3.51	15
Corn	Stalk	5.91	4.97	2.98	60
	Stover	0.59	1.90	1.14	60
Cotton	Stalk	6.13	2.52	1.51	60
	Ginning res.	0.48	0.73	0.58	80
Barley	Straw	9.99	8.96	1.34	15
Sun flower	Stalk	2.30	2.26	1.35	60
Rye	Straw	0.40	0.35	0.05	15
Oat	Straw	0.41	0.32	0.04	15
Rice	Straw	0.58	0.21	0.12	60
	Hull	0.08	0.07	0.06	80
Tobacco	Stalk	0.36	0.41	0.24	60
Peanut	Straw	0.12	-	-	-
	Hull	0.02	0.02	0.02	80
Soybean	Straw	0.06	0.02	0.01	60

1.1.2. Structure of Lignocellulosic Biomass

Lignocellulosic biomass composed of three main biopolymers; cellulose, hemicellulose and lignin along with small amounts of pectin, inorganic compounds, protein, ash and extractives such as waxes and lipids. The exact composition of lignocellulose varies depending on the plant source, species, plant tissue and the growth conditions. Typically, a given type of lignocellulosic biomass consists of 40-50% cellulose, 20-40% hemicellulose whereas the lignin content varies roughly between 18-35% (Sun et al., 2011; Brandt et al., 2013).

The composition of lignocellulose constituents' in common agricultural residues can be seen in Table 4. According to this table, some plant residues are rich in cellulose while others have plenty of hemicellulose or lignin. For instance, corncobs and cotton seeds have greater amounts of cellulose, whereas wheat straw and leaves have more hemicellulose (Jorgensen et al., 2007; Kumar et al., 2009).

Table 4. Cellulose, Hemicellulose, and Lignin Contents in Common Agricultural Residues (Jorgensen et al., 2007; Kumar et al., 2009).

Lignocellulosic Residue	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40 - 55	24 - 40	18 - 25
Softwood stems	45 - 50	25 - 35	25 - 35
Nut shells	25 - 30	25 - 30	30 - 40
Corn cobs	45	35	15
Grasses	25 - 40	35 - 50	10 – 30
Wheat straw	30	50	15
Leaves	15 - 20	80 - 85	0
Cotton seed	80 - 95	5 - 20	0
Switchgrass	45	31.4	12
Coastal bermudagrass	25	35.7	6.4

Plant cell walls are complex and dynamic constructions. In these structures; cellulose polymers creates rigid bundles and each bundle surrounding by hemicellulose and forms larger structures called microfibrils. Lignin is considered as the essential ‘glue’ that holds these microfibrils together and all together these polymers build the plant cell wall, which is the leading constituent of lignocellulosic biomass (Sannigrahi et al. 2010). The structural organization of plant cell wall can be seen in Figure 1.

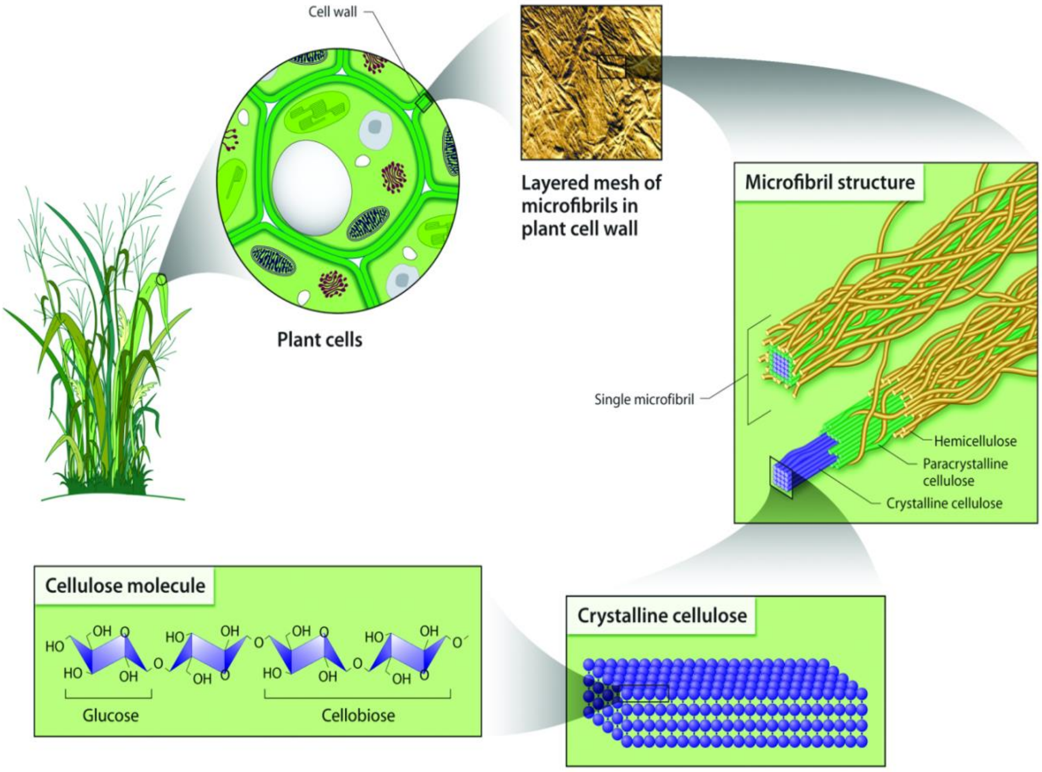


Figure 1. Structural organization of the plant cell wall (Office of Biological and Environmental Research of the U.S. Department of Energy Office of Science. science.energy.gov/ber/)

One of the components which forms the plant cell wall; cellulose, is a long linear polymer consisting solely of glucose units, whereas hemicelluloses are branched heteropolymers, consisting of different sugar monomers including glucose, xylose, mannose, galactose with 500–3000 sugar units per molecule (Coughlan et al., 1993; Sannigrahi et al., 2010; Brandt et al., 2013). On the other hand lignin is relatively hydrophobic and aromatic in nature, but lacks a defined primary structure where, softwood lignin is mainly composed of guaiacyl units while hardwood lignin is composed of both guaiacyl and syringyl units (Hu et al., 2002).

The detailed view of the lignocellulosic structure demonstrates the connections of these three components given in Figure 2 where branched hemicellulose surrounds cellulose piles and creates bundles and lignin bonds these bundles tightly.

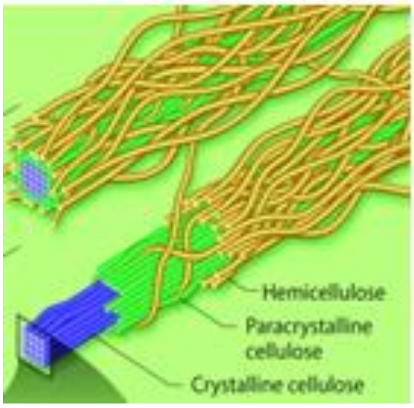


Figure 2. Closer look to the structure of cellulose, hemicellulose and lignin (Office of Biological and Environmental Research of the U.S. Department of Energy Office of Science. science.energy.gov/ber/)

1.1.3. Composition of Lignocellulosic Biomass

Lignocellulose is a composite material synthesized by plant cells, consisting of polymeric carbohydrates cellulose and hemicellulose with the aromatic polymer lignin.

1.1.3.1. Cellulose

Cellulose is the most abundant biopolymer on earth owing to this situation being the major component of the lignocellulosic biomass. The monomer of cellulose is glucose and two glucose molecules build a cellobiose unit as can be seen in Figure 3. The chemical formula of the cellulose is $(C_6H_{10}O_5)_{n.}$

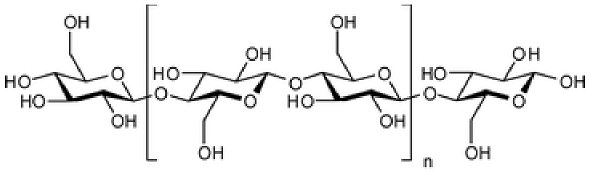


Figure 3. Structure of cellulose (Kobayashi et al., 2011)

Cellulose, is a homo-polysaccharide which composed entirely of d-glucose linked together by β-1,4-glucosidic bonds (Jorgensen et al., 2007). The β configuration in the polymer causes a stretched chain conformation, the chains creates flat sheets with hydrogen bonds. In contrary to cellulose, starch has a helical shape due to α conformation (Brandt et al., 2013).

The linear structure of cellulose chain allows the formation of intra and intermolecular hydrogen bonds. These bonds cause the accumulation of the chains and build parallel alignment crystalline fibrils of 36 cellulose chains. Although overall structures of the fibrils are crystalline, some sources claim that the surface could has an amorphous view (Ding et al., 2006).

In biosynthetic (native) cellulose, namely cellulose Ia and cellulose Ib; there are three hydrogen bonds per glucosyl unit. Two of them are intramolecular hydrogen bonds and the other one is intermolecular hydrogen bond to a bordering cellulose molecule in the same sheet (Qian et al., 2005). These sheets cooperate mostly through Van der Waals interactions and support extensively the stabilization of the cellulose fibrils

(Nishiyama et al., 2002). Cellulose II, a non-natural however thermodynamically more stable form of cellulose can be obtained by transformation of cellulose Ia and Ib by swelling (mercerization) and dissolution/ regeneration (Dinand et al., 2002). With this transformation, the new form of celluloses crystal symmetry changed and between sheets, hydrogen-bonds occur (Kolpak et al., 1976).

Cellulose is a relatively hygroscopic biopolymer which absorbs approximately 8-14% water under normal atmospheric conditions. Although it swells in water, it is insoluble. It is soluble in dilute acid solutions at high temperatures. It dissolves in concentrated acids where hydrogen bonds can break however severe degradation by hydrolysis may occur (Harmsen et al., 2010). Alkaline solutions cause swelling of the cellulose also dissolution of some low molecular weight fractions of the cellulose (Krassig and Schurz, 2002). Furthermore solutions of aqueous salt such as zinc chloride dissolve partial amounts of cellulose (Kirk-Othmer, 2001). Although cellulose does not melt down with temperature, its decomposition starts at 180°C (Thermowoodhandbook, 2003).

Degree of polymerization (DP) which described as the number of glucose units found in one polymer molecule, also determines the properties of cellulose polymer. Among the lignocellulosic polymers, cellulose has the highest degree of polymerization up to 10 000 or higher (Jorgensen et al., 2007; Brandt et al., 2013).

The configuration of the cellulose with intermolecular hydrogen bonds provides fibrils stable, straight, multimolecular forms and high tensile strength (Jorgensen et al., 2007). Although the monomer (glucose) is water-soluble; cellulose is not. High molecular weight which relates the polymer length and relatively low flexibility of the cellulose molecule chains contributes to the polymers insolubility in water and most solvents (Armeniades et al., 1977; Brandt et al., 2013). These features also support to have resistance against microbial degradation (Ward et al., 1989). The hydrophobic surface of cellulose forms a dense layer of water which prevents the diffusion of enzymes and other degradation products (Matthews et al., 2006).

In order to use the lignocellulosic biomass and its component cellulose as a raw material for glucose and ethanol production, pretreatment and hydrolysis steps are applied. The physical, chemical and biological pretreatment methods are employed prior to the enzymatic hydrolysis of cellulose to glucose monomers. Pretreatment procedure is required to be able to break down the shield formed by lignin and hemicellulose so the hydrolysis enzymes can attack the cellulose structures easily and efficiently. Glucose molecules can be transformed into numerous biochemicals as well as bioethanol via fermentation. Thus bioethanol which is an essential biofuel can be produced by using non-food renewable source instead of feedstock like starch and sugar crops (Zheng et al., 2009).

Highly functionalized, linear stiff-chain homopolymer, cellulose is known by its hydrophilicity, chirality, biodegradability and broad chemical modifying capacity (Klemm et al., 2005). Cellulose has versatile application areas in many industries such as wood and paper, fibers and clothes, veterinary foods, cosmetics and pharmaceuticals (Ven and Godbout, 2013). Wood pulp is the main cellulose source for the paper and cardboard production. Some part of the cellulose is used for the manufacturing fibers and films; a significant amount is utilized for the synthesis of cellulose esters and ethers which produced on an industrial scale these derivatives are employed for coatings, optical films, laminates, foodstuffs and cosmetics (Klemm et al., 2005). Cellulose and its derivatives as cellulose ethers and esters with different physicochemical and mechanical properties are extensively used in pharmaceutical products. Such as extended and delayed released coated dosage forms and matrices, osmotic drug delivery systems, bio adhesives and mucoadhesives, compressibility enhancers in compression tablets, thickening agents and stabilizers in liquid forms, binders in granules and tablets, gelling agents, also as fillers and taste maskers (Ven and Godbout, 2013). Cellulose is the main component of the textiles obtained from cotton, linen other plant fibers. It can be converted to rayon an important fiber with viscose process. Lyocell process, in which cellulose regenerated from a non-toxic solution with spinning, made a notable revolution for the field of synthetic fiber field as an environmentally friendly alternative to the viscose process. Owing to its biocompatibility and chirality in proteins, antibodies and heparins plus formation of composites with synthetic and biopolymers, celluloses application areas have extended.

1.1.3.2. Hemicellulose

Hemicellulose is the second most abundant polysaccharide in nature following cellulose also it is the most abundant heteropolysaccharide (Gatenholm and Tenkanen, 2004). Along with cellulose and lignin, hemicellulose is the core structural component of plant cell wall. Contrary to cellulose, hemicellulose polysaccharides have amorphous and branched structure which makes its solubility behavior distinctly different. For instance hemicellulose can be separated from cellulose and plant cell walls by alkaline treatment (Aspinall et al., 1959).

The monomers of the hemicellulose are simple sugars as hexoses and pentoses with uronic acids. The hexoses are 6 carbon sugars and mainly include D-glucose, D-galactose and D-mannose. Uronic acids includes D-glucuronic acid, D-galactoronic acid and 4-O-metyl-D-glucuronic acid. Pentoses contain arabinose, xylose and rhamnose (Kumaret al., 2009). In Figure 4, the principal monomers of hemicellulose can be viewed.

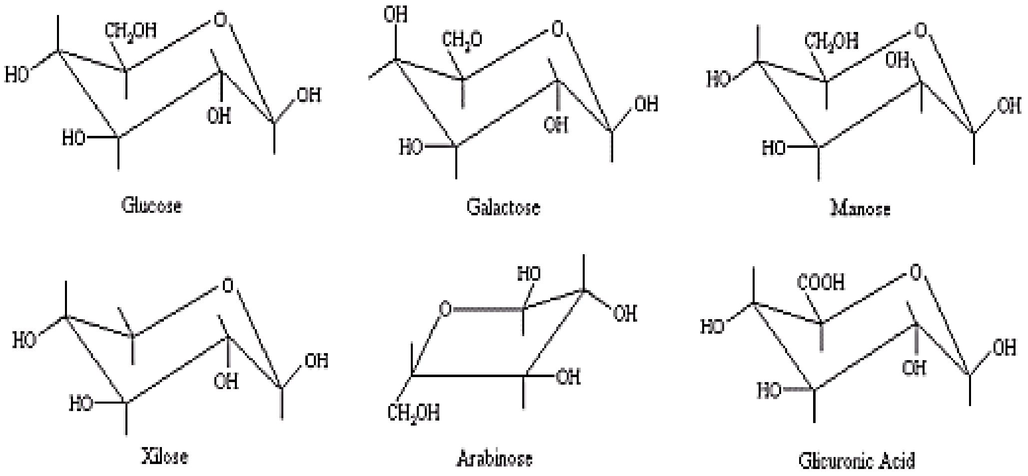


Figure 4. Monomers of hemicellulose (Stöcker et al., 2008)

As mentioned earlier, hemicellulose consist 20-40% of the plant cell wall. Based on the origin; softwoods (gymnosperms), hardwoods (angiosperms) and grass and cereals (gramineae) the composition of the constituents varies. For instance the cell walls of maize stems and barley straw composed of rigid cellulose microfibrils (37-38%), heteropolysaccharide matrix (28-35%) and connected lignin (15-16%) (Plackett, 2011). The components of some lignocellulosic fibers are shown in Table 5.

Table 5. Components of some lignocellulosic fibers (Adapted from Bismark et al. 2005)

Fiber	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**	**Pectin (%)**
Flax	71	18.6 – 20.6	2.2	2.3
Hemp	70 – 74	17.9 - 22.4	3.7 – 5.7	0.9
Jute	61 – 71.5	13.6 – 20.4	12 – 13	0.2
Ramie	68.6 – 76.2	13.1 – 16.7	0.6 – 0.7	1.9
Sisal	66 – 78	10 – 14	10 – 14	10
Banana	63 – 64	10	5	
Oil Palm	65		19	
Coir	32 – 43	0.15 – 0.25	40 - 45	3.4
Cereal Straw	38 - 45	15 – 31	12 - 20	8

Xylans and mannans are the most abundant hemicelluloses. The subgroups of hemicellulose are named with the backbone type, for instance arabinoxylan which is the most abundant hemicellulose in annual plant contains D-xylopyranosyl backbone with a number of L-arabinofuranose and D-glucuronic acid side chains (MacGragor & Fincher, 1993; Höije et al., 2005). Generally xylan contains O-acetyl groups that located at hydroxyl groups in the xylan backbone which can be removed with isolation using alkali (Gabrieli et al., 2000). Xylans are the leading hemicellulose in hardwoods around 25-35% where the main hemicellulose in softwoods is galactoglucomannan (GGM) about 20% (Mikkonen et al., 2012; Brandt et al., 2013).

The monosaccharide types and amounts of hemicellulose change broadly from one plant to another. Frequently, two or more types of hemicellulose can be co-exist in the same plant, only there are composition changes in the different parts of the plant (fibers, branches, knots, roots and core). Moreover the composition of hemicellulose can change within the wood construction (between latewood, earlywood, heartwood, sapwood and compression wood) and layer of the plant cell wall (Plackett, 2011). Table 6 presents the sugar monomer composition of hemicellulose found in variety of plants.

Table 6. Monosaccharide amounts (%) of hemicellulose in variety of plants (Plackett, 2011)

Plant Source	**Xylose**	**Arabinose**	**Glucose**	**Galactose**	**Mannose**	**Uronic acids**
Spruce mannan			15	1	62	
Spruce arabino galactan		11	8	35	30	8
Larch arabino galactan		16	1	79	1	1
Pine arabino galactan		14	3	69	7	4
Birch xylan	92.6	1.2	2			4.1
Birch mannan	1	2	28	1	68	
Beech xylan	91.6	1.2	2			5.2
Aspen xylan	95		0.7	0.6		3.8
Aspen mannan	2	1	41	1	55	
Sugarcane bagasse	55	13	28	2.6	1.5	3
Wheat straw xylan	56.9	17.1	12.1	5.6		8.3
Rye straw xylan	78.3	12.4	5.9	2.5	0.4	5
Passion fruit rind	29	1	42	15	9	<0.5
Date palm leaf	75	6.3	0.3	1		17
Flax xylan	83.2	1	2.8	3.4	0.6	9
Flax mannan	7.4	3.9	42.2	8.8	37.8	

Hemicellulose has non-covalent bonds with the surface of cellulose fibrils, while holds these fibrils together it behaves as an amorphous matrix material (Hansen et al., 1998). As a result of its non-crystalline nature, hemicellulose is more sensitive than cellulose on the subject of depolymerization particularly in acidic media (Brandt et al., 2013).

The most remarkable difference between hemicellulose and cellulose is hemicellulose has short branches consisted of various sugar monomers. The backbone of hemicellulose structure has either a homopolymer or a heteropolymer with short branches connected by β-(1, 4)-glycosidic and β-(1, 3)-glycosidic bonds (Kuhad et al., 1997). On the contrary to cellulose, the polymers within hemicellulose hydrolyze easily besides they do not aggregate even if they crystallize with chains of cellulose (Kumar et al., 2009). Hemicellulose has lower molecular weight than cellulose owing to its degree of polymerization around 100 – 200 which also has side chains that can be acetylated (Timell et al., 1967; Kuhad et al., 1997; Jorgensen et al., 2007; Brandt et al., 2013).

1.1.3.3. Lignin

Lignin is the most complex component which formed by polymerization of phenyl propanoid units and unlike cellulose and hemicellulose it is the most abundant non-polysaccharide portion in lignocellulose.

The monomers of lignin are three phenyl alcohols; coniferyl alcohol (guaiacyl propanol), coumaryl alcohol (p-hydroxyphenyl propanol), and sinapyl alcohol (syringyl alcohol) which can be seen in schematic representation in Figure 6. Alkyl-alkyl, alkyl-aryl and aryl-aryl ether bonds connect these phenolic monomers together. Cellulose is embedded into lignin hence lignin provides a protection against microbial and chemical degradation. Lignin also creates covalent bonds with hemicelluloses such as benzyl ester bonds with the carboxyl group of 4-O-methyl-d-glucuronic acid in xylan. Between lignin and arabinose or galactose side groups in xylans and mannans, stable ether bonds can be formed and named as lignin carbohydrate complexes (LCC). (Jorgensen et al., 2007; Kumar et al., 2009)

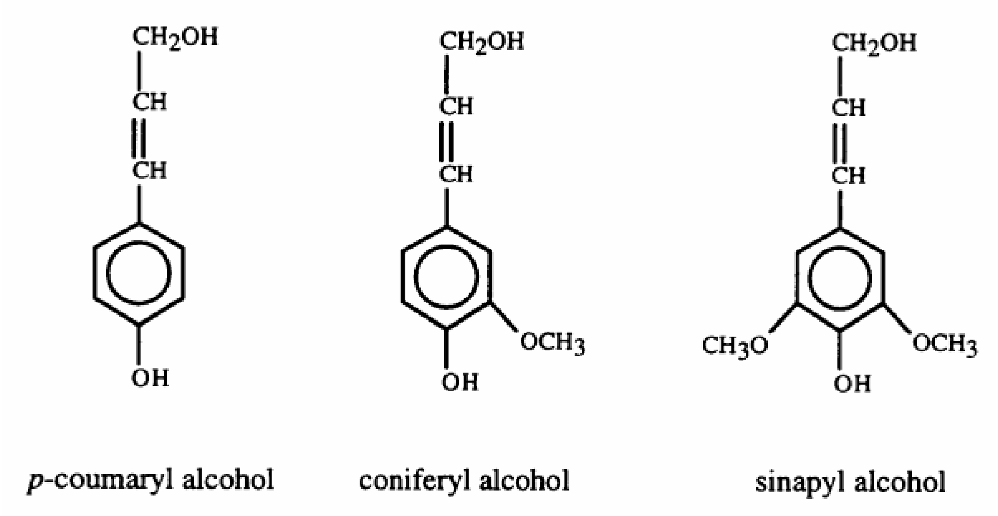


Figure 5. Structure of three phenyl alcohol monomers of lignin (Harmsen et al., 2010)

In general the abundance of lignin in lignocellulosic biomass is softwood 25-35%, hardwood 18-25% and grass 17-24% respectively. The composition of the lignin is different for softwoods (gymnosperm) and hardwoods (angiosperm). Softwood lignin is made up of more than 90% of coniferyl alcohol and the rest is being mostly p-coumaryl alcohol units. Contrary to this, hardwood lignin contains varying ratios of sinapyl and coniferyl alcohol units (Kirk-Othmer 2001; Harmsen et al., 2010). The diversity in compositions of different types of biomass has a great influence on delignification chemistry hence deconstruction of biomass. Guaiacyl units have C-C cross-links at C-5 position of the ring which can form both during lignification and delignification. The C-5 position is replaced in the syringyl unit therefore it cannot take part in substitution reactions. Because the C-C crosslinks cannot be hydrolyzed by acid or base, delignification of softwood is more challenging than hardwood (Harmsen et al., 2010; Saningrahi et al., 2010; Brandt et al., 2013).

Lignin is a relatively hydrophobic polymer with aromatic structure but its exact construction is still unknown (Sannigrahi et al., 2010). Lignin is soluble in alcohols such as ethanol and methanol, ketones such as cyclohexanone or methyl ethyl ketone; or ethers such as diethyl ether (Hu et al., 2002; Sun et al., 2011).

Lignin has a significant effect on the cell’s persistence and improvement since it involves the transport of water, nutrients and other metabolites in the plant cell wall. It behaves as binder between plant cells and forms composite materials that have extraordinary resistance to impact, bending and compression. At high temperatures, thermal softening of lignin occurs that ease the depolymerization reactions by alkaline or acidic solutions (O’Connor et al., 2007; Harmsen et al., 2010).

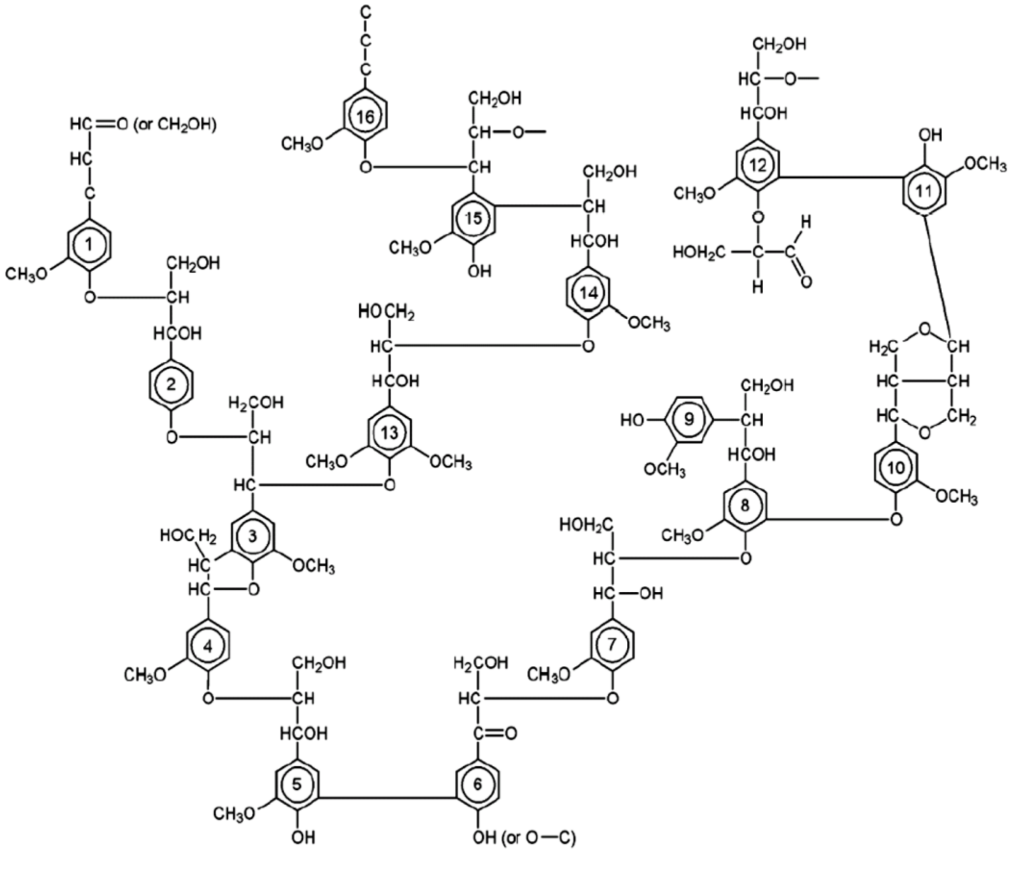


Figure 6. Structure of spruce lignin (Harmsen et al., 2010)

The lignin content of a plant provides insight about the applications of biomass. As the proportion of lignin increases, the bioavailability of the substrate for bioethanol production decreases. While cellulose, hemicellulose and lignin are interconnected also lignin is considered as the glue that holds these polysaccharides, especially hemicellulose in a plant cell wall (Sanningrahi et al., 2010). Since there are stable lignin-carbohydrate bonds and cross linkages in the biomass, it becomes one of the main reasons that prevent separation of the components for biorefinery process (Aimi et al., 2005; Lawoko et al., 2005).

The greater amount of technical lignin (more than 50 million tons) are produced by pulping industries which can be classified as sulfur-containing lignin (kraft lignin and lignosulfonate lignin) and sulfur-free lignin (alkali lignin and organosolv lignin) (Faix et al., 1992). Kraft lignin, produced via kraft pulping, utilized mostly for in house fuel for chemical recovery. Alkali lignin is manufactured from non-wood feedstock such as straw, flax and bagasse via soda pulping while organosolv lignin has high purity and low molecular weight (Lora et al., 2002; Arato et al., 2005; Pan et al., 2006).

Potential lignin applications can be seen in Figure 7. High quality lignin can be employed as substitutions for polymeric materials: epoxy resins, phenolic powder resins, polyurethane and polyisocyanurate foams. Phenolic powder resin is utilized as binder for fractured products, automative break pads and molding. Due to it’s a good adsorbent and has outstanding rheological, adhesive and colloidal properties, it is used as partial replacement for phenolic binders in oriented-strand board manufacturing. Additionally lignin is a raw precursor for phenol, DMSO, ethylene and can be converted to carbon fiber (Lora et al., 2002; Eckert et al., 2007).

Another feature that lignin was related to was the oxygen barrier property of the films. In a study conducted by Ryberg et al. (2011) the existence of lignin in the hemicellulose based coatings which were applied on the polyethylene terephthalate films decreases the oxygen permeability more than 5 fold when compared with the coatings attained with delignified hemicellulose. This new feature of lignin enhances the film properties in terms of their utilization in food packaging and the hemicellulose production without delignification step becomes an attractive method.

