

HEMICELLULOSE BASED BIODEGRADABLE FILM PRODUCTION

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

EMEL IRAZ GÖKSU

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

FEBRUARY 2005

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Nurcan Baç
Head of Department

This is to certify that we have read this thesis and that in our department it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Ülkü Yılmazer
Co-Supervisor

Prof. Dr. Ufuk Bakır
Supervisor

Examining Committee Members

Prof. Dr. Levent Yılmaz (METU, CHE)_____

Prof. Dr. Ufuk Bakır (METU, CHE)_____

Prof. Dr. Ülkü Yılmazer (METU, CHE)_____

Assoc. Prof. Dr. Göknur Bayram (METU, CHE)_____

Assoc. Prof. Dr. Gülüm Şumnu (METU, FDE)_____

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

Name, Last name : Emel Iraz Göksu

Signature :

ABSTRACT

HEMICELLULOSE BASED BIODEGRADABLE FILM PRODUCTION

Göksu, Emel Iraz

M.Sc., Department of Chemical Engineering

Supervisor: Prof. Dr. Ufuk Bakır

Co-Supervisor: Prof. Dr. Ülkü Yılmaz

February 2005, 78 pages

Xylan was extracted from cotton waste, characterized by DSC and TGA analysis and used in biodegradable film production. Pure cotton waste xylan did not form film. The presence of an unknown compound, as an impurity, yielded composite films. The unknown compound was determined as a phenolic compound, and most probably lignin, by using DSC and TGA analysis and Folin-Ciocalteu method. The effects of xylan concentration of the film forming solutions, glycerol (plasticizer) and gluten additions on thickness, mechanical properties, solubility, water vapor transfer rate, color and microstructure of the films were investigated.

Films were formed within the concentration range of 8-14%. Below 8%, film forming solutions did not produce films, whereas xylan concentrations above 14% was not used because of high viscosity problems. The average tensile strength, strain at break, water vapor transfer rate and water solubility of the cotton waste xylan

films were determined as about 1.3 MPa, 10%, 250 g/m².24h and 99%, respectively. The addition of glycerol as the plasticizer resulted in a decrease in the tensile strength and an increase in strain at break. The change in water solubility due to the addition of glycerol was very small. In addition, water vapor transfer rate and the deviation of the color from the reference color for the plasticized films were found to be higher than the unplasticized films.

The effect of addition of wheat gluten in cotton waste xylan film forming solutions on film formation was investigated at different concentration ratios. However, the incorporation of wheat gluten worsen the film quality.

Keywords: Xylan, cotton waste, biodegradable film, glycerol

ÖZ

HEMİSELÜLOZ BAZLI BİYOBOZUNUR FİLM ÜRETİMİ

Göksu, Emel Iraz

Yüksek Lisans, Kimya Mühendisliği

Tez Yöneticisi: Prof. Dr. Ufuk Bakır

Yardımcı Tez Yöneticisi: Prof. Dr. Ülkü Yılmaz

Şubat 2005, 78 sayfa

Pamuk atığından ksilan özütlenmiş, DSC ve TGA analizleriyle karakterize edilmiş ve biyo-bozunur film üretiminde kullanılmıştır. Saf pamuk atığı ksilanı film oluşturamamıştır. Bilinmeyen bir katışık maddenin varlığı kompozit film oluşmasını sağlamıştır. Bilinmeyen maddenin fenolik bir bileşik, büyük ihtimalle lignin, olduğu yapılan DSC ve TGA analizleri ve Folin-Ciocalteu yöntemiyle tespit edilmiştir. Film oluşturma çözeltisinin ksilan konsantrasyonu, gliserol ve gluten ilavesinin filmlerin kalınlığı, mekanik özellikleri, sudaki çözünürlükleri, su buharı geçirme hızları, renkleri ve mikroyapıları üzerindeki etkileri incelenmiştir.

Filmler %8-14 konsantrasyon aralığında oluşturulmuştur. Film oluşturma çözeltisi %8 ksilan konsantrasyonunun altında film oluşturamazken, %14 ksilan konsantrasyonunun

üzeri yüksek viskozite problemlerinden dolayı kullanılmamıştır. Ortalama çekme dayanımı, kopma anındaki uzama, su buharı geçirme hızı ve sudaki çözünürlük sırasıyla 1.3 MPa, 10%, 250 g/m².24saat ve %99 olarak bulunmuştur. Gliserolün plastikleştirici madde olarak eklenmesi, çekme dayanımını azaltmış ve kopma anındaki uzama değerlerini arttırmıştır. Gliserolün eklenmesi sebebiyle oluşan çözünürlük değişimi oldukça az bulunmuştur. Bunlara ek olarak, plastikleştirilmiş filmlerin su buharı geçirme hızı ve renklerinin referans renkten farklarının plastikleştirilmemiş filmlerden daha fazla olduğu gözlenmiştir.

Buğday gluteninin, pamuk atığı ksilanı film oluşturma çözeltisine değişik konsantrasyon oranlarında ilave edilerek film oluşturması üzerindeki etkileri incelenmiştir. Fakat buğday gluteninin eklenmesi film kalitesini bozmuştur.

Anahtar sözcükler: Ksilan, pamuk atığı, biyo-bozunur film, gliserol

To Mummy

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my supervisor Prof. Dr. Ufuk Bakır for her guidance, patience and unforgettable encouragement throughout not only this study and my academic career but also my hopeless times.

I extent my sincere appreciation to Prof. Dr. Ülkü Yılmaz and Prof. Dr. Levent Yılmaz for their solutions and suggestions throughout this study. Their continuous supports are greatly acknowledged.

I wish to thank to Assoc. Prof. Dr. Serpil Şahin and Assoc. Prof. Dr. Gülüm Şumnu for their help in the color measurements.

I am very grateful to Prof. Dr. Ruşen Geçit for the psychological and technical support he provided during thesis writing and for his tolerance.

To my all friends, Didem Sutay, Ayşegül Kavas, Ayşegül Ersayın, Özlem Ak, Beril Korkmaz, Deniz Öztürk, Tijen Seyidođlu, Selin Aytar, Arcan Erkan, Nazar İleri and Aytaç Kocabaş, I thank them for their love and support.

Special thanks are due to Volkan Ortalan for his endless support and encouragement.

I wish to thank to my father, my grandmother and my aunt for their extraordinary help.

Finally, I would like to appreciate to my mother. Words are meaningless. I love you.

TABLE OF CONTENTS

PLAGIARISM	iii
ABSTRACT	iv
ÖZ	vi
DEDICATION	viii
ACKNOWLEDGMENTS	ix
TABLE OF CONTENTS	x
LIST OF TABLES	xiii
LIST OF FIGURES	xiv
CHAPTER	
1. INTRODUCTION	1
1.1 Application of Biological Polymers as Packaging Materials	1
1.2 Hemicelluloses	4
1.2.1 Xylans	5
1.3 Gluten	8
1.4 Xylan and Xylan-Gluten Films	10
1.5 Cotton Waste	11
1.6 Objectives of the Study	13
2. MATERIALS AND METHODS	15
2.1 Materials	15
2.2 Xylan Extraction	16
2.3 Phenolic Measurement	16
2.4 Film Production	17

2.4.1	Unplasticized Xylan Films	17
2.4.2	Plasticized Xylan Films	17
2.4.3	Xylan-Gluten Composite Films	17
2.5	Film Characterization	18
2.5.1	Thickness Measurements	18
2.5.2	Tensile Test Measurements	18
2.5.3	Solubility Measurements	20
2.5.4	Water Vapor Transfer Rate (WVTR) Measurements ..	20
2.5.5	Color Measurements	21
2.5.6	Moisture Content Determination	22
2.6	Differential Scanning Calorimetry (DSC) Analysis	22
2.7	Thermogravimetric Analysis (TGA)	22
2.8	Scanning Electron Microscopy (SEM) Analysis	22
2.9	Statistical Analysis	23
3.	RESULTS AND DISCUSSION	24
3.1	Film Formation	24
3.2	Characterization of the Unknown Compound	30
3.3	Effect of Xylan Concentration of the Film Forming Solutions on Film Properties	36
3.3.1	Film Thickness	36
3.3.2	Mechanical Properties	37
3.3.3	Film Solubility	43
3.3.4	Water Vapor Transfer Rates	44
3.3.5	Color of the Films	45
3.4	Effect of Plasticizer on Film Properties	49
3.4.1	Film Thickness	50
3.4.2	Mechanical Properties	52
3.4.3	Film Solubility	55
3.4.4	Water Vapor Transfer Rates	56
3.4.5	Color of the Films	57
3.5	Incorporation of Wheat Gluten	58

4. CONCLUSION AND RECOMMENDATIONS	64
REFERENCES	65
APPENDIX A	71

LIST OF TABLES

TABLE

1.1	Commonly used packaging films (Tharanathan, 2003)	1
1.2	Composition of cotton gin waste (Jeoh and Agblevor, 2001)	12
2.1	Composition of the wheat gluten used in the experiments	15
3.1	Tensile strengths of various packaging films	39
3.2	Strain at break values of various packaging films	40
3.3	Elastic modulus of various packaging films	42
A.1	Data for xylan concentration in film forming solution	71

LIST OF FIGURES

FIGURE

1.1	Naturally occurring biopolymers used in biodegradable packaging films and composites (Tharanathan, 2003)	3
1.2	Structure of <i>O</i> -acetyl-4- <i>O</i> -methylglucuronoxylan from hardwood (Puls and Schuseil, 1993)	6
1.3	Structure of arabinoxylan from grasses (Puls and Schuseil, 1993)	7
1.4	Structure of arabino-4- <i>O</i> -methylglucuronoxylan from softwoods (Puls and Schuseil, 1993)	9
2.1	Shape and dimensions of specimen	19
2.2	Graph for the WVTR calculations	21
3.1	Photograph of a 10% (w/w) cotton waste xylan film	25
3.2	SEM images of 10% cotton waste xylan films (A) surface area (B) cross-sectional	26
3.3	Photograph of casted and dried birchwood xylan containing solutions: (A) purchased birchwood xylan; (B) extracted birchwood xylan	27
3.4	Photograph of 10% (w/w) birchwood xylan film prepared by using the washing solution left after the xylan extraction	28
3.5	SEM images of 10% birchwood xylan and unknown molecule composite films (A) surface area (B) cross-sectional area	29
3.6	DSC diagram of extra washed cotton waste xylan dried at 60°C	31
3.7	DSC diagram of birchwood xylan dried at 60°C	32
3.8	DSC diagram of cotton waste xylan dried at 60°C	33

3.9	DSC diagram of the unknown compound	34
3.10	Photograph of 5% (w/w) cotton waste xylan film	36
3.11	The effect of xylan concentration on cotton waste xylan film thickness .	37
3.12	The effect of xylan concentration on the tensile strength of the cotton waste xylan films	38
3.13	The effect of xylan concentration on strain at break values of the cotton waste xylan films	40
3.14	The effect of xylan concentration on the elastic modulus values of the cotton waste xylan films	41
3.15	The effect of xylan concentration on the hypothetical coating strength of the cotton waste xylan films	42
3.16	The effect of xylan concentration on water solubility of the cotton waste xylan films	44
3.17	The effect of xylan concentration on water vapor transfer rate of the cotton waste xylan films	45
3.18	The effect of concentration on the lightness of the cotton waste xylan films	46
3.19	The effect of xylan concentration on the “redness-greenness” of the cotton waste xylan films	47
3.20	The effect of xylan concentration on the “yellowness-blueness” of the cotton waste xylan films	48
3.21	The effect of xylan concentration on the total color change (ΔE) values of the cotton waste xylan films with respect to white paper	49
3.22	SEM images of plasticized cotton waste xylan films (A) surface area (B) cross-sectional area	51
3.23	The effect of glycerol on thickness of the cotton waste xylan films	52
3.24	The effect of glycerol on tensile strength of cotton waste xylan films	53
3.25	The effect of glycerol on strain at break values of cotton waste xylan films	54
3.26	The effect of glycerol on elastic modulus of cotton waste xylan films ...	54

3.27	The effect of glycerol on hypothetical coating strength of cotton waste xylan films	55
3.28	The effect of glycerol on water solubility of cotton waste xylan films ...	56
3.29	The effect of glycerol on the water vapor transfer rate of cotton waste xylan films	57
3.30	The effect of glycerol on the total color change (ΔE) of the cotton waste xylan films with respect to white paper	58
3.31	Photographs of cotton waste xylan and wheat gluten composite film with different xylan to gluten ratios of (A) 8:2 (B) 5:5 (C) 2:8	60
3.32	SEM images of cotton waste xylan and wheat gluten composite films with xylan to gluten ratio of 8:2 (A) surface area (B) cross-sectional area	61
3.33	SEM images of cotton waste xylan and wheat gluten composite films with xylan to gluten ratio of 2:8 (A) surface area (B) cross-sectional area	62
3.34	Photograph of extra washed cotton waste xylan and wheat gluten composite film with xylan to gluten ratio of 2:8	63
A.1	TGA diagram of extra washed cotton waste xylan	72
A.2	TGA diagram of birchwood xylan	73
A.3	TGA diagram of cotton waste xylan	74
A.4	DSC diagram of tannic acid	75
A.5	DSC diagram of extra washed cotton waste xylan dried at 90°C	76
A.6	DSC diagram of birchwood xylan dried at 90°C	77
A.7	DSC diagram of cotton waste xylan dried at 90°C	78

CHAPTER 1

INTRODUCTION

1.1 Application of Biological Polymers as Packaging Materials

Food packaging, an important discipline in the area of food technology, is concerned with the preservation and protection of all types of foods and their raw materials (Tharanathan, 2003). The characteristics required in packaging depend on what item will be packaged as well as the environment in which the package will be stored. Foods require more stringent packaging requirements than nonperishable goods. Physical characteristics of the packaging films are greatly influenced by the chemical structure, molecular weight, crystallinity and the processing conditions of the polymers used (Chandra and Rustgi, 1998). There is a variety of materials used in packaging. The most commonly used ones and their monomeric units are listed in Table 1.1.

Table 1.1 Commonly used packaging films (Tharanathan, 2003).

<i>Film type</i>	<i>Monomeric unit</i>
Polyethylene	Ethylene
Polyvinylidene	Vinylidene
Polyester	Ethyleneglycol + terephthalic acid
Polyamide	Diamine + various acids
Cellophane	Glucose

Petrochemical based plastics such as polyolefins, polyesters, polyamides, etc. have been increasingly used as packaging materials, because of their availability in large quantities at low cost and favorable characteristics such as good mechanical properties. However, they have a very low water vapor transmission rate and most significantly they are totally non-biodegradable leading to ecological problems. Therefore, their use has to be restricted and may be gradually abandoned to circumvent problems concerning waste disposal (Tharanathan and Saroja, 2001). Consequently, there is a shift to the biodegradable packaging materials (Tharanathan, 2003).

Polymer degradation may result from biodegradation, photo-degradation or chemical degradation (Petersen et al., 1999). Biodegradation is a natural process by which organic chemicals in the environment are converted to simpler compounds, mineralized and redistributed through elemental cycles such as the carbon and nitrogen cycles. Biodegradation can only occur within the biosphere in as much as microorganisms such as bacteria, yeast and fungi play a central role in biodegradation process (Chandra and Rustgi, 1998). The final products of the degradation process are carbondioxide, water and biomass under aerobic conditions and hydrocarbons, methane and biomass under anaerobic conditions (Lim et al., 1999).

One group of biodegradable materials is natural biodegradable polymers or biopolymers. They are formed in the nature during the growth cycles of all organisms. Their synthesis generally involves enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex metabolic processes (Chandra and Rustgi, 1998). Use of such biological polymers as packaging materials will open up potential economic benefits to the farmers and agricultural processors (Tharanathan, 2003). The classification for the naturally occurring biopolymers used in packaging is given in Figure 1.1.