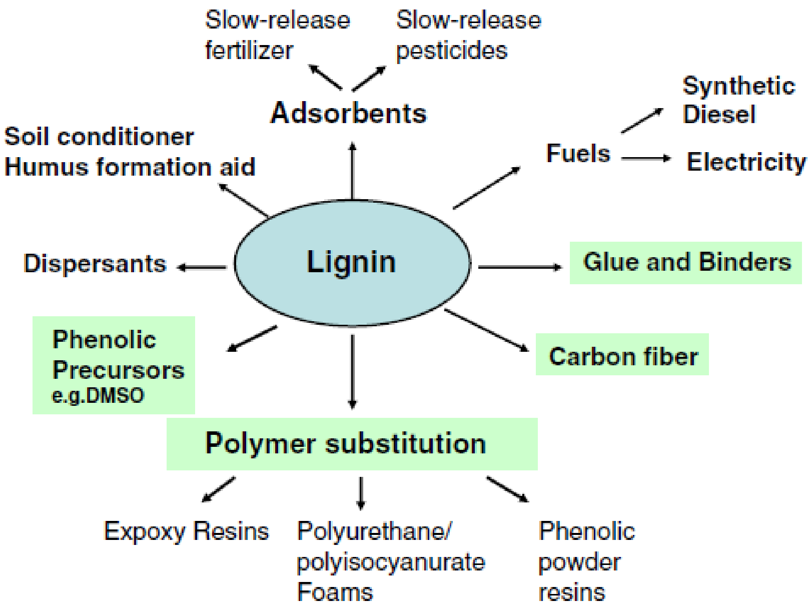


Figure 7. Applications of lignin (Zhang et al., 2008)

1.2. Hemicellulose

Hemicellulose is the second most abundant biopolymer in nature as it is a constituent of plant cell walls. Although this polysaccharide is insoluble in water, it can be hydrolyzed in dilute acids or dissolve with aqueous alkali and separated from lignocellulose. The structure of hemicellulose is heterogeneous consisting of sugar monomers. The types of hemicellulose vary according to backbone monosaccharides. These types are xylans (β-1,4-linked ᴅ-xylose units), mannans (β-1,4-linked ᴅ-mannose units), arabinans (β-1,5-linked L-arabinose units) and galactans (β-1,3-linked ᴅ-galactose units). Structure of this biopolymer consists of a backbone and side chains which gathered by linkages. The monosaccharides and connections determine major properties such as three-dimensional configuration as well as the solubility of the polymer (Spiridon and Popa, 2008). Table 7 presents types of hemicellulose contain in hardwood and softwood plants.

Table 7. Hemicellulose types in hardwood and softwood (Spiridon and Popa, 2008).

Hemicellulose type	Hardwood (%)	Softwood (%)
Methylglucuronoxylan	80 -90	5 - 15
Arabinomethylglucuronoxylan	0.1 - 1	15 -30
Glucomannan	1 - 5	1 - 5
Galactoglucomannan	0.1 - 1	60 -70
Arabinogalactan	0.1 - 1	1 -15
Other galactans	0.1 -1	0.1 -1

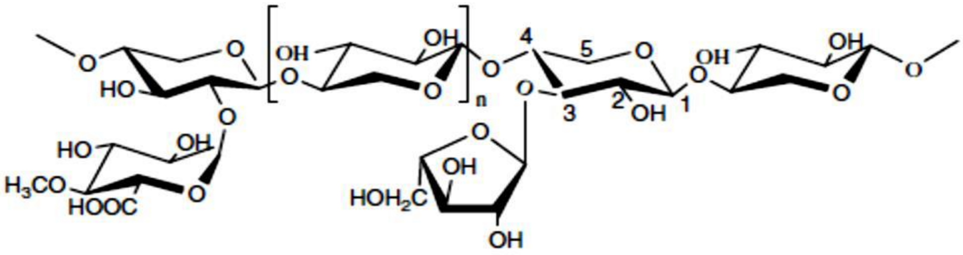
1.2.1. Types and structures of hemicellulose

While there are xylan, mannan, arabinan and galactan types of hemicelluloses, xylans and mannans are the leading biopolymers among them according to their abundance in nature.

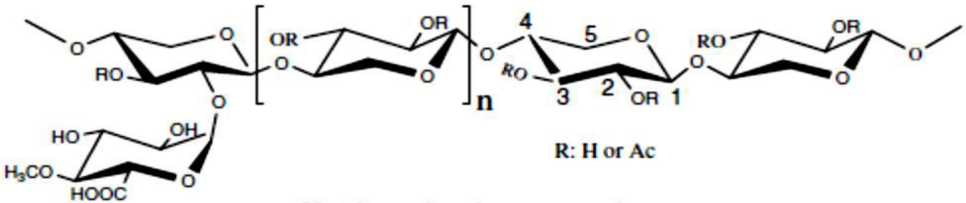
1.2.1.1. Xylans

Xylan is one of the main components in lignocellulosic residues which has a structure of backbone consist of β-1,4-linked D-xylopyronose. The construction has also branches of arabinosyl, acetyl or glucuronosyl components where they changes with the source and extraction type of lignocellulosic biomass (Spiridon and Popa, 2008).

Xylans are mostly found in annual plants and such as corn, rice and cereals. Wheat, oat and switch grass are composed of essentially glucuronoarabinoxylans (Carpita et al., 1996; Jorgensen et al., 2007). Within the hardwood species for example aspen, poplar, birch or oak; glucuronoxylans are the most abundant hemicelluloses where glucomannans follow them as second (Willför et al., 2005; Jorgensen et al., 2007). Xylans can be attained from many sources by the extraction of agricultural residues, forestry waste and by-products as stalks, straws and hulls of harvests also wood chip and saw dust.



Softwood - arabinoglucuronoxylan



Hardwood - glucuronoxylan

Figure 8. The structure of xylan types found in softwood and hardwood (Pu et al., 2011)

1.2.1.2. Mannans

In softwoods such as fir, pine and spruce; the leading hemicellulose type is glucomannans in particular galactoglucomannans with proportion of 20 % of the dry wood whereas the amounts of arabinogalactans and xylans are minor (Wilför et al., 2005). Glucomannans composed of an O-acetylated β-(1,4) linked glucomannan backbone with D-galactose α-(1,6) side groups that connect to some of the mannosyl units (Timell, 1967; Lundqvist et al., 2002).

The structures of d-galacto-d-mannan and d-gluco-d-mannan are shown in Figure 9.

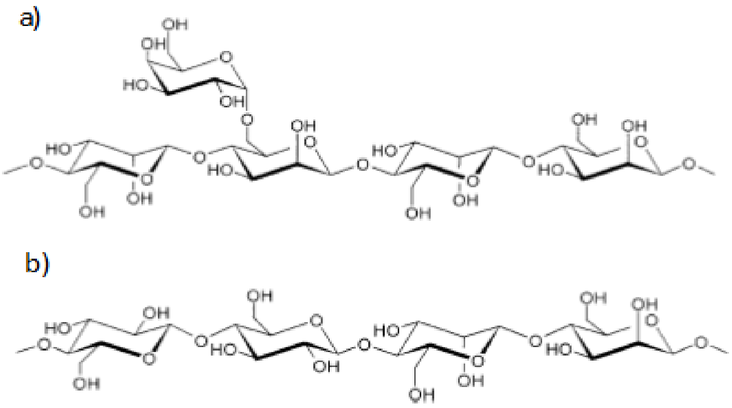


Figure 9. Primary structure of a) d-galacto-d-mannan (GaM) b) d-gluco-d-mannan (GM) (Ebringerova, 2005)

1.2.2. Isolation Methods of Hemicellulose

The separation of the biopolymers in lignocellulosic biomass is crucial since it is a necessity to get pure biopolymers as they become a feedstock for both polymeric composite materials and base chemicals and fuels. The fractionation of the biomass however is not an easy task. Due to the covalent bonds between lignin and carbohydrates (cellulose and hemicellulose) which form a highly cross linked network, it is prevented to dissolve or fractionate in conventional solvents (Kumar et al., 2009). Therefore several pretreatment methods have been developed to open the compact structure and make separations or conversions easier. These methods are;

- Physical (pulverization, irradiation)
- Chemical (alkali, acid, organosolv, ammonia explosion)
- Physicochemical (steam explosion, CO_2 explosion, wet oxidation),
- Biological (enzymolysis),
- Electrical or some combinations of these (Kumar et al., 2009)

The isolation of hemicellulose from a broad variety of plants, agricultural and forestry residues is a challenge since the closely integrated structure of carbohydrates and lignin in the plant cell wall. The separation methods are commonly multi-step procedures includes mechanical and chemical treatments. Hemicellulose can be isolated with various technics including alkaline, acidic hot water, ammonia dimethyl sulfoxide (DMSO) extraction, heat fractionation using steam or microwave (Ebringerova et al., 2005; Plackett, 2011).

As these methods are applying to the lignocellulosic residues, the risk of hydrolysis of backbone always exists. This causes extracted hemicellulose has lower molecular weight and/or less branches than the previous condition (Hoffman et al., 1976).

The prior purpose of extraction is to expose the cell walls to extraction solvent for liquid penetration. For a better extraction, the surface of the material get extended by mechanical processing the wood and plants into shive, dust and chips (Plackett, 2011).

Following the mechanical treatment, usually the removal of lignin fractions comes. This procedure is named as delignification done through acid chlorite treatment which involves $NaClO_2$ and glacial acetic acid at around 60°C (Campbell et al., 1952). Delignification process may cause degradation of hemicellulose occasionally. After removal of lignin the product is called as holocellulose. Delignification is not a mandatory procedure for hemicellulose separation, in some cases lignin can stay with hemicellulose and provides new features for polysaccharide.

One of the isolation methods is extraction with acidic hot water which is an effective way of releasing hemicellulose into the solvent. When using this method, degradation of chain and furfural formation may occur (Plackett, 2011). Steam explosion is another way of separation the lignocellulose in which the wood chips can be impregnated with water and exposed to hot water steam for a few minutes and creates separable slurry (Plackett, 2011). Microwave irradiation is an alternative hemicellulose isolation technique of heat fractionation. In this method; first lignocellulosic waste such as wood and straw chips immersed into water or basic medium then heat fractionated up to half an hour approximately at 200 °C which results with proper yield of hemicellulose (Lundqvist et al., 2002; Stalbrand et al., 2004).

A much common and successful method is extraction in alkaline media. Hemicellulose can be extracted with alkaline solutions such as NaOH or KOH effectively. Extraction is commonly combined with fractionation using ethanol/benzene solutions where ethanol is used as precipitation liquid (Höije et al., 2005; Plackett, 2011). Within the precipitation process, higher molecular weight fraction precipitated while oligomer fraction remains in the solution. Another fractionation method that is joint the extraction procedure is filtration (e.g. gel filtration). For instance after extraction, soluble parts of hemicellulose can be collected by ultrafiltration and/or diafiltration where the polysaccharide fractions are concentrated and filtered through pressurized membranes (Andersson et al., 2007; Plackett, 2011). The ultrasound application seems to be very effective during the alkaline extraction of xylans from corncob, wheat straw, buckwheat seed, corn hull and sugarcane bagasse. The sono-mechanical effects of ultrasound is disintegrated the cell walls and help to achieve high yields of xylans without any structural modifications (Ebringerova et al., 2005).

1.2.3. Application Areas of Hemicellulose

Nowadays wide variety of plastic materials and chemicals is almost entirely produced from petroleum (Höije et al., 2005). These fossil based polymeric materials are non-renewable and most importantly not biodegradable so they become harmful for nature since the disappearance takes long period of time and they increase greenhouse effect when burned (Gröndahl et al., 2004). As oil sources come to an end, it becomes much more expensive to produce these synthetic materials (Höije et al., 2005). The pursuit for a replacement to petroleum source is an attractive topic in the last decades.

Lignocellulosic biomass is a promising resource substitute to fossil based products since it is abundant in nature with less or no economic value and environmentally friendly natures. The polymers that are produced from these wastes are biodegradable so after use, they can be incinerated, recycled or composted with minimum or no environmental damage (Gröndahl et al., 2004).

As being at the second most abundant polymer in plant cell walls, hemicellulose is an attractive resource for green polymers and chemicals, wide range of valuable products (sugar, ethanol and organic acids) via hydrolysis, fermentation and degradation. (Plackett, 2011). In Figure 10 the application areas of hemicellulose can be observed.

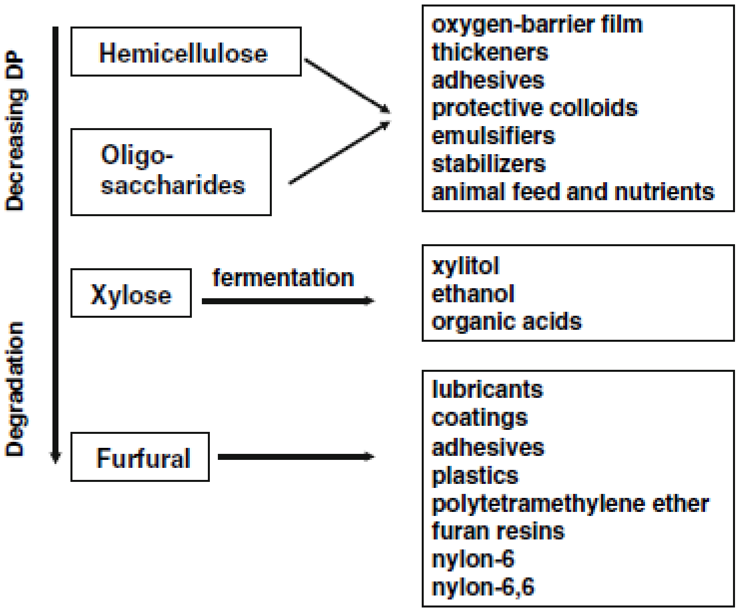


Figure 10. Hemicellulose applications (Zhang et al., 2008)

Hemicellulose has been used as plant gum for adhesives, thickeners emulsifiers, protective colloids and stabilizers (Kamm et al., 2004), while oligosaccharides can be utilized as animal feed additives and nutrients (Davis et al., 2002; Fernandez et al., 2002).

Main monomeric sugar of hemicellulose, xylose, can be fermented to xylitol a type of sweetener that is a sucrose substitute for diabetes patients (Walther et al., 2001; Buhner et al., 2004). Furfural is valuable solvent obtained from chemical degradation of hemicellulose-rich lignocellulose and used for coatings, lubricants, resins and adhesives. It is also the starting material for the production of Nylon-6 and Nylon-6.6 (Kamm et al., 2004; Kamm et al., 2006).

In chemical pulping industry; hemicellulose has remarkable roles, it is discharged into the cooking liquor and removed from fibers by washing also burned for energy recovery (Plackett, 2011). Moreover by using as wet-end additive, this biopolymer enhances the mechanical properties and yield of the paper when retained in the pulp of pulp and paper industry (Meller et al., 1965; Molin et al., 2002).

Within the food sector, hemicellulose has also been applied for a long time due to its water solubility, nontoxicity, biocompatibility and ability to form gels. Mannans such as guar gum, locust bean gum and konjac glucomannan are the commercial sweetening agents, thickeners and emulsifiers (Popa et al., 1996; Zhang et al., 2001).

The biomedical field interests the film and gel forming properties of this polysaccharide. Hemicellulose films have been discovered for wound–dressing intents and xyloglucan gels for controlled drug-delivery treatment (Miyazaki et al., 1998; Melandri et al., 2006). Furthermore this biopolymer is employed as nutreceutical, in chiral separations and as a HIV inhibitor (Gröndahl et al., 2004).

The best known and most significant features of this renewable biopolymer are its effective barrier and film forming nature. Arabinoxylan for instance, have been utilized to protect protein foam while it has a great potential for packaging applications (Ebringerova et al., 1999; Zhang et al., 2004). Similarly a mannan family hemicellulose konjac glucomannan or galactoglucomannan have been used for preparation of packaging films (Hartman et al., 2006; Mikkonen et al., 2008). The film-forming function and biodegradability of xylans and mannans make them attractive alternatives to petroleum based materials especially used as food packaging (Mikkonen et al., 2012). The special characteristics that make them applicable for this purpose are barrier properties such as low oxygen and grease permeability, thermal behavior and high tensile strength (Mikkonen et al., 2012).

The requirements for food packaging;

- To protect the food from outside environment (gases, volatiles, odors, water, grease, water vapor, dust, microorganisms, vibrations, shocks, compressive forces)
- The food packaging material has to be processable, heat stable, recyclable or compostable and low price

These parameters support a better food protection for both safety of nutrition and human health. Oxygen gas has to be blocked by packaging films since it causes microbial growth, color changes, rancidity and senescence of fruits, vegetables and various other foods (Robertson et al., 2010). Water is another obstacle for storage of the foods due to acceleration of the chemical reactions, microbial growth, enzymatic changes and structural deteriorations (Roos et al., 2001). The packaging materials are an essential necessity in terms of protecting the foods from mentioned biological, chemical and physical effects to preserve the nutritional value of the food products.

CHAPTER 2

LITERATURE SURVEY

2.1. Hemicellulose Based Films

In literature the main method to form hemicellulose based films is solvent casting. The steps of this technique can be described as the dissolution the polymer for this case hemicellulose, in a solvent mostly in water, casting the solution in a petri dish then evaporation of the solvent.

The effects of extraction conditions and alkali type of wheat straw hemicellulose were investigated by Lawther et al. (1996). In the study, various alkali types (sodium hydroxide, calcium hydroxide, lithium hydroxide and liquid ammonia), several alkali (KOH) and boric acid concentrations, different extraction temperatures and times were examined. Increase in extraction time, temperature and alkali concentration resulted in the rise of hemicellulose yield. According to this study, when 10% KOH with 2% H_3BO_3 was used, optimum extraction time at 20°C, was determined as between 21 and 26 hours, optimum alkali (KOH) concentration at 20°C for 2 hours extraction time was found as between 20 and 30% and optimum H_3BO_3 concentration at 20°C, 24% KOH for 2 h was obtained as either 2 or 5%. Among them the preferred extraction conditions were found as 24% KOH / 2% H_3BO_3 at 20°C for 2 hours and at this conditions hemicellulose yield was 34 %. Although KOH, NaOH and LiOH gave similar and much more hemicellulose yields than $Ca(OH)_2$ and NH_3/H_2O, KOH was considered as the best alkali solution since the extraction product KAc salt can be removed with ethanol dissolving.

Composite arabinoxylan-based films from maize bran were prepared with various emulsified fats by Peroval and coworkers (2002). To investigate the effects of different types of fats palmitic acid (C16), stearic acid (C18), triolain and hydrogenated palm oil (OK35) were employed. Pure arabinoxylan films with glycerol additive showed the best mechanical properties, elongation as 7.4±2.9 %, tensile strength as 26.5±4.1MPa and elastic modulus as 72.4±35.2 MPa were obtained. The only film showed better mechanical property than pure arabinoxylan film was triolein-AX based with 10.8±3.3 % elongation value. On the other hand OK35 film had the lowest water vapor permeability (WVP) so OK35 enhanced the functional properties of AX-based films in terms of vapor barriers.

Biodegradable composite films with the blends of wheat gluten and xylan from birchwood, corncob and grass were produced by Kayserilioğlu et al. (2003). Xylan was extracted from corncob and grass with alkaline solution and birchwood xylan was purchased. The films composed of wheat gluten as the matrix and xylan (birchwood, corncob, grass) as an additive at different fractions of 0-40% (w/w). The films were prepared at different pH conditions ranging from 4 to 11 and dried at either uncontrolled or controlled conditions (80°C and 35%RH). Tensile strength of the films were not affected by gluten-xylose ratio (G: X) however the films that were prepared at alkaline conditions have higher tensile strength than the ones at acidic conditions. Additionally the films that dried at controlled conditions resulted as more stretchable than controlled ones. Film forming behaviors of the gluten-xylan solutions were deteriorated when xylan content increased above 20% at pH 4. Strain at break was decreased as the xylan ratio increases at same conditions and opposite to tensile strength, films prepared at acidic conditions were more stretchable. For the comparison of xylan source and non-composite films, the properties of films were examined while G: X ratio was kept constant. Tensile strength of the grass and corn cob based films was lower (1-3 MPa) while birchwood and pure wheat gluten films were nearly the same (7 MPa). Corncob xylan films were much more stretchable than other films with approximately 600% strain at break while other two xylan films were 50%.

Gröndahl et al. (2004) studied the material properties of glucuranoxylan films isolated from aspen wood. Glucuronoxylan was separated by alkali extraction while the isolated material was mostly composed of xylose (83%) with rest of methyl glucuronic acid, mannose and other sugars. The films were prepared by solvent casting method with addition of xylitol or sorbitol plasticizers at different concentrations between 20-50% (w/w). Films that were prepared without any additive became very brittle and fractionated after drying due to the high glass transition temperature. Following addition of plasticizers transparent films with good mechanical unity were formed which resulted with enhanced material properties. With addition of 20% xylitol or sorbitol these semicrystalline films demonstrate 40 MPa ultimate tensile strength with only 2% elongation. As the amount of plasticizers increases, strain of the films increase but tensile strength and Young's modulus decrease. Polyvinyl alcohol (PVA), a commercially utilized synthetic polymeric material was also prepared as film for the comparison of the oxygen permeability properties. The glucuronoxylan films with 35 (w/w) % sorbitol showed excellent oxygen barrier properties (0.21 $cm^3 \mu m/m^2 dkPa$) at 50% RH which was equal to PVA and lower than plasticized starch and synthetic polymer EVOH.

Zhang and Whistler (2004) produced edible corn hull arabinoxylan films. The mechanical and water vapor permeability properties of unplasticized and plasticized with glycerol, propylene glycol and sorbitol (0-22 (w/w) %) films were compared. They observed that propylene glycol plasticized arabinoxylan films were more fragile and changes in plasticizer amount did not make any positive or negative difference for mechanical properties. For instance tensile strengths were changing from 53 to 61 MPa where elongations were 5.9 and 6% approximately. On the other hand, mechanical properties of the films that plasticized with sorbitol and glycerol changed considerably as the tensile strengths were reduced with increasing glycerol and sorbitol content, from 47 to10 MPa and 48 to20 MPa, respectively while elongations were raised from 6 to 12% and 6 to 9%, respectively. Sorbitol-plasticized arabinoxylan films had the best moisture barrier properties while glycerol and propylene glycol containing films had lower WVP values. Also all of the plasticized AX films had lower WVP values than those unplasticized ones, this situation was attributed to antiplasticization effect of these plasticizers at low concentrations. High concentrations of plasticizer (above 10% for glycerol) resulted with increased permeability due to the hygroscopic character of plasticizer. The produced films in this study were strong, stable, transparent and smooth. They had good moisture barrier property which was resulted in the reduction of weight loss from 82 to 59%.

Different isolation methods for arabinoxylans from barley husks were investigated by Höije et al. (2005). The isolation methods including enzyme and hydrochloric acid (HCl) pretreatment, delignification with chlorite or organosolv and extraction with alkali solution. Chlorite delignification was found effective since it removes both starch and lignin hence the pretreatment step considered unnecessary. Alkali extraction was performed with NaOH and 0.5% $NaBH_4$ to prevent degradation of polymers. Among the isolated hemicelluloses, the highest yield of 57% was obtained by HCl pretreatment following by chlorite delignification and alkali extraction. The ultimate tensile strength (UTS) of the film obtained with this method was 50 MPa and the elongation was 2.5% where water content was approximately 35% at 50%RH. Water content of the films was important since water acts like a plasticizer and softens the film.

Hartman et al. (2006a) isolated O-acetyl-galactoglucomannan (AcGGM) type hemicellulose from industrial process water that attained from ultrafiltrated mechanical wood pulping. They investigated the film forming capacity of AcGGM and oxygen barrier properties of this hemicellulose film. The films were prepared using solvent casting method with the help of glycerol, sorbitol or xylitol plasticizers to avoid the brittleness. Although plasticizers were used to increase the ductility of the films, these additives cause higher sensitivity to moisture which is an undesirable property for some applications. To obtain hemicellulose films with good oxygen barrier and mechanical properties, Hartman et al. (2006a) created physical blends of AcGGM with either carboxymethylcellulose (CMC) or alginate, which both have much higher molecular weights than AcGGM. The storage modulus values which represent the stiffness of the material were decreased sharply with increased relative humidity for plasticized films especially glycerol AcGGM films. On the other hand, alginate or CMC blend films had higher storage modulus than plasticized ones even at elevated humidity. The highest elongation was 195±12 % and belonged to glycerol plasticized AcGGM film. The mechanical strength of the two component films composed of alginate or CMC were high, however they had low elongation values around the elongation of the films were improved due to the addition of 4.1±0.8 % and 3.1±0.1 %, respectively. The three component film, containing AcGGM, alginate and glycerol had 17.1±2.6 % elongation, the elongation of the films were improved due to the addition of glycerol. The hybrid films that blend of alginate or CMC with AcGGM were the most resistant ones towards oxygen permeability with 0.55±0.06 ($cm^3 \mu m$)/ ($m^2 dkPa$) and 1.28±0.15 ($cm^3 \mu m$)/($m^2 dkPa$) permeability values, respectively. Sorbitol-AcGGM and Xylitol-AcGGM films follow them with 2.00±0.08 ($cm^3 \mu m$)/ ($m^2 dkPa$) and 4.40±0.14 ($cm^3 \mu m$)/($m^2 dkPa$), respectively. Whereas the highest oxygen permeability value, 4.56±0.10 ($cm^3 \mu m$)/($m^2 dkPa$) was established by glycerol plasticized alginate-AcGGM film.

Another study conducted by Hartman et al. (2006b) was focused on the promising barrier properties of AcGGM films from their previous work. Their aim was to produce modified O-acetyl-galactoglucomannan (AcGGM) films with good barrier property and low moisture sensitivity. For this purpose unmodified AcGGM was accepted as base material, three different strategies were applied; styrene grafting by plasma (1), vapor-phase treatment of styrene (2) and lamination with benzylated AcGGM (3). Benzylated AcGGM (BnGGM) films were transparent, flexible and water resistant. The film properties were compared to AcGGM-alginate and AcGGM-CMC blend films (weight ratio of 7:3). BnGGM films had higher oxygen permeability values than blend films. Vapor-phase-grafted films had better moisture resistance than the plasma-treated films. Lamination procedure created films with good barrier property at higher humidity.

The effect of lignin content on film forming and mechanical properties was studied by Göksu et al. (2007). Xylan and lignin were separated from cotton stalk by alkali extraction and lignin was removed from xylan with ethanol washing. The lignin-free xylan namely pure xylan could not form self-supporting continuous films. Nevertheless without totally removal and keeping approximately 1% (w/w) lignin in xylan was established to be sufficient for the film formation. They compared the different concentrations of additional birchwood xylan (8, 10, 12 and 14% w/w) for their effect to mechanical properties. The films that had 14% (w/w) xylan showed better mechanical properties in terms of strength, strain and elastic modulus. Increasing xylan concentration decreased the water vapor transfer rate which parallels to the thickness of the films. Glycerol addition to the films increased the ductility of the films.

Höije et al. (2008) studied the properties of enzymatically tailored arabinoxylan(AX) films. They used rye arabinoxylan which had arabinose/xylose ratio (Ara/xyl) of 0.50 initially. These AX were modified with α-L-arabinofuranosidase at different dosages and varying arabinose content thus (Ara/xyl) between 0.2-0.5 hemicellulose was obtained. All AX types formed solid films without any additional plasticizer. Untreated AX films were entirely amorphous while enzyme-treated AX films were semicrystalline. An enzyme treated AX film, (Ara/xyl 0.37) had higher strength 57.7±5.9 MPa and strain 10.4±4.2% values than untreated AX films and the films that had lower Ara/xyl. Oxygen permeability of the films also decreased with the decreasing Ara/xyl content. These results attributed to the enzymatic debranching of arabinoxylan made arrangements as physical cross-linking.

Plasticized oat spelt arabinoxylan (osAX) films were prepared by Mikkonen and coworkers (2009). The effect of plasticizers, glycerol and sorbitol with 10 and 40% (w/w) ratios were compared. Firstly, without the removal of insoluble parts of plasticized osAX suspension, films became heterogeneous, discontinuous and weak. When the insoluble parts were removed, film formation improved. They observed that without plasticizer (even if the insoluble part was removed), the osAX did not form self-support films. Low plasticizer content led to higher tensile strength than the higher ones. Tensile strength of the glycerol plasticized films were higher than sorbitol plasticized films with 10% (w/w) plasticizer content however with 40% (w/w) sorbitol addition the results were reversed. Furthermore the use of sorbitol resulted in more effective water vapor barrier properties than glycerol and sorbitol plasticized films retained their tensile properties during 5 months of storage.

Edlund et al. (2010) created biobased films and coatings from spruce wood hemicellulose that was regained from the wastewater of hydrothermal treatment wood chips. The wastewater was filtered with membrane to achieve oligo and polysaccharide-rich, noncellulosic fraction, namely hemicellulose. Despite many of the studies in literature, in this work no plasticizer was utilized so the films can be named free standing. However to improve the mechanical strength and barrier properties, blend mixtures of wood hydrolysate with carboxymethtyl cellulose (CMC) or chitosan were prepared. The casted CMC or chitosan films were transparent, smooth, shiny and had good mechanical properties with low oxygen permeability values. The tensile strength and tensile strain values increased as the proportion of CMC or chitosan was increased. In general chitosan blend films had higher strength and strain values than CMC containing ones. The best mechanical properties were belonged to 50% (w/w) chitosan blend film, which had tensile strength of 62.4±4.3 MPa, strain at break of 7.2±2.6 % and elastic modulus of 2365±706 MPa. Wood hydrolysate with co-component blends were applied onto PET films as coating to analyze the utilization of this blend films in packaging applications. The coated and uncoated PET films were compared in terms of mechanical properties and oxygen permeability values. Chitosan-wood hydrolysate coated PET films had higher tensile strength and accordingly lower strain values than CMC coated ones. While tensile strain and elastic modulus of the uncoated and coated films were alike, uncoated PET films had relatively high tensile strength values. However water vapor transmission rate and oxygen permeability (OP) of the films dropped significantly when the films coated these blends especially with CMC. For instance, OP of the uncoated PET was 14.6 ($cm^3 \mu m/m^2 daykPa$) while chitosan and CMC coated films had 6.2 ($cm^3 \mu m/m^2 daykPa$) and 1.9 ($cm^3 \mu m/m^2 daykPa$) values, respectively. The blend coatings enhanced the OP values and became a promising material for packaging applications.

Peng et al. (2011) interested in nanocomposite films with improved mechanical properties by the combination of cellulose nanofibers (CNF) into xylan-rich hemicellulose (XH). The solvent casted films composed of the aqueous mixtures of XH (64-75 wt%), sorbitol used as plasticizer (16-22 wt%) and CNF used as nanoreinforcement (0-20 wt%). XH films plasticized with 25 wt% sorbitol (based on dry XH weight) demonstrated inadequate mechanical properties whereas incorporation of CNF (5-20 wt%, based on the total dry mixture) into films had better film forming property, thermal stability with enhanced mechanical properties due to the mechanical strength provided by reinforcement CNF and strong interactions between XH matrix and CNF.

Bahcegul et al. (2012) studied the effect of alkaline pretreatment temperature on a multi-product basis for the co-production of glucose and hemicellulose films from cotton stalk. Within this study, alkaline pretreatment was conducted at three different temperatures (25, 60 and 90°C) and both cellulose and hemicellulose portions of the biomass were obtained. Among these co-products, hemicellulose was more affected from the pretreatment temperatures. The most important difference was observed as visual and film forming properties of elevated temperature pretreated films (90°C), since significant long cracks occurred. Furthermore the mechanical properties, strength and elongation, of these films were reduced with increased temperature. All three types of films had similar water content which is important for their mechanical properties since water acts like plasticizer. Low mechanical properties and poor film formation properties of the films could be due to lignin agglomeration at 90°C reported by Westby et al. (2007).

Solvent casting was the only method to produce hemicellulose based films in literature. The extrusion of hemicellulose based films was introduced by our research group. The extrusion of the xylans from corn cob into bioderadable polymeric materials developed by Bahcegul et al. (2013). The aim was to produce hemicellulose films using an industrially utilized method instead of a high energy consuming solvent casting method. Corn cobs were extracted with an alkaline solution (24% KOH) then precipitated with acetic acid-ethanol mixture (1:10 volumetric ratio) followed by the removal of potassium acetate salt by washing (water – ethanol) and end with drying at room temperature, arabinoglucuranoxylan (AGX) type hemicellulose was obtained. The extrusion was performed with twin screw, co-rotated mini extruder which can work with small amounts of polymer. Prior to extrusion, AGXs were conditioned in desiccators at three different relative humidities 10%, 55% or 90%, to obtain extractable polymers, since water acts as plasticizer. The extrusions were performed at 50 rpm of screw speed and each batch of hemicellulose was extruded at three different temperatures (60°C, 90°C and 120°C). The outcomes showed the significance of extrusion temperature and water content on the production of hemicellulose based films since the only biopolymer which had about 27% water content could be extruded at 90°C. The obtained strips had better mechanical properties as 76±6 MPa tensile strength and 35±8% elongation at break than a commercially used poly(lactic acid). Homogeneous internal structure and good mechanical properties of the strips proved the extrusion method can be utilized for large scale production.

2.2. Aim of the Study

Nowadays, ecologically friendly biodegradable polymers and materials manufactured from agricultural and forestry wastes became one of the most attractive research subjects due to the depletion of fossil sources and environmental damages of synthetic products. The biomass and its components cellulose, hemicellulose and lignin are utilized in various industries in which hemicellulose, the second most abundant polymer in nature, may have a utilization area in the production of biodegradable films for food packaging applications.

The present study focuses on the production of hemicellulose based polymeric materials from two different agricultural residues, corn cob and cotton stalk. Hemicelluloses were isolated from these biomasses via alkaline extraction and extrusion process was utilized for production of hemicellulose based materials instead of highly used solvent casting method. The study aims to investigate the effects of different extraction and extrusion parameters on the properties of hemicellulose based materials and hemicellulose yield. Another aim of the study is to compare the film production methods, extrusion and solvent casting, by studying the properties (mechanical, thermal, and morphological) of the produced films.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Corn cob and cotton stalk as the biomass of this study was provided from Hatay (Turkey). Sodium hydroxide (NaOH), boric acid (H_3BO_3), sodium borohydride ($NaBH_4$), sulfuric acid (H_2SO_4), D-(+)-xylose and D-(+)-galactose were purchased from Merck (Darmstad, Germany).

Potassium hydroxide (KOH), acetic acid (CH_3COOH), alkali lignin, calcium carbonate ($CaCO_3$), D-(+)-glucose, L-(+)-arabinose and D-(+)-mannose were purchased from Sigma-Aldrich (St.Louis, Missouri, USA). Ethanol was obtained from Colony Sugar Mills (Lahore, Pakistan).

3.2. Experimental Methods

3.2.1. Alkaline Extraction from Different Agricultural Residues

For the extraction of hemicellulose from lignocellulosic biomass, the reported methods by Lawther et al. (1996) and Zilliox and Debeire (1998) were used as a starting point. To obtain the highest hemicellulose yields from different lignocellulosic biomasses, small modifications were applied to these methods.

3.2.1.1. Alkaline Extraction from Corn Cobs

Alkaline extraction method was mainly derived from the previously reported procedures by Zilliox and Debeire (1998) and Bahcegul et al. (2013) with some minor changes. Before the extraction process, corn cobs were crushed with a mill (Arthur Thomas Co., Philadelphia, USA) and sieved through 10, 16, 30 and 100 mesh with Retsch Analytical Sieve Shaker (Retsch GmbH, D- Haan, Germany). Thus 2-1.19 mm, 1.19- 0.6 mm, 0.6-0.15 mm and <0.15 mm particle sized corn cobs were obtained.

Milled and sieved (1.19-0.15 mm particle sized) 50 grams of dry biomass was swollen in 1000 ml deionized water for 30 minutes at room temperature with a magnetic stirrer. Swollen particles having large surface area provide effective alkaline extraction. The suspension was filtered and the biomass was mixed with 425 ml of 24% (w/v) KOH solution for 2 hours at room temperature with a magnetic stirrer (RCT Basic Safety Control, IKAWerke, Staufen, Germany) at approximately 600 rpm. At the end of extraction; liquid alkali soluble fraction (hemicellulosic portion of the biomass) was filtered through a cloth and separated from the solid alkali insoluble fraction (cellulosic portion). For further separation; the liquid hemicellulosic portion was centrifuged (Hettich Centrifuge, Rotina 380R, Germany) at 5000xg for 5 minutes. After obtaining clear solution of hemicellulosic portion without any small alkali insoluble particles; 1250 ml of acetic acid-ethanol solution in 1:10 volumetric ratio was added to precipitate hemicellulose from the solution as suggested by Zilliox and Debeire (1998). The precipitated hemicellulose was separated by filtration through a cloth. Following filtration, hemicellulose was washed with 100 ml deionized water and 300 ml ethanol 3 times to remove potassium acetate (CH_3COOK abbreviate as KAc) salt which is formed during the neutralization of KOH with acetic acid at the precipitation step. The rinsed hemicellulose polymers were recovered and left to dry at room conditions.

Within the scope of this study, the effects of different parameters; particle size of the biomass (2-1.19 mm, 1.19- 0.6 mm, 0.6-0.15 mm and <0.15 mm), extraction time (1, 2, 6 and 12 hour(s)), alkali(KOH) concentration (5, 10, 15, 20, 24% (w/v))and addition of boron compounds during extraction (0.5, 1 and 2% (w/v) of H_3BO_3 or 0.5, 1% (w/v) of $NABH_4$) on extraction, extrusion and production of hemicellulose based films were investigated. Each parameter was tested three times for the reliability of the study. Schematic demonstration of corn cob extraction steps is shown in Figure 11.

3.2.1.2. Alkaline Extraction from Cotton Stalk

For the extractions from cotton stalk, it was intended to obtain the highest hemicellulose yield. Therefore some extraction trials were conducted and the best method was selected. Before the extraction process, the cotton stalks were cleaned from its leaves and small cotton parts, then were crushed with a mill (Arthur Thomas Co., Philadelphia, USA) to obtain particles less than 2 mm (sieve size).

200 g of cotton stalk particles were swollen and mixed with 4000 ml deionized water for 16 hours at room conditions in a temperature controlled vessel with mechanical mixer. The suspension was filtered and the biomass was mixed with 1700 ml of 24% (w/v) KOH + 1% $NaBH_4$ (w/v) solution for 24 hours in the same vessel at room temperature. After the extraction; hemicellulosic portion was filtered using a cloth and separated from the cellulosic portion. For further separation, the centrifugation was employed at 5000xg for 5 minutes. Then clear hemicellulose solution was precipitated using 5000 ml of acetic acid-ethanol solution in 1:10 volumetric ratio. After the filtration of precipitated hemicellulose, this biopolymer was washed with 400 ml deionized water and 1200 ml ethanol 3 times to remove the KAc salt which is formed during precipitation. The rinsed hemicellulose polymers were recovered and left to dry at room conditions.

Within the scope of this study, the effect of extraction temperature (room temperature and 60°C) on hemicellulose yield, extrusion and production of hemicellulose based materials was investigated. Each extraction parameter was tested twice for the reliability of the study. Schematic demonstration of cotton stalk extraction steps was shown in Figure 12.

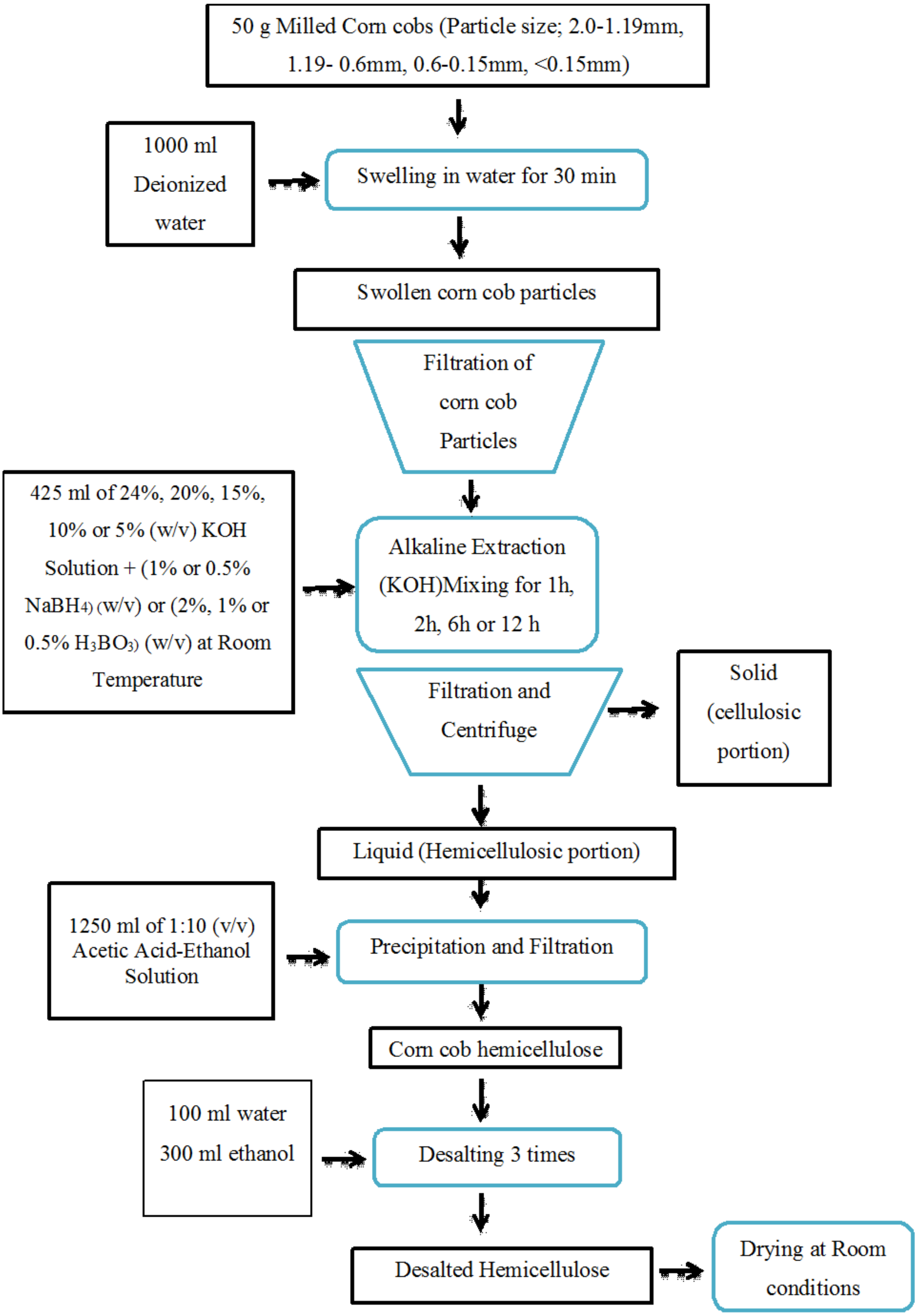


Figure 11. Schematic demonstration of corn cob extraction steps

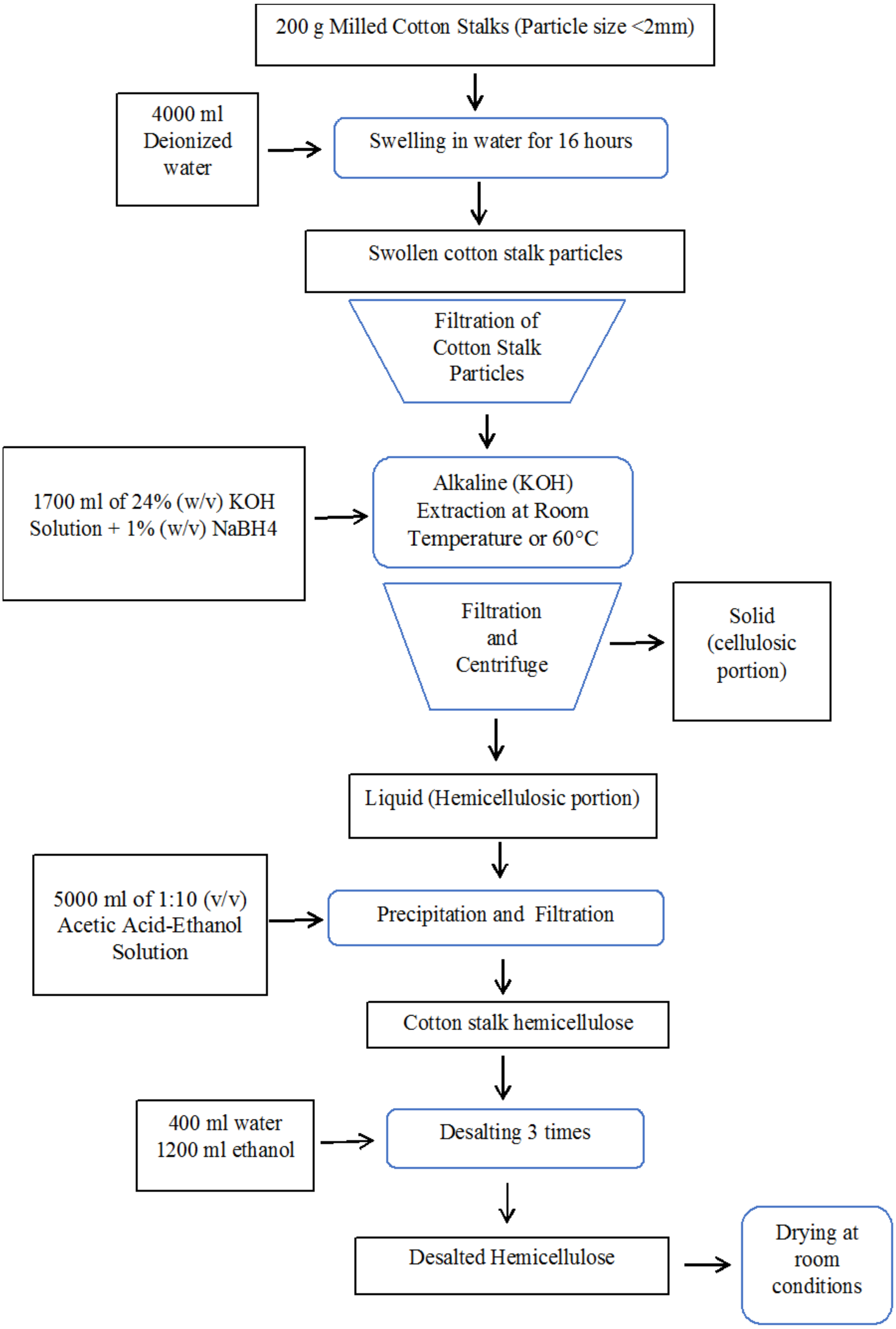


Figure 12. Schematic demonstration of cotton stalk extraction steps

3.2.2. Hemicellulose Film Production

3.2.2.1. Hemicellulose Film Production via Solvent Casting

Hemicellulose biopolymer (0.5 g) was dissolved in 15 ml deionized water via magnetic stirrer at room temperature for 18 to 24 hours, depending on their dissolution rate. To be able to compare the properties of extruded films and solvent casting films, the thickness of the films had to be similar to each other. In order to obtain thicker films, larger amounts of hemicellulose were dissolved in 15 ml deionized water. The polymer solution was ultrasonificated at 40% amplitude for 8 minutes to provide enhanced dispersion of solid particles. Subsequently, the solution was poured into petri dishes with a diameter of 9 cm and left to dry at 23°C and 50% relative humidity in a conditioning cabinet (Medcenter 111 Climacell, MMM Group, Munich, Germany) for two days to obtain solvent casted polymer films.

3.2.2.2. Hemicellulose Film Production via Extrusion

A twin screw co-rotating extruder (Thermo HAAKE Mini CTW) which has conical screws (screw length: 109.4 mm, screw diameter: 4-15 mm) and two heating zones was used for the extrusion of the hemicelluloses polymers (Figure 13). The extruder contains a ribbon die plate with a rectangular opening of 5 x 0.5 mm (width x length) in order to obtain a strip shaped extruded material. The extruded strip was collected on a mini moving belt. Extrusion parameters including temperature, screw speed and torque were controlled and monitored via a computer which has software and connected to extruder.

Prior to the extrusion process; 5 grams of dried hemicellulose polymers were conditioned at 90 ± 5 % relative humidity and room temperature using a desiccator containing water for 24 hours. The conditioned and water plasticized hemicellulose was manually fed into the twin-screw extruder at 90ºC. Screw speed was started with

20 rpm then increased to 50 rpm. After the extrusion process, 5 mm wide strips were obtained from the hemicellulose polymer (Bahcegul et al., 2013).

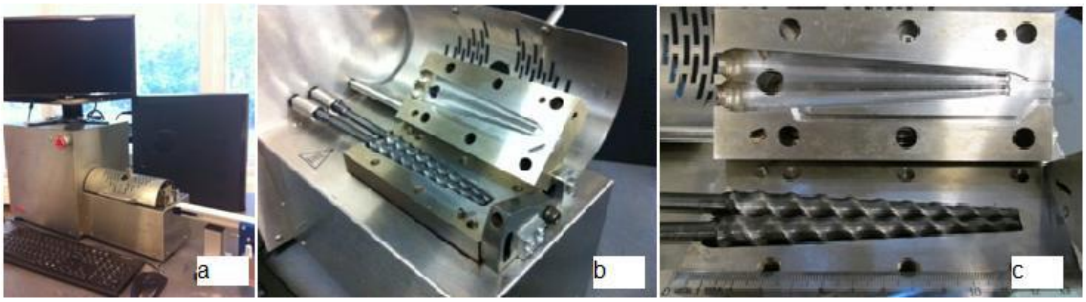


Figure 13. The view of twin-screw mini-extruder (a), inside (b), screws (c)

Within the scope of this study, the extrusion parameters of cotton stalk hemicellulose were investigated. These parameters were extrusion temperature (75 ºC and 90 ºC) and extrusion speed (50 rpm and 100 rpm). Each extrusion parameter was tested twice for the reliability of the study.

One of the objectives of this study is to examine and compare the properties of the films produced by two methods (the extrusion and solvent casting processes). To compare the properties of the films produced by these methods, the thicknesses of the extruded and solvent casted films should be similar; therefore the extruded strips were made thinner by rolling through a roller (Yilmaz Machine Industry, Turkey). Prior to rolling, the strips were held in desiccators with 90% relative humidity for 24 hours. The rolled films were cut into a dog bone shape before the tensile testing. The images of the extruded strip, the rolled film and the dog bone shaped polymer film are shown in Figure 14.

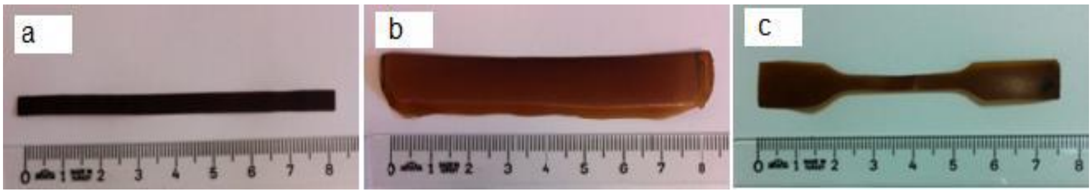


Figure 14. The images of the extruded strip (a), the rolled film (b) and the dog bone shaped film before the tensile testing.

3.2.3. The Characterization of Hemicellulose

3.2.3.1. Lignin Content

Lignin content of the hemicellulose samples was obtained using the UV-VIS Spectrophotometry (Nicolet Evolution 100, Thermo Fisher Scientific Inc., USA). For analysis; 0.1g hemicellulose from each sample was solved in 5 ml of 4% NaOH solution for overnight then the solution was filtered through a 0.2µm filter and the absorbance of this solution at 280 nm was measured as suggested by Westbye et al. (2007). Alkali lignin was used as the standard lignin and standard solutions were prepared as diluting 0.1 mg/ml stock lignin solution in 4% NaOH solution at different concentrations. Using the standard lignin solutions, a lignin concentration vs. absorbance calibration curve was established and the lignin contents were determined.

3.2.3.2. Potassium Acetate (KAc) Salt Content

Potassium acetate (CH_3COOK abbreviate as KAc) salt content of the hemicellulose was measured according to the conductivity of hemicellulose. 0.4 g hemicellulose was dissolved in 40 ml deionized water. For the standard KAc solutions; 10% stock KAc solution was prepared and diluted with deionized water for different concentrations. KAc Concentration – Conductivity Calibration Curve was established using electrical conductivity meter (Inolab, WTW Cond. 720). Using the calibration curve, KAc concentration of the hemicelluloses was determined.

3.2.3.3. Water Content

Water content of the hemicellulose polymer and strips were determined by calculating the difference between sample weight before and after oven drying. For oven drying, the samples were left to dry in an oven at 105°C for 1 day until it reached a constant weight. The water content was determined by using the formula given below;

$$Water\ Content(\%) = \frac{Sample\ weight(initial - after\ drying)(g)}{Initial\ sample\ weight(g)} \times 100$$

3.2.3.4. Viscosity

Viscosity of hemicellulose polymers was measured using a capillary rheometer (Dynisco LCR-7001, located at Central Laboratory, METU). Prior to this analysis, the hemicellulose polymers were conditioned at 90% relative humidity for 1 day. The viscosity values of the polymers were determined at 90°C and 75°C which are the extrusion temperatures for these polymers in this study. The capillary rheometer which has a die of 2.096 mm diameter and 23.05 mm length was used for viscosity measurement. Viscosity values were determined at various shear rates ranging from 1.3s^{-1} to 6.6 s^{-1}.

3.2.3.5. Hemicellulose Yield

Hemicellulose yield represents the hemicellulose (dried at room conditions) amount which was obtained after the extraction process. The hemicellulose yield (%) was calculated by the formula given below;

$$Hemicellulose\ Yield\ (\%) = \frac{Recovered\ Hemicellulose\ weight}{Initial\ Biomass\ weight} \times 100$$

3.2.3.6. Monosaccharide Analysis

Monosaccharide analysis of the extracted hemicelluloses were performed using High Pressure Liquid Chromatography (HPLC, Shimadzu LC-20AD Series Kyoto, Japan). Sample preparation and compositional analysis were carried out according to the National Renewable Energy Laboratory (NREL, Golden, CO) analytical procedure of biomass (NREL, 1996; 2011).

Compositional analysis mainly based on hydrolysis of the biomass to simple monomers and determination of the amount of these monomers in the sample. First, 3 ml of H_2SO_4 (72%) was added to 300 ± 10 mg of biomass in glass tubes and the tubes were placed in a water bath at 30°C for 1 hour. The suspensions in the tubes were stirred at every 10 minutes with glass rods. After 1 hour, H_2SO_4 was diluted to 4% (w/w) with the addition of 84 ml deionized water and the suspensions were taken into autoclave bottles with screw caps. The bottles were placed into an autoclave (Hirayama, Hiclave HVE-50) at 121°C for 1 hour for further digestion. At the end of 1 hour, the bottles were removed from the autoclave and cooled to room temperature.

To determine the monomers of biomass, 20 ml of the filtrate was taken into a beaker to adjust the pH approximately to 6-7 with the addition of sufficient $CaCO_3$. The solution was filtered through 0.2 μm syringe filter into HPLC vial. The samples in the vials which contained simple sugar monomers were subjected to HPLC to determine the simple sugar amounts in the biomass (Haykir, 2013).

HPLC Analysis was performed using Shimadzu –Liquid Chromatography (LC-20AD Series) with Refractive Index Detector (RID-10A). The HPLC column was Transgenomic CarboSep Coregel 87P and the analysis conditions were 85 °C with a flow rate of 0.6 ml/min. 0.45 µm filtered and 15 min degassed deionized water was used as the mobile phase. Analyses were performed at 30 minutes and the injection volumes of the samples were 40 um. D(+)xylose, D(+)glucose, D(+)galactose, L(+)arabinose and D(+)mannose were used as standard sugar monomers and the standard solutions were prepared for different concentrations in order to obtain a calibration curve in the range of 0-2 mg/ml. All samples were filtered through 0.22 µm syringe filters into the HPLC vials.

The compositional analysis was carried out using the software (LC Solution) of HPLC. The areas under the monosaccharide peaks were evaluated with the assistance of another software program (PeakFit v4.12). Glucose, xylose, galactose and arabinose concentrations in the biomass were calculated using calibration curves prepared.

3.2.3.7. Solubility in Water

0.4 g hemicellulose was dissolved in 40 ml de-ionized water with a stirrer for 24 hours at room conditions. The solution was centrifuged at 8000xg for 5 min to precipitate the undissolved hemicellulose portion. This solid part was firstly dried in at 60 ºC for two days, then at 105 ºC for one day then weighed. The solubility of hemicellulose in water was calculated by the formula given below;

$$Solubility(\%) = \frac{Soluble\ Hemicellulose\ weight}{Initial\ Hemicellulose\ weight} X100$$

3.2.4. Characterization of the Films and Strips

3.2.4.1. Mechanical (Tensile) Testing

Tensile testing of the films and strips produced from the hemicellulose polymer was performed using a universal testing machine (Zwick/Roell Z250, Zwick GmbH & Co., Germany) located at Middle East Technical University (METU) Central Laboratory.

Prior to the tensile testing, the hemicellulose strips were cut into pieces with 6 cm length while the solvent casted and the rolled films were cut into dog bone shapes and conditioned at 23ºC and 50% relative humidity for 1 day using a climacell (Medcenter 111 Climacell, MMM Group, Munich, Germany). The test conditions of the machine were; initial grip separation was 20 mm for strips and 10 mm for films, the crosshead speed was 5 mm/min and the load cell used was 10 kN for the strips and 100 N for the films. The test room conditions were 23±1ºC and 50±5% relative humidity and controlled by a climatic room conditioner (Technair LV). Ultimate tensile strength (UTS), percent elongation at break (εB) and elastic modulus (E) were obtained via the software (testXpert2) of the universal testing machine. The toughness of the hemicellulose strips/films were calculated using the test data. The thickness and width of the test specimens were measured by a digital micrometer (40 EXL, Mahr GmbH, Esslingen, Germany).

The stress-strain curve and associated mechanical properties of the polymer strips/films are shown in Figure 15. According to this curve; the ultimate tensile strength (UTS) is the maximum tensile stress sustained by the sample during the test. Elongation at break (εB) is expressed as the percentage of the change of the original length of a specimen between grips at break. The elastic modulus (E) is determined as the slope of the linear part of the stress-strain curve and it is the measure of stiffness and resistance to the elastic deformation. Tensile energy to break in other words the toughness (T) is the required energy to break a unit volume of a material and this value is expressed as the area under the stress-strain curve up to the point of fracture.

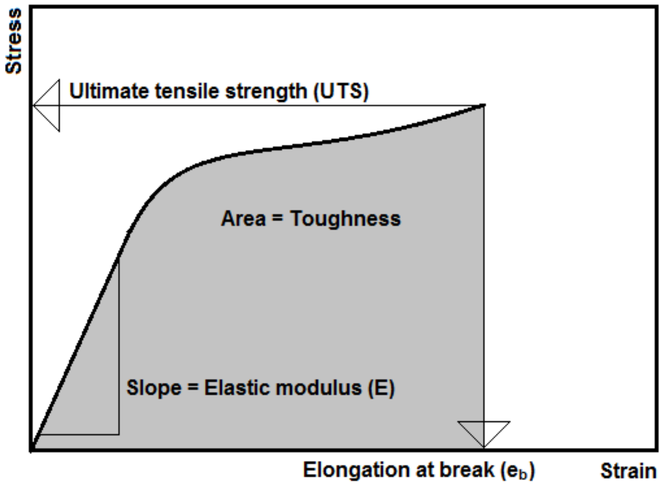


Figure 15. Stress- Strain Curve (Bahcegul et al., 2013)

3.2.4.2. Scanning Electron Microscopy (SEM Analysis)

SEM analysis was performed using a Quanta 400F Scanning Electron Microscope at METU Central Laboratory. Scanning electron microscope was used to characterize the surface and cross-sectional morphology of the strips and films at a voltage of 10 kV. Prior to the SEM analysis, the samples were immersed into a liquid nitrogen bath and fractured in order to obtain the necessary cross-sectional surface then coated with gold/palladium.

3.2.4.3. Statistical Analysis

Statistical analysis was performed using Microsoft Office Excel Software Program. The statistical significance of the differences between the experimental data was determined using T-Test. As the result of the T-Test, *p value* was calculated and if the p value was less than 0.05 the difference was statistically significant.

3.2.4.4. Thermogravimetric Analysis (TGA)

Thermal analysis of the films was conducted using thermogravimetric analysis equipment (Pyris 1, Perkin Elmer, located at METU Central Laboratory). To obtain the thermogravimetric curves, film samples were heated from room temperature to 900°C, with a heating rate of 10°C/min in a nitrogen gas medium.

3.2.4.5. Water Vapor Transfer Rate (WVTR)

Glass bottles were completely filled with silica gels to maintain 0% relative humidity (RH) inside the bottles. Hemicellulose films with dimension of 0.5cm x 2cm were sealed on top of the bottles with an aluminum tape. The bottles were placed into the closed desiccators which had water inside to keep relative humidity around 96%. The weight difference of the bottles was monitored for 24 hours. The experiment was carried for two different biomass (corn cob and cotton stalk) films with different thickness values. Two samples were tested for each type of film. Net weight (grams) versus time (hours) plots were obtained. Net weight of the water was the difference between the measured weight of the bottle and the weight of the bottle at the beginning of the analysis. The water vapor transfer rate (WVTR) of the films was calculated as follows and the normalized values with respect to film thickness were reported to eliminate the effect of film thickness on permeability. Water vapor transfer rate and normalized equation were calculated by the formula given below (Kayserilioğlu et al. 2001; 2003).

$$WVTR = \frac{slope\ of\ the\ plot(g/h)x\ (24h/day)}{area\ of\ the\ film\ (m^2)}$$

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

CHAPTER 4

RESULTS AND DISCUSSION

In this study, effect of alkali extraction and extrusion parameters on the properties of hemicellulose based biodegradable polymeric materials from different agricultural feedstocks including corn cob and cotton stalk was investigated.