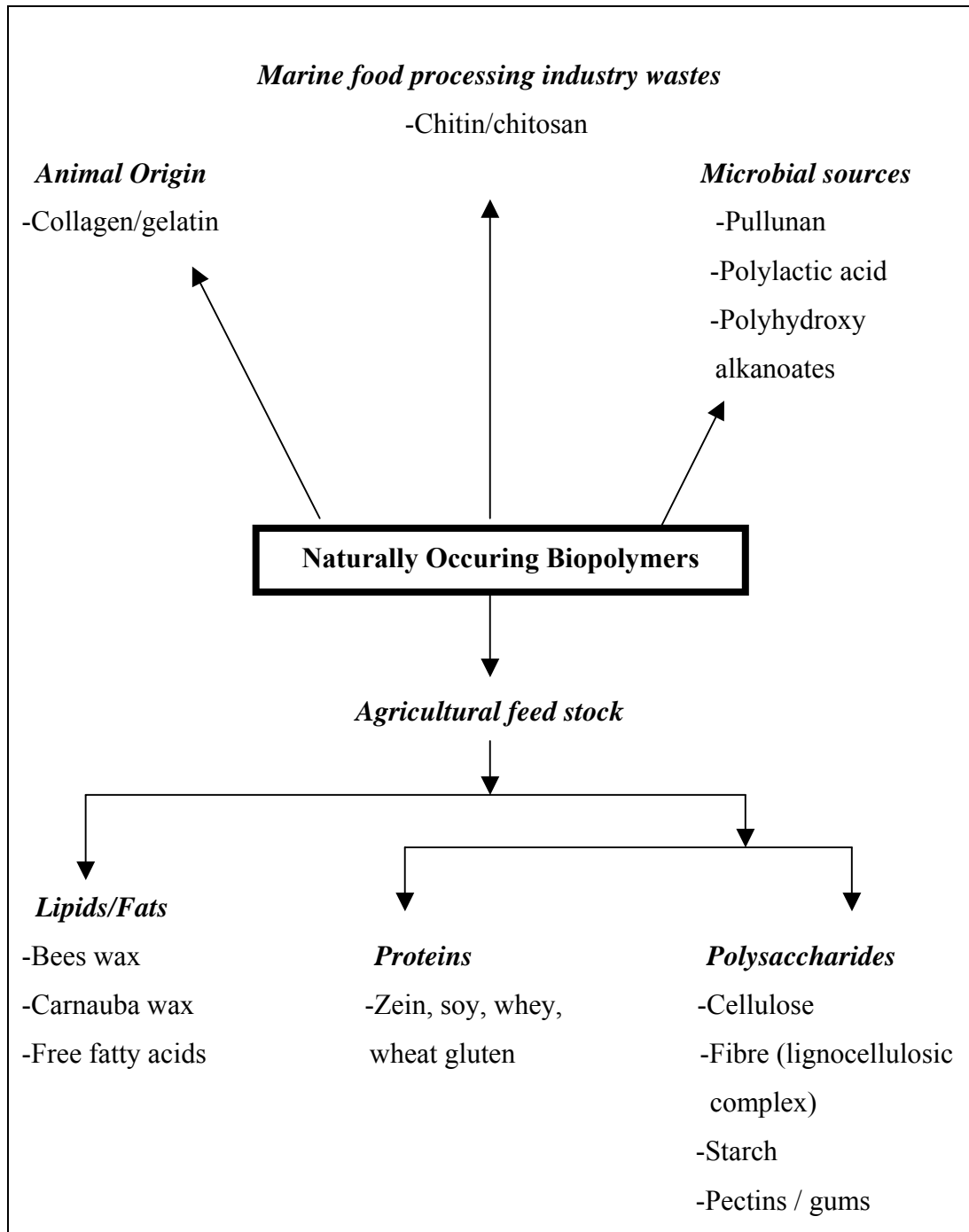


Figure 1.1 Naturally occurring biopolymers used in biodegradable packaging films and composites (Tharanathan, 2003).

Applications of biopolymers for food packaging were reviewed by Peterson et al. (1999). Fresh mushrooms were packaged with glass jar covered with gluten films and stored at 10°C for approximately 6 days. A modified atmosphere containing 2-

3% carbondioxide and 2-3% oxygen was developed (Guilbert et al., 1997). Fresh products such as lettuce, cabbage, brocolli and tomatoes were packaged with chitosan-cellulose and polycaprolactone and stored at 10-25°C for 4-6 days. This biodegradable laminate was found suitable as a packaging material with modified atmosphere packaging in the inert temperature range (Makino and Hirata, 1997). Bread, brocolli and ground beef were stored at temperatures appropriate for recommended storage periods in cornstarch-containing polyethylene type of packaging materials. The film was found out to be effective in protecting the stored food (Holton et al., 1994). Kim and Pometto III (1994) worked on the packaging of ground beef with starch-polyethylene films containing corn starch, oxidized polyethylene and pro-oxidant. It was decided that those films had potential use as primary food containers for ground beef.

1.2 Hemicelluloses

Plant cell walls are known to be the main polysaccharide-containing renewable resources in nature and they are composed of three major polymeric constituents, namely; cellulose, hemicellulose and lignin (Biely, 1993). Hemicelluloses are heteroglycans with low molecular weights and include glucans, mannans, arabinans and xylans. They can be removed from the tissue by extraction with aqueous alkali or, less frequently with water. Only one hemicellulose, arabinogalactan, can be directly extracted from fully lignified wood with water in reasonable yield (Biely, 1993; Puls and Schuseil, 1993).

Hemicelluloses are synthesized by a different pathway from the cellulose and, in contrast to cellulose, many hemicelluloses are branched and composed of a mixture of different sugars and other substituents (Gabriellii and Gatenholm, 1998). Hemicelluloses of woody plants are built up from relatively few sugar residues, the most common of which are D-xylose, D-mannose, D-glucose, L-arabinose, 4-*O*-methylglucuronic acid, D-galacturonic acid and glucuronic acid. The variety of sugar residues of those from grasses and cereals is smaller; the most common ones are D-xylose, L-arabinose, D-glucose and D-galactose. However, there is a variety of

linkages and abundance of branching types in graminaceous hemicelluloses (Puls and Schuseil, 1993).

1.2.1 Xylans

Xylans are the most common hemicelluloses and they are considered to be the most abundant polysaccharide in nature after cellulose (Biely, 1993; Ebringerová and Heinze, 2000). They are estimated to account for one third of all renewable biomass available on earth (Gabielli and Gatenholm, 1998).

The main sugar component of xylan is D-xylose and these D-xylosyl units are β -1,4 linked in xylan structure. The structure of xylan is not uniform. Depending on the source, it varies from linear β -1,4-polyxylose main chains to highly branched heteropolysaccharides substituted with mainly acetyl, arabinosyl and glucuronosyl residues (Biely, 1993; Hazlewood and Gilbert, 1993).

The principle xylan of hardwood, *O*-acetyl-4-*O*-methylglucuronoxylan, consists of a backbone of 1,4-glycosidic bond linked β -xylopyranose residues as it can be seen in Figure 1.2. Nearly every tenth xylose unit carries a single, terminal side chain, consisting of 4-*O*-methylglucuronic acid attached directly to the 2-position of xylose. Seven out of ten xylose residues contain an *O*-acetyl group at C-2 and C-3 positions. In addition, hardwood xylans contain minor amounts of rhamnose and galacturonic acid integrated to the xylan main chain. The degree of polymerization of hardwood xylan is 150-200 (Coughlan et al., 1993; Puls and Schuseil, 1993).

Xylan structure of grasses represented in Figure 1.3 differs depending on the species and the tissue within a single species. These xylans, arabinoxylans, have the same backbone as the wood xylans, however, they contain smaller portions of uronic acid and they are more highly branched. In addition, they contain large proportions of L-arabinofuranosyl units, linked probably mainly to the C-2 position of xylose (Puls and Schuseil, 1993).

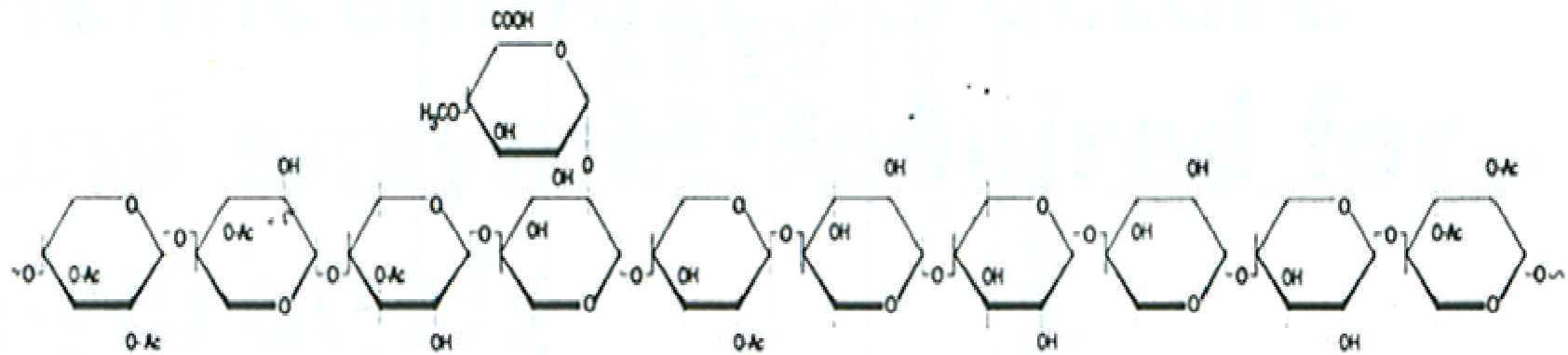


Figure 1.2 Structure of *O*-acetyl-4-*O*-methylglucuronoxylan from hardwood (Puls and Schuseil, 1993).

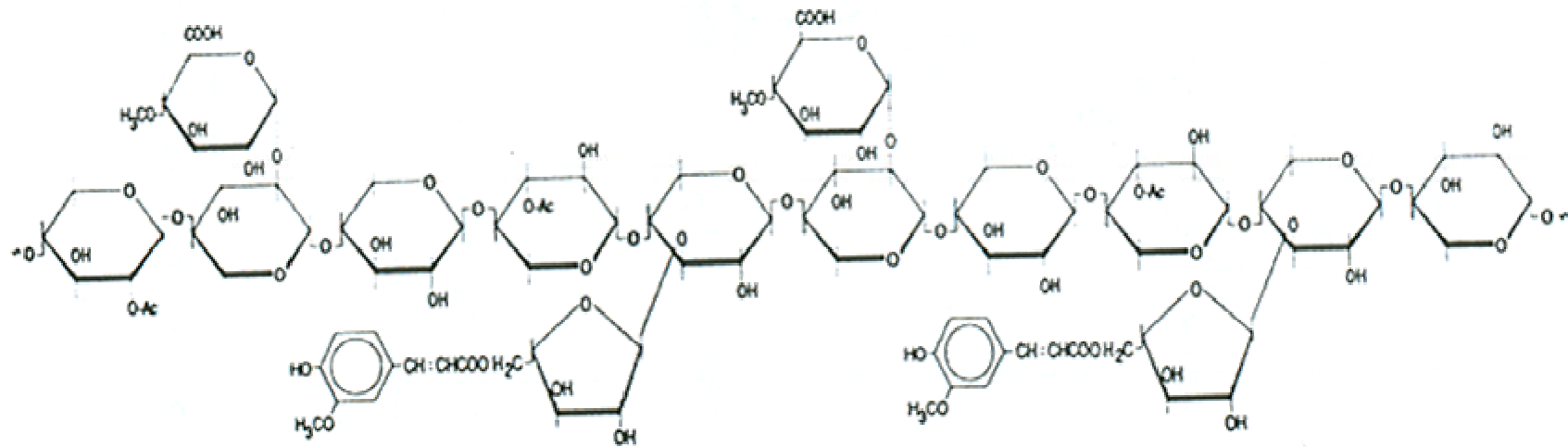


Figure 1.3 Structure of arabinoxylan from grasses (Puls and Schuseil, 1993).

Softwood xylans, arabino-4-*O*-methylglucuronoxylans whose structure is represented in Figure 1.4, consist of a backbone of β -1,4-linked D-xylopyranose residues. They contain α -L-arabinofuranose residues directly linked to C-3 of the xylose, instead of acetyl-substituents found in hardwoods. Nearly seven out of ten xylose units are substituted by terminal 4-*O*-methylglucuronic residues linked to C-2. The degree of polymerization of softwood xylan is 70-130 (Coughlan et al., 1993; Puls and Schuseil, 1993).

1.3 Gluten

Gluten is the major storage protein in wheat and corn (Weber, 2001). It is a substance which is intended to be used in food and non-food applications such as protective coatings, films, thermoplastic material, adhesives and surfactants. Its complex mixture consists of proteins, carbohydrates, lipids and fibers, however, it is mainly composed of two proteins; glutenin and gliadin (Kersting et al., 1994).

Glutenin has many subunits linked together via intermolecular disulfide bonds in its structure and it is responsible for the elasticity. On the other hand, gliadin is a single-chained molecule and the major bonds encountered are the intramolecular disulfide bonds. Gliadin is responsible for the extensibility (Kasarda et al., 1978).

Glutamic acid and proline contents of gluten proteins are high (Kasarda et al., 1978). Peptide bonds of proline are not flexible since the amino groups are involved in the ring structure. There is a large number of nonpolar side chains resulting in an increase in the possibility of apolar bonding. In addition, the gluten proteins have a low ionic character. 35% of the total amino acids have hydrophobic side chains indicating that the apolar residues are not accommodated in the hydrophobic core of the protein. Therefore, it is believed that hydrophobic interactions between the proteins have a significant role in structure stabilization (Kasarda et al., 1976).

The gluten proteins are easy to isolate since they are insoluble in water (Kasarda et al., 1978). The isoelectric point of the gluten proteins generally is in between 6 and 9

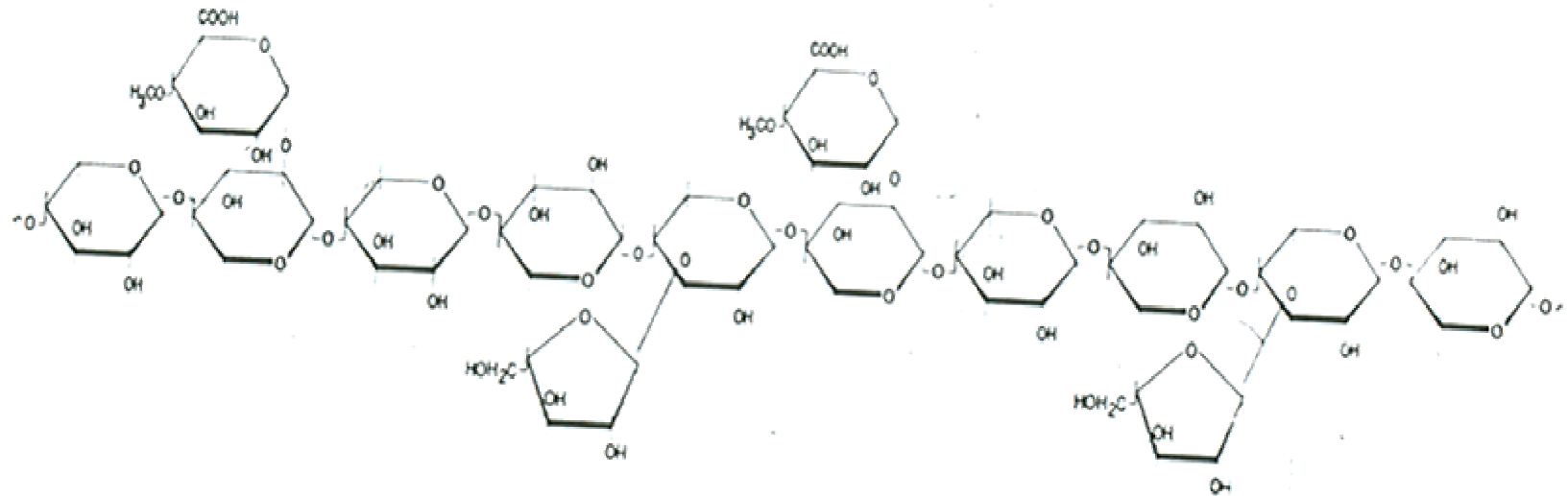


Figure 1.4 Structure of arabinano-4-O-methylglucuronoxylan from softwoods (Puls and Schuseil, 1993).