In the literature, the only method given for the production of hemicellulose based films is solvent casting which consists of several steps including dissolution of hemicellulose in a solvent, casting the film, and evaporating the solvent. With these steps, the solvent casting method was not only time consuming but also costly. On the other hand, extrusion technique, which has already been a utilized method for many polymeric materials in large scale productions, was started to be used for hemicellulose based film production in our laboratory in 2011(Bahcegul et al., 2013).

In this study, the extrusion technique was used for the production of hemicellulose based materials while alkali extraction method was conducted for the isolation of hemicellulose from two different agricultural biomass, corn cob and cotton stalk.

In the first stage of this study, the effects of several alkaline extraction parameters including, particle size of biomass, alkaline concentration, extraction time, and boron compound utilization, on the properties of hemicellulose based strips were investigated. For each parameter, three batches of the hemicellulose were extracted from the corn cobs and to compare the effects of these parameters, some analyses were applied.

In the second stage of the study, the effects of extraction temperature, together with different extrusion conditions were examined. Cotton stalk was utilized as the biomass and the properties of the extruded films were compared with the ones that were formed via solvent casting technique. Although it was intended to keep the extraction parameters similar with the first part except the temperature, due to the low hemicellulose yield of cotton stalk, some modifications were made.

In the last stage of the study, the film qualities and properties of two different biomass, corn cob and cotton stalk, were compared. To be able to make an accurate comparison, the extraction and extrusion conditions for both of the biomass were kept constant. Within this part of the study, both the film formation properties of two biomass and two different film manufacturing methods, solvent casting and extrusion, were compared and investigated.

4.1. Effect of Alkali Extraction Parameters on the Properties of Corn Cob Hemicellulose Based Polymeric Materials Obtained Via Extrusion

One of the most important factors when producing hemicellulose based polymeric materials is the extraction procedure. It affects the amount and purity of product as well as energy consumption, therefore determines the cost of the product. In this part of the study the most effective alkali extraction conditions were investigated.

Suitable extraction conditions were determined based on the properties of the hemicellulose strips obtained with different isolation parameters, including particle size of the corn cob (2-1.19 mm, 1.19-0.6 mm, 0.6-0.15mm and less than 0.15 mm), extraction time (1, 2, 6 and 12 hours), alkali concentration (5%, 10%, 15%, 20% and 24% KOH), boron compound utilization (0.5%, 1% and 2% boric acid, 0.5% and 1% $NaBH_4$) at room temperature.

Within this part of the study, all extrusions were conducted at 90°C and 50 rpm and hemicellulose strips with a thickness of approximately 0.5 mm and a width of 4.5 mm were obtained.

4.1.1. Effect of Corn Cob Particle Size

In the previous studies done by our research group, it was noticed that, there are large standard deviations in the mechanical properties, between batches of corn cob based extruded strips. While investigating the reasons for these differences, the variations in the particle size of the corn cobs were observed.

Before the extraction process, the corn cobs were crushed with a mill and sieved through 10, 16, 30 and 100 mesh sieve shaker. Thus 2.0-1.19 mm, 1.19-0.6 mm, 0.6-0.15 mm and <0.15 mm particle sized corn cobs were obtained. Two hours of extraction time using 24% KOH were applied on the corn cobs with different particle sizes at room temperature.

4.1.1.1. Corncob Hemicellulose Yield

The amounts of the recovered hemicelluloses from different particle size corn cobs increased by increasing particle size as shown in Table 8. The maximum hemicellulose yield was achieved with the 1.19-2.0 mm corn cobs. However the decrease in yield was related with the decreased efficiency of the filtering system used. In other words, this reduction in the hemicellulose yield was attributed to the material loss during the isolation process as the size of particles decrease, they can easily pass through the filtering cloth. Therefore, the more effective extraction was provided by using large particle corn cobs.

Table 8. The hemicellulose yields extracted from different particle size corn cobs

Particle Size of The Corn Cobs (mm)	Hemicellulose Yield (%)
< 0,15	20.73 ± 0.79
0,15 - 0,6	21.47 ± 0.77
0,6 - 1,19	25.54 ± 0.55
1,19 - 2,0	28.88 ± 1.23

4.1.1.2. Compositional Properties of Corncob Hemicellulose

Monosaccharide composition of hemicellulose was determined by acidic hydrolysis of the polymer and a subsequent HPLC analysis and the lignin content of the hemicellulose was determined using UV-Vis spectroscopy. During the extraction procedure, KAc salt was produced when the precipitation of the hemicellulose in KOH solution with acetic acid/ethanol mixture and salt existence in hemicellulose may decrease the mechanical properties of films. So after extraction, hemicellulosic precipitate is washed with water and ethanol. Nevertheless a small percent of salt remains in the polymer as residual salt.

The residual KAc salt percent of the polymer was determined by the conductivity measurements of hemicellulose solutions.

The sugar monomers of hemicellulose is given in Table 9. From the table, xylose was found as the major monosaccharide of hemicellulose with approximately 64%. It was followed by arabinose with 21% and galactose with 12%. Glucose was the minor sugar monomer of corn cob hemicellulose. All of the hemicellulose extracted from different particle size corn cobs showed similar monomer compositions. The minor changes were observed in xylose ratios of the polymers, with decreasing corn cob particle size, xylose content decreased from 68% to 62%. Even though, there were small quantities of other sugar monomers, the hemisellulosic fraction of isolated corn cobs was referred as xylan in this study, considering the large proportion of xylose.

The alkali soluble lignin and residual salt contents of hemicellulose isolated from different particle size corn cobs are also given in Table 9. According to these results there was no trend in either lignin or salt contents in the hemicelluloses depending on particle size. The alkali extracted hemicellulose contained approximately 12% of alkali soluble lignin and between 2-4% of KAc salt.

Table 9. Lignin, residual KAc Salt and sugar monomer concentrations (%) of the hemicellulose biopolymers extracted from different particle size corn cobs

	Particle Size of The Corn Cobs (mm)			
	1.19 – 2.0	0.6 – 1.19	0.15 – 0.6	< 0.15
Lignin (%)	12.7 ± 0.6	13.8 ± 2.9	10.8 ± 0.5	12.9 ± 1.3
Residual Salt (%)	1.5	3.9	2.3	1.8
Glucose (%)	2	3	5	5
Xylose (%)	68	64	62	62
Galactose (%)	10	12	12	12
Arabinose (%)	20	21	21	21

4.1.1.3. Tensile Properties of Extruded Corncob Hemicellulose Strips

The tensile properties of extruded hemicellulose strips extracted from various particle size corn cobs are shown in Table 10 and Figure 16.

A significant difference was observed especially between flexibilities and toughness of the extruded strips which were produced from various particle size corn cobs ($p<0.005$). According the data in Table 10, the highest tensile properties were obtained when the 1.19-0.6 mm corn cobs were utilized. These strips had the highest mechanical properties: 78.54 MPa ultimate tensile strength, 51.41% elongation, and 33.8 MJ/m^3 toughness values. The following particle sizes were 0.6-0.15mm, <0.15 mm and 2.0- 1.19 mm in terms of mechanical properties. The most recognizable and poor tensile properties of the strips were observed when the largest particle size corn cobs (2.0- 1.19 mm) were employed. Particularly there was a sharp drop of the elongation value of these strips and it affected the toughness value directly. The reasons of the mechanical divergence of these strips were investigated by water content, SEM, TGA analysis and viscosity measurements hence viscosity dependence of hemicellulose on corn cob particle size was observed as the main problem as observed in the following pages.

Table 10. Tensile properties of the hemicellulose based strips produced from hemicellulose extracted using different particle size corn cobs

Particle Size of The Corn Cobs (mm)	Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)
2.0 – 1.19	1179.7±204.9	69.9±4.7	27.2±8.7	16.4±6.6
1.19 – 0.6	1284.2±157.9	78.5±3.0	51.4±4.5	33.8±3.4
0.6 – 0.15	1092.0±156.4	74.8±5.7	46.0±4.0	28.5±3.6
< 0.15	1089.2±105.3	70.3±3.8	37.7±9.0	22.3±6.2

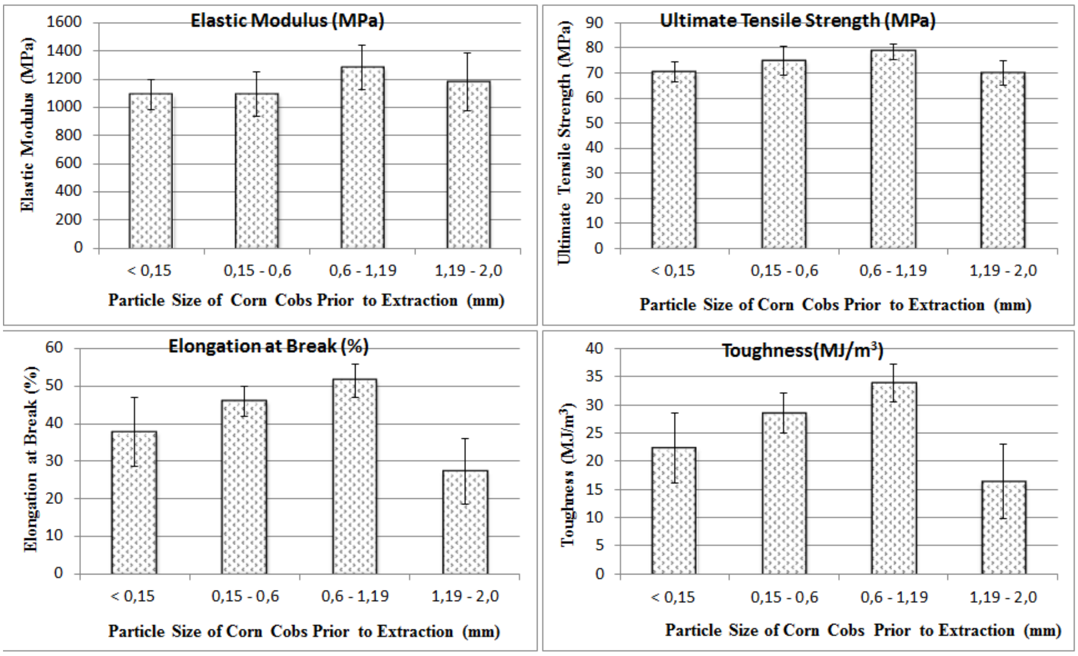


Figure 16. Tensile properties of the hemicellulose based strips extracted from different particle size corn cobs

The water content of the hemicellulose had significant impact on extrusion process since water acts as a plasticizer for polymers and plasticizers enhanced the mechanical properties especially the elongation of the strips. The water content (%) of the hemicellulose polymers prior to the extrusion and the initial portion of the extruded strip are given in Table 11. According to this water content values, there is no significant difference in the water contents of the polymers when various size of corn cob particles were used as biomass.

Table 11. Water content of the hemicellulose polymer prior to the extrusion and at the beginning of the extruded strip

Particle Size of The Corn Cobs (mm)	Water Content (%)	
	Hemicellulose	Beginning of the Strip
< 0,15	28.70 ± 1.66	25.61 ± 1.84
0.15 – 0.6	30.97 ± 6.45	21.21 ± 3.86
0.6 – 1.19	28.12 ± 1.75	24.77 ± 1.45
1.19 – 2.0	30.75 ± 2.35	25.97 ± 1.80

4.1.1.4. Cross sectional and Surface Morphologies (SEM) of Extruded Corncob Hemicellulose Strips

According to scanning electron microscopy results, the cross sectional and surface area of extruded strips obtained from largest particle size corn cobs demonstrates non-uniform structure with big voids within the strips (see Figure 17 and 18). The reason of the defected structure was a result of problems during the extrusion process. The variations in the mechanical properties of these extruded strips can be related to these defects that were observed by SEM analysis. The extruded strips that extracted from other particle size corn cobs showed homogenous, smooth and compact structure construction.

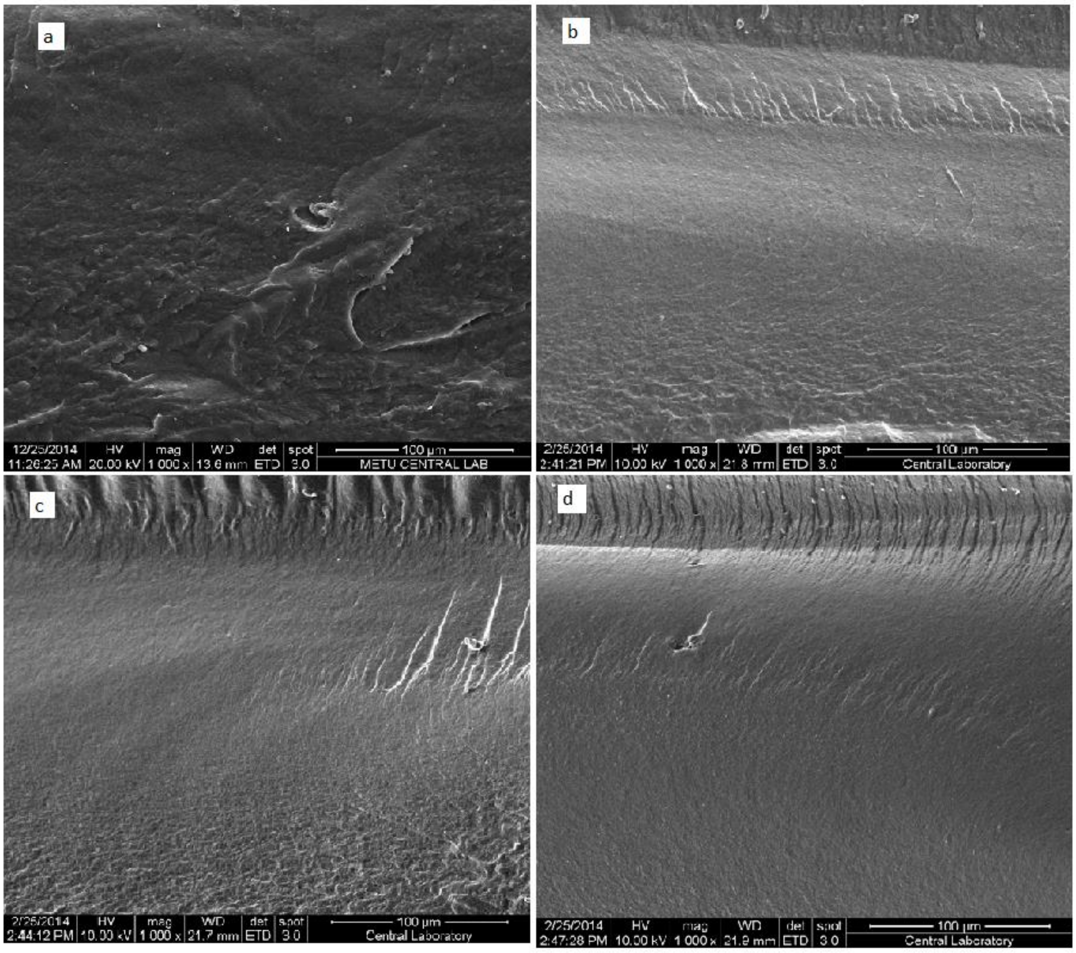


Figure 17. Cross sections of the extruded strips obtained from corncobs having particle size of a) 2.0-1.19 mm, b) 1.19- 0.6 mm, c) 0.6-0.15 mm and d) <0.15 mm

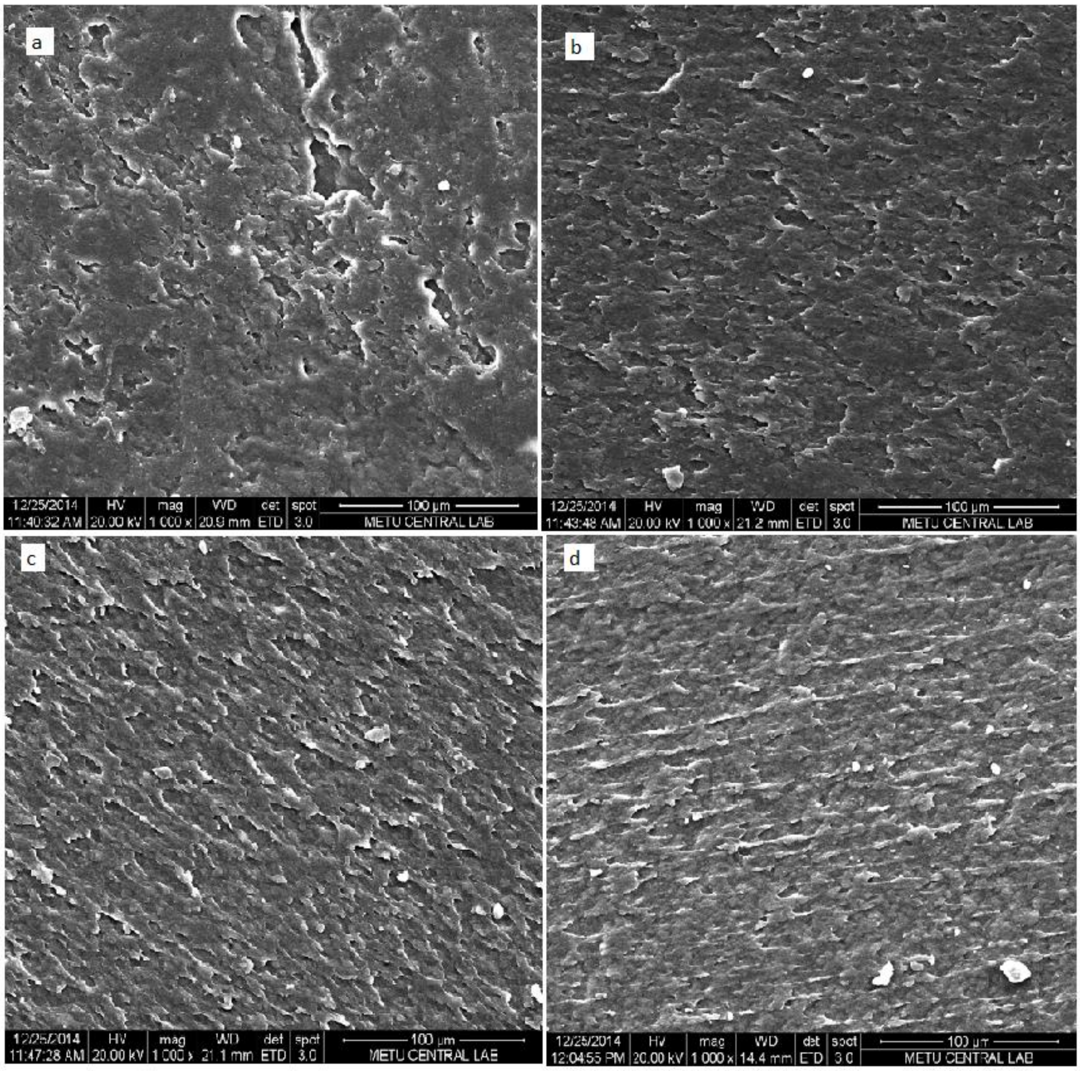


Figure 18. Surfaces of the extruded strips obtained from corncobs had particle size of a) 2.0-1.19 mm, b) 1.19- 0.6 mm, c) 0.6-0.15 mm and d) <0.15 mm

4.1.1.5. Physical Properties of Corncob Hemicellulose

The viscosity of hemicelluloses was calculated using a capillary rheometer. The rheometer was operated at 90°C which was the same as the extrusion temperature. A trend was observed between the particle size and viscosity values (Figure 19). The viscosity of the hemicelluloses increased with the increasing of the corn cob particle size.

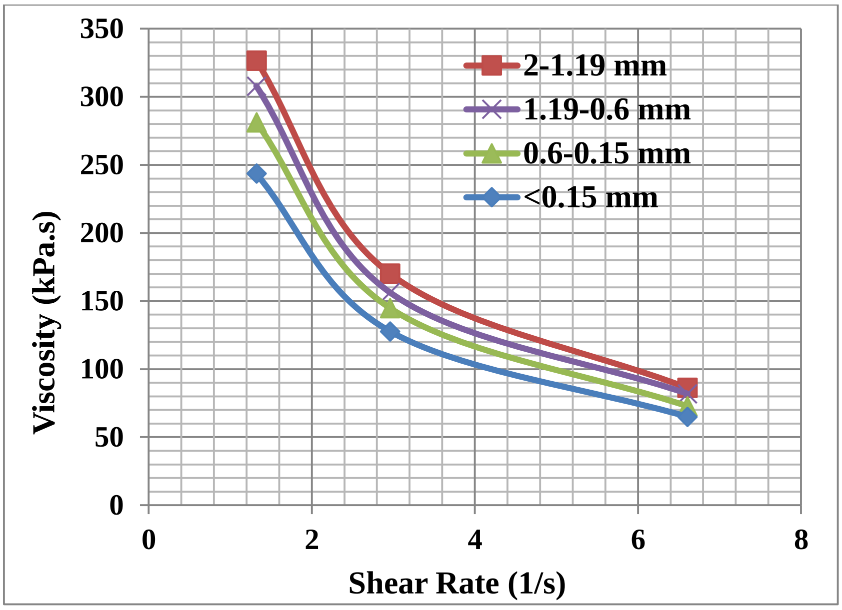


Figure 19. Viscosity of the hemicelluloses extracted from different particle size corn cobs.

The average torque (force required for extrusion) values during the extrusion process are given in Figure 20. The average torque values of the extrusion increased significantly with the increasing of corn cob particle size, especially the hemicellulose samples with the largest particle sizes had a noticeable high torque value which might be the reason for the extrusion defects observed in these extruded strips. The higher torque values means difficulty in extrusion process and higher viscosity values, owned by largest particle size corn cob hemicellulose, may probably induced this situation. In consideration of the reduced mechanical and film forming properties with extrusion problems obtained by largest particle size corn cobs (2.0-1.19 mm) and low hemicellulose yield of the smallest particle size corn cobs (< 0.15 mm), the following experiments, were done using the corncobs with medium size particles ranging from 0.15 mm to 1.19 mm throughout the study.

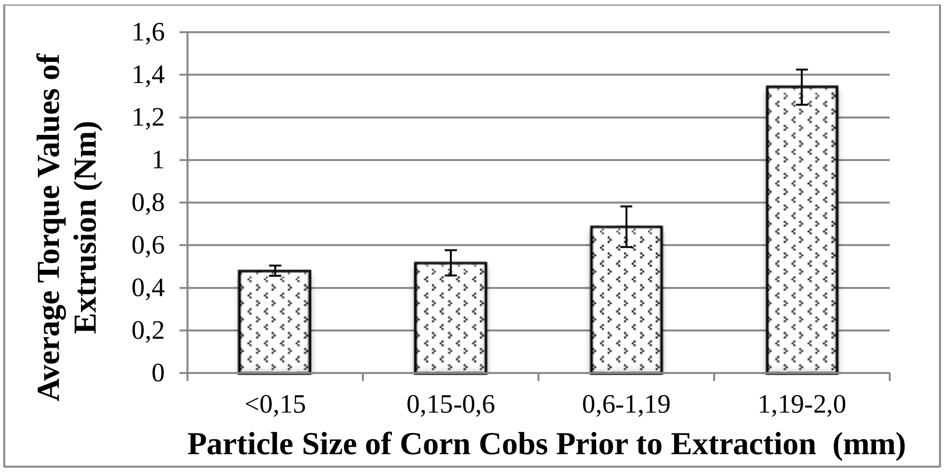


Figure 20. Average torque values during the extrusion of the hemicellulose extracted from different particle size corn cobs

4.1.1.6. Thermal Properties of Extruded Corncob Hemicellulose Strips

The thermal gravimetric analysis (TGA) results for the extruded strips, which are produced from hemicelluloses extracted using corn cobs with different particle sizes, are given in Figure 21. As can be seen in the TGA curves of the extruded strips, the particle size of the corn cobs did not influence the degradation behavior of these extruded strips. The maximum degradation temperatures of the extruded strips were determined as approximately 285°C.

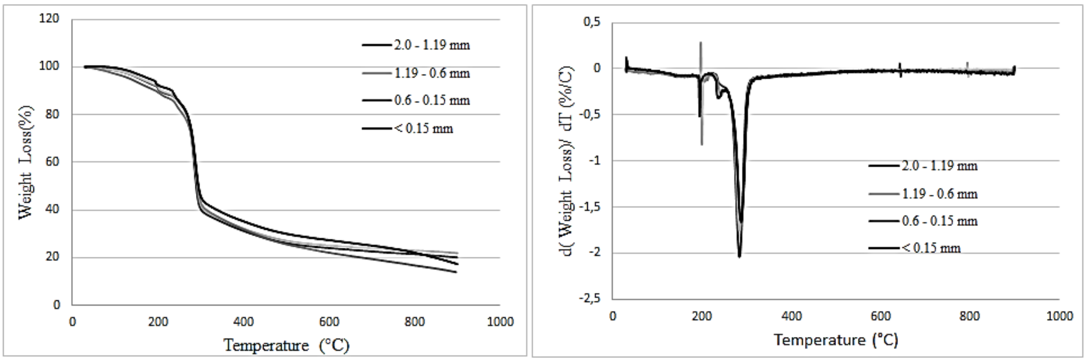


Figure 21. TGA graph of the strips extracted from different particle size corn cobs.

4.1.2. Effect of Alkali Concentration on Corncob Hemicellulose

The alkali extraction method that was used in this study was adapted from Zilliox and Debeire (1998) and Lawther et al. (1996). The method was based on the isolation of hemicellulose from lignocellulosic biomasses using 24% KOH. One of the main purposes in this study was to drop the cost of biopolymeric material production and using less alkali was considered to maintain this goal. Therefore in this part, the extraction of the corn cobs were performed using 5%, 10%, 15%, 20% and 24% KOH and the influence of alkali concentration on the properties of corn cob hemicellulose based strips were investigated with extraction conditions: for 2 hours at room temperature.

4.1.2.1. Hemicellulose Yield from Corncobs

As shown in Table 12, with the increasing of alkaline concentration from 5% to 24% the amount of recovered hemicellulose was increased which was in agreement with the previous studies done by Lawther et al. (1996) and Toraman (2012). The hemicellulose yield showed a significant rise with the increasing of KOH concentration from 2.5% to 23.2%. The reason of the increase in yield might be due to the increasing dissolution power at higher alkaline concentrations. When the KOH concentration was low (5% and 10%), less hemicellulose was dissolved from the biomass. In this study, it was found that, when the KOH concentration was increased beyond 15%, the dissolution efficiency did not change considerably, as a result the yield of the hemicellulose was nearly the same (about 23%).

Table 12. The hemicellulose yields extracted with the different concentrations of alkali (KOH) solutions

Alkali (KOH) Concentration (%)	Hemicellulose Yield (%)
5	2.5 ± 0.6
10	12.7 ± 0.6
15	22.1 ± 0.6
20	23.5 ± 0.2
24	23.2 ± 0.7

4.1.2.2. Compositional Properties of Corncob Hemicellulose

The isolation of hemicellulose using various concentrations of KOH did not influence the alkali soluble lignin content, which was about 13%. The hemicelluloses, extracted using 10%, 15%, and 20% KOH, had nearly the same amount of residual salt (about 1%). On the other hand, increasing the KOH content to 24% resulted in a small increase in the salt content. The sugar monomer concentrations was not changed significantly with different alkali concentrations, for instance the xylose monomer content was generally about 71-74%.

Table 13. Lignin, residual KAc salt and sugar monomer concentrations (%) of the hemicellulose biopolymers extracted with different concentrations of alkali (KOH) solutions

	Alkali (KOH) Concentration (%)				
	5	10	15	20	24
Lignin (%)	13.1 ± 0.0	13.5 ± 1.3	12.5 ± 0.7	13.3 ± 0.6	13.4 ± 0.2
Residual Salt (%)	0.3	1.1	0.9	0.9	1.8
Glucose (%)	4.8±0.9	4.2±0.4	3.6±0.8	9.2±0.5	3.2±0.5
Xylose (%)	70.3±3.2	71.7±1.7	71.3±1.1	71.1±1.1	74.2±0.9
Galactose (%)	8.5±0.9	9.3±0.6	9.4±0.2	8.8±0.4	10.6±1.3
Arabinose (%)	16.3±1.3	14.7±0.6	15.6±0.5	12.1±0.7	12.0±0.1

4.1.2.3. Tensile Properties of Extruded Corncob Hemicellulose Strips

Increasing the alkali concentration of extraction solution results in the strips with the higher mechanical properties. This may be due to the efficiency of the extraction process: it may not be possible to extract high molecular weight hemicellulose when sufficient amount of KOH was not used. Table 14 and Figure 22 show the tensile properties of hemicellulose based strips obtained using various alkali concentrations. The ultimate tensile strength, the elongation at break, and the toughness values of the extruded strips were ranged between 60.3 – 76.9 MPa, 36.6 - 48.7 % and 19.1- 31.1 MJ/ m^3, respectively.

The extruded strip with the highest mechanical properties was obtained when 24% KOH was used during the extraction process. However, the mechanical properties of the strips obtained using 15 % KOH was not significantly lower than those of the strips obtained using 24 % KOH. As a result, the extraction process can be carried out using 15% KOH for more economical production.

Table 14. Tensile properties of the hemicellulose based strips extracted using different concentrations of alkali (KOH) solutions

Alkali Concentration (%)	Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)
5	942.0 ± 23.5	60.3 ± 1.2	36.6 ± 2.7	19.1 ± 1.6
10	974.0 ± 53.4	64.6 ± 2.2	44.0 ± 5.2	24.3 ± 3.5
15	935.0 ± 123.8	67.7 ± 2.5	48.2 ± 3.9	27.5 ± 2.4
20	966.5 ± 56.5	69.8 ± 1.6	49.9 ± 2.9	29.3 ± 2.1
24	1184.5 ± 66.1	76.9 ± 3.8	48.7 ± 6.4	31.1 ± 4.9

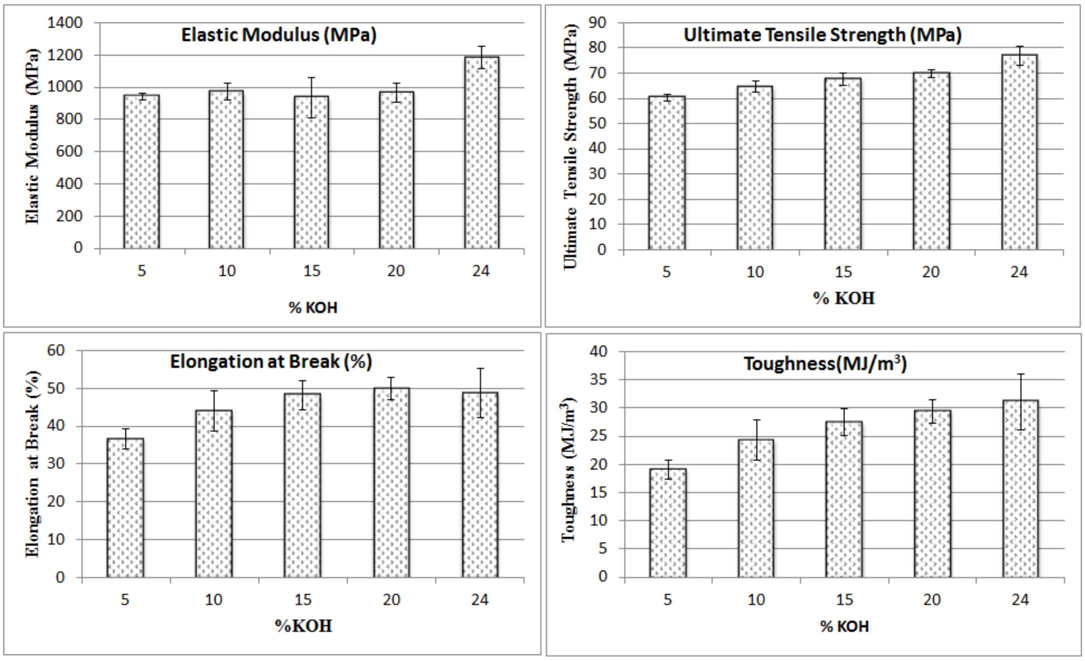


Figure 22. Tensile properties of the hemicellulose based strips extracted using different concentrations of alkali (KOH) solutions

The water contents of the hemicelluloses prior to extrusion and the strips just after extrusion were similar as shown in Table 15.