(Wrigley, 1968 a,b). At high pH values or at pH values lower than 4 or 5, they are moderately soluble, however, disulphide bridges can be broken at high pH (Donavan, 1967).

1.4 Xylan and Xylan-Gluten Films

The studies about xylan films in the literature are limited. Film forming properties of xylan extracted from aspen (Gabrielli and Gatenholm, 1998) and birchwood (Gabrielli et al., 2000) were studied. Pure xylan solution did not form films. The surfaces of the xylan flakes were investigated and the surface was observed to be composed of small particles that are loosely connected with each other. Mixtures of xylan and various amounts of chitosans were prepared and it was observed that at as little as 5% chitosan and above, the solutions started to form films upon drying. At 10% and above, continuous, self-supporting films were achieved.

The authors suggested that the electrostatic interaction between glucuronic acid functionalities of xylan and amino groups of chitosan is responsible for the film formation as well as the crystalline domains of xylan tied together with the chitosan chains. Researcher also suggested that addition of chitosan might promote an increase in the degree of order of xylan in the films. The films with high xylan/chitosan ratio were brittle, probably because of lower mass of xylan.

Acetyl groups present in the native xylan molecules which prevent the crystallization of xylan are removed in the extraction process. The relative crystallinities of the samples were found to decrease with an increasing amount of chitosan, and the film of pure chitosan had virtually no crystallinity (Gabrielli and Gatenholm, 1998).

Kayserilioğlu and coworkers (2003a) worked on the incorporation of xylan into wheat gluten films. Birchwood, corncob and grass xylan were added into gluten in various quantities, namely 10:0, 9:1, 8:2, 7:3 and 6:4 gluten to xylan ratios. The film forming properties were investigated. It was observed that the composition of the solution, xylan type, pH and drying conditions had affected the film properties.

The film forming solutions with a pH value of 11 formed continuous, self supporting films. The tensile strengths of the composite films prepared by using birchwood xylan were similar to the other biodegradable films in the literature. It was concluded that birchwood xylan might be added up to 40% without any loss in tensile strength. The elongation at break values decreased whereas the elastic modulus values increased as the concentration of the xylan in the solution increased. It was observed that higher temperature drying did not enhance the strength of the films.

Films containing birchwood xylan gave the highest tensile strength, on the other hand, films containing corncob xylan gave the lowest tensile strength. No differences in elongation at break values between films containing birchwood and grass xylan were observed. Addition of corncob xylan resulted in more stretchable and less stiff films than corncob and grass xylan.

No change in the gluten solubility was observed by changing the type of xylan used, however, as the concentration of the xylan increased, the protein solubility decreased. Moreover, it was observed that the addition of xylan only slightly affected water vapor transfer rate of films and alteration of xylan type had no negative effect on water vapor transfer rate of the films.

The microstructures of the films were investigated by using scanning electron microscopy. Xylan type was observed to affect the microstructure of the films. Corncob xylan added films had a more uniform surface than the other films, which explains the high stretchability of corncob xylan films. Films with grass xylan showed little globular formation on the surface. Use of birchwood xylan resulted in more heterogeneous films.

1.5 Cotton Waste

Cotton is a natural fibre, and makes up nearly half of all fibre sold in the world. The cotton grows on a plant that is a member of the *Hibiscus* family, botanically known as *Gossypium Hirsutum*. Approximately 19.3 million tons of cotton is produced in

the world annually and nearly 0.7 million tons of this cotton is produced in Turkey (DPT, 2004). In the cotton industry, the ginning process generates a considerable amount of waste. About 18-65 kg of cotton gin waste is produced per 100 kg of cotton (Thomasson, 1990). The composition of cotton gin waste is given in Table 2 below.

Table 1.2 Composition of cotton gin waste (Jeoh and Agblevor, 2001).

<i>Component</i>	<i>Weight %</i>
Lignin	28.83
Ash	10.46
Extractives	7.74
Cellulose	37.1
Xylan	9.41
Mannan	1.13
Arabinan	2.3
Galactan	2.38

One of the ways to treat cotton waste is disposing by combustion, however, this application is known to cause air pollution and the cost of meeting particulate emission standards can be prohibitive (Fuller et al., 1997). Another way to treat the waste is ploughing the waste into the soil as an organic soil amendment. However, this alternative promotes weed, diseases, insect infestation and excess chemicals in the receiving soil (Jeoh and Agblevor, 2001). Therefore, conversion of the cotton waste into value-added product is a significant concept, however, the number of the studies in the literature is limited.

Researchers worked on the conversion of cotton gin waste to ethanol and concluded that 157 liters of ethanol could be produced from one ton of waste (Brink, 1981; Beck and Clements, 1982). Other researchers analyzed cotton gin waste to assess its fuel value for combustion and proposed using the feed stock for the production of

char, hydrogen, protein and prolysis gases (Griffin, 1974; Schacht and Lepori, 1978). Parnell and coworkers (1991) investigated the gasification of cotton gin waste in a fluidized bed reactor and observed that the gas produced had a low heating value.

1.6 Objectives of the Study

Biodegradable packaging films have received great attention in different fields, especially in food packaging, due to some of their superior properties to most commonly used petroleum based packaging materials. The use of those films is advantageous not only in economic point of view but also in environmental point of view depending on their source (Tharanathan and Saroja, 2001). There are numerous studies about biodegradable films prepared from polysaccharides, lipids, proteins or combination of those constituents in the literature. The mostly used polysaccharides in the biodegradable film production are starch, cellulose, gums, chitosan, xanthan, pullulan and curdlan (Weber, 2001). However, there occur some different application fields of those polysaccharides resulting in an increase in their cost. Therefore, use of biological molecules with limited or no use may be beneficial.

Hemicelluloses are noncellulosic polysaccharides found in the cell wall structure of the plants associated with cellulose and lignin (Puls and Schuseil, 1993). The use of hemicelluloses in industry is limited. Being the most widely distributed component in the nature after cellulose, the hemicellulosic component xylan accounts for roughly one third of the biomass on the earth (Gabielli and Gatenholm, 1998). There is an increasing interest in the application potential of xylan polymers both in food and non-food area. Promising results were obtained in the field of papermaking, baking and food additives (Ebringerová and Heinze, 2000). Widening the application of xylan by using it in the biodegradable film production seems to be a good idea.

Cotton waste, a by-product of the cotton production, creates some problems. It is the part of the cotton plant that is left after harvesting period and contains burs, pieces of stems, leaves, motes, cotton lint and ash. Combustion of cotton waste leads to some environmental problems such as air pollution, whereas ploughing it into the soil as an

organic amendment enhances the growth of some undesired organisms (Fuller et al., 1997; Jeoh and Agblevor, 2001). Therefore, conversion of cotton waste into value-added products was studied by various researchers.

Approximately, 11% (w/w) of the dried cotton waste is composed of xylan molecules. However, this may change depending on the climacteric conditions (Jeoh and Agblevor, 2001). An alternative way for the conversion of cotton waste into value-added products may be the utilization of the xylan in the cotton waste in the biodegradable film production.

The use of xylan in the biodegradable film production was not extensively studied in the literature. The film forming properties of pure xylan isolated from birchwood and aspenwood was studied but the results were not promising. Pure xylan did not form continuous and self-supporting films in its pure form (Gabrielli and Gatenholm, 1998; Gabrielli et al., 2000). The incorporation of xylan from different sources into wheat gluten was studied and it was observed that birchwood, corncob and grass xylan could be used as an additive in wheat gluten film production. The composition and the type of the xylan affected the mechanical properties of the films. It was observed that those types of xylan molecules did not form films in their pure form (Kayserilioğlu et al., 2003). However, the use of cotton waste xylan in biodegradable film production has not been studied yet.

In this study, the major aim was to produce hemicellulose based biodegradable films from cotton waste. For this purpose, xylan was extracted from cotton waste and utilized for the film production. The extracted xylan samples by different procedures were characterized by using DSC and TGA analysis. The effect of pH and drying conditions on xylan was observed. Film forming solutions with different xylan concentrations were prepared and the films were characterized in terms of thicknesses, mechanical properties, solubilities, water vapor transfer rates, colors and microstructures. Moreover, effect of addition of glycerol as the plasticizer and the effect of incorporation of wheat gluten on the film forming properties was investigated.

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

Cotton waste was obtained from a local cotton producer in Urfa, Turkey. Wheat gluten was obtained from Kröner Stärke (Germany). The composition of the purchased gluten is given in Table 2.1.

Table 2.1 Composition of the wheat gluten used in the experiments.

<i>Material</i>	<i>Weight %</i>
Water (max)	8.0
Protein (min)	78.0
Fat	1.4
Fibre	0.5
Ash	0.9

Potassium hydroxide, sodium hydroxide, sodium borohydride, acetic acid, sodium bromide, potassium bromide, ethanol and silica gel were purchased from Merck (Germany).

2.2 Xylan Extraction

The method used by Zilliox and Debeire (1998) was followed for the xylan extraction. Dried cotton waste was milled. 100 ml of distilled water was added to 2 g of milled cotton waste sample and the sample was swelled at 60°C for 16 hours in an incubator (Nüve, Turkey). The swollen sample was filtered by means of a filter paper (Whatman 41) and the pellet was mixed with 17 ml of 24 %w/v KOH + 1 %w/v NaBH₄ containing solution and stirred for 3 hours at room temperature. Afterwards, the suspension was filtered and the supernatant was mixed with 5 ml cold ethanol and 0.5 ml acetic acid solution and shaken for several minutes for standard extraction procedure. For extra washed xylan preparation, the supernatant was mixed with 85 ml cold ethanol and 8.5 ml acetic acid solution and shaken for several minutes. A centrifugation step was performed at 8300xg for 20 minutes and the pellet was dried at 60°C for 24 hours and used as xylan source.

2.3 Phenolic Measurement

Folin-Ciocalteu method was followed for this purpose. 5 ml of standard catechol solutions at different concentrations in a range of 0-0.01 mg/ml were prepared by diluting 0.1 mg/ml stock solutions with distilled water in test tubes. 25 ml of sodium carbonate solution at a concentration of 0.2 g/ml was prepared. 0.75 ml of sodium carbonate and 0.25 ml of Folin-Ciocalteu phenol reagent was added to catechol standard and sample solutions. After incubation for 1 hour at room temperature, the absorbances of the solutions were measured at 750 nm in 4 ml plastic spectrophotometer cuvettes against distilled water. The standard curve for catechol was plotted. The phenolic compound concentration in the sample which is the solution left from the extra washing step was estimated by using the standard curves.

2.4 Film Production

2.4.1 Unplasticized Xylan Films

Film forming solutions with concentrations of 8%, 10%, 12% and 14% (w/w) were prepared by dissolving cotton waste xylan in distilled water. After 8 hours of stirring on a magnetic stirrer (Heidolph, MR3001, Germany), the beakers were placed into a water bath at 70°C for 10 minutes to prevent bubble formation in the films upon casting. Then, 20 g of the solution was cast into petri disks with diameter of 9.0 cm. The films were dried in a controlled environment at a temperature of 20±2°C and a relative humidity of 40±4 up to a condition that they could be peeled from the petri plates.

2.4.2 Plasticized Xylan Films

Film forming solutions were prepared by dissolving 10 g of extracted xylan in solvents (10% w/w) containing 2 g glycerol as the plasticizer. After 8 hours of stirring, the beakers were placed into a water bath at 70°C for 10 minutes to prevent bubble formation in the films upon casting. Then, 20 g of the solution was cast into petri disks with diameter of 9.0 cm. The films were dried in a controlled environment at a temperature of 20±2°C and a relative humidity of 40±4% up to a condition that they could be peeled from the petri plates.

2.4.3 Xylan-Gluten Composite Films

10% (w/w) film forming solutions with xylan:gluten ratios of 2:8, 5:5 and 8:2 were prepared. The mixtures were dissolved in water containing 2 g glycerol as the plasticizer. After 8 hours of stirring, the beakers were placed into a water bath at 70°C for 10 minutes to prevent bubble formation in the films upon casting. Then, 20 g of the solution was cast into petri disks with diameter of 9.0 cm. The films were dried in a controlled environment with a temperature of 20±2°C and a relative humidity of 40±4% up to a condition that they could be peeled from the petri plates.

2.5 Film Characterization

Films were conditioned in the presence of a saturated NaBr solution at 20°C and 60%RH for at least 48 hours prior to all measurements.

2.5.1 Thickness Measurements

Film thickness was measured by using a digital micrometer (Pass, China). Filmstrips were placed within the micrometer and the gap was reduced until the first indication of contact was noted. Measurements were performed at 10 different locations on the films and the average value was calculated.

2.5.2 Tensile Test Measurements

Test specimens having the shape and dimensions given in Figure 2.1 were cut from the flat films. Tensile properties were determined from three individual cast films, with two subsamples tested from each film replicate. The tests were performed in an environment at a temperature of 20±2°C and a relative humidity of 40±4%. A Lloyd Material Testing Machine (Lloyd Instruments Ltd., Fareham) supported with Lloyd Windap and L Series Console software was used for the measurements. The grip separation and the crosshead speed were set to 50 mm and 10 mm/min, respectively. Stress versus strain curves, tensile strength and strain at break values were obtained for each film.

Stress and strain values was obtained as follows:

$$\sigma = F / A$$

where σ is the tensile stress expressed in MPa, F is measured force in N, A is the initial cross-sectional area of the specimen expressed in mm².

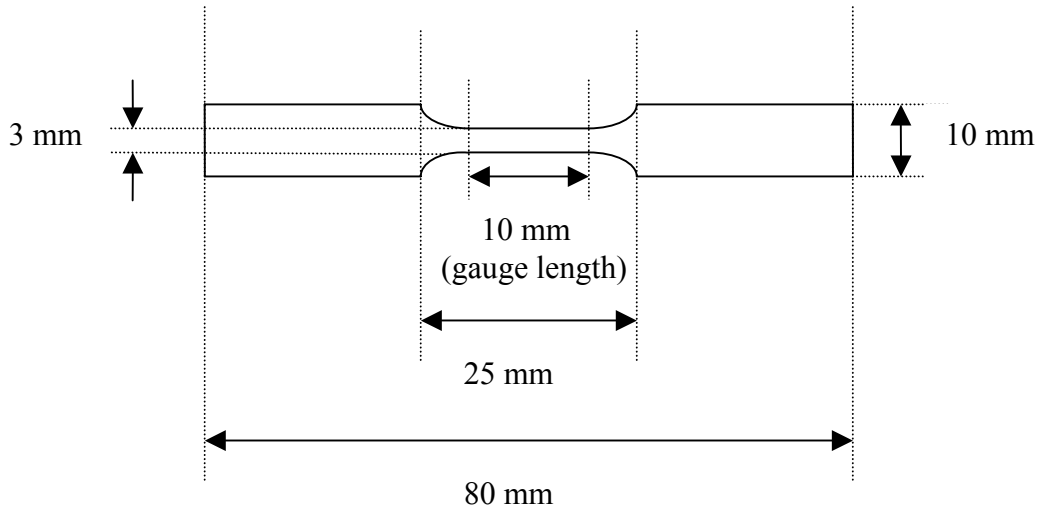


Figure 2.1 Shape and dimensions of specimen.

$$\varepsilon = \Delta L / L_0$$

$$\varepsilon (\%) = (\Delta L / L_0) \times 100$$

where ε is the strain value expressed as a dimensionless ratio, or in percentage; L_0 is the gauge length of the test specimen taken as 10 mm; ΔL_0 is the increase in the specimen length between gauge marks, expressed in mm.

Tensile strength (σ_{\max}) was calculated by dividing the peak load by the initial cross-sectional area of the specimen. Strain at break (ε_b) was expressed as percentage of the change of the original length of a specimen between grips at break.

The modulus of elasticity (E) was determined as the slope of linear part of the stress-strain curves. Calculation of E value was as follows:

$$E = \left. \frac{\partial \sigma}{\partial \varepsilon} \right|_{\varepsilon \rightarrow 0}$$

where the modulus of elasticity is expressed in terms of MPa.

In addition to these properties, hypothetical coating strength (HCS) was calculated as follows:

$$\text{HCS} = \sigma_{\text{max}} / E$$

2.5.3 Solubility Measurements

Films were cut and 0.2 g of film was put into 20 g of distilled water and swollen for 24 hours. Afterwards, the piece of film was taken out and dried in an environment at a temperature of $20 \pm 2^\circ\text{C}$ and a relative humidity of $40 \pm 4\%$ for 48 hours and weighed. The solubility (%) values were calculated as follows:

$$\text{solubility (\%)} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100$$

2.5.4 Water Vapor Transfer Rate (WVTR) Measurements

Glass bottles were completely filled with dry silica particles to maintain 0%RH within the bottles. Films were clamped on top of the bottles and these bottles were placed in an environmental chamber at 20°C and 80%RH in the presence of saturated KBr solution. After incubation for 24 hours, the increase in weight of the bottles was monitored in time up to 3 days to assess the water vapor transfer rate of the films. Two measurements were performed for each day. The following graph represented in Figure 2.2 was utilized to calculate WVTR of the films:

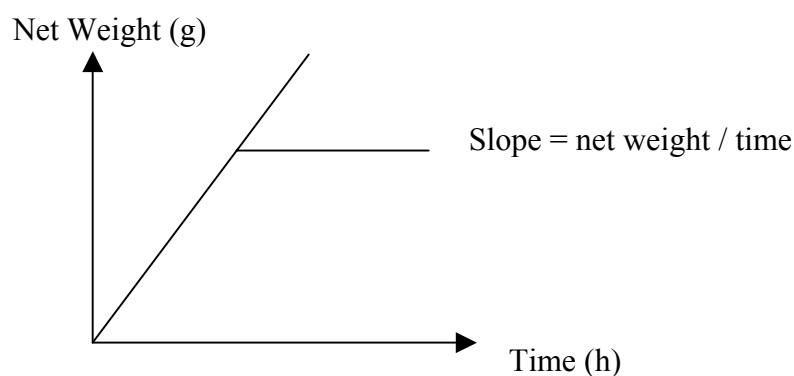


Figure 2.2 Graph for the WVTR calculations.

Net weight of the bottle was the difference between the measured weight of the bottle and the weight of the bottle at the first day. The WVTR of the films were calculated as follows:

$$\text{WVTR} = \frac{\text{Slope (g/h)} \times (24 \text{ h/day})}{\text{Area of the film (m}^2\text{)}}$$

Two samples were tested for each type of film, each obtained from a separately cast film.

2.5.5 Color Measurements

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

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

2.5.6 Moisture Content Determination

The sample was cut into pieces and the weights of the pieces were measured. The pieces were placed in an incubator (Nüve, Turkey) at 105°C and waited for 24 hours. The final weight of the sample was measured. The moisture content of the films were calculated as follows:

$$\text{moisture content (\%)} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100$$

2.6 Differential Scanning Calorimetry (DSC) Analysis

10 mg of sample placed in a pan, and the reference (empty pan) were heated at a rate of 5°C/min to keep the two pans at the same temperature. The difference in power needed to keep both at the same temperature was amplified and provided the information about thermal transitions. The samples were heated from room temperature to 250-300°C. Nitrogen was used as the inert gas.

2.7 Thermogravimetric Analysis (TGA)

10 mg of sample was placed in a pan. The weight of the sample was measured continuously on a sensitive balance as sample temperature was increased in an inert atmosphere in which nitrogen was used. The heating rate used was 5°C/min. The sample was heated from room temperature up to 500°C. Data was recorded as a thermogram of weight versus temperature.

2.8 Scanning Electron Microscopy (SEM) Analysis

Differences in surface film morphology were investigated using a scanning electron microscope (JEOL JSM-6400). The samples were sputter-coated with gold prior to examination.

2.9 Statistical Analysis

Statistical analysis were performed by using SPSS 10.0 software. The comparisons were performed by Duncan's test with a significance level of 0.05.

CHAPTER 3

RESULTS AND DISCUSSION

In this study, xylan extracted from cotton waste was used to produce biodegradable films. First of all, the film formation properties of the xylan extracted from cotton waste and birchwood by using extraction methods having different washing levels were compared and discussed. The characterization of the extracted xylan molecules was performed. The effects of drying conditions on the xylan structure and xylan solubility were investigated.

Afterwards, the effects of xylan concentration in film forming solution on the thickness, mechanical properties, solubility, water vapor transfer rate, color and microstructure of the films were determined. In addition, the effect of the incorporation of the glycerol as the plasticizer and gluten addition were studied.

3.1 Film Formation

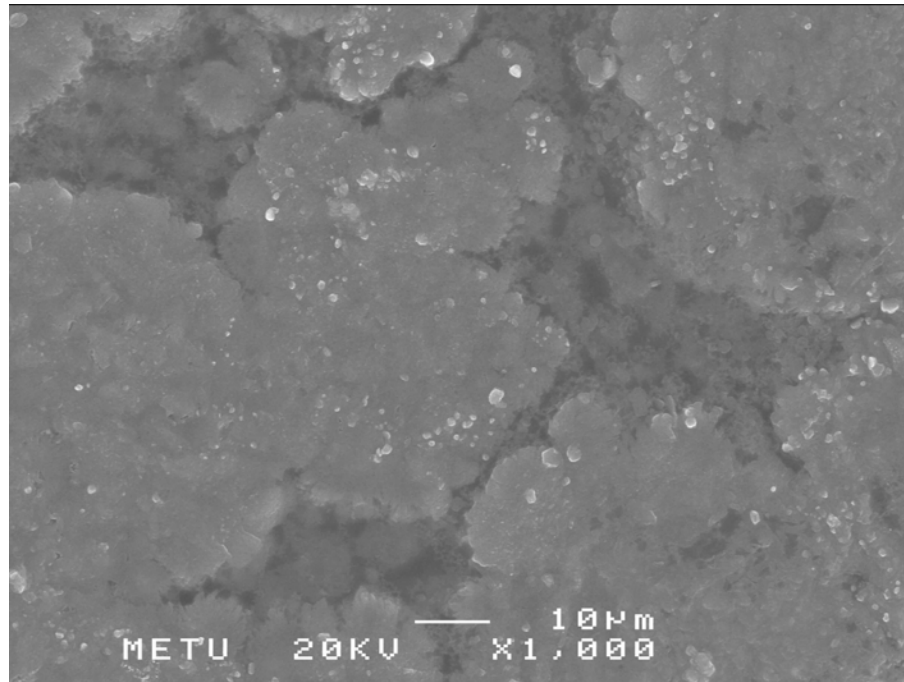
At the beginning of this study, xylan was extracted from the cotton waste as explained in Chapter 2 in section 2.2. First of all, films were formed from the extracted xylan by dissolving it in distilled water. 10% (w/w) xylan containing film forming solution was prepared, casted and dried. To our surprise, continuous and self-supporting films, as shown in Figure 3.1, were obtained.



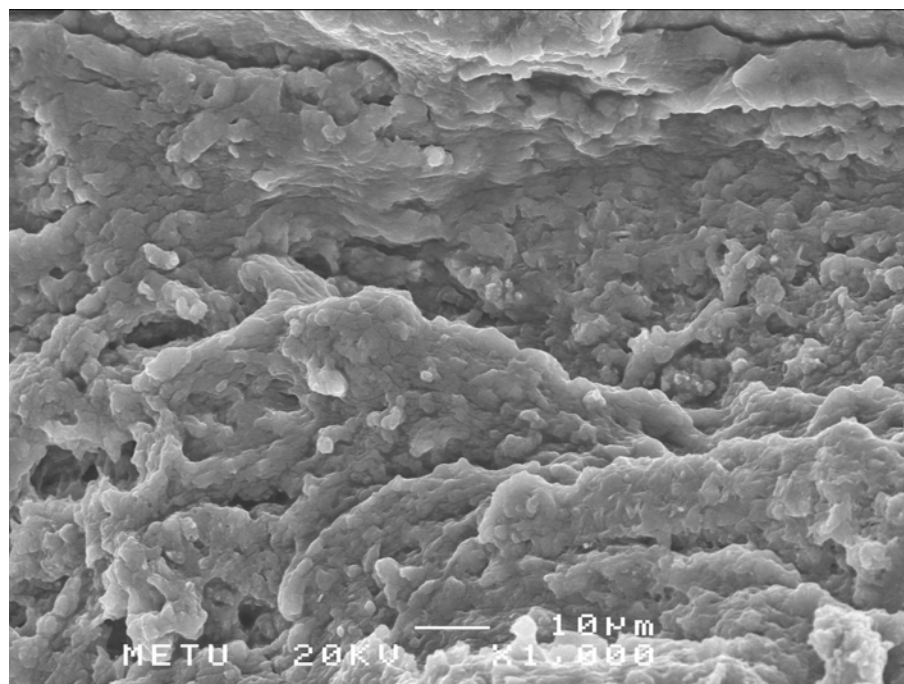
Figure 3.1 Photograph of a 10% (w/w) cotton waste xylan film.

Additionally, SEM images of the surface and cross-sectional areas are shown in Figure 3.2. As observed from Figure 3.2, the cross-sectional areas of the films are rougher than the surface area. Moreover, both surfaces seem to have globular structures.

This result is contradictory to the results obtained with the birchwood xylan. Birchwood xylan, which is also a hardwood like cotton waste (Puls and Schuseil, 1993), did not form films in its pure form as reported in the literature and observed in our laboratory (Gabrielli and Gatenholm, 1998; Kayserilioğlu, 2003a). However, in these studies, commercial birchwood xylan (Sigma) was used. Considering the possible differences of the extraction methodology between commercial extraction and the one used in the laboratory, and their possible effect on film formation, two birchwood xylan film solutions by using either commercial (Sigma) or extracted birchwood xylan, were prepared. Exactly the same procedure used to extract cotton waste xylan was followed during the xylan extraction from birchwood. As observed from Figure 3.3, neither commercial nor extracted birchwood xylan samples produced films. However, much larger film patches formed by using extracted than commercial birchwood xylan.



A



B

Figure 3.2 SEM images of 10% cotton waste xylan films (A) surface area (B) cross-sectional area.

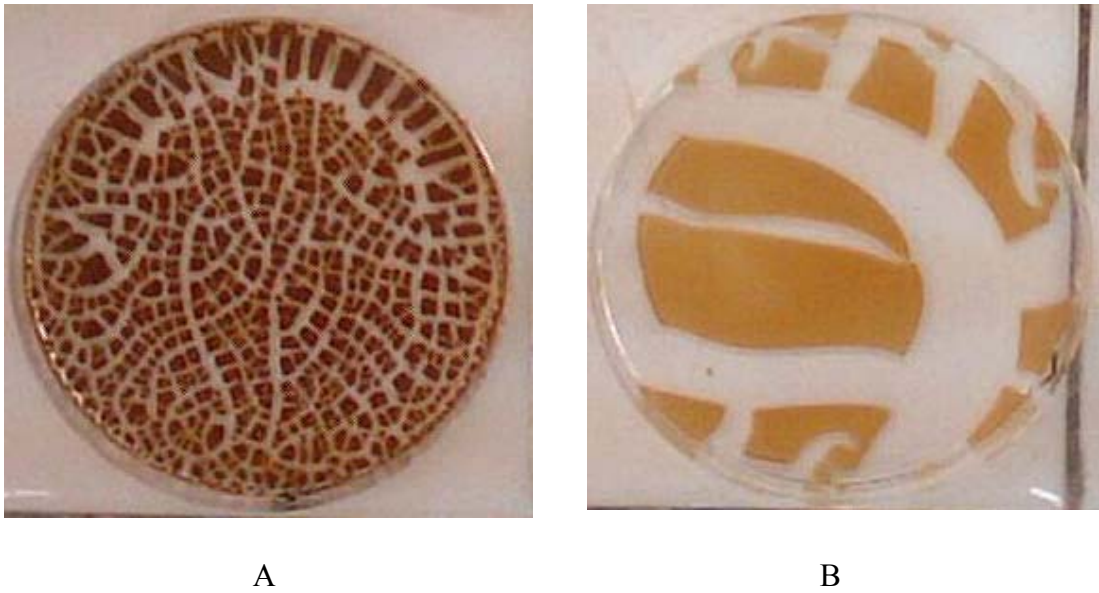


Figure 3.3 Photograph of casted and dried birchwood xylan containing solutions: (A) purchased birchwood xylan; (B) extracted birchwood xylan.

This surprising result probably showed the presence of another compound, yielding film formation, in the xylan extract as an impurity. Therefore, an analysis program was followed to identify the unknown compound. First of all, the extracted xylan was washed more by using fresh ethanol/acetic acid solution to remove the unknown compound. The xylan extracted by these extra washing steps will be referred to “extra washed xylan” (EWX) to distinguish from the xylan extracted by using the standard protocol, which will be referred to “extracted xylan” (EX). As expected, extra washed xylan did not produce films verifying the presence of another compound having film formation effect.

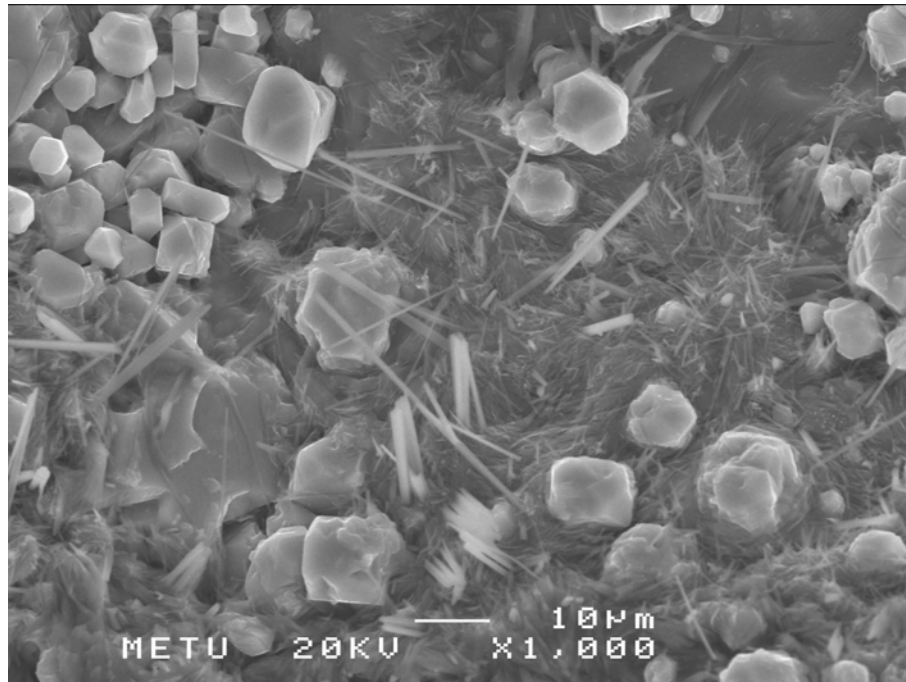
To confirm the film forming effect of the unknown compound, birchwood xylan which did not form films, was dissolved (10%) in the washing solution of the EWX extraction after vaporization of ethanol. As a result, continuous, self-supporting films formed as shown in Figure 3.4. Therefore, it was concluded that the unknown compound which could not be removed by the standard washing during xylan extraction led to film formation when combined with the xylan molecules.



Figure 3.4 Photograph of 10% (w/w) birchwood xylan film prepared by using the washing solution left after the xylan extraction.