Table 15. Water content of the hemicellulose polymer prior to the extrusion and at the beginning of the extruded strip

Alkali (KOH) Concentration (%)	% Water Content	
	Polymer	Beginning of the Strip
5	30.51 ± 0.00	25.94 ± 0.00
10	28.08 ± 1.00	25.41 ± 1.88
15	28.38 ± 0.92	26.74 ± 3.01
20	26.50 ± 0.62	23.75 ± 1.56
24	27.38 ± 1.02	26.68 ± 1.01

4.1.2.4. Cross Sectional and Surface Morphologies (SEM) of Extruded Corncob Hemicellulose Strips

Cross sectional and surface morphologies of the extruded strips obtained by extraction with different concentrations of KOH solutions are shown in Figures 23 and 24 According to the cross-sections of the strips, all of the strips exhibited homogenous structure. However the surfaces of the strip extracted using 5%KOH was less uniform compared to the strips extracted using higher concentrations of KOH. The reduced mechanical properties of this strip can be due to defects observed on the surface of the strip.

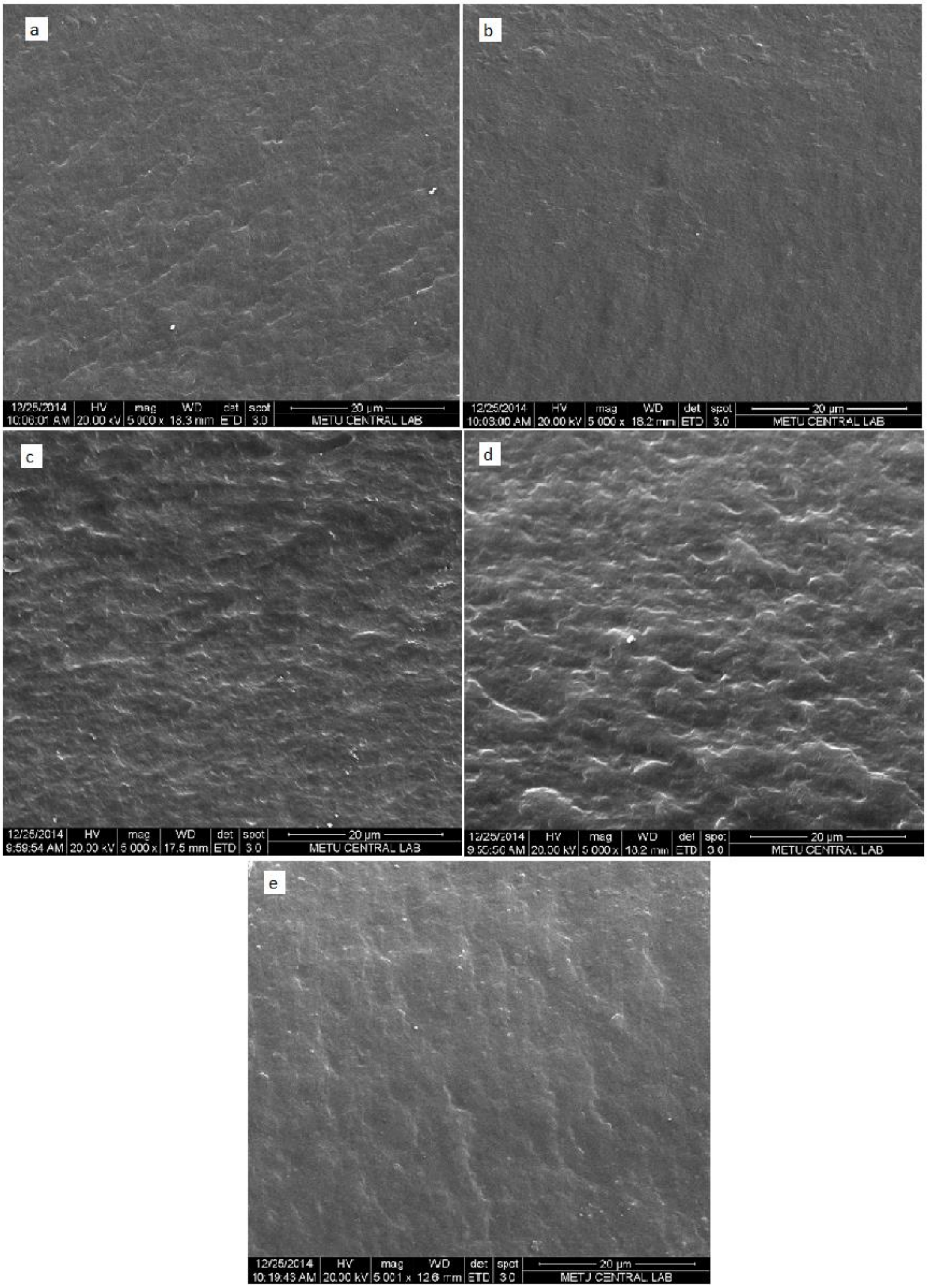


Figure 23. Cross sections of the extruded strips obtained by extraction using a) 5%, b) 10%, c) 15%, d) 20% and e) 24% KOH solutions

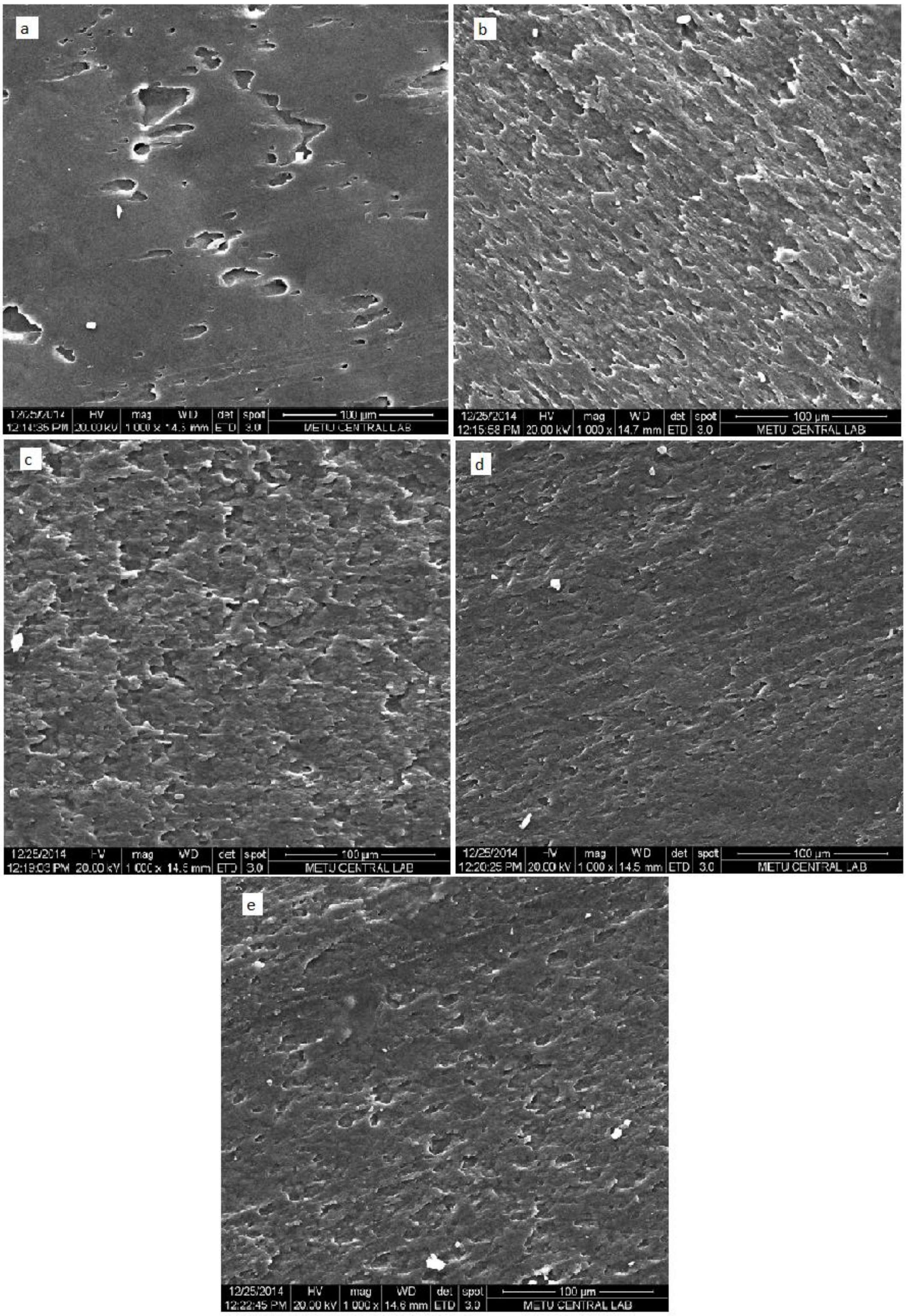


Figure 24. Surfaces of the extruded strips obtained by extraction with a) 5%, b) 10%, c) 15%, d) 20% and e) 24% KOH solutions

4.1.2.5. Thermal Properties of Extruded Corncob Hemicellulose Films

The thermal gravimetric analysis (TGA) results for the extruded strips produced from hemicelluloses extracted with different alkaline concentrations of KOH are given in Figure 25. There was not a significant difference between maximum degradation temperatures (approximately 285°C) for different alkali concentrations.

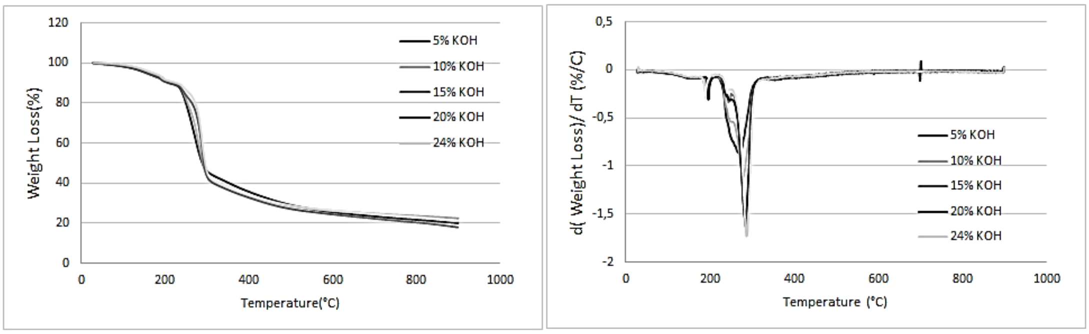


Figure 25. The TGA graphs of the extruded strips obtained from the hemicelluloses extracted using a) 5%, b) 10%, c) 15%, d) 20% and e) 24% KOH solutions

4.1.3. Effect of Extraction Time on Corncob Hemicellulose

Time of extraction was another significant parameter of hemicellulose based polymeric material production. Throughout this study, 2 hours of extraction time was utilized according to the previous studies. Within this part, different extraction times (1h, 2h, 6h and 12 h) were applied and the influence of the extraction time on the material properties of the hemicellulose strips were studied where extractions conducted with 24% KOH at room temperature.

4.1.3.1. Corncob Hemicellulose Yield

Hemicellulose yields which were achieved after various extraction times are demonstrated in Table 16. Although it was observed that the hemicellulose yield was slightly increased with increasing extraction time, this difference was not significant.

Table 16. Yields of hemicellulose obtained with different extraction hours

Extraction Time (hour)	Hemicellulose Yield (%)
1	22.42 ± 0.61
2	23.20 ± 0.71
6	24.17 ±0.70
12	24.96 ± 0.68

4.1.3.2. Compositional Properties of Corncob Hemicellulose

The alkali soluble lignin and residual KAc salt contents of the hemicellulose biopolymers obtained at different extraction times are given in Table 17. The lignin content of hemicelluloses, which were extracted at different times, range between approximately 12-14% and there was not a trend between the extraction time and lignin content. The highest lignin content was achieved when the extraction time was 6 hours. On the other hand, there was not a trend among the samples in terms of residual salt content. The sugar monomer concentrations did not change much with different extraction times, however strips which had the best mechanical properties (1h) in the range tested had slightly higher xylose content as 75%.

Table 17. Lignin, residual KAc salt and sugar monomer concentrations (%) of the hemicellulose biopolymers obtained with different extraction hours

	Extraction Time (hours)			
	1	2	6	12
Lignin (%)	11.8 ± 0.3	13.4 ± 0.2	14.0 ± 0.5	12.6 ± 0.8
Residual Salt (%)	1.2	1.8	2.5	2.0
Glucose (%)	3.6±0.1	3.2±0.5	3.8±0.9	3.6±0.6
Xylose (%)	75.8±0.9	74.1±0.9	72.8±3.0	72.8±2.3
Galactose (%)	8.9±0.8	10.6±1.3	8.6±0.1	9.6±0.7
Arabinose (%)	11.5±0.1	12.0±0.1	14.6±2.2	13.8±0.9

4.1.3.3. Tensile Properties of Extruded Corncob Hemicellulose Strips

The mechanical properties of the extruded strips of corn cob hemicellulose obtained at different extraction times are given in Table 18 and Figure 26. According to the tensile test results, there was not a significant difference between the mechanical properties of extruded hemicellulose strips isolated at various times (1, 2, 6 and 12 hours) especially for ultimate tensile strength. 1 hour of extraction resulted with the strongest strips, having 80.6 ± 2.1 MPa of ultimate tensile strength.

The lowest elongation at break values (34%) was obtained for the strips produced from the hemicellulose with an extraction time of 6 hours. The low ductility of this strip may be related to the lignin content of this polymer. The presence of lignin together with hemicellulose may promote the agglomeration of lignin-hemicellulose complexes (Westbye et al. 2007) and it would negatively influence the mechanical properties of the hemicellulose-based films (Bahcegul et al. 2012). The high lignin content of the 6 hour extracted hemicellulose might be responsible for the lower elongation values due to the agglomeration mechanism reported by Westbye et al. (2007).

Table 18. Tensile properties of the hemicellulose based strips obtained with different extraction hours

Extraction Time (hour)	Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)
1	1232 ± 77.8	80.6 ± 2.1	44.3 ± 5.8	29.7 ± 4.4
2	1184.5 ± 66.1	76.9 ± 3.8	48.7 ± 6.4	31.1 ± 4.9
6	1290 ± 63.3	76.7 ± 3.4	34.3 ± 8.2	22.3 ± 6.0
12	1172.8 ± 107.7	78.7 ± 6.8	48.2 ± 6.0	31.5 ± 5.7

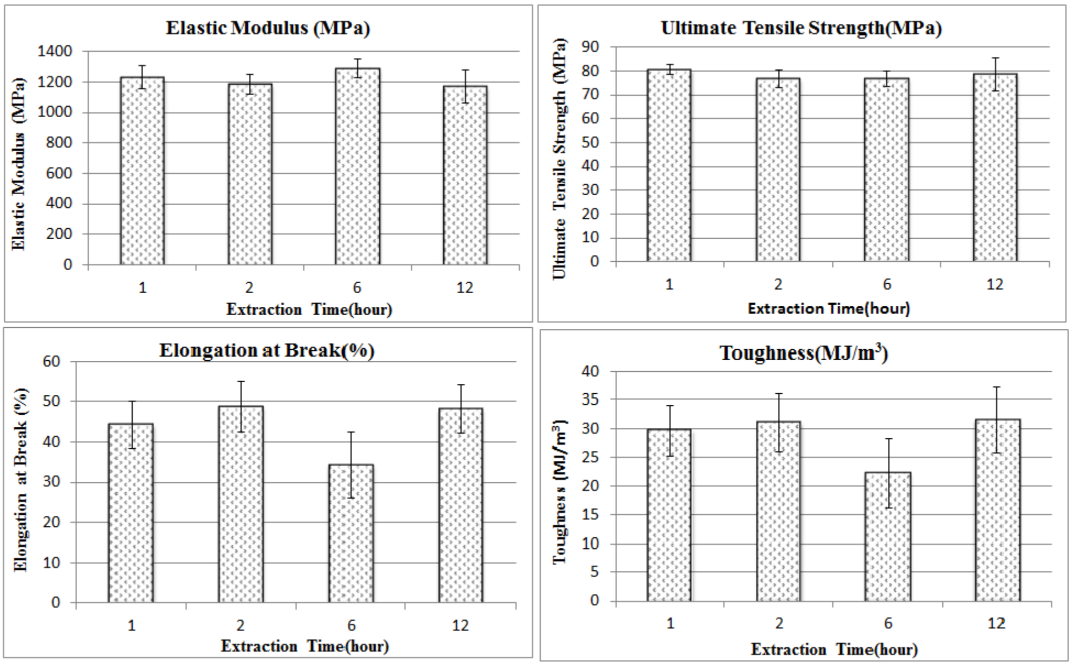


Figure 26. Tensile properties of the hemicellulose based strips obtained with different extraction hours

The water contents of hemicellulose polymer prior to extrusion and the extruded strips just after the extrusion process are given in Table 19. According to these values, 6 and 12 hour- extracted hemicelluloses had higher water content than shorter time extracted polymers. However this situation did not affect the elongation values of the extruded strips.

Table 19. Water content of the hemicellulose polymer prior to the extrusion and the extruded strip just after the extrusion.

Extraction Time (hour)	% Water Content	
	Polymer	Beginning of the Strip
1	26.74 ± 2.83	25.12 ± 2.73
2	27.38 ± 1.02	26.68 ± 1.01
6	30.95 ± 2.41	27.19 ± 0.96
12	30.86 ± 0.66	28.23 ± 1.15

4.1.3.4. Cross Sectional and Surface Morphologies (SEM) of Extruded Corncob Hemicellulose Strips

SEM images of the cross-sections and surfaces of the extruded strips obtained at different extraction times are given in Figures 27 and 28, respectively. Both the cross-sections and surfaces of the strips, which were produced from the hemicelluloses with different extraction times, exhibited a relatively homogenous structure.

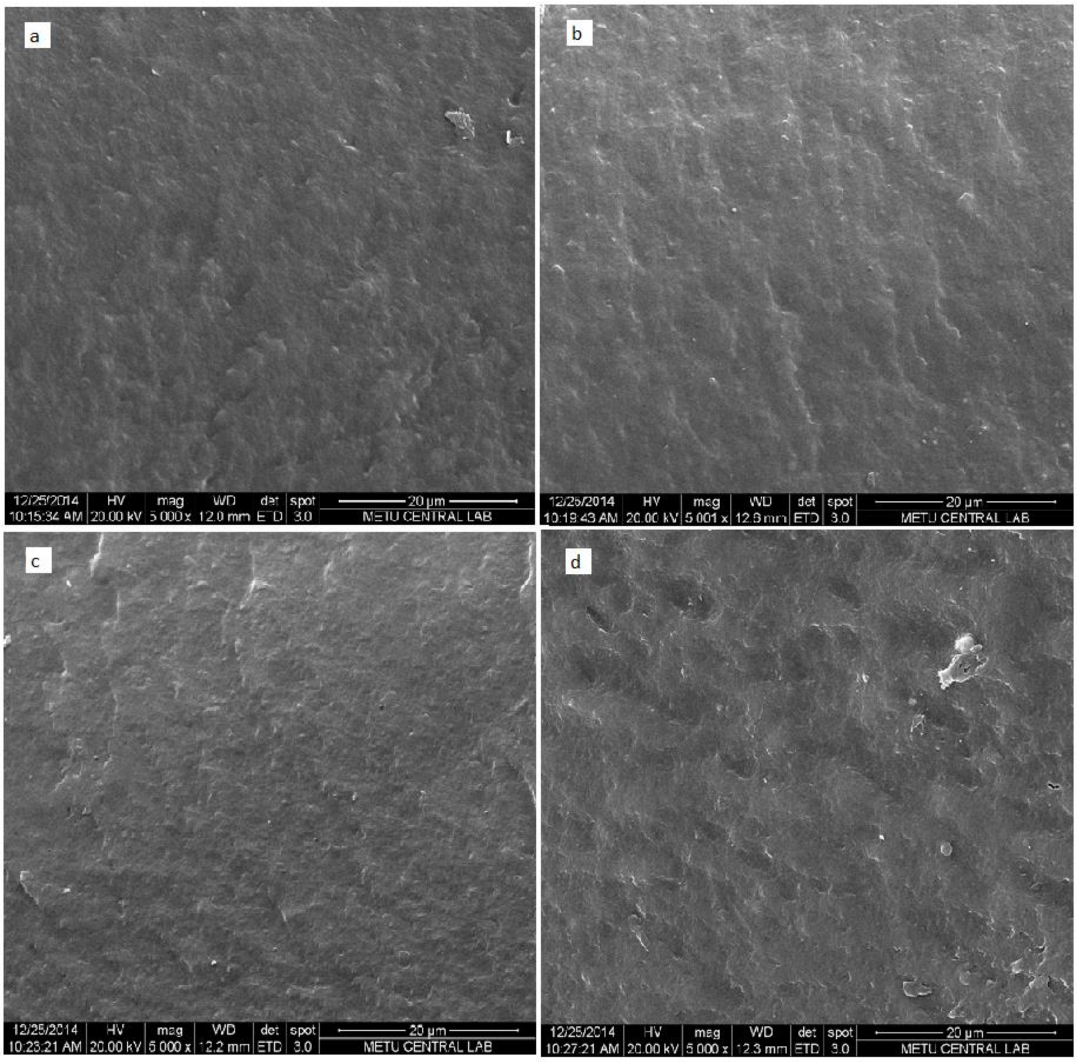


Figure 27. The cross sections of the extruded strips produced from the hemicelluloses with different extraction times a) 1 hour, b) 2 hours, c) 6 hours and d) 12 hours

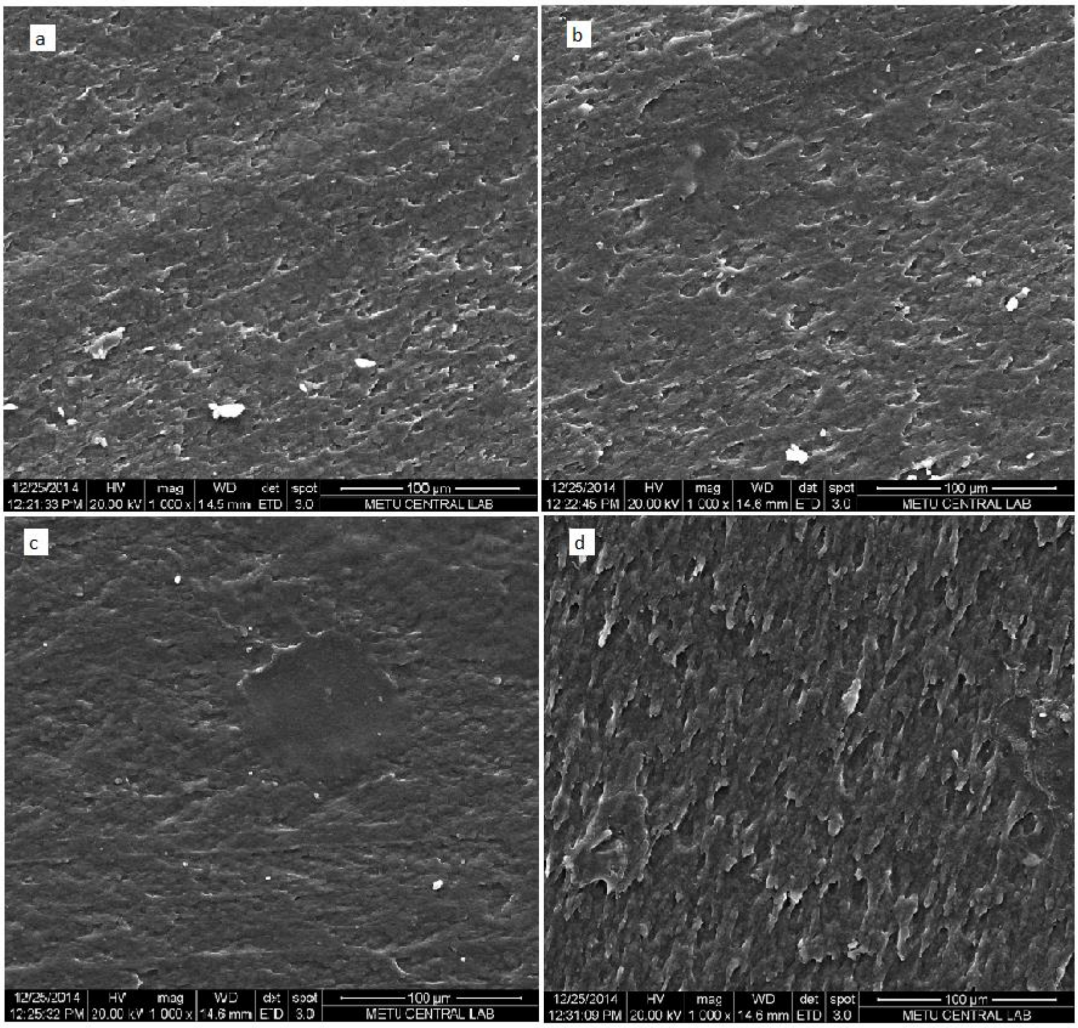


Figure 28. The SEM pictures from the surfaces of the extruded strips produced using the hemicelluloses with different extraction times a) 1 hour, b) 2 hours, c) 6 hours and d) 12 hours

4.1.3.5. Thermal Properties of Extruded Corncob Hemicellulose Films

The thermal gravimetric analysis (TGA) results for the extruded strips produced using the hemicelluloses with different extraction times are given in Figure 29. As can be seen in the TGA curves of the extruded strips, the extraction time of the hemicelluloses did not influence the thermal stability of these strips. The maximum degradation temperatures of the extruded strips were determined as approximately 286°C.

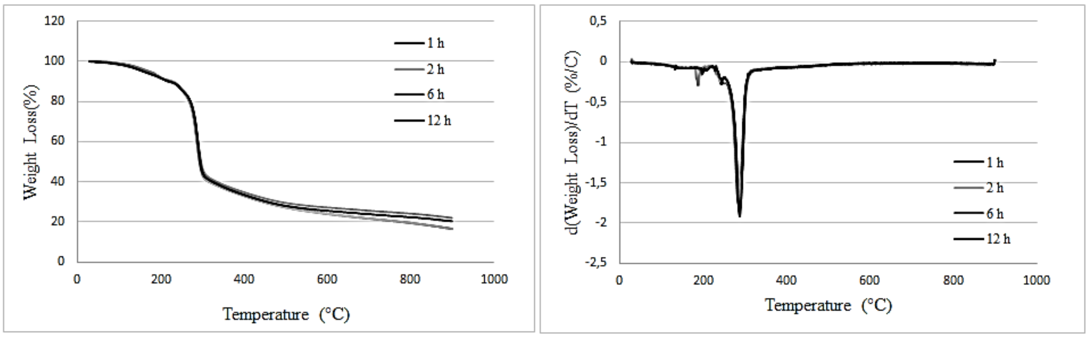


Figure 29. The TGA graphs of the extruded strips obtained by extraction for a) 1 hour, b) 2 hours, c) 6 hours and d) 12 hours

The strips produced using the hemicellulose with 1 hour extraction time did not have worse mechanical properties and hemicellulose yield. So this observation suggest that it is not necessary to use longer extraction times.

4.1.4. Effect of Boron Compound Addition on Corncob Hemicellulose

In this part of the study, the effects of boron compound (boric acid or $NaBH_4$) addition to the alkali extraction solution on the hemicellulose and hemicellulose based strips were investigated.

In literature, boric acid (H_3BO_3) or sodium borohydride ($NaBH_4$) were utilized as additional chemicals in the extraction procedure. The addition of these boron compounds into the alkali solutions (NaOH or KOH) increases the dissolving power of some types of biomass which are highly resistant to extraction (Gonzalez et al., 1986; Lawther et al., 1996).

In the following part of the study, the extractions were carried out with the addition of various concentrations of H_3BO_3 (0.5%, 1% and 2%) or $NaBH_4$ (0.5% and 1%) and without any boron compound to understand the effect of boron compound on the properties of hemicellulose and extruded strips.

4.1.4.1. Corncob Hemicellulose Yield

Hemicellulose yields which were obtained after alkali extraction of corn cobs with the addition of boron compounds are shown in Table 20. Although it was observed that the hemicellulose yield was slightly increased with the addition of boron compounds, this difference was not significant.

Table 20. The hemicellulose yields extracted with boric compounds

Boron Compound Content (%)		Hemicellulose Yield (%)
0		23.2 ± 0.7
H_3BO_3 (%)	0.5	24.8 ± 0.4
	1.0	23.9 ± 0.3
	2.0	24.2 ± 0.7
$NaBH_4$ (%)	0.5	25.6 ± 0.5
	1.0	25.7 ± 1.3

4.1.4.2. Compositional Properties (Lignin, Salt, Sugar Monomers) of Corncob Hemicellulose

Lignin, residual salt and sugar monomer concentration (%) of hemicelluloses extracted with boron compound addition are given in Table 21. While there was not a significant difference between sugar monomers of the hemicelluloses, 1% $NaBH_4$ added hemicellulose, having reduced mechanical properties, had low xylose content too.