The surface and cross-sectional SEM images of the birchwood xylan/unknown compound composite films are given in Figure 3.5. The surface and cross-sectional areas of the films resemble to each other; both of them have distinguishable globular solid structures. The presence of those structures might be due to the high potassium hydroxide content of the solution used to prepare film forming solution. When the surface is exposed to air, potassium hydroxide molecules might form crystalline structures. Another reason may be the presence of undissolved birchwood xylan.

Afterwards, characterization studies such as DSC and TGA, were performed to identify the unknown compound. On the other hand, in parallel to the identification studies, composite xylan films containing this unknown compound were continued to prepare at various conditions and the film characterization studies were performed.



A



B

Figure 3.5 SEM images of 10% birchwood xylan and unknown molecule composite films (A) surface area (B) cross-sectional area.

3.2 Characterization of the Unknown Compound

Three xylan samples, EX, EWX and commercial birchwood, were characterized and compared by using their DSC and TGA diagrams. One can note the high similarities of the DSC diagrams of commercial birchwood and EWX samples verifying both complete removal of the impurity, and structural similarity between birchwood and cotton waste xylylans (Figures 3.6 and 3.7). However, DSC diagram of the EX (Figure 3.8) is quite different than the other two diagrams. The big difference between the DSC diagrams of the two cotton waste xylan samples (EX and EWX) and, on the other hand, the high resemblance between DSC diagrams of the EWX and birchwood xylan samples fortified the presence of the unknown compound in the extracted cotton waste xylan. The same results were also observed in TGA analysis (Figures A.1, A.2 and A.3 in Appendix).

To identify the unknown compound, ethanol in the washing solution left from the extra washing step was vaporized and the solution was cooled and centrifuged. After drying the pellet at 60°C for 48 hours, DSC analysis of this component was performed and diagram was given in Figure 3.9. The DSC diagram indicates either this unknown compound is a relatively low molecular weight compound exhibiting two characteristic melting peaks or two individual low molecular weight compounds with distinguished melting points.

Considering the possibility of the unknown compound being lignin which is a phenolic compound, the phenolic concentration was measured in the washing solution of EWX by using Folin-Ciocalteu method. As a result, the phenolic nature of the unknown compound was verified and its concentration was determined as 170 µg/ml by using catechol as standard.

Other than lignin, the phenolic compound may also be tannin. Therefore, to determine whether this phenolic compound is tannic acid or not, the DSC analysis of the tannic acid was performed and given in Figure A.4 in the Appendix A. Depending on the dissimilarity between DSC diagrams of the unknown compound

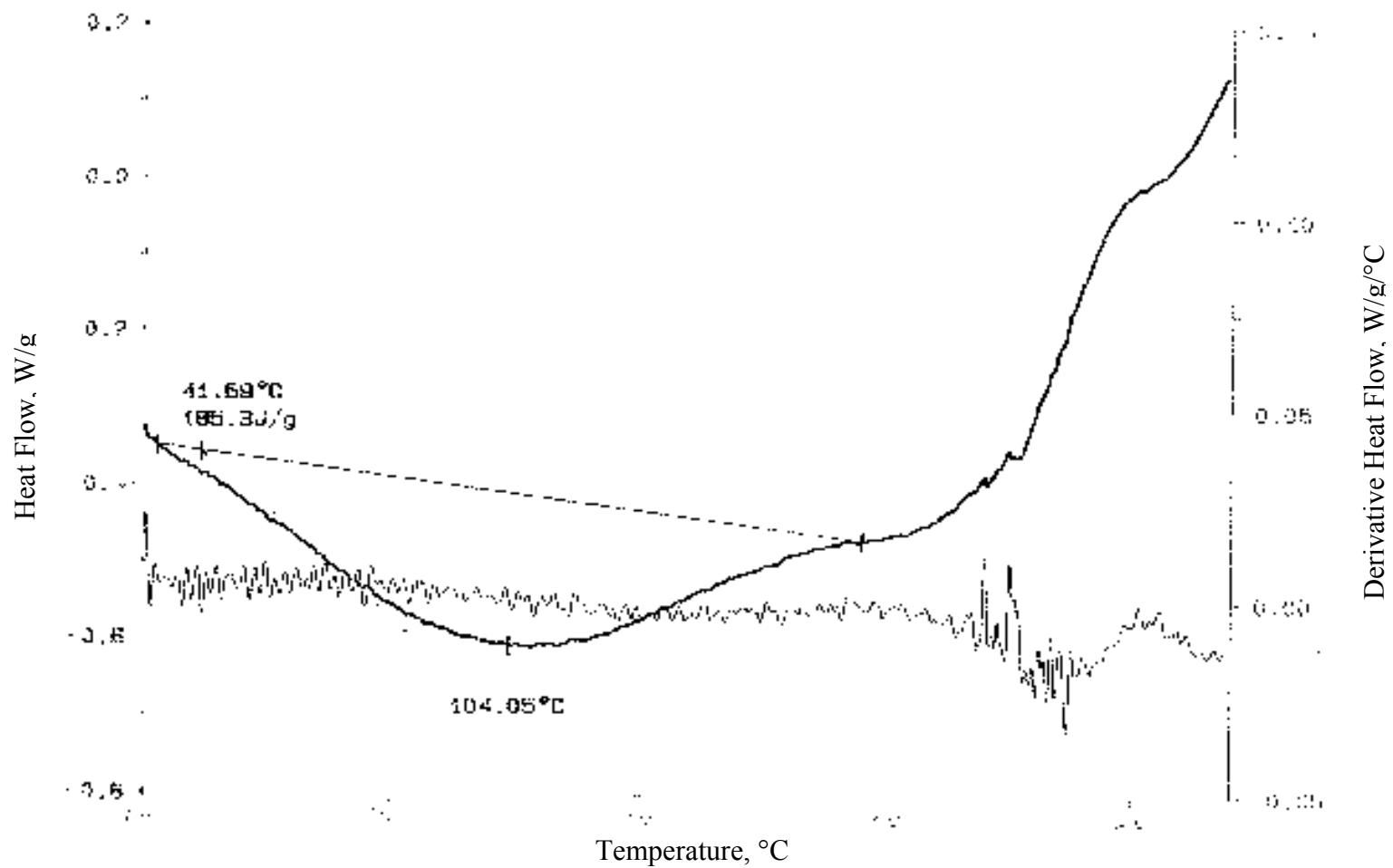


Figure 3.6 DSC diagram of extra washed cotton waste xylan dried at 60°C.

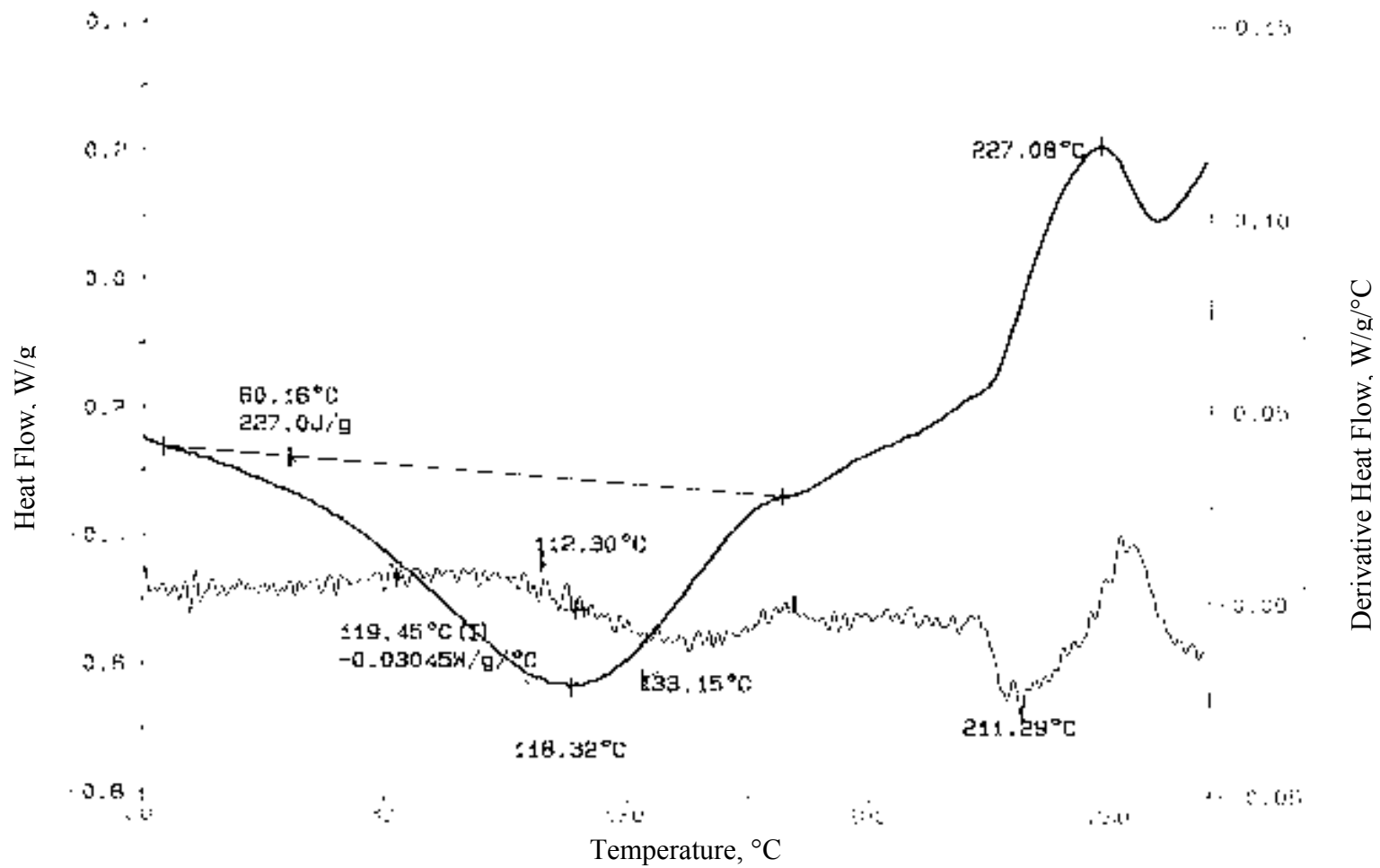


Figure 3.7 DSC diagram of birchwood xylan dried at 60°C.

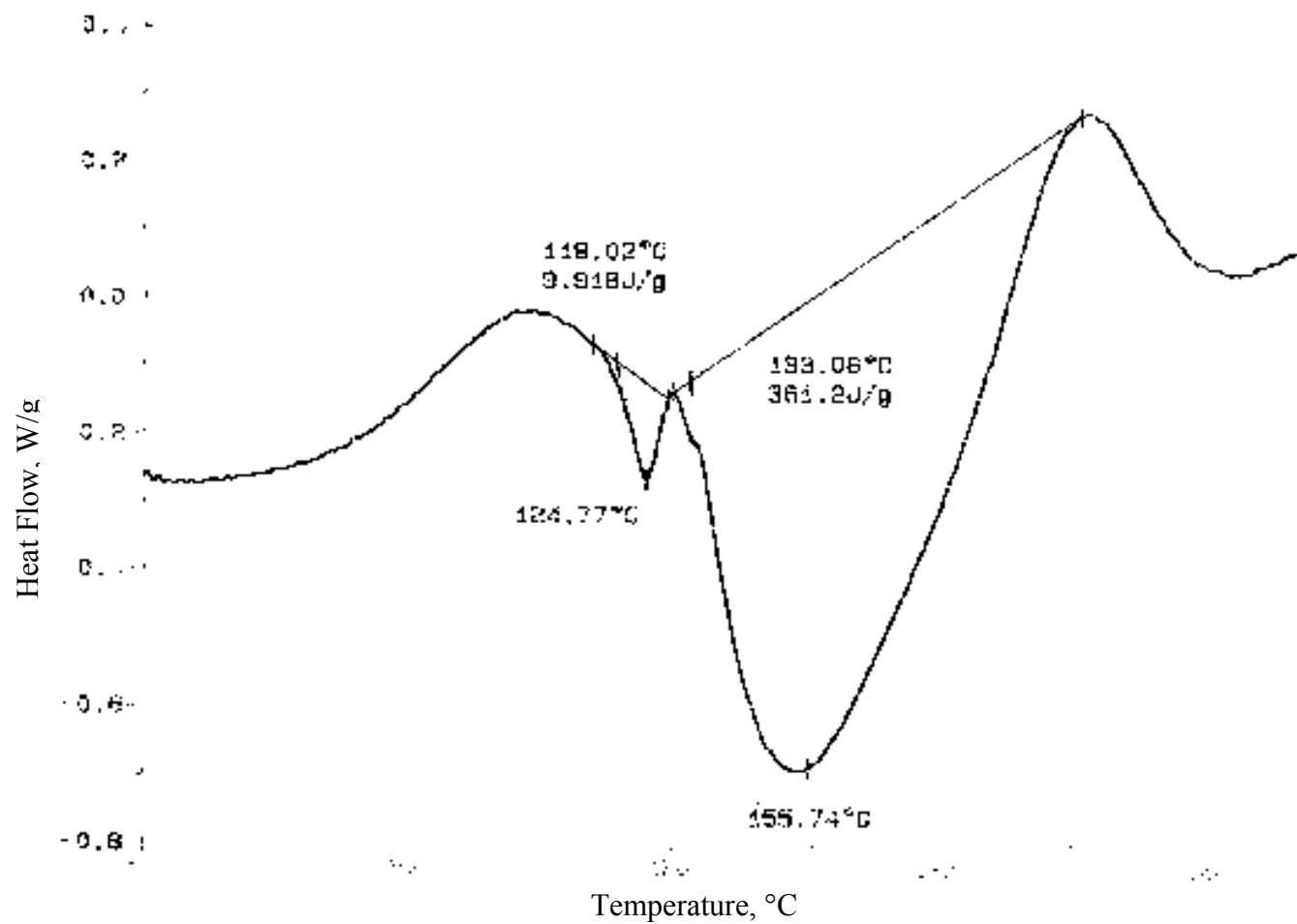


Figure 3.8 DSC diagram of cotton waste xylan dried at 60°C.

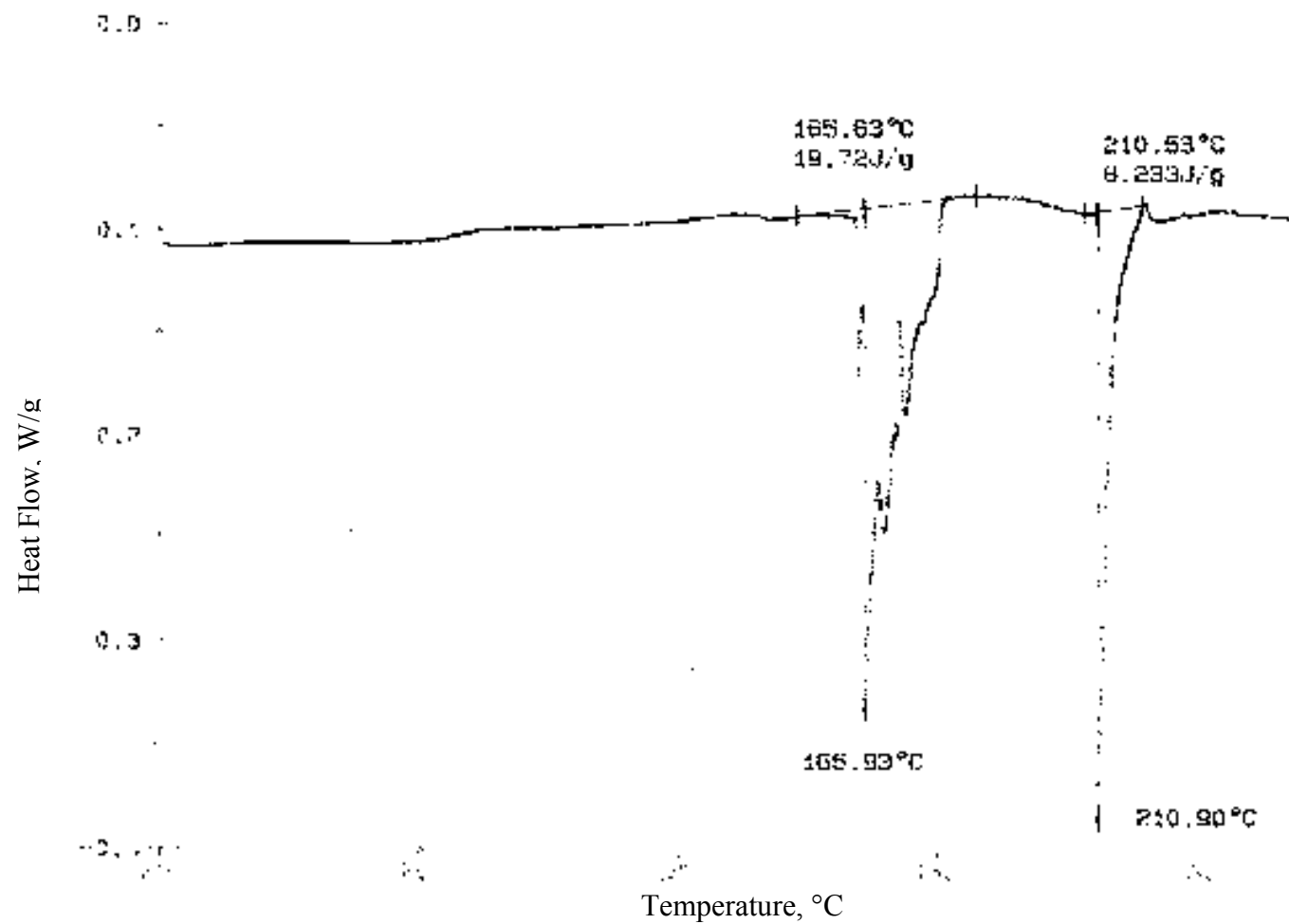


Figure 3.9 DSC diagram of the unknown compound.

and tannic acid, the possibility of the unknown compound being tannic acid was invalidated.

In addition, considering the reason of ethanol washing in the xylan extraction as lignin removal step as reported by Gabriellii and coworkers (2000), the unknown compound is determined as, most probably, lignin. Depending on mass balances, addition of 70 mg lignin to one gram of cotton waste xylan seems enough for film formation. Moreover, the aforementioned structural differences of the films prepared from the commercial and extracted birchwood xylan solutions may be the presence of lignin in the extracted xylan samples as observed in Figure 3.3. However, lignin extraction from cotton waste xylan should be done and the DSC analysis should be performed for definite verification of the unknown compound as lignin. After verification of the unknown compound as lignin, a systematic study to optimize lignin/xylan ratio should be performed to increase the quality of the lignin/xylan composite films.

On the other hand, the effect of the drying conditions on the xylan structures was studied. The DSC diagrams of the xylan samples dried at 90°C are given in Figures A.5, A.6 and A.7. Comparing these with DSC diagrams in which xylans were dried at 60°C (Figures 3.6, 3.7 and 3.8), shift of the peaks were observed indicating cross-linking at high temperature drying. That is the reason of the lack of water solubility of the xylan molecules dried at higher temperature or stored at 60°C for a prolonged period.

In the following experiments, xylan extraction was performed without extra washing step in order to obtain biodegradable films. Effects of cotton waste xylan concentration, plasticizer and gluten additions on film properties were investigated.

3.3 Effect of Xylan Concentration of the Film Forming Solution on Film Properties

For optimization studies, film forming solutions were prepared at different xylan concentrations. Using concentrations above 14% (w/w) resulted in too viscous film forming solutions so that the solution could not be mixed efficiently. On the other hand, decreasing xylan concentration to 5% or lower, the film forming solutions did not form continuous and self-supporting films as given in Figure 3.10.



Figure 3.10 Photograph of 5% (w/w) cotton waste xylan film.

Therefore, film forming solutions having the xylan concentrations of 8%, 10%, 12% and 14% (w/w) were prepared. The moisture content of the extracted xylan was found to be 25.46%. Actual xylan content of the film forming solutions are given in Table A.1 in Appendix. The films were tested for their thickness, mechanical properties, water solubility, water vapor transfer rate and color.

3.3.1 Film Thickness

Thickness of the packaging films is an important parameter especially in terms of the mechanical properties. The effect of xylan concentration on the film thicknesses of

the cotton waste xylan films, as given in Figure 3.11, indicated that the film thicknesses increased as the xylan concentration of the film forming solution increased, as expected. With the increasing quantity of xylan in the films, the number of the xylan layers and the number of the entrapped water molecules within the films are increasing which result in an increase in the film thickness. In order to validate this phenomenon, the moisture content of the 8% and 10% films were determined as 17.3% and 20.33%, respectively.

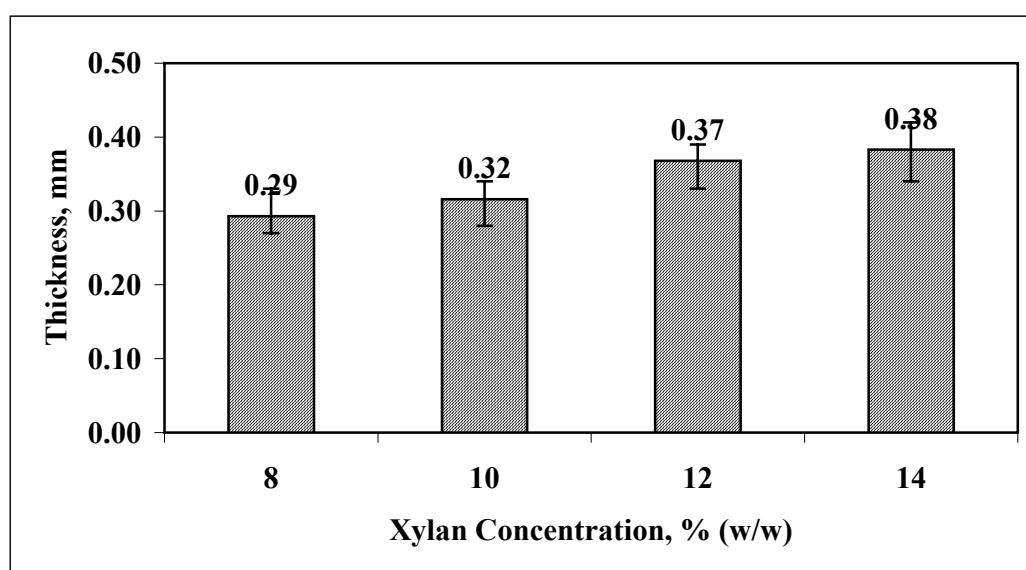


Figure 3.11 The effect of xylan concentration on cotton waste xylan film thickness.

The average thickness of the films is 0.34 mm which is approximately the same as the gluten films prepared by using a similar procedure and dried at 20°C and 35% RH (Kayserilioğlu, 2003b). The comparison of the thicknesses of the films present in the literature is difficult since the thickness is directly related with the amount of the solution casted.

3.3.2 Mechanical Properties

Mechanical properties of cotton waste xylan films were obtained from the tensile tests and hypothetical coating strength (HCS). Figures 3.12, 3.13, 3.14 and 3.15

show the effect of xylan concentration on the tensile strength, strain at break, elastic modulus and HCS values, sequentially.

Tensile strength expresses the maximum stress developed in a film during a tensile test and offers a measure of integrity and heavy-duty use potential of films (Gennadios et al., 1993). Figure 3.12 reflects the effect of xylan concentration in the film forming solution on the tensile strength of the films. The tensile strength values of the films having xylan concentrations of 10%, 12% and 14% are close to each other. The tensile strength of the 8% films is lower. The low quantity of the xylan molecules or the xylan layers may be the major factor of this decrease. Drying period might be another reason affecting the tensile strength of the films. The films were dried until they could be easily peeled from the petri plates. The drying period of the 8% films was approximately 65 hours, whereas the drying period for the others was around 48 hours. The increase in the drying period might have caused a decrease in the tensile strength of the films.

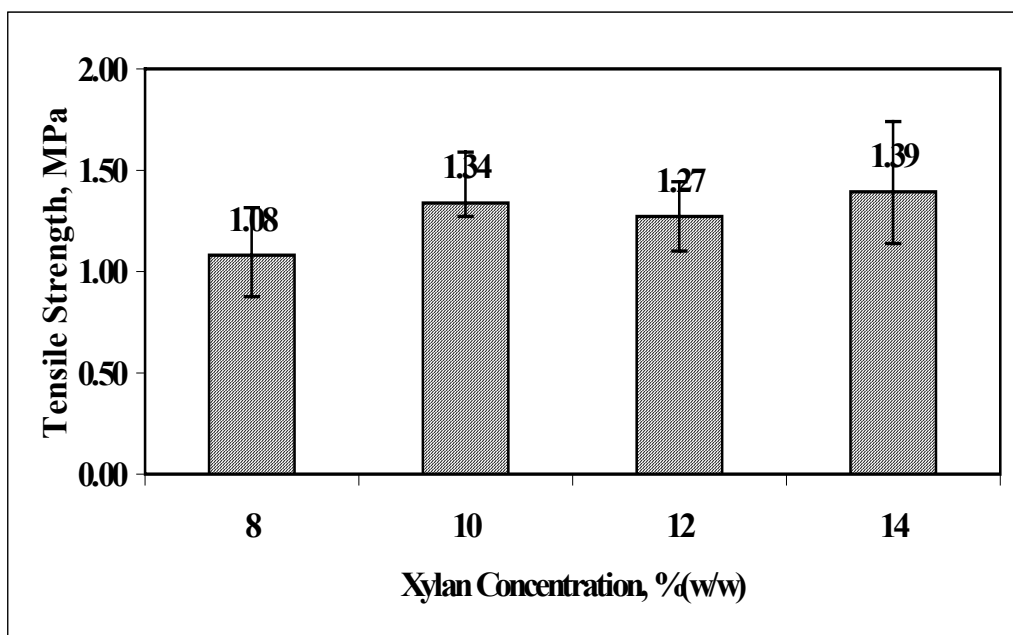


Figure 3.12 The effect of xylan concentration on the tensile strength of the cotton waste xylan films.

The average tensile strength of the cotton waste xylan films was calculated as 1.27 MPa. In the literature, the range of the tensile strength values of the packaging films is too wide. In order to make a comparison, Table 3.1 was prepared. This value is comparable with the tensile strengths of the corncob xylan-gluten and grass xylan-gluten composite films having gluten to xylan ratios of 8:2 (Kayserilioğlu et al., 2003a).

Table 3.1 Tensile strengths of various packaging films.

<i>Component</i>	<i>Tensile Strength,</i>	
	<i>MPa</i>	<i>Reference</i>
Cotton waste xylan	1.27	This study
Corn cob xylan-wheat gluten	1.30	Kayserilioğlu et al. (2003a)
Grass xylan-wheat gluten	2.00	
Wheat gluten	4.00	Kayserilioğlu et al. (2003b)
Cellulose (wheat bran and maize)	1.80-2.50	Chauvelon et al. (2000)
LDPE	13.10-27.60	Tharanathan (2003)
Hydroxypropyl cellulose	14.79-15.32	
Methyl cellulose	55.62-61.15	

Strain at break is quantitative representation of the film's ability to stretch (Gennadios et al., 1993). Figure 3.13 indicates that as the xylan concentration in the film forming solution increased, the strain at break values increased. This is probably due to the increase in the amount of the entrapped water molecules.

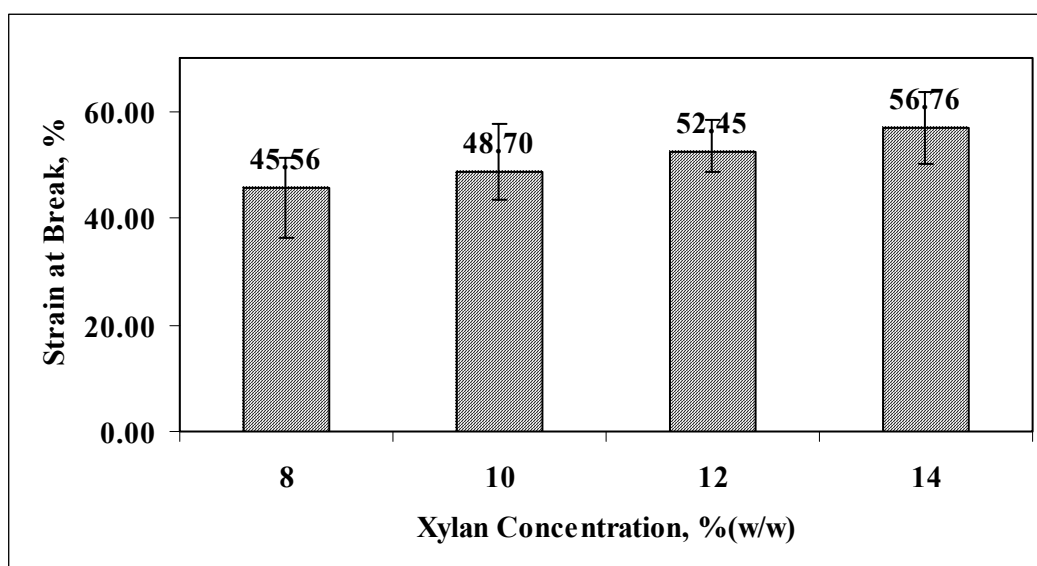


Figure 3.13 The effect of xylan concentration on strain at break values of the cotton waste xylan films.

The average value for the strain at break is 50.9%. In order to make a comparison among the strain at break values of packaging films, Table 3.2 below was prepared. As observed from the table, average strain at break value of the cotton waste xylan film is higher than the birchwood xylan-wheat gluten, grass xylan-wheat gluten, hydroxypropyl cellulose and methyl cellulose films.

Table 3.2 Strain at break values of various packaging films.

<i>Component</i>	<i>Strain at Break,</i>	
	<i>%</i>	<i>Reference</i>
Cotton waste xylan	51	This study
Birchwood xylan-wheat gluten	20	Kayserilioğlu et al. (2003a)
Grass xylan-wheat gluten	20	
Wheat gluten	250	Kayserilioğlu et al. (2003b)
LDPE	100-965	Tharanathan (2003)
Hydroxypropyl cellulose	33	
Methyl cellulose	17	

Elastic modulus is the ratio of stress to strain over the linear range and measures the intrinsic stiffness of the film (Chen, 1995). The elastic modulus values for the cotton waste xylan films are given in Figure 3.14. The increase of the xylan concentration in the film forming solution resulted in an increase in the elastic modulus values of the films indicating a rise in the intrinsic stiffness. As the number of the bonds between the molecules increase, the flexibility of the films decreased, as expected. The increase in elastic modulus by increasing xylan concentration is not linear but there is a jump between the films having 8% and 10% xylan concentration probably due to the aforementioned reasons, i.e., very low quantity of xylan or the length of the drying period of the films.

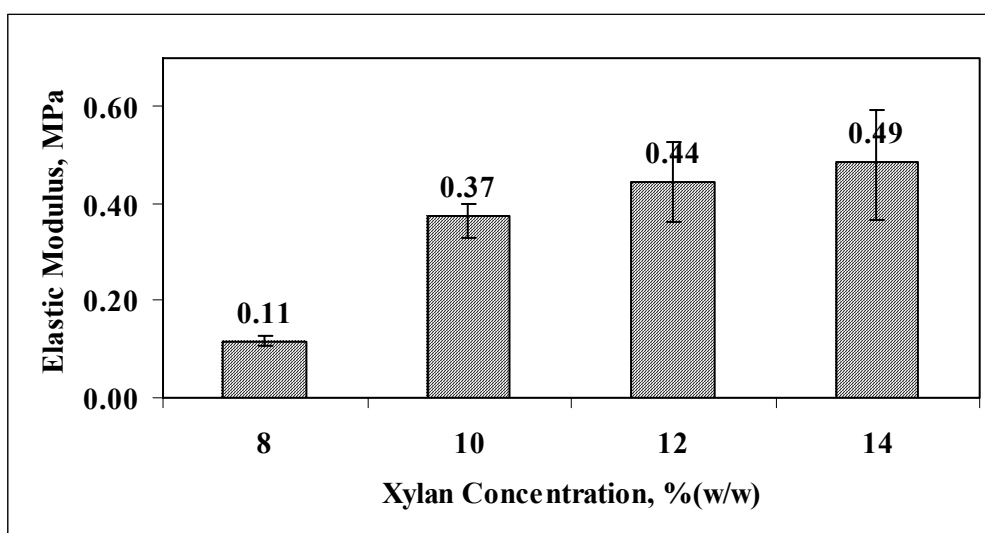


Figure 3.14 The effect of xylan concentration on the elastic modulus values of the cotton waste xylan films.