Table 21. Lignin, residual salt and sugar monomer concentration (%) of hemicellulose extracted with boron compound addition

Boron Compound Content (%)		Lignin (%)	Residual Salt (%)	Glucose	Xylose	Galactose	Arabinose
0		13.4 ± 0.1	1.8	3.2±0.5	74.1±0.9	10.5±1.3	12.0±0.1
H_3BO_3 (%)	0.5	11.8 ± 0.7	2.7	2.6±0.4	71.3±1.0	12.7±0.5	13.3±0.1
	1.0	12.5 ± 0.3	1.7	2.4	74.2	13.0	10.3
	2.0	11.5 ± 0.1	3.9	3.6±0.1	71.5±0.3	11.4±1.3	13.3±2.5
$NaBH_4$ (%)	0.5	9.9 ± 0.4	1.1	4.3±0.2	73.1±1.3	9.5±0.7	13.1±0.3
	1.0	10.5 ± 0.7	0.9	5.4±0.2	69.7±1.1	9.1±1.5	15.7±2.3

4.1.4.3. Tensile Properties of Extruded Corncob Hemicellulose Strips

The effect of boron compound addition on the mechanical properties of hemicellulose based strips can be seen in Table 22 and Figure 30. According to these results, the boron compound addition has no positive effect on the mechanical properties of corn cob hemicellulose based strips.

Compared to the films produced from corn cob hemicellulose in the previous studies(Toraman, 2012), 1% $NaBH_4$ addition to the extraction improved the UTS and modulus of the films from 9.7 to 38.8 MPa and from 364.2 to 1742.5 MPa, respectively, while decreasing the elongation values from 14.4 to 5.5 % for solvent casted films. Another study done by Akınalan (2014), additional boron compounds showed no improvement mechanically, the UTS and toughness values of the extruded films produced from sunflower stalk hemicellulose, were around 48 MPa and 2 MJ/ m^3 which was lower than other extruded films. And the reason of the ineffective presence of the $NaBH_4$ was attributed to the behavior of some particles observed in the SEM images as impurities. Similar to the study done by Akınalan (2014), in this work, additional $NaBH_4$ reduced mechanical properties of hemicellulose strips especially the UTS values. The UTS and toughness values of the strips decreased from 76.8 to 61.1 MPa and from 31.1 to 24.5 MJ/m^3 when 1% $NaBH_4$ were utilized.

Consequently, considering the effect of boron compound utilization on both the hemicellulose yield and mechanical properties, it was decided when the corn cob used as biomass there was no need for boron compound addition for hemicellulose based film formation.

Table 22. Tensile properties of the hemicellulose based strips extracted with boron compound addition

Boron Compound Content (%)		Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)
0		1184.5± 66.1	76.8 ± 3.8	48.7 ± 6.4	31.1 ± 4.9
H_3BO_3 (%)	0.5	1110.7 ± 88.3	74.5 ± 3.8	50.5 ± 4.6	31.6 ± 3.6
	1.0	1190.0 ± 85.5	77.4 ± 5.1	48.6 ± 4.0	31.5 ± 3.9
	2.0	1062.6 ± 112.2	70.1 ± 6.1	42.6 ± 5.8	25.5 ± 4.9
$NaBH_4$ (%)	0.5	966.0 ± 65.7	62.4 ± 2.9	44.0 ± 4.1	23.1 ± 2.8
	1.0	917.1 ± 89.3	61.1 ± 3.9	47.8 ± 3.7	24.5 ± 2.3

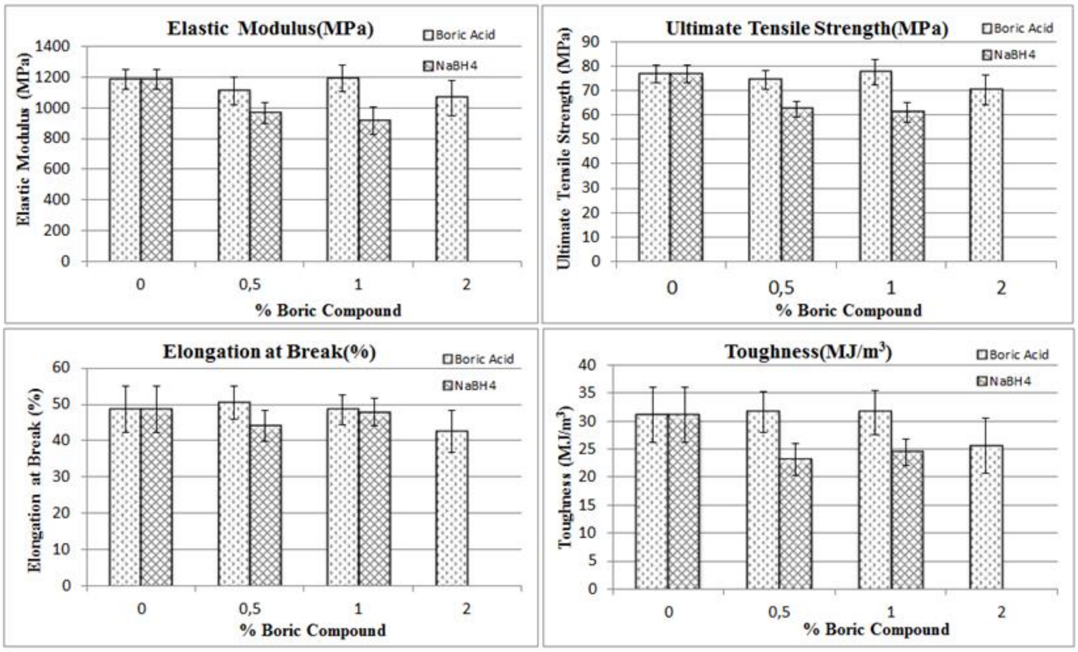


Figure 30. Tensile properties of the hemicellulose based strips extracted with boron compound addition

The water content of the hemicelluloses when boron compound used prior to extrusion and at the beginning of the extruded strip can be seen in Table 23. It was observed that when the concentration of the boron compound increased, the water content of hemicellulose increased slightly. However this did not affect the elongation value of the strips as expected.

Table 23. Water content of the hemicellulose polymer prior to the extrusion and at the beginning of the extruded strip

Boron Compound Content (%)		% Water Content	
		Polymer	Beginning of the Strip
0		27.3 ± 1.0	26.6 ± 1.0
H_3BO_3 (%)	0.5	28.6 ± 0.3	25.8 ± 1.9
	1.0	29.8 ± 1.7	27.8 ± 1.9
	2.0	29.8 ± 4.8	29.4 ± 1.9
$NaBH_4$ (%)	0.5	29.4 ± 0.6	26.2 ± 1.1
	1.0	32.3 ± 3.0	27.5 ± 2.0

4.1.4.4. Cross Sectional and Surface Morphologies (SEM) of Extruded Corncob Hemicellulose Strips

SEM images of the cross-sections and surfaces of extruded strips obtained by extraction with the addition of boron compounds are given in Figures 31 and 32, respectively. Surface areas of these strips looked uniform. While cross sectional images of the strips obtained either without boron compound addition or 0.5% H_3BO_3 and 1.0% H_3BO_3 addition demonstrated relatively homogenous structures. However, 2% H_3BO_3 and 0.5% $NaBH_4$ added strips had voids and cracks within the structure. These non-uniformities could be the result of the impurities formed by precipitation of boron compounds with acetic acid solution during the extraction which affected the mechanical properties of these strips.

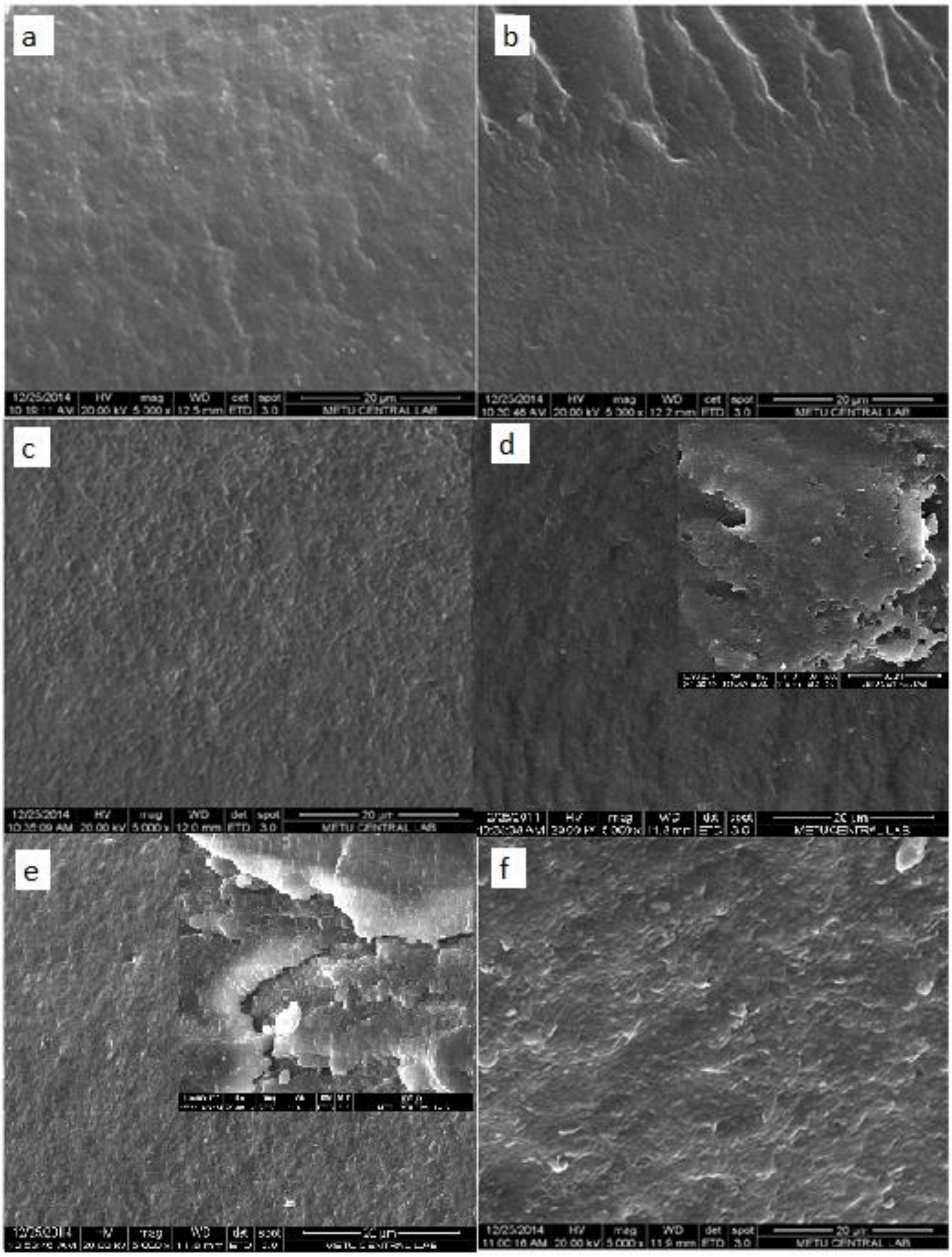


Figure 31. Cross sections of the extruded strips obtained by extraction with a) 0% boron compound, b) 0.5% H_3BO_3, c) 1.0% H_3BO_3, d) 2% H_3BO_3, e) 0.5% $NaBH_4$ and f) 1.0% $NaBH_4$ addition

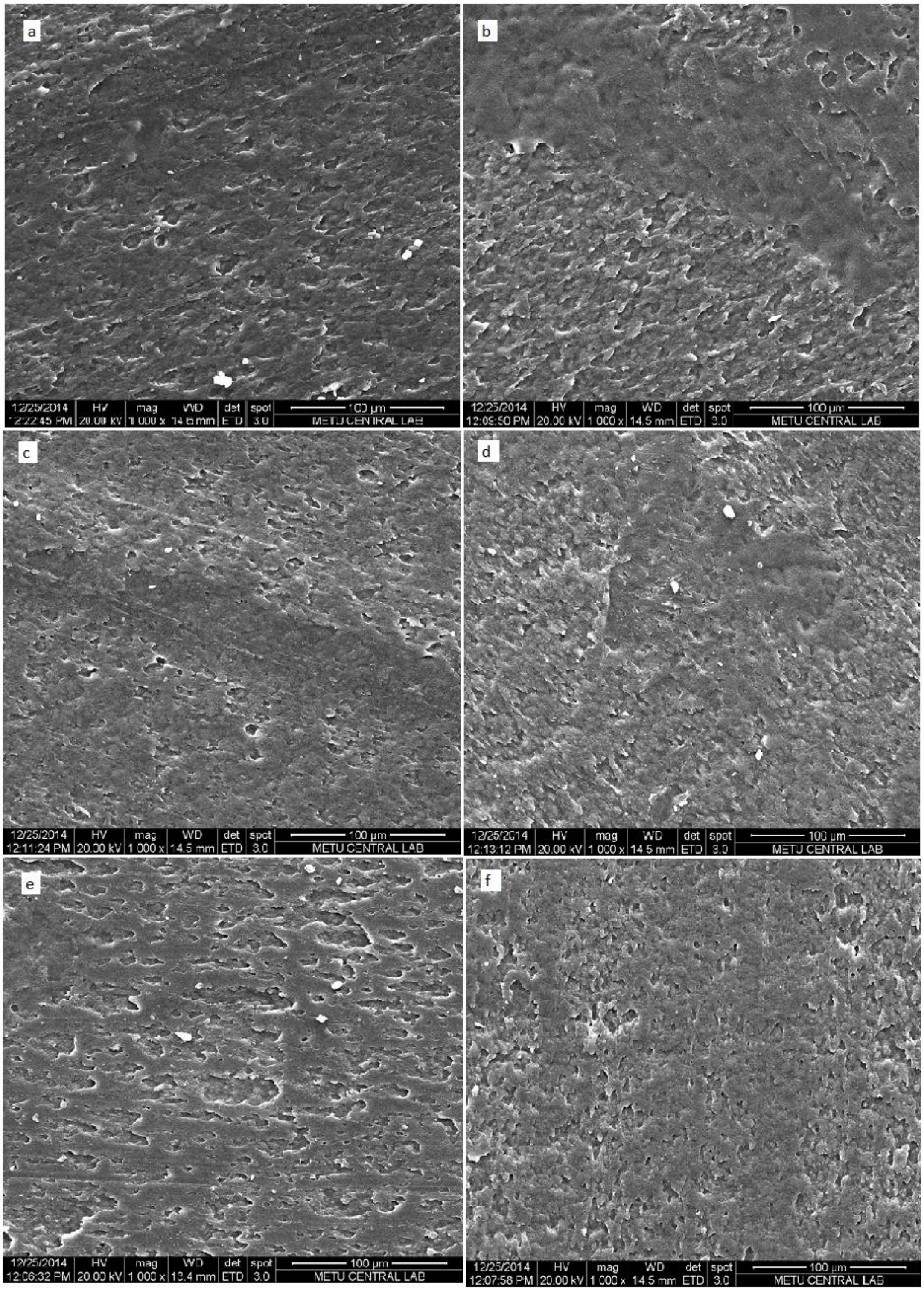


Figure 32. Surface areas of the extruded strips obtained by extraction with a) 0% boron compound, b) 0.5% H_3BO_3, c) 1.0% H_3BO_3, d) 2% H_3BO_3, e) 0.5% $NaBH_4$ and f) 1.0% $NaBH_4$ addition

4.1.4.5. Thermal Properties of Extruded Corncob Hemicellulose Strips

The thermal gravimetric analysis (TGA) results for the extruded strips produced from hemicellulose extracted with the addition of different boron compounds at different concentrations are given in Figure 33. As can be seen in the TGA curves of the extruded strips, addition of boron compounds at different concentrations did not influence the degradation behavior of these strips considerably. The maximum degradation temperatures of the extruded strips were determined as approximately 290°C for boric acid added strips and 286 °C for $NaBH_4$ added strips

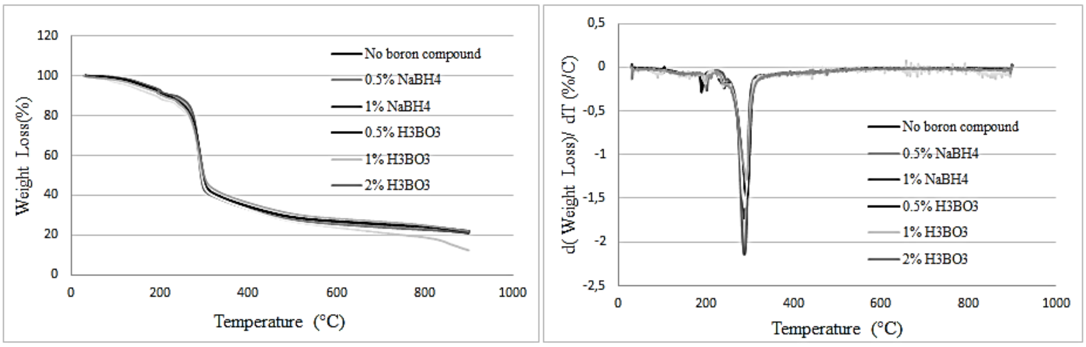


Figure 33. TGA Graphs of the extruded strips obtained by extraction with a) 0% boron compound, b) 0.5% H_3BO_3, c) 1.0% H_3BO_3, d) 2% H_3BO_3, e) 0.5% $NaBH_4$ and f) 1.0% $NaBH_4$ addition

4.2. Effect of Alkali Extraction Temperature and Extrusion Conditions on the Properties of Cotton Stalk Hemicellulose Based Polymeric Materials Obtained Via Extrusion

Within the second part of the study, the effect of extraction temperature and extrusion conditions on the properties of cotton stalk hemicellulose based polymeric materials were investigated.

The extraction procedure of the cotton stalk had to be changed since the hemicellulose extraction yield was very low when the current method utilized

(1.7%). Therefore some preliminary extractions were done to obtain higher amounts of hemicellulose. First, the time for swelling the biomass with water was raised to 16 hours since the large particle surface enhances the alkali solution interactions. Then extraction time was raised to 24 hours with the purpose of increase the interaction time, which increased the hemicellulose yield up about 2%. However the main problem was the difficulty to dissolve the hemicellulosic portion of the cotton stalk in the alkali solution. To overcome this problem 1% $NaBH_4$ was added to the extraction solution of 24% KOH to increase the dissolution power. With applying only 1%$NaBH_4$, yield raised to 6.3%. All of these changes were employed to the extraction process and approximately 9.89% of hemicellulose yield was obtained at room temperature.

In this part of the study, solvent casted films, extruded strips and extruded films which were obtained by rolling of the strips, were produced from cotton stalk hemicellulose. These materials were compared in terms of their mechanical properties.

4.2.1. Effect of Alkali Extraction Temperature on Cotton Stalk Hemicellulose

Extractions of cotton stalk were conducted at two different temperatures at room temperature and 60°C. Extrusion of the cotton stalk hemicellulose was performed at 90°C and 50 rpm. The extruded strips were slenderized using a roller.

4.2.1.1. Cotton Stalk Hemicellulose Yield

Hemicellulose yields achieved with the extraction of cotton stalks at different temperatures are given in Table 24. With increasing extraction temperature, the amount of recovered hemicellulosic portion increased from 9.9 to 12.2% in accordance with the previously reported results by Lawther et al. (1996) and Bahcegul et al. (2011).

Table 24. The hemicellulose yields of cotton stalk extracted at different temperatures

Extraction Temperature (°C)	Hemicellulose Yield (%)
Room Temperature	9.9 ± 0.9
60 °C Extraction	12.2 ± 1.2

4.2.1.2. Compositional Properties of Cotton Stalk Hemicellulose

The lignin and residual KAc salt content of the hemicelluloses obtained at different temperatures is given in Table 25. The lignin content of hemicellulose extracted at 60ºC was nearly 2 fold of the ones extracted at room temperature. The appearances of the solvent casted films obtained from cotton stalk extraction at different temperatures is demonstrated in Figure 34. The color of the film extracted at 60ºC was darker and this darkening with increasing extraction temperature was likely a result of increasing lignin content which might have a negative effect on oxygen permeability and mechanical properties (Bahcegul et al., 2011). On the other hand KAc salt content was not affected by extraction temperature as can be seen in Table 25. However xylose content probably dropped to 64% from 72% and arabinose content increased from 4.5 to 13.8% with increasing extraction temperature showing extraction of shorter xylan molecules with more arabinose side groups at higher temperatures.

Table 25. Lignin, residual KAc salt and sugar monomer concentrations (%) of the cotton stalk hemicellulose biopolymers extracted at different temperatures

	Cotton Stalk Hemicellulose Extracted at Different Temperatures	
	Room Temp.	60 º C
Lignin	6.5 ± 2.2	11.7 ± 2.0
Residual KAc Salt (%)	5.9	6.3
Glucose (%)	3.4 ± 0.0	5.7 ±0.8
Xylose (%)	72.0 ±2.8	64.6 ±4.7
Galactose (%)	20.0 ± 3.9	15.8 ±1.8
Arabinose (%)	4.5 ±1.2	13.8 ± 2.0

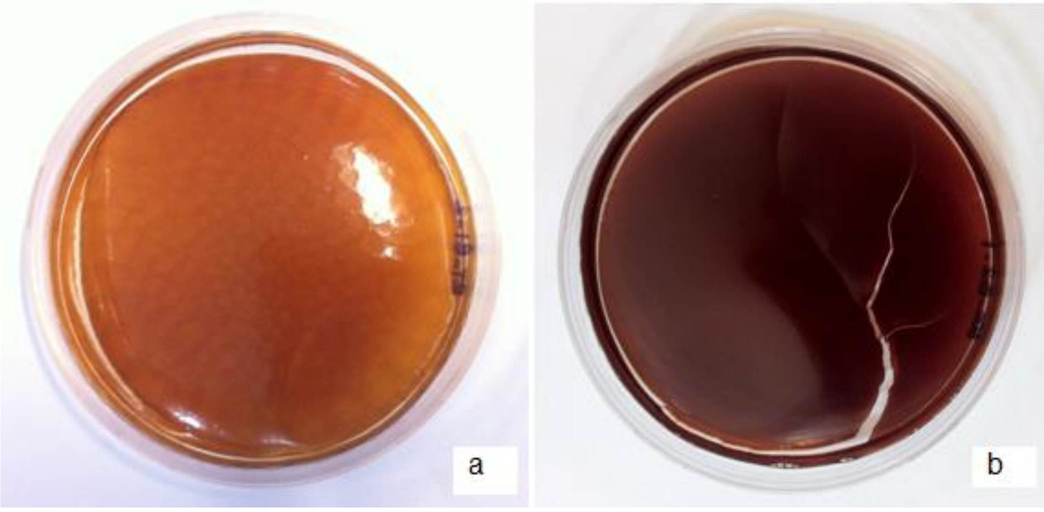


Figure 34. The appearances of the solvent casted films obtained from cotton stalk hemicellulose extracted at a) room temperature and at b) 60°C

4.2.1.3. Tensile Properties of Extruded Cotton Stalk Hemicellulose Films

Mechanical properties of the hemicellulose based films obtained from cotton stalks at different extraction temperatures are given in Table 26. The films which extracted at different temperatures had similar tensile properties.

The rolling process applied to the extruded strips to obtain films, decreased the mechanical properties. For instance the tensile strength and elongation values of a strip were approximately 71 MPa and 15% respectively, however after rolling 42 MPa of tensile strength and 4.4% of elongation values were obtained (Table 26). Similar to this study, decreased mechanical properties after rolling were observed from the previous studies by Akınalan (2014). The mechanical properties of the films might be affected by the thickness of the films, since the thicker ones keep more water within, which enhances the elongation as a plasticizer. However, the reduction in the mechanical properties of the films might also be a result of defects on the film surfaces that formed during the rolling process.

Table 26. Tensile properties of the hemicellulose based films obtained from cotton stalk at different extraction temperatures

Film Type	Extraction Temp.(°C)	Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)
Rolled Film	Room Temp.	1235 ± 200	42 ± 4	4.4 ± 0.9	1.1 ± 0.3
	60ºC	1191 ± 68	49 ± 3	5.5 ± 1	1.7 ± 0.5
Strip	Room Temp.	1210 ± 25	71.8 ± 2.7	15 ± 2.3	8.3 ± 1.7
	60ºC	1187 ± 56	70.9 ± 2.3	13.8 ± 2.2	7.5 ± 1.4
Casted Film	Room Temp.	1999 ± 79	92 ± 5	6.5 ± 0.8	3.8 ± 0.8
	60ºC	1461 ± 122	85 ± 3	9.4 ± 0.9	5.3 ± 0.8

Water content of the hemicelluloses that extracted at different temperatures was almost the same (see Table 27).

Table 27. Water content of the hemicellulose polymer prior to the extrusion and at the beginning of the extruded strip

Extraction Temperature (°C)	% Water Content	
	Polymer	Beginning of the Strip
Room Temp.	29.9	27.9
60°C	29.3	27.5

4.2.1.4. Cross Sectional and Surface Morphologies (SEM) of Extruded Cotton Stalk Hemicellulose Films

Cross sectional and surface morphologies of the extruded strips obtained by extraction at different temperatures were demonstrated in Figure 35. According to cross-sectional areas of the strips, they exhibited homogenous structure.

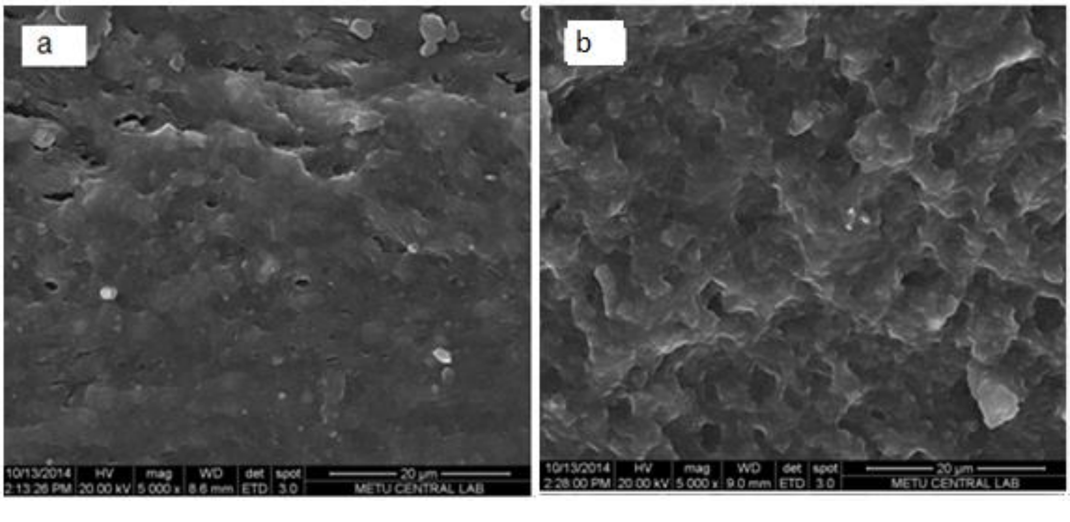


Figure 35. Cross sectional areas of extruded strips obtained by extraction at a) room temperature, b) 60 °C

4.2.1.5. Physical Properties of Cotton Stalk Hemicellulose

The viscosity- shear rate curve of the cotton stalk hemicellulose is given in Figure 36. The viscosity values decreased with increasing shear rate. The viscosity of the room temperature extracted hemicellulose was higher than the one extracted at 60 °C.

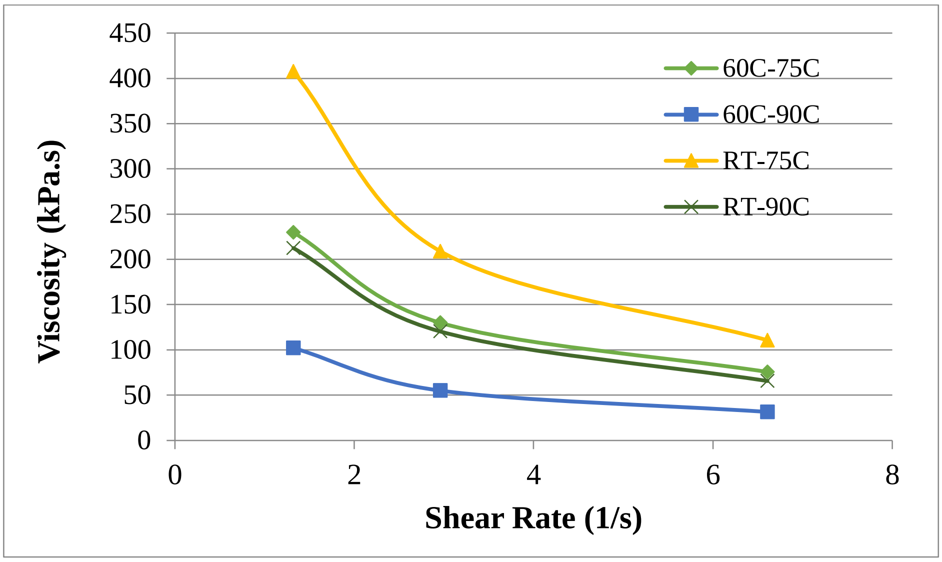


Figure 36. Viscosity – shear rate curves of cotton stalk hemicellulose (Extraction Temperatures; RT: room temperature, 60°C, Extrusion temperatures: 75°C, 90°C)

4.2.1.6. Thermal Properties of Extruded Cotton Stalk Hemicellulose Films

The thermal gravimetric analysis (TGA) results for the extruded films and solvent casted films produced from cotton stalk hemicellulose extracted at different temperatures are given in Figure 37. Maximum degradation temperature of the cotton stalk hemicellulose films did not change with extraction temperature or film production method (about 285°C).

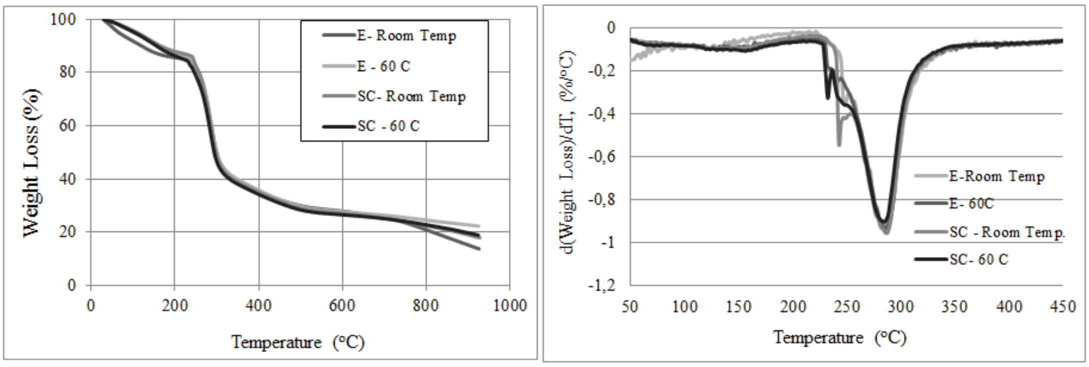


Figure 37. TGA curves of extruded (E-RT, E1-60°C) and solvent casted (SD-RT, SD-60° C) films extracted at different temperatures from cotton stalks

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4.2.2. Effect of Extrusion Conditions on Cotton Stalk Hemicellulose Strips and Films

To observe the effects of extrusion conditions of hemicellulose, two different temperatures (75°C and 90°C) and two different screw speeds (50 rpm and 100 rpm) were applied. 90°C of extrusion temperature had already been determined, as a suitable condition for extrusion since at either 60°C or 120°C, strips did not form (Bahcegul et al., 2013). Therefore another temperature, 75°C which was closer to 90°C was chosen as the second temperature.