The average elastic modulus value for films is found to be 0.35 MPa which is quite lower than the values obtained for the other types of packaging films as given in Table 3.3. Therefore, it can be concluded that the cotton waste xylan films are not as stiff as the gluten, gluten-xylan and chitosan-methylcellulose composite films.

Table 3.3 Elastic modulus of various packaging films.

<i>Component</i>	<i>Elastic Modulus, MPa</i>	<i>Reference</i>
Cotton waste xylan	0.35	This study
Birchwood xylan-wheat gluten	140	Kayserilioğlu et al. (2003a)
Corn cob xylan-wheat gluten	10	
Grass xylan-wheat gluten	25	
Wheat gluten	70	Kayserilioğlu et al. (2003b)
Chitosan-methylcellulose	2.5	Garcia et al. (2004)

Hypothetical coating strength (HCS) is the ratio of the tensile strength to elastic modulus and is an indicator for a film's hypothetical performance as a coating material (Joshi et al., 1989). The larger ratio would suggest the most desired coating for mechanical protection (Rowe, 1983). The HCS values for the cotton waste xylan films are given in Figure 3.15. The values for 10%, 12% and 14% films are close to each other. As mentioned before, the increase in the drying time might have affected the results.

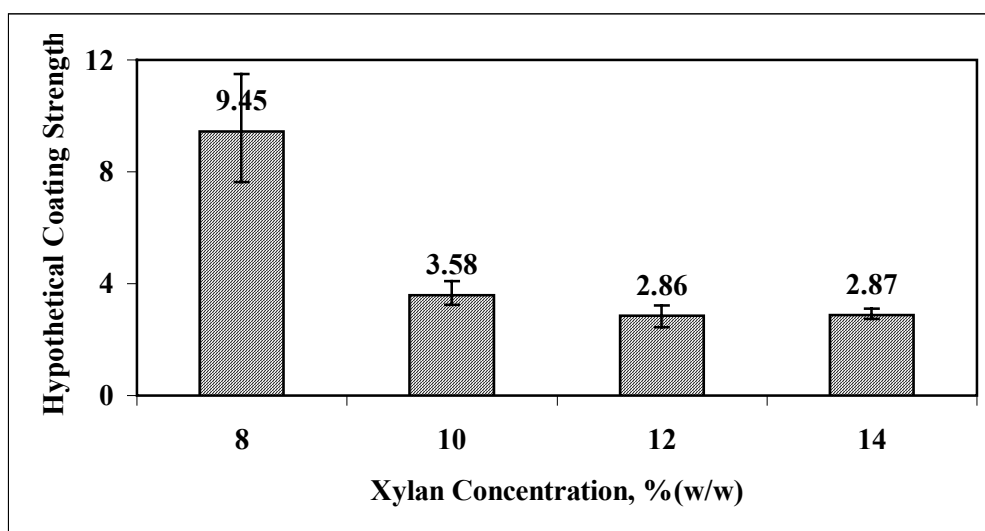


Figure 3.15 The effect of xylan concentration on the hypothetical coating strength of the cotton waste xylan films.

The average HCS value for the films is found to be in the magnitude of 4.7. This value is smaller than the value obtained for the plasticized wheat gluten films which is approximately 7.3. However, the value for the 8% films is compatible with the gluten films having a value of approximately 9.5. Another point is that the HCS values for the 10%, 12% and 14% films are close to each other and lower than the gluten films.

3.3.3 Film Solubility

Film solubility is a significant parameter for the application of packaging films. Potential applications may require low water solubility to enhance product integrity and water resistance. On the other hand, in some cases such as food coating, high film solubility in water, before consumption of the product, might be beneficial (Perez-Gago and Krochta, 2000).

The solubility of the cotton waste xylan films are given in Figure 3.16. There is no significant difference between the solubilities of the films in water. The average solubility value of the films is found to be greater than 99%, indicating that the films are nearly totally soluble in water. This value is much larger than the values obtained for other type of the packaging materials. Since the pH of the film forming solutions is high, potassium hydroxide molecules precipitate on the film surfaces resulting in an increase of the pH during film dissolution within water. The characteristic property of the hemicellulosic components; solubility at high pH values, makes the films totally soluble in water. If low solubility in water is desired, addition of some hydrophobic molecules with low solubility in water might be the solution.

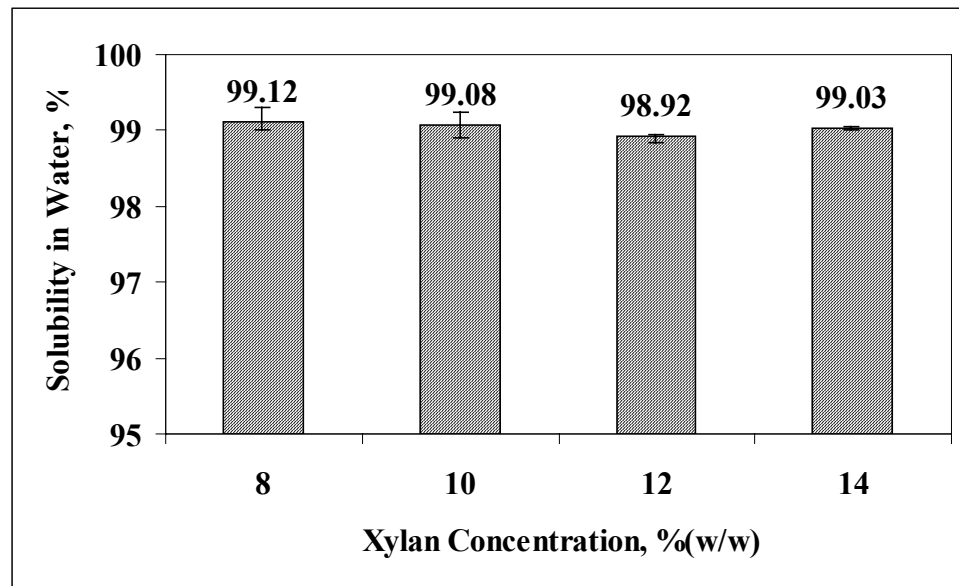


Figure 3.16 The effect of xylan concentration on water solubility of the cotton waste xylan films.

3.3.4 Water Vapor Transfer Rates

The water vapor transfer rate of the packaging films is another important property to be considered. The critical points to be considered during decision on water vapor transfer rate are the type of the material to be packaged and the storage conditions. If the packaging material is used for vegetable or fruit packaging purposes, high water transfer rate is desired considering the continuation of respiration and some of the metabolic activities. Otherwise, water vapor will condense and accumulate within the package resulting in the spoilage of the food. On the other hand, if the material is stored in a humid environment, the packaging material should withstand the humidity in order to protect the food material from bacterial or other types of spoilage.

The water vapor transfer rates of the cotton waste xylan films are given in Figure 3.17. The water vapor transfer rates of the films decreased as the concentration of the xylan in the film forming solution increased. Since the number of the xylan layers increased, the thicknesses of the films increased and the film became better barriers

to water vapor than the films having low xylan concentrations in the film forming solution.

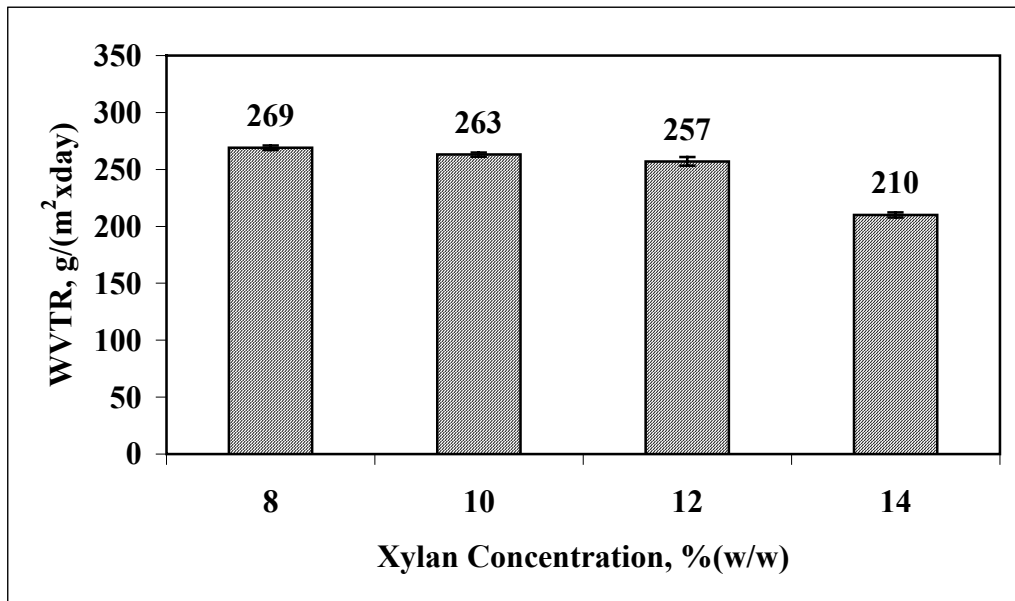


Figure 3.17 The effect of xylan concentration on water vapor transfer rate of the cotton waste xylan films.

The average water vapor transfer rate value is approximately 250 g/(m²xday). This value is much higher than other type of the packaging film materials that were studied in the literature. To illustrate, the water vapor transfer rate of the gluten and gluten-xylan composite films is in the order of the magnitude of 0.07 g/m²xday (Kayserilioğlu et al., 2003b). This is expected since the solubility of the films in water is also too high. If a lower water vapor transfer rate is required, the surface of the films might be coated by hydrophobic molecules such as lipids.

3.3.5 Color of the Films

The color of the packaging films is a significant factor that may affect the consumer choice. A dark colored packaging material might not be preferred. However, it may be desired if the packaged material is sensitive to light. The investigation of the color

of the packaging films in the literature is limited. The color of the films was measured by using a white paper as the reference color.

Figure 3.18 represents the L* values of the cotton waste xylan films. The L* value represents 'lightness', from zero (black) to one hundred (white). There seems to be no significant difference between the lightness of the films prepared at concentrations with 8%, 10% and 12%. However, the lightness of the 14% films was measured to be lower than the others. The average lightness of the cotton waste xylan films is lower than the value obtained for chitosan-methylcellulose composite films which is approximately 96 (Garcia et al., 2004).

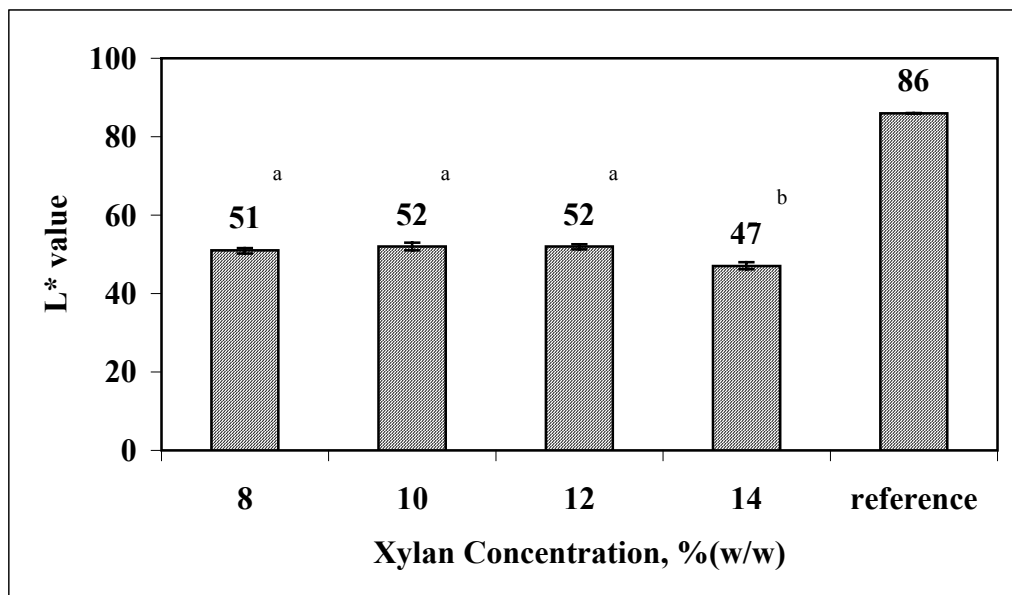


Figure 3.18 The effect of concentration on the lightness of the cotton waste xylan films.

Figure 3.19 shows the a* values of the cotton waste xylan films. The a* value represents, 'redness' or 'greenness' ranging from +60 to -60. Higher a* values indicate the presence of the redness in the films. The a* values of the films with the concentrations of 10% and 14% are found to be similar to each other. On the other hand, redness of the 8% film was observed to be a little higher and 12% film was observed to be a little lower than the others.

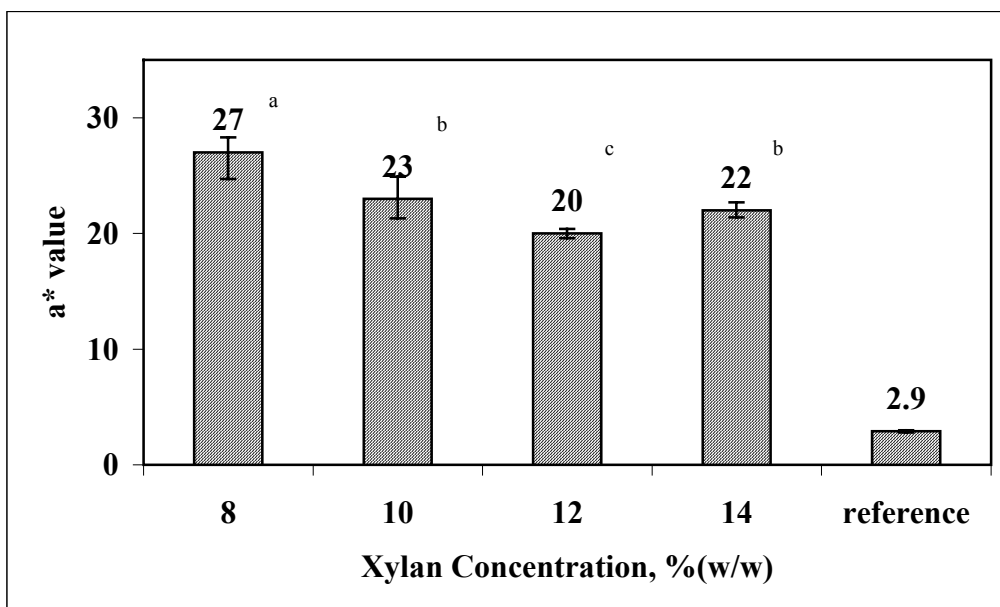


Figure 3.19 The effect of xylan concentration on the “redness-greenness” of the cotton waste xylan films.

Figure 3.20 shows the b^* values of the cotton waste xylan films. The b^* value represents, ‘yellowness’ or ‘blueness’ ranging from +60 to –60. High b^* value indicates that the color is close to yellow. As observed from the figure, the color of the films is closer to yellow. The average b^* for the films was found to be approximately 40.7. The yellowness of the films is found to be quite higher than the chitosan-methylcellulose composite films which ranges between 1- 7 (Garcia et al., 2004).