Two different extruder screw speeds, 50 and 100 rpm, were selected as the other extrusion parameters. All of the extrusion parameters were applied to the hemicelluloses extracted at both temperatures (room temp. and 60°C). The effects of extrusion parameters as well as the extraction temperature on the mechanical, thermal, rheological and morphological properties were investigated.

4.2.2.1 Tensile Properties of Cotton Stalk Hemicellulose Films

Mechanical properties of the strips extruded at different extrusion conditions are given in Table 28. In general it was observed that, room temperature extracted hemicellulose strips showed better mechanical properties than strips that extracted at

60°C. Furthermore it can be seen that, extrusion temperature of 90°C resulted strips having higher mechanical properties including both strength and elongation, than 75°C extruded ones. Although the difference between these properties were not significant ($p > 0.005$), there might be some reasons for better film properties. Throughout the extrusion procedure, hemicellulose polymers were molten and shaped under the heat and shear forces at the extrusion temperature. When the extrusion temperature was increased at some level it provides more heat to hemicellulose particles however it is crucial not to conduct extrusion at elevated temperatures since it evaporates the water inside these particles and prevent extrusion (Bahcegul et al., 2013). Thus it was observed that the strips extruded at 90°C became more uniform than the strips extruded at 75°C. Additionally formation of extrusion defects on strip surfaces decreased when more heat was provided. As a result, especially elongation and toughness values of the strips extruded at 90°C were (approximately 15 MPa and 8.3 MJ/m^3) higher than the strips extruded at 75°C (11.8 MPa and 5.9 MJ/m^3).

Table 28. Mechanical properties of the strips obtained from cotton stalk hemicellulose extracted at different temperatures and extruded at different conditions

Extraction Temp. (°C)	Extrusion Conditions (°C – rpm)	Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)
Room Temp.	90 - 50	1210 ± 25	71.8 ± 2.7	15 ± 2.3	8.3 ± 1.7
	90 - 100	1231 ± 57	71.7 ± 3.3	18.6 ± 2.7	10.9 ± 2.0
	75 - 50	1121 ± 105	69.4 ± 4.6	11.8 ± 3.0	5.9 ± 2.3
	75 - 100	1036 ± 79	66.3 ± 4.5	14.7 ± 2.8	7.3 ± 2.1
60ºC	90 - 50	1187 ± 56	70.9 ± 2.3	13.8 ± 2.2	7.5 ± 1.4
	90 - 100	1072 ± 115	67.9 ± 2.4	16.1 ± 2.4	8.5 ± 1.6
	75 - 50	1024 ± 79	65.6 ± 6.5	9.3 ± 1.3	3.9 ± 1.2
	75 - 100	996 ± 154	61.2 ± 4.7	10.4 ± 1.6	4.4 ± 1.2

Table 29 shows the mechanical properties of rolled extruded films produced from cotton stalk hemicellulose extruded at different conditions. According to these values, neither extrusion temperature nor extrusion speed affected the mechanical properties of the films significantly ($p>0.005$). The tensile modulus, tensile strength, elongation at break and toughness values of these films were approximately 1200 MPa, 45 MPa, 4.8% and 1.3 MJ/m^3 , respectively.

Table 29. Mechanical properties of the films obtained from cotton stalk hemicellulose extracted at different temperatures and extruded at different conditions

Extraction Temp. (°C)	Extrusion Conditions (°C – rpm)	Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)
Room Temp.	90 - 50	1235 ± 200	42 ± 4	4.4 ± 0.9	1.1 ± 0.3
	90 - 100	1047 ± 167	39 ± 7	4.5 ± 1	1.0 ± 0.4
	75 - 50	1183 ± 173	42 ± 5	4.5 ± 0.8	1.1 ± 0.4
	75-100	1256 ± 136	47 ± 3	5.4 ± 1.5	1.6 ± 0.7
60ºC	90 - 50	1191 ± 68	49 ± 3	5.5 ± 1	1.7 ± 0.5
	90 - 100	1156 ± 119	47 ± 3	5.2 ± 0.4	1.4 ± 0.1
	75 - 50	1244 ± 62	47 ± 2	5.0 ± 1.3	1.4 ± 0.6
	75 - 100	1289 ± 125	47 ± 5	4.3 ± 0.8	1.2 ± 0.4

Table 30 shows the mechanical properties of solvent casted films obtained from cotton stalk hemicellulose extracted at different temperatures. The strength values of these films were higher than strips and rolled films even though the thickness of casted films were higher. This outcome indicated that the solvent casted films of cotton stalk hemicellulose were stronger than extruded films.

Table 30. Mechanical properties of the solvent casted films obtained from cotton stalk hemicellulose extracted at different temperatures

Extraction Temp. (°C)	Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)
Room Temp.	1999 ± 79	92 ± 5	6.5 ± 0.8	3.8 ± 0.8
60^{o}C	1461 ± 122	85 ± 3	9.4 ± 0.9	5.3 ± 0.8

4.2.2.2. Cross Sectional and Surface Morphologies (SEM) of Extruded Cotton Stalk Hemicellulose Films

Morphological properties of the extruded films were investigated by SEM analysis. The SEM images of the cross-sectional areas of the cotton stalk hemicellulose films extruded at different conditions are given in Figures 38 and 39. According to cross-sectional and surface areas of the strips, all of the strips exhibited homogenous structure.

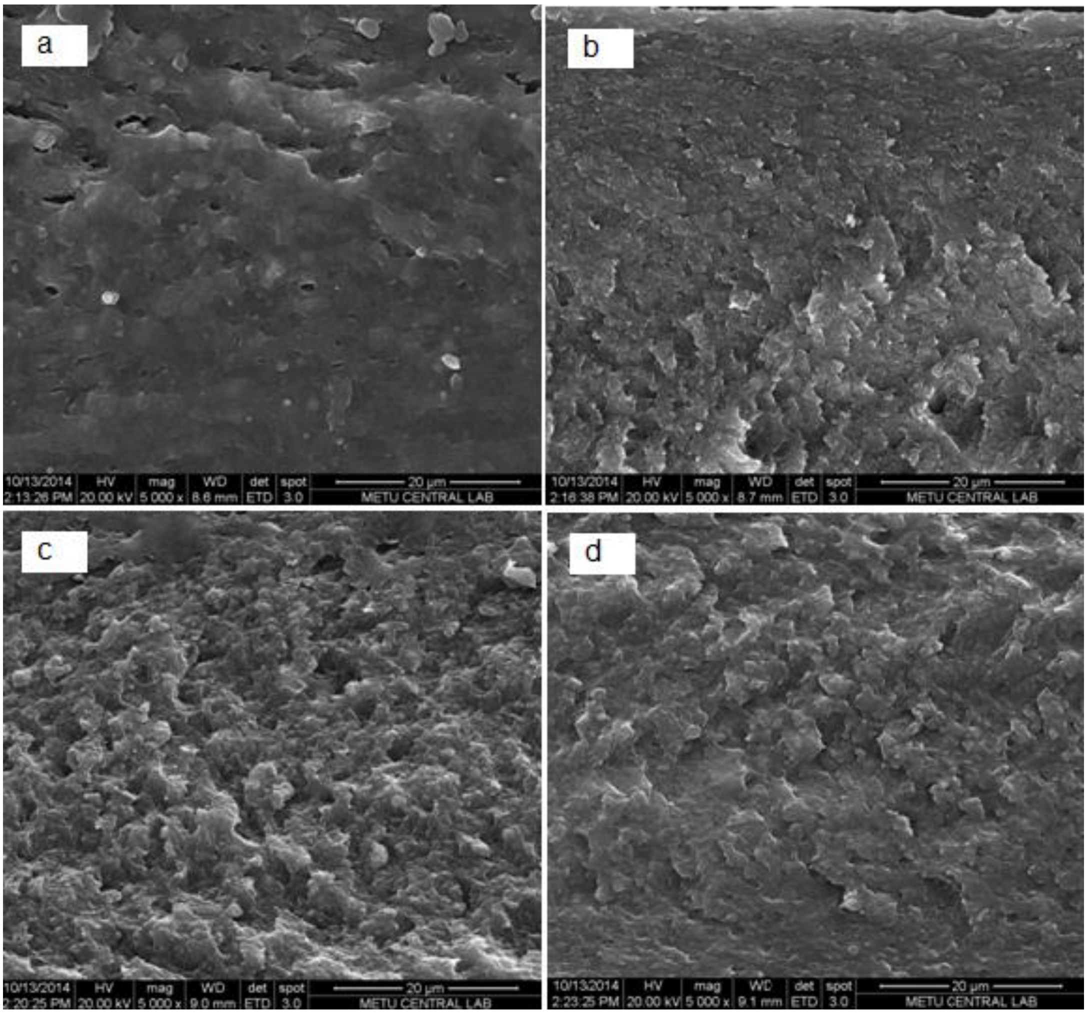

Figure 38. The cross sections of extruded films extracted from cotton stalk hemicellulose at room temperature. Extrusion conditions; a) 90°C-50 rpm, b)90°C-100 rpm, c) 75°C- 50 rpm and d) 75°C- 100 rpm

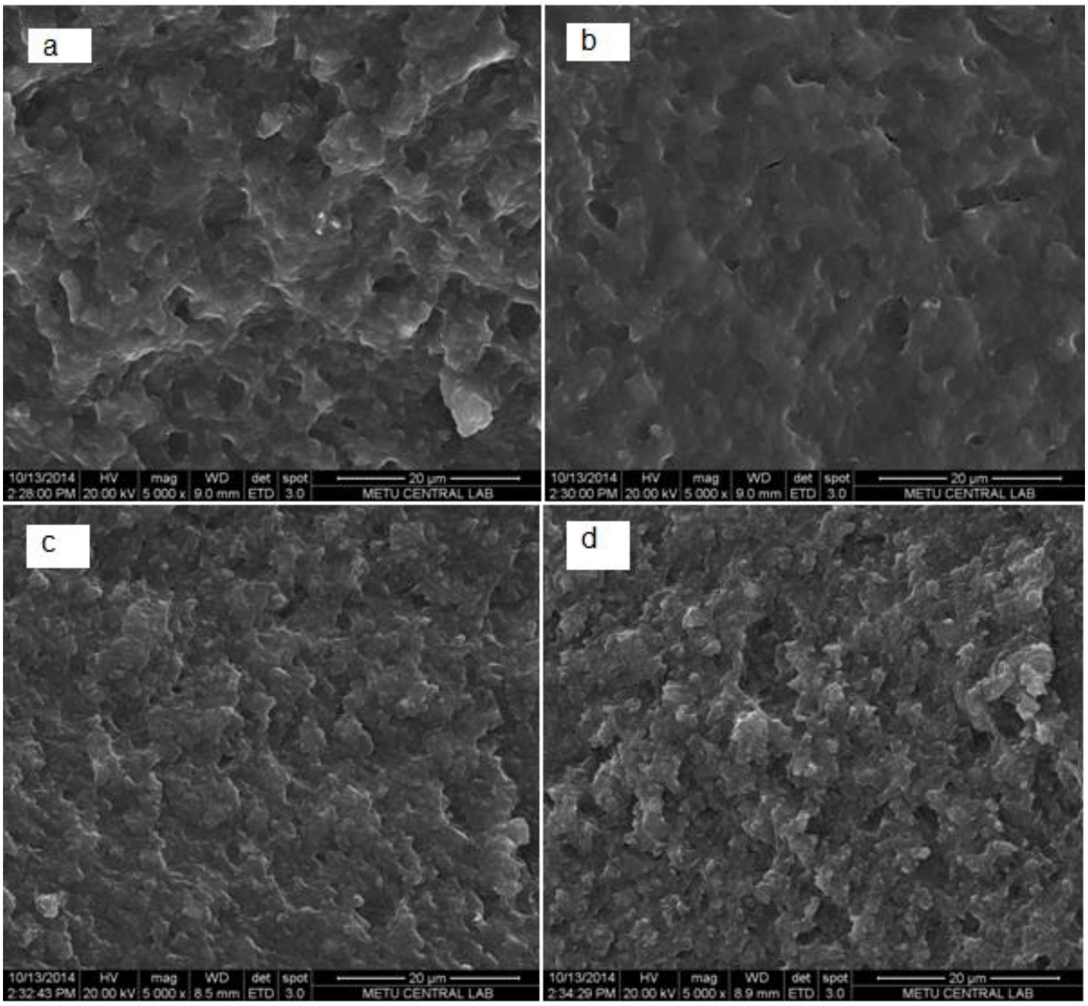

Figure 39. The cross sections of extruded films extracted from cotton stalk hemicellulose at 60°C. Extrusion conditions; a) 90°C-50 rpm, b)90°C- 100 rpm, c) 75°C- 50 rpm and d) 75°C- 100 rpm

In Figure 40, the surfaces of the solvent casted film was observed as homogenous and smooth while there were long cross scratches on the surface of the extruded film. Similar scratches can be seen on the surfaces of the extruded films extracted from other types of agricultural biomass was reported by Akınalan (2014). The scratches were appeared after the slendering procedure that were applied on the extruded strips by a roller.

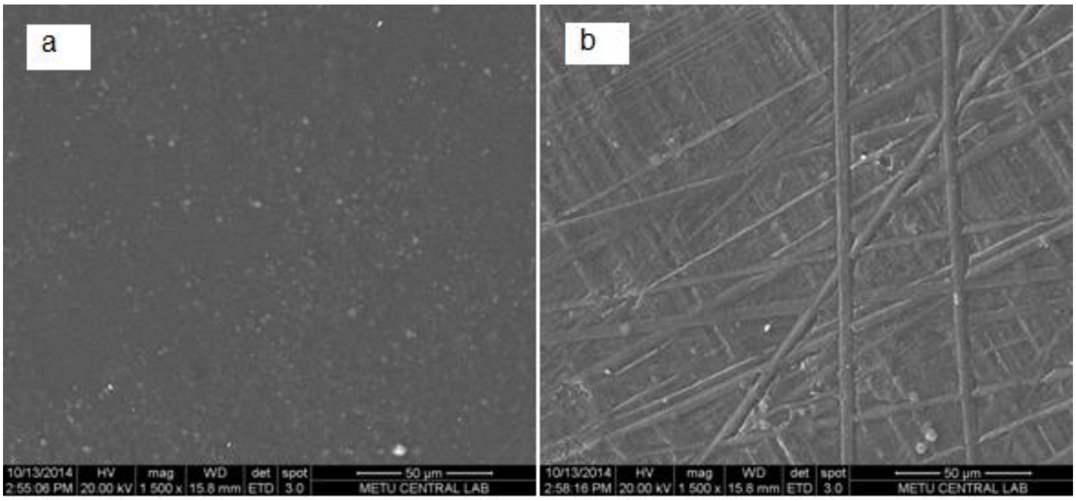

Figure 40. The surfaces of the hemicellulose films extracted at room temperature a) Solvent casted film, b) Extruded and rolled film.

4.3. Comparison of Corncob and Cotton Stalk Hemicellulose Based Materials Obtained via Extrusion

In the last part of the study, the effect of different types of lignocellulosic biomass on properties of hemicellulose based materials were investigated.

With this purpose, it was essential to obtain the hemicellulose based materials with identical extraction and extrusion conditions except their biomass sources. The biomass were corn cobs from the first part of the study and cotton stalk from the second part. The extraction and extrusion conditions were determined regarding the limiting extraction conditions of cotton stalk. As mentioned in the second part of the study, hemicellulose yield of the cotton stalk was low when the current extraction conditions conducted and they were changed to improve the yield. The extractions in this part was operated at these conditions; overnight (approximately 16 hours) swelling of the biomass in water, extraction with 24% of KOH and 1% of $NaBH_4$ addition for 24 hours at room temperature. The isolated hemicellulose was extruded at 90°C and 50 rpm. The extruded strips, rolled films and solvent casted films were produced from both types of biomass and compared in terms of their mechanical, thermal and morphological properties.

4.3.1. Hemicellulose Yield Obtained From Extraction of Different Biomass

The yield of hemicellulose extracted from different types of biomass are shown in Table 31. The extracted hemicellulose amount of the corn cobs were approximately 3 folds of cotton stalk. Thus this result indicated the efficiency of corn cob extraction for the production of hemicellulose based polymeric materials.

Table 31. Yields of hemicellulose extracted from different biomass

Biomass	Hemicellulose Yield (%)
Cotton Stalk	9.9 ± 0.8
Corn Cob	29.5 ± 0.6

4.3.2. Compositional Properties of Hemicellulose

The lignin and KAc salt content of the hemicellulose biopolymers extracted from corn cob and cotton stalk are given in Table 32. Corn cob hemicellulose had higher lignin content as 9.0% than cotton stalk hemicellulose which had 6.5%. However cotton stalk hemicelluloses KAc salt content was higher than corn cob.

Table 32. Lignin, residual KAc salt and sugar monomer concentrations (%) of the hemicellulose biopolymers extracted from different biomass

	Cotton Stalk Hemicellulose	Corn Cob Hemicellulose
Lignin (%)	6.5 ± 2.2	9.0 ± 0.2
Residual Salt (%)	5.9	4.3
Glucose (%)	3.3 ±0.01	4.6 ±0.5
Xylose (%)	72.0 ± 2.8	67.4 ±3.3
Galactose (%)	20.0 ± 3.9	8.9 ± 2.1
Arabinose (%)	4.5 ± 1.2	18.9 ± 0.7

4.3.3. Tensile Properties of the Extruded Films from Different Biomass Hemicelluloses

The mechanical properties of the hemicellulose based materials from different types of biomass are given in Table 33. The best ultimate tensile strength values of cotton stalk hemicellulose films were obtained solvent casting method as 91.5 MPa followed by extrusion as 71,8 MPa and rolling 42,4 MPa while their elongation values were 6.5%, 15% and 4.4% respectively. This outcome showed the strongest films from cotton stalk were produced by solvent casting whereas the most flexible films were produced with extrusion. The reason of higher strength might be the better solubility of the cotton stalk hemicellulose in water for the solvent casting procedure. The higher elongation of the extruded strip can be attributed to the thickness of the strip which enables to keep more water inside the strip.

Although the data demonstrating the mechanical properties of corn cob hemicellulose based materials showed the highest tensile strength values belongs to solvent casted films as approximately 70MPa, extruded corn cob strips could have higher strength values as 80 MPa from the previous part of this study. Furthermore the elongation and toughness values of corncob strips from the previous part were approximately 45% and 30 MJ/m^3. The reason of the reduced mechanical properties of extruded corncob hemicellulose strips and films might be addition of 1% $NaBH_4$ into the extraction environment. The negative effect of $NaBH_4$ addition was discussed in the previous chapter.

Moreover the strips produced from corn cob hemicellulose in this study had higher mechanical properties (80 MPa tensile strength and 48% elongation) than commercially used biodegradable PLA strips which had 52 MPa tensile strength and 12% (Bahcegul, 2013).

Therefore it can be concluded that solvent casting was a suitable method for cotton stalk hemicellulose while extrusion was more convenient for corn cob hemicellulose considering the mechanical properties of the films.

Table 33. Comparison of the mechanical properties of hemicellulose films extracted from different biomass

Biomass/ Film Type	Elastic Modulus (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Toughness (MJ/m^3)	Thickness of the films (µm)
Corn Cob					
Strip	800.0 ± 182.0	53.5 ± 6.7	28.8 ± 5.3	13.1± 3.8	575.3± 73.8
Rolled Film	1201.2 ± 137.9	54.9 ± 2.1	16.7 ± 6.1	7.6 ± 3.4	161.8± 39.4
Casted Film	1244.3 ± 144.1	68.9 ± 2.9	10.8 ± 1.8	5.4 ± 1.1	176.5 ± 9.0
Cotton Stalk					
Strip	1210.0 ± 25.2	71.8 ± 2.7	15.0 ± 2.3	8.3 ± 1.7	419.4± 12.2
Rolled Film	1234.5 ± 200.0	42.4 ± 4.2	4.4 ± 0.9	1.1 ± 0.3	127.6± 67.5
Casted Film	1998.6 ± 79.1	91.5 ± 5.2	6.5 ± 0.9	3.8 ± 0.9	117.9 ± 9.7

The water content of the hemicellulose polymer prior to the extrusion and at the beginning of the extruded strip are given in Table 34 which shows that corncob hemicellulose had more water content than cotton stalk.

Table 34. Water content of the hemicellulose polymer prior to the extrusion and at the beginning of the extruded strip

Biomass Type	% Water Content	
	Polymer	Beginning of the Strip
Cotton Stalk	29.9 ± 0.01	27.9 ± 0.3
Corn Cob	32.1 ± 2.14	27.4 ± 1.5

4.3.4. Physical Properties of Hemicellulose Obtained from Extraction of Different Biomass

The solubility values of hemicellulose extracted from different biomass are given in Table 35. There were a dramatic difference between the solubility of cotton stalk hemicellulose and corn cob hemicellulose where cotton stalk hemicellulose solubility was more than 2 folds of corn cob. This high solubility of cotton stalk hemicellulose (approximately 97%) explained the better mechanical properties of solvent casted films which directly related to the better film forming feature of this polymer. As is known, if a polymer dissolves in a solvent completely and homogenously, the films became stronger. In this study both kinds of solvent casted films were self-supporting and continuous but cotton stalk films were mechanically better probably due to their high solubility in water.

Table 35. Solubility of hemicellulose in water

Biomass Type	Solubility (%) of hemicellulose in water
Corn Cob	43.9 ± 2.6
Cotton Stalk	96.5 ± 0.1

Viscosity graph shows cotton stalk hemicellulose and corn cob hemicellulose with no $NaBH_4$ addition had similar and lower viscosity values than corn cob xylan obtained with $NaBH_4$ which can also be the reason of lower mechanical properties of the strips produced with $NaBH_4$ utilization.

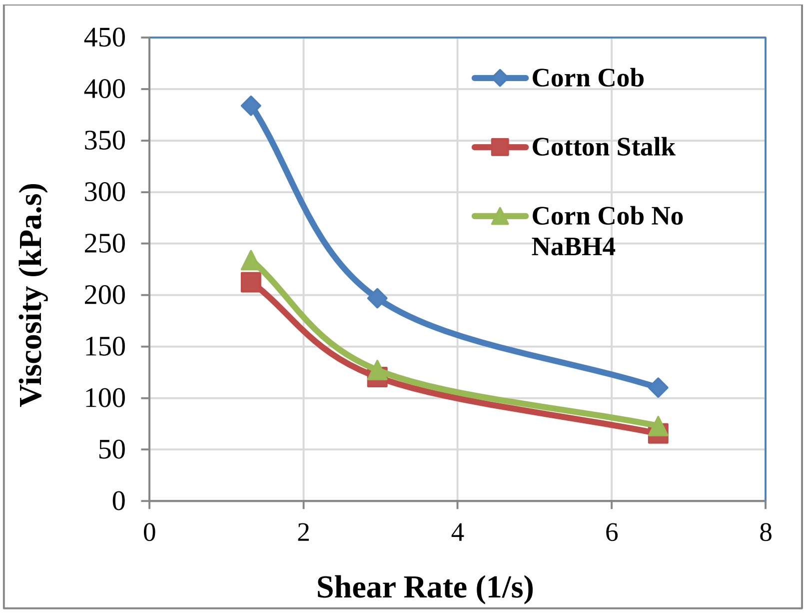

Figure 41. Viscosity values of hemicellulose extracted from cotton stalk, corncob and corncob without $NaBH_4$ addition

4.3.5. Cross Section and Surface Morphologies of Extruded Films

Morphological properties of the extruded films and strips were investigated by SEM analysis. The SEM images of the cross-sectional areas of the cotton stalk and corn cob hemicellulose films and strips are given in Figures 42 and 43. According to cross-sectional and surface areas of the strips, all of the strips and films exhibited homogenous structure except cotton stalk based film. This film had less homogenous structure with small voids within which might explain the lower mechanical properties of the films compared the solvent casted ones.

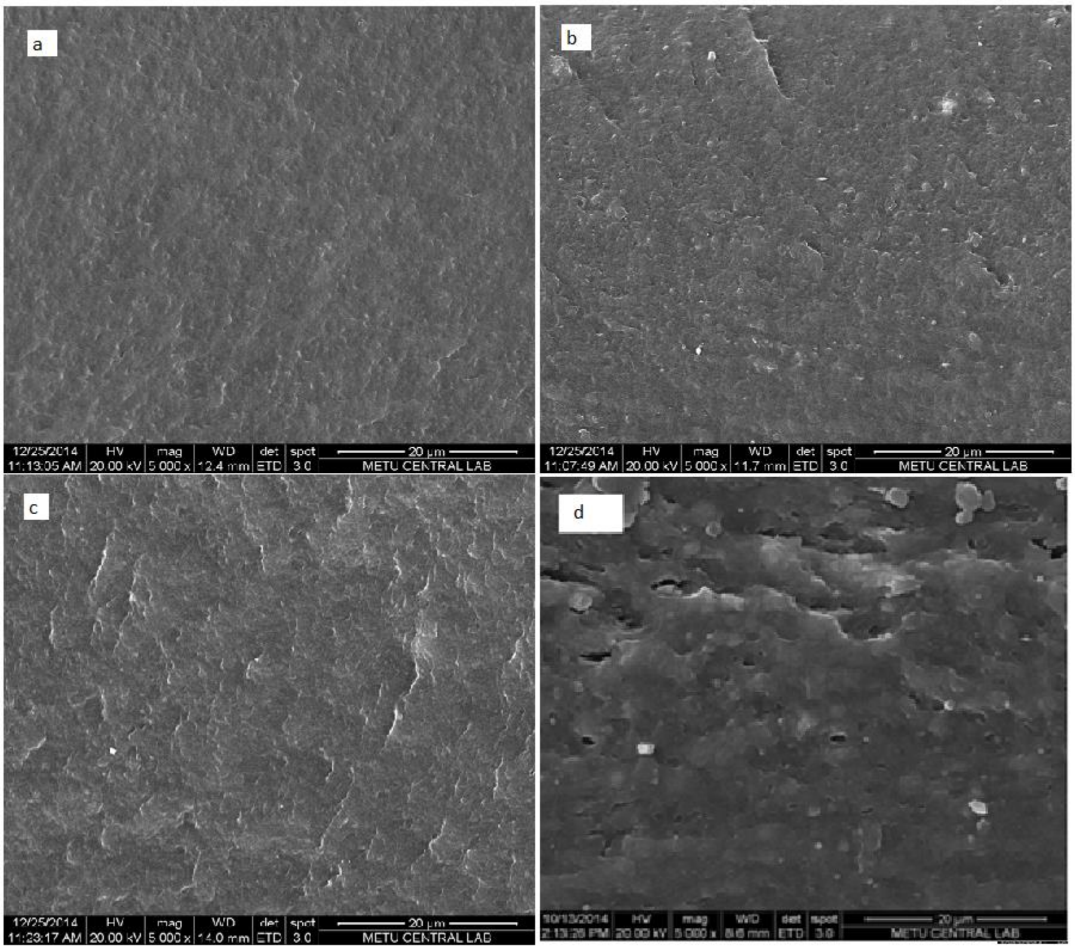

Figure 42. Cross sections of the a) corn cob strip, b) cotton stalk strip, c) corn cob film, d) cotton stalk film

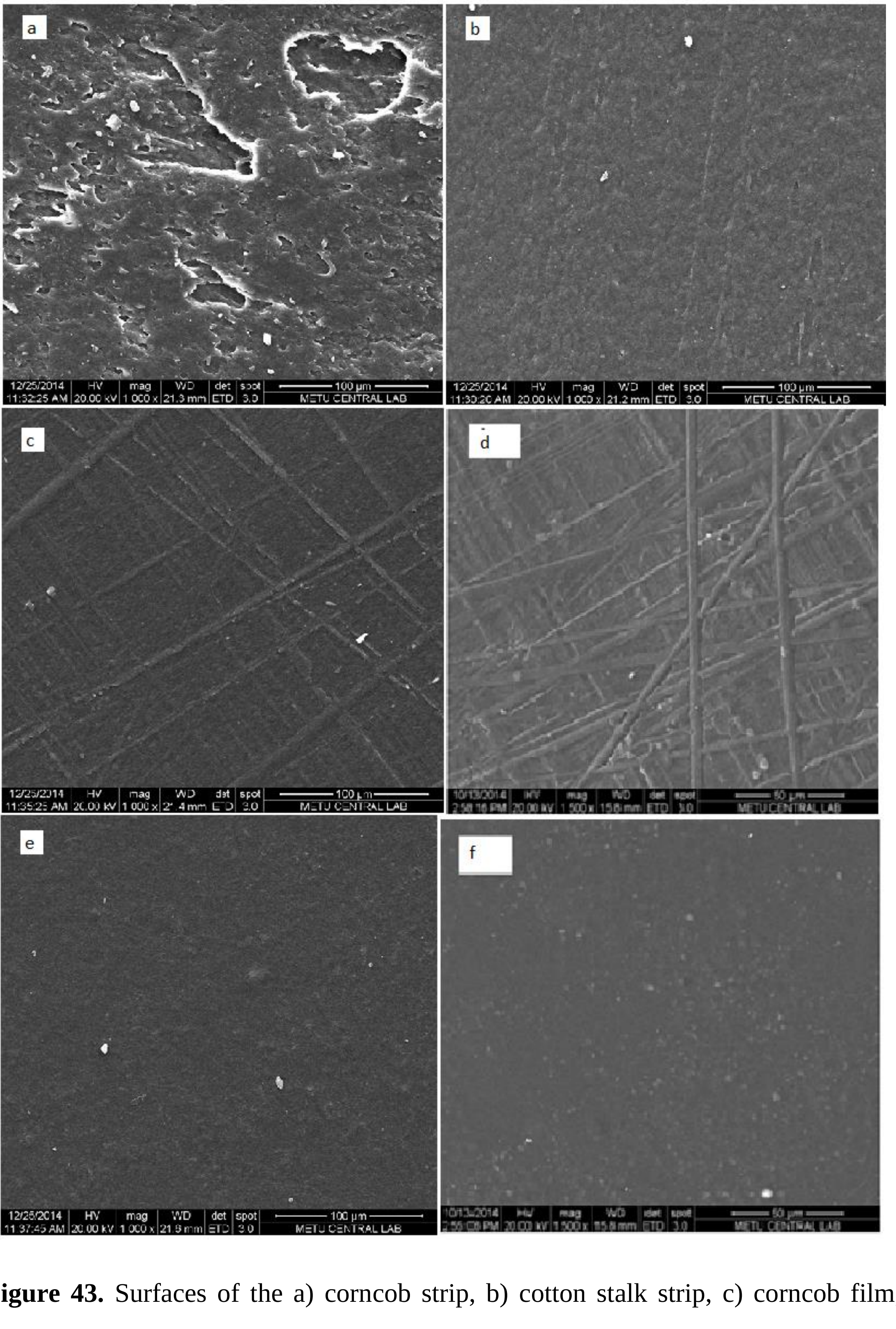

Figure 43. Surfaces of the a) corncob strip, b) cotton stalk strip, c) corncob film, d)cotton stalk film, e) solvent casted corncob film and f) solvent casted cotton stalk film

4.3.6. Thermal Properties of Extruded Films

The thermal gravimetric analysis (TGA) results for the extruded films produced with extrusion and solvent casting methods from different biomass type of hemicellulose are given in Figure 44. As can be seen in the TGA curves of the extruded films, film forming method of hemicellulose did not affect the degradation behavior of these materials. The maximum degradation temperatures of the extruded strips from corn cob and cotton stalk were determined as approximately 285°C.

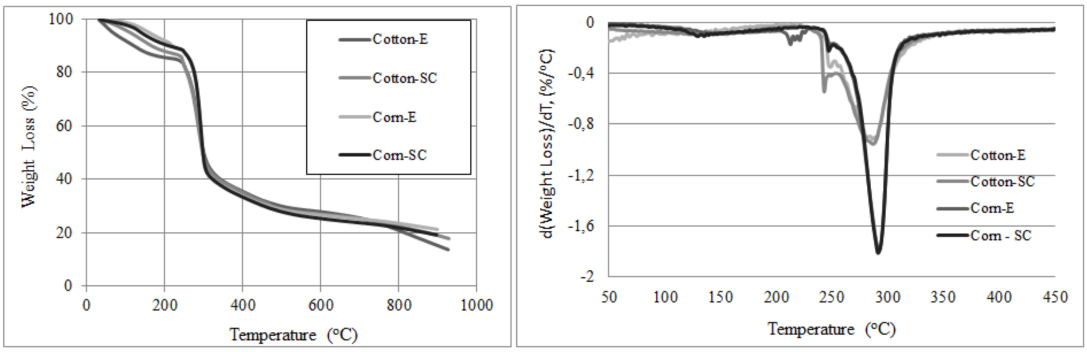

Figure 44. TGA graphs of the Corn-E (corn cob strip), Cotton – E (cotton stalk strip), Corn – SC (solvent casted corncob film) and Cotton – SC (solvent casted cotton stalk film)

4.3.7. Water Vapor Transfer Rate of the Extruded Films

The water vapor transfer rates were analyzed by measuring the water gain of the extruded films. The experiment was performed for extruded films obtained from cotton stalk and corn cob hemicellulose, with different thickness values. Water vapor transfer rates were calculated using the slope of the net weight gained by films versus time plot.

The water vapor transfer rate (WVTR) and normalized water vapor transfer rate (NWVTR) values with respect to film thickness are given in Table 36. As expected WVTR reduced with increasing thickness of the films for both of the biomass.

Besides, cotton stalk hemicellulose films had higher WVTR than corn cob hemicellulose films at the similar film thickness. The reason of the higher results might be higher solubility of the cotton stalk hemicellulose. Consequently extruded films from corn cob hemicellulose would be a better candidate for food packaging at humid environments.

Table 36. Water vapor transfer rates of the extruded films obtained from different types of biomass

Biomass Type	Film Thickness (m)	Water Vapor Transfer Rate (g/day.m^2)	Normalized Water Vapor Transfer Rate (g/day.m^3)
Corn Cob	1.945×10^{-4}	1440	740×10^4
	2.345×10^{-4}	1440	614×10^4
	2.49×10^{-4}	1176	472×10^4
Cotton Stalk	1.365×10^{-4}	2160	$1\,582 \times 10^4$
	1.85×10^{-4}	1584	856×10^4
	2.125×10^{-4}	1752	824×10^4

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Two types of hemicelluloses were isolated from corn cobs and cotton stalks and hemicellulose based biopolymeric strips were obtained via the extrusion technique. The extruded strips were compared with the films produced using the solvent casting technique. First, the effect of extraction parameters including particle size of the biomass, alkali concentration, extraction time and boron compound utilization, on the properties of corn cob hemicellulose based strips were investigated. And it was observed that the lowest mechanical and film forming properties was obtained when the largest particle size corn cobs was used probably due to the high viscosity and extrusion problems of this hemicellulose. The highest tensile strength (about 76 MPa) and elongation at break values (about 48%) for the extruded strips were attained when using 24% of KOH for extraction in the range tested. However, when 15% KOH was used during the extraction process, the mechanical properties of the corresponding strips were slightly reduced. Therefore 15% KOH can be utilized to reduce high alkaline consumption leading to additional cost and environmental problems. Elevated extraction times did not make any significant difference for the strips mechanically, thus reducing the time to 1 hour will reduce energy consumption for large scale productions. Boron compound utilization for the extraction process did not make a positive influence on the strips in fact it was observed that there was no need for additional boron compound for the production of corn cob hemicellulose based materials.

Extraction temperature did not affect the properties of cotton stalk films. The strips produced at the extrusion temperature of 90°C have better mechanical properties compared to the strips produced at the extrusion temperature of 75°C. The extrusion speed did not influence the properties of the extruded strips significantly.

In order to make a comparison between the film forming features between two biomasses, the corn cob and the cotton stalk hemicelluloses were isolated and extruded at the same conditions. The hemicellulose yield of the corn cobs were approximately 3 folds of cotton stalk, as about 10% for the cotton stalk and about 30% for the corncobs. The best ultimate tensile strength (91.5 MPa) was obtained for the solvent casted films of cotton stalk, followed by the extruded strips (72 MPa) and the extruded plus rolled films (42 MPa). The tensile strength and elongation at break values of the extruded corn cob strips were approximately 80 MPa and 48%, respectively. However, when the extruded corn cob strips were rolled to obtain thinner films, the mechanical properties of the films reduced (the tensile strength 55 MPa and elongation at break 16 %). These observations suggest that the solvent casting was a suitable method for the cotton stalk hemicellulose while the extrusion was more convenient technique for the corn cob hemicellulose. The reason for obtaining better mechanical properties for the solvent casted cotton stalk films probably is the good solubility of the cotton stalk hemicellulose. Furthermore, the WVTR of the cotton stalk films was higher than that of corn cob films at the similar film thickness, which can also be related to higher solubility of the cotton stalk hemicellulose. This study shows that different biomass demands different types of processing.

Addition of plasticizers, which are commonly used during solvent casting based studies, to the hemicellulose in the extrusion process should be studied for further studies to enhance the ductility of hemicellulose based materials. Moreover composite materials can be produced by using synthetic polymers and biomass based hemicellulose, which will resulted in materials with improved mechanical strength and semi-biodegradable nature. Nanocomposite materials based on hemicellulose and generated with extrusion method could also be investigated where nanofibrillated cellulose or nanoclays could be selected as reinforcements. Additionally, the water sensitivity of hemicellulose based materials can be studied.

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APPENDIX A

ALKALI SOLUBLE LIGNIN CALIBRATION CURVE

The lignin content of hemicellulose was calculated by using the following formula:

$$Lignin\ content(\%) = (A - n) * m * DF * \frac{V}{100} * 100$$

where A is the absorbance of the sample, V is the sample volume, DF is the dilution factor of the sample, n is the y-intercept and m is the slope of the calibration curve.

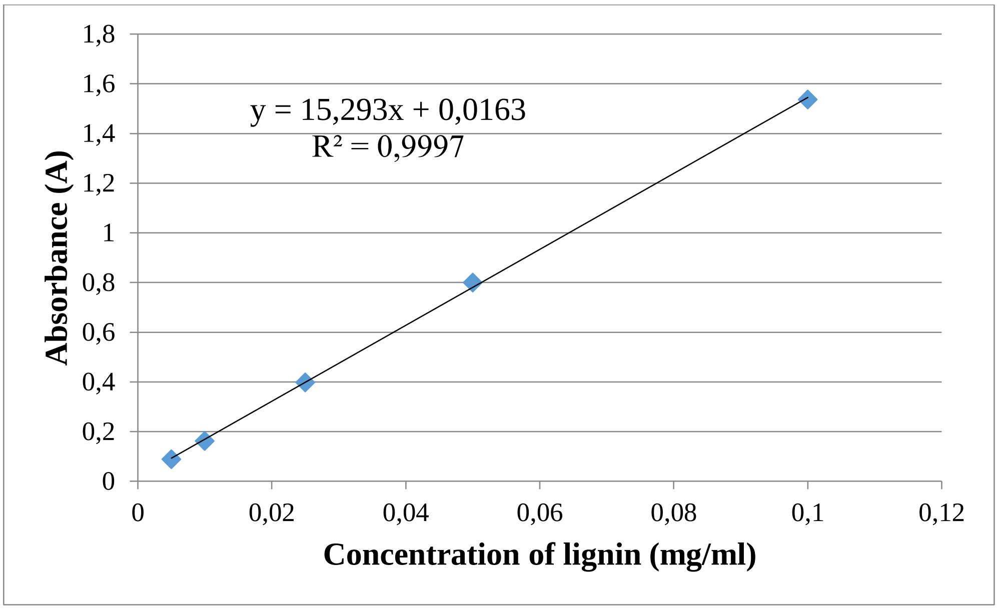

Figure 45. Calibration curve of the alkali soluble lignin

APPENDIX B

SAMPLE OF EXTRUSION DATA PROFILE

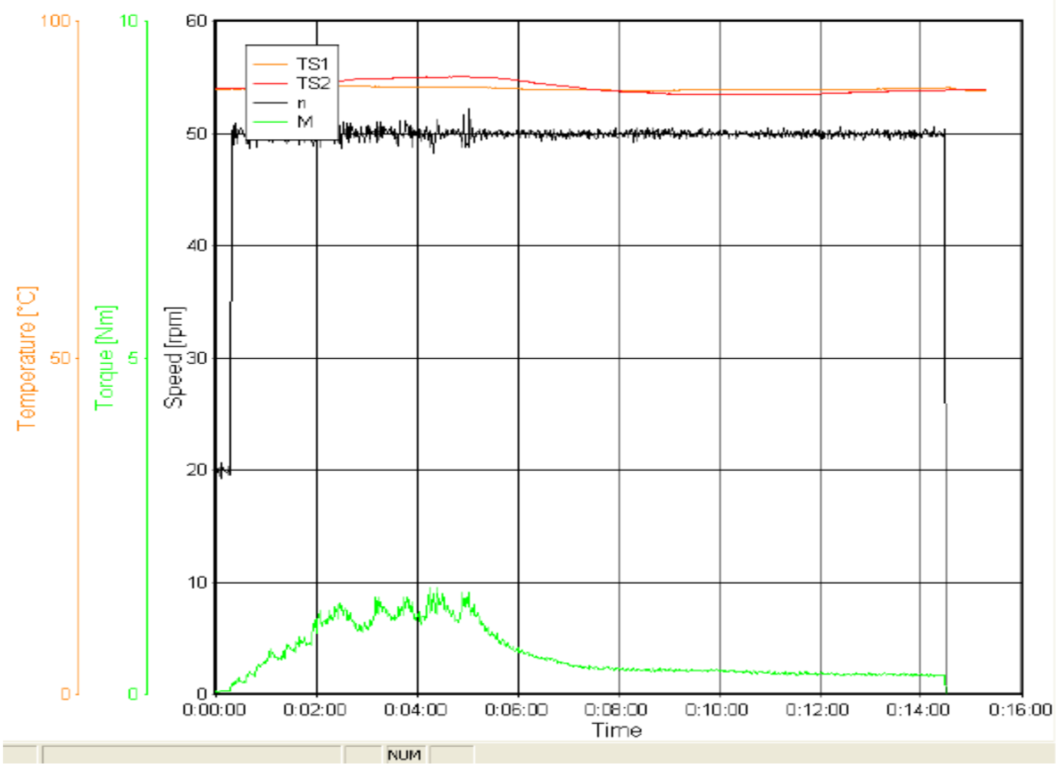

Figure 46. A sample extrusion data profile of room temperature extracted corn cob hemicellulose extruded at 90°C and 50 rpm

APPENDIX C

SAMPLE OF HPLC RESULTS OF PEAK FIT PROGRAM

Sample: Corn Cob Biomass, Extraction Time: 1h, Batch 1

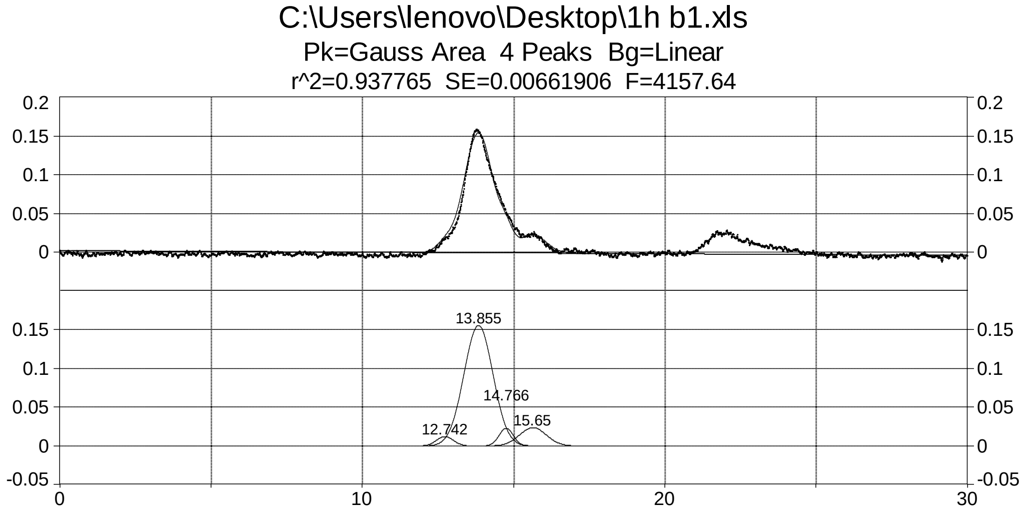

Figure 47. A sample HPLC result of peak fit program

Fitted Parameters

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.93776500	0.93752203	0.00661906	4157.64480

Peak	Type	a_0	a_1	a_2
1	Gauss Area	0.00820565	12.7419253	0.27417297
2	Gauss Area	0.18371584	13.8549693	0.47167702
3	Gauss Area	0.01311807	14.7658745	0.23090168
4	Gauss Area	0.02581374	15.6500984	0.43736732
B	Linear Bg	0.00196168	-0.0002015	

Measured Values

Peak	Type	Amplitude	Center	FWHM	Asym50	FW Base
1	Gauss Area	0.01193984	12.7419253	0.64562800	1.00000001	1.29235889
2	Gauss Area	0.15538602	13.8549693	1.11071450	1.00000000	2.22332635
3	Gauss Area	0.02266485	14.7658746	0.54373189	0.99999948	1.08839261
4	Gauss Area	0.02354587	15.6500984	1.02992133	1.00000000	2.06160200

Peak	Type	Anlytc Area	% Area	Int Area	% Area	Centroid
1	Gauss Area	0.00820565	3.55448657	0.00820565	3.55448657	12.7419253
2	Gauss Area	0.18371584	79.5812054	0.18371584	79.5812054	13.8549693

```
  3    Gauss Area    0.01311807    5.68242693    0.01311807    5.68242693    14.7658745
  4    Gauss Area    0.02581374    11.1818811    0.02581374    11.1818811    15.6500984
       Total         0.23085330    100.000000    0.23085330    100.000000
```

Parameter Statistics

```
Peak 1  Gauss Area
 Parm    Value         Std Error     t-value       95
 Area    0.00820565    0.00172929    4.74508927    0.00481515    0.01159615
  Ctr    12.7419253    0.04861380    262.105091    12.6466118    12.8372387
  Wid    0.27417297    0.04262488    6.43222853    0.19060154    0.35774440

Peak 2  Gauss Area
 Parm    Value         Std Error     t-value       95
 Area    0.18371584    0.00361068    50.8811793    0.17663664    0.19079504
  Ctr    13.8549693    0.00560519    2471.81200    13.8439796    13.8659590
  Wid    0.47167702    0.01080031    43.6725560    0.45050166    0.49285238

Peak 3  Gauss Area
 Parm    Value         Std Error     t-value       95
 Area    0.01311807    0.00294834    4.44930854    0.00733748    0.01889866
  Ctr    14.7658745    0.02515725    586.943192    14.7165506    14.8151985
  Wid    0.23090168    0.02917310    7.91488187    0.17370414    0.28809921

Peak 4  Gauss Area
 Parm    Value         Std Error     t-value       95
 Area    0.02581374    0.00181723    14.2050325    0.02225084    0.02937664
  Ctr    15.6500984    0.03439832    454.966910    15.5826562    15.7175406
  Wid    0.43736732    0.03369397    12.9805831    0.37130607    0.50342857

Baseline  Linear Bg
 Parm    Value         Std Error     t-value       95
   a0    0.00196168    0.00022727    8.63130217    0.00151608    0.00240728
   a1    -0.0002015    1.2764e-05    -15.785136    -0.0002265    -0.0001765
```

Analysis of Variance

```
r2 Coef Det    DF Adj r2     Fit Std Err
0.93776500     0.93752203    0.00661906
Source    Sum of Squares    DF      Mean Square         F
Regr      2.3680099         13      0.18215461          4157.6448
Error     0.15715354        3587    4.381197e-05
Total     2.5251635         3600
```

Details of Fit

```
Set Convergence      State          Iterations      Minimization        Extent
   1E-6             Converged          58           Least Squares        1/1
Curvature Matrix                Constraints                                Violated
   Sparse-Roots       25.0000-5.00000-50.0000- None  - None                   0
```

APPENDIX D

STATISTICAL ANALYSIS (P VALUES) BETWEEN THE MECHANICAL PROPERTIES OF FILMS PRODUCED USING DIFFERENT EXTRACTION AND EXTRUSION PARAMETERS

Table 37. P values of the corncob hemicellulose strips extracted from different particle size (mm) corncobs

P Values				
	Elastic Modulus (MPa)			
Particle Size (mm)	**2.00 - 1.19**	**1.19 - 0.6**	**0.6 - 0.15**	**< 0.15**
2.00 - 1.19	1	0.0679	0.1331	0.0829
1.19 - 0.6	0.0679	1	0.0005	6.34E-05
0.6 - 0.15	0.1331	0.1331	1	0.9512
< 0.15	0.0829	6.34E-05	0.9512	1
	Ultimate Tensile Strength (MPa)			
Particle Size (mm)	**2.00 - 1.19**	**1.19 - 0.6**	**0.6 - 0.15**	**< 0.15**
2.00 - 1.19	1	2.26E-08	0.0069	0.7489
1.19 - 0.6	2.26E-08	1	0.0213	6.69E-08
0.6 - 0.15	0.0069	0.0213	1	0.0117
< 0.15	0.7489	6.69E-08	0.0117	1
	Elongation at Break (%)			
Particle Size (mm)	**2.00 - 1.19**	**1.19 - 0.6**	**0.6 - 0.15**	**< 0.15**
2.00 - 1.19	1	7.60E-13	4.23E-10	0.0008
1.19 - 0.6	7.60E-13	1	0.0003	9.77E-06
0.6 - 0.15	4.23E-10	0.0003	1	0.0023
< 0.15	0.0008	9.77E-06	0.0023	1
	Toughness (MJ/m^3)			
Particle Size (mm)	**2.00 - 1.19**	**1.19 - 0.6**	**0.6 - 0.15**	**< 0.15**
2.00 - 1.19	1	3.03E-12	1.93E-08	0.0073
1.19 - 0.6	3.03E-12	1	3.79E-05	4.31E-07
0.6 - 0.15	1.93E-08	3.79E-05	1	0.0013
< 0.15	0.0073	4.31E-07	0.0013	1

Table 38. P values of the corncob hemicellulose strips extracted with different concentrations of KOH

P Values					
	Elastic Modulus (MPa)				
% KOH	**5**	**10**	**15**	**20**	**24**
5	1	0.0338	0.8047	0.1324	2.35E-13
10	0.0338	1	0.1840	0.6601	1.48E-13
15	0.8047	0.1840	1	0.2934	1.71E-09
20	0.1324	0.6601	0.2934	1	2.93E-13
24	2.35E-13	1.48E-13	1.71E-09	2.93E-13	1
	Ultimate Tensile Strength (MPa)				
% KOH	**5**	**10**	**15**	**20**	**24**
5	1	2.85E-06	5.46E-10	1.50E-10	2.37E-15
10	2.85E-06	1	6.64E-05	5.48E-11	1.45E-13
15	5.46E-10	6.64E-05	1	0.0024	1.61E-10
20	1.50E-10	5.48E-11	0.0024	1	4.21E-08
24	2.37E-15	1.45E-13	1.61E-10	4.21E-08	1
	Elongation at Break (%)				
% KOH	**5**	**10**	**15**	**20**	**24**
5	1	6.44E-05	2.91E-07	2.06E-07	3.84E-07
10	6.44E-05	1	0.0042	5.21E-05	0.0131
15	2.91E-07	0.0042	1	0.1145	0.7547
20	2.06E-07	5.21E-05	0.1145	1	0.4523
24	3.84E-07	0.0131	0.7547	0.4523	1
	Toughness (MJ/m^3)				
% KOH	**5**	**10**	**15**	**20**	**24**
5	1	1.40E-05	2.47E-08	4.39E-09	9.18E-10
10	1.40E-05	1	0.0009	1.53E-06	1.32E-05
15	2.47E-08	0.0009	1	0.0156	0.0070
20	4.39E-09	1.53E-06	0.0156	1	0.1537
24	9.18E-10	1.32E-05	0.0070	0.1537	1

Table 39. P values of the corncob hemicellulose strips extracted at different extraction times

P Values								
	Elastic Modulus (MPa)				**Ultimate Tensile Strength (MPa)**			
Time	**1 h**	**2 h**	**6 h**	**12 h**	**1 h**	**2 h**	**6 h**	**12 h**
1 h	1	0.0444	0.0172	0.0542	1	0.0005	0.0003	0.2295
2 h	0.0444	1	1.9E-1	0.6817	0.0005	1	0.8973	0.3091
6 h	0.0172	1.9E-05	1	0.0002	0.0003	0.8973	1	0.2670
12 h	0.0542	0.6817	0.0002	1	0.2295	0.3091	0.2670	1
	Elongation at Break (%)				**Toughness (MJ/m^3)**			
Time	**1 h**	**2 h**	**6 h**	**12 h**	**1 h**	**2 h**	**6 h**	**12 h**
1 h	1	0.0282	0.0002	0.0459	1	0.3456	0.0002	0.2504
2 h	0.0282	1	1.7E-1	0.7792	0.3456	1	3.8E-1	0.7819
6 h	0.0002	1.7E-06	1	2.7E-1	0.0002	3.8E-1	1	3.5E-1
12 h	0.0459	0.7792	2.7E-1	1	0.2504	0.7819	3.5E-1	1

Table 40. P values of the corncob hemicellulose strips extracted with addition of different concentrations of boric acid (H_3BO_3)

P Values								
	Elastic Modulus (MPa)				**Ultimate Tensile Strength (MPa)**			
% H_3BO_3	**0**	**0.5**	**1**	**2**	**0**	**0.5**	**1**	**2**
0	1	0.0037	0.8437	0.0003	1	0.0568	0.7433	0.0003
0.5	0.0037	1	0.0145	0.1408	0.0568	1	0.0973	0.0142
1	0.8437	0.0145	1	0.0010	0.7433	0.0973	1	0.0011
2	0.0003	0.1408	0.0010	1	0.0003	0.0142	0.0011	1
	Elongation at Break (%)				**Toughness (MJ/m^3)**			
% H_3BO_3	**0**	**0.5**	**1**	**2**	**0**	**0.5**	**1**	**2**
0	1	0.3037	0.9631	0.0035	1	0.6664	0.7499	0.0013
0.5	0.3037	1	0.2176	3.6E-1	0.6664	1	0.9489	9.9E-1
1	0.9631	0.2176	1	0.0018	0.7499	0.9489	1	0.0006
2	0.0035	3.6E-1	0.0018	1	0.0013	9.9E-1	0.0006	1

Table 41. P values of the corncob hemicellulose strips extracted with addition of different concentrations of $NaBH_4$

	Elastic Modulus (MPa)			**Ultimate Tensile Strength (MPa)**		
% $NaBH_4$	**0**	**0.5**	**1**	**0**	**0.5**	**1**
0	1	2.63E-11	5.70E-10	1	1.48E-14	1.02E-12
0.5	2.63E-11	1	0.0964	1.48E-14	1	0.2976
1	5.70E-10	0.0964	1	1.02E-12	0.2976	1
	Elongation at Break (%)			**Toughness (MJ/m^3)**		
% $NaBH_4$	**0**	**0.5**	**1**	**0**	**0.5**	**1**
0	1	0.0127	0.6051	1	1.05E-06	1.4E-05
0.5	0.0127	1	0.0138	1.05E-06	1	0.1577
1	0.6051	0.0138	1	1.47E-05	0.1577	1

Table 42. P values of the cotton stalk hemicellulose strips extracted at different temperatures (room temperature (RT) or 60°C) and produced at different extrusion conditions (at 90°C or 75°C extrusion temperature, 50 rpm or 100 rpm screw speed)

	Elastic Modulus (MPa)							
P Values	**RT_90_50**	**RT_90_100**	**RT_75_50**	**RT_75_100**	**60_90_50**	**60_90_100**	**60_75_50**	**60_75_100**
RT_90_50	1.000	0.030	0.521	0.771	0.506	0.291	0.885	0.444
RT_90_100	0.030	1.000	0.082	0.005	0.026	0.118	0.005	0.001
RT_75_50	0.521	0.082	1.000	0.274	0.884	0.686	0.283	0.105
RT_75_100	0.771	0.005	0.274	1.000	0.162	0.090	0.784	0.531
60_90_50	0.506	0.026	0.884	0.162	1.000	0.447	0.062	0.025
60_90_100	0.291	0.118	0.686	0.090	0.447	1.000	0.066	0.021
60_75_50	0.885	0.005	0.283	0.784	0.062	0.066	1.000	0.258
60_75_100	0.444	0.001	0.105	0.531	0.025	0.021	0.258	1.000

Table 43. P values of the cotton stalk hemicellulose strips extracted at different temperatures (room temperature (RT) or 60°C) and produced at different extrusion conditions (at 90°C or 75°C extrusion temperature, 50 rpm or 100 rpm screw speed) continued

	Ultimate Tensile Strength(MPa)							
P Values	**RT_90_50**	**RT_90_100**	**RT_75_50**	**RT_75_100**	**60_90_50**	**60_90_100**	**60_75_50**	**60_75_100**
RT_90_50	1.000	0.276	1.000	0.007	0.000	0.022	0.005	0.020
RT_90_100	0.276	1.000	0.299	0.009	0.002	0.015	0.010	0.013
RT_75_50	1.000	0.299	1.000	0.016	0.002	0.038	0.015	0.034
RT_75_100	0.007	0.009	0.016	1.000	0.182	0.798	0.892	0.909
60_90_50	0.000	0.002	0.002	0.182	1.000	0.159	0.101	0.221
60_90_100	0.022	0.015	0.038	0.798	0.159	1.000	0.299	0.906
60_75_50	0.005	0.010	0.015	0.892	0.101	0.299	1.000	0.989
60_75_100	0.020	0.013	0.034	0.909	0.221	0.906	0.989	1.000

Table 44. P values of the cotton stalk hemicellulose strips extracted at different temperatures (room temperature (RT) or 60°C) and produced at different extrusion conditions (at 90°C or 75°C extrusion temperature, 50 rpm or 100 rpm screw speed) continued

	Elongation at Break (%)							
P Values	**RT_90_50**	**RT_90_100**	**RT_75_50**	**RT_75_100**	**60_90_50**	**60_90_100**	**60_75_50**	**60_75_100**
RT_90_50	1.000	0.761	0.924	0.060	0.017	0.018	0.235	0.680
RT_90_100	0.761	1.000	0.822	0.115	0.049	0.076	0.395	0.492
RT_75_50	0.924	0.822	1.000	0.065	0.018	0.017	0.257	0.596
RT_75_100	0.060	0.115	0.065	1.000	0.927	0.671	0.420	0.596
60_90_50	0.017	0.049	0.018	0.927	1.000	0.477	0.293	0.005
60_90_100	0.018	0.076	0.017	0.671	0.477	1.000	0.507	0.002
60_75_50	0.235	0.395	0.257	0.420	0.293	0.507	1.000	0.116
60_75_100	0.680	0.492	0.596	0.596	0.005	0.002	0.116	1.000

Table 45. P values of the cotton stalk hemicellulose strips extracted at different temperatures (room temperature (RT) or 60°C) and produced at different extrusion conditions (at 90°C or 75°C extrusion temperature, 50 rpm or 100 rpm screw speed) continued

	Toughness (MJ/m^3)							
P Values	**RT_90_50**	**RT_90_100**	**RT_75_50**	**RT_75_100**	**60_90_50**	**60_90_100**	**60_75_50**	**60_75_100**
RT_90_50	1.000	0.589	0.995	0.034	0.005	0.011	0.100	0.656
RT_90_100	0.589	1.000	0.633	0.022	0.004	0.017	0.063	0.374
RT_75_50	0.995	0.633	1.000	0.043	0.010	0.039	0.133	0.700
RT_75_100	0.034	0.022	0.043	1.000	0.949	0.340	0.410	0.059
60_90_50	0.005	0.004	0.010	0.949	1.000	0.152	0.276	0.012
60_90_100	0.011	0.017	0.039	0.340	0.152	1.000	0.968	0.034
60_75_50	0.100	0.063	0.133	0.410	0.276	0.968	1.000	0.187
60_75_100	0.656	0.374	0.700	0.059	0.012	0.034	0.187	1.000