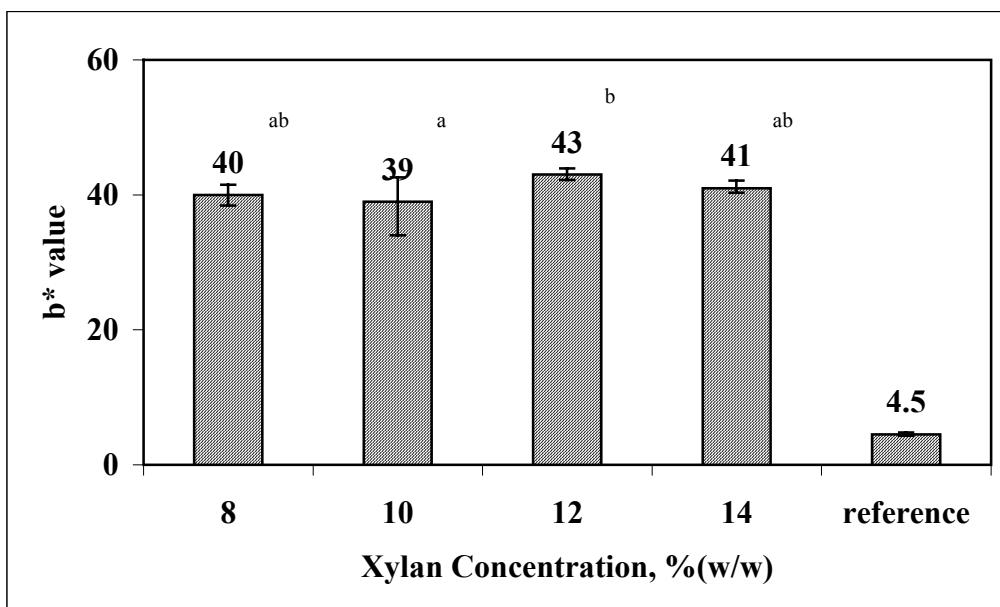


Figure 3.20 The effect of xylan concentration on the “yellowness-blueness” of the cotton waste xylan films.

Total color change from white (ΔE) was calculated from the following equation in which white color was used as the reference point, which was denoted by L_0 , a_0 and b_0 :

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

Figure 3.21 shows the total color change of the cotton waste xylan films in comparison with white paper. The values for the 10% and 12% films are close to each other. The values for 8% and 14% films are higher than the other ones. As it was mentioned previously, the main reason of the higher values should be the higher redness of 8% films and the lower lightness of the 14% films. Nevertheless, the values are not much different from each other.

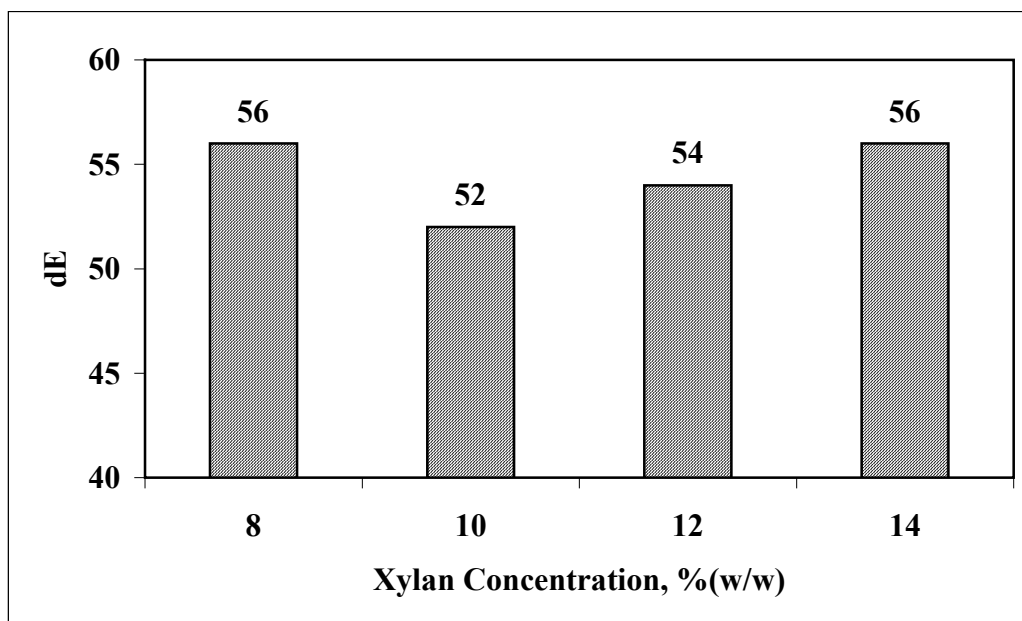


Figure 3.21 The effect of xylan concentration on the total color change (ΔE) values of the cotton waste xylan films with respect to white paper.

3.4 Effect of Plasticizer on Film Properties

A plasticizer has been defined as a small, low-volatile molecule of a chemical nature similar to that of the film forming polymer. The addition of the plasticizers in polymeric materials leads to modifications in the molecular three dimensional organization and therefore in functional properties. The highest plasticizing effects are generally observed when highly hydrophilic and small plasticizers are used. They generally increase extensibility, distensibility and flexibility and decrease cohesion, elasticity, mechanical resistance and rigidity by interfering with the bonds of the polymeric molecules. Large amounts of plasticizers facilitate diffusion of molecules and have negative effects on the barrier properties of the films (Cuq et al., 1997). The commonly used plasticizers are polyols, mono-, di-, or oligosaccharides, lipids and derivatives (Gontard et al., 1993).

In this study, glycerol (2% w/w), being the most commonly used plasticizing agent in the packaging films, was added to the film forming solutions as plasticizer. As

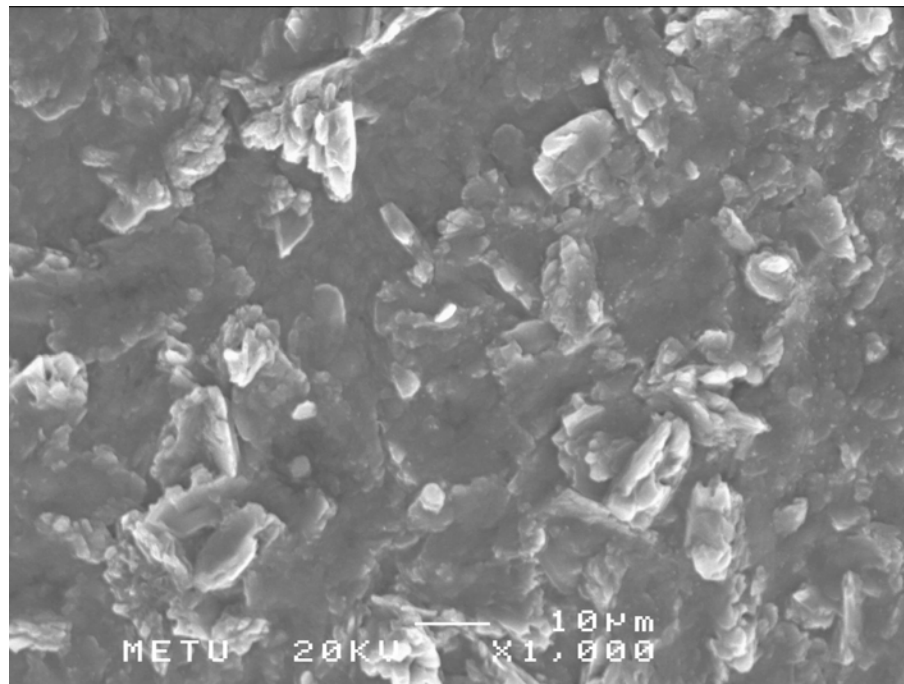
discussed in the previous section, 10% xylan concentration was used representing average properties. The films were tested for their thickness, mechanical properties, water solubility, water vapor transfer rate and color. Although the effect of glycerol addition into the film forming solution on the film properties can be guessed, the magnitude of the contribution is important in order to be used in industrial applications.

The SEM images of the surface and the cross-sectional areas of plasticized xylan films are given in Figure 3.22. The outer surface of the plasticized films is rougher than the surface area of the unplasticized xylan films. The cross-sectional area of the films looks similar to the unplasticized films. However, the layers are more globular.

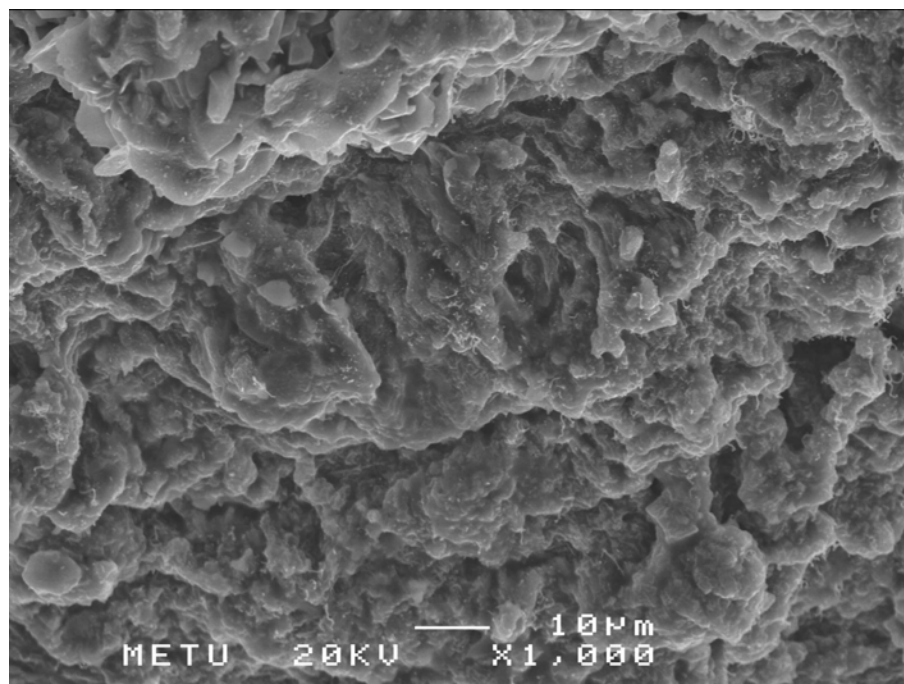
3.4.1 Film Thickness

The effect of plasticizer on the thickness values for the cotton waste xylan films is given in Figure 3.23. The thickness of the films was not significantly affected by the addition of the plasticizer into the film forming solution.

The minimal decrease of the thickness may be owing to the fact that the plasticizer molecules increase the free volume within the film structure and allow the water molecules to vaporize easily during drying. Another factor to be considered may be the average drying temperature and humidity changes during the drying step. Nonetheless, the values did not change to a great extent and they are comparable with the values obtained for the gluten films prepared by following a similar procedure which is approximately 0.31 mm (Kayserilioğlu et al., 2003b).



A



B

Figure 3.22 SEM images of plasticized cotton waste xylan films (A) surface area (B) cross-sectional area.

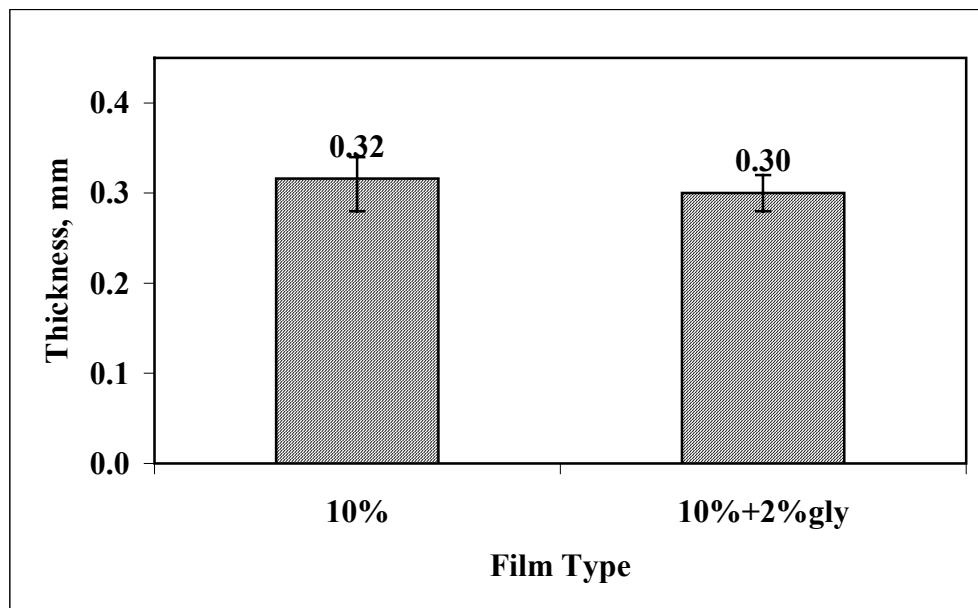


Figure 3.23 The effect of glycerol on thickness of the cotton waste xylan films.

3.4.2 Mechanical Properties

As mentioned before, mechanical properties of cotton waste xylan films were obtained from the tensile tests and hypothetical coating strength (HCS). Figures 3.24-3.27 show the effects of glycerol addition on tensile strength, strain at break, elastic modulus and HCS values, sequentially.

The tensile strength of the films decreased with the introduction of the plasticizer into the film forming solutions. On the contrary, the strain at break values increased up to 90%. Although the decrease of the tensile strength to approximately 0.8 MPa, the strain at break value of the plasticized films became comparable with the plasticized gluten films. The SEM images of the surface and cross section of the plasticized films, as given in Figure 3.22, are not as uniform as the unplasticized films. In addition, the continuity of the structures decreased. These effects may cause tensile strength to decrease and strain at break values to increase.

The elastic modulus values of the films decreased from 0.38 MPa to 0.08 MPa indicating a decrease in the stiffness of the films. Another point is that the addition of

the plasticizer increased the HCS value from approximately 4 to 10, i.e., plasticized films are more suitable for the coating purposes than the unplasticized films.

Making use of those differences in the mechanical properties of the films depends on the packaging application. In this section, the cotton waste xylan concentration in the film forming solution was used as 10%. However, this concentration might be decreased or increased depending on the desired property by using the available data given in the previous sections.

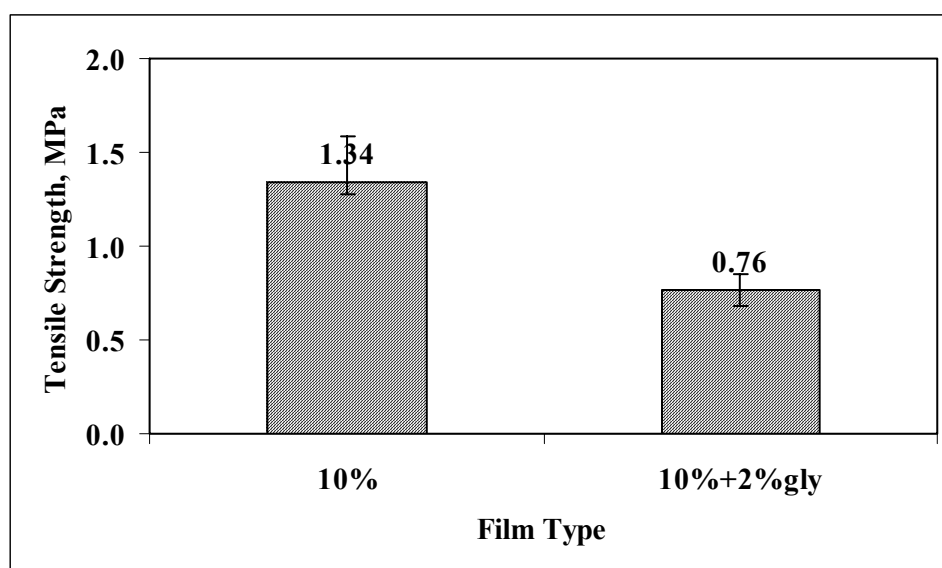


Figure 3.24 The effect of glycerol on tensile strength of cotton waste xylan films.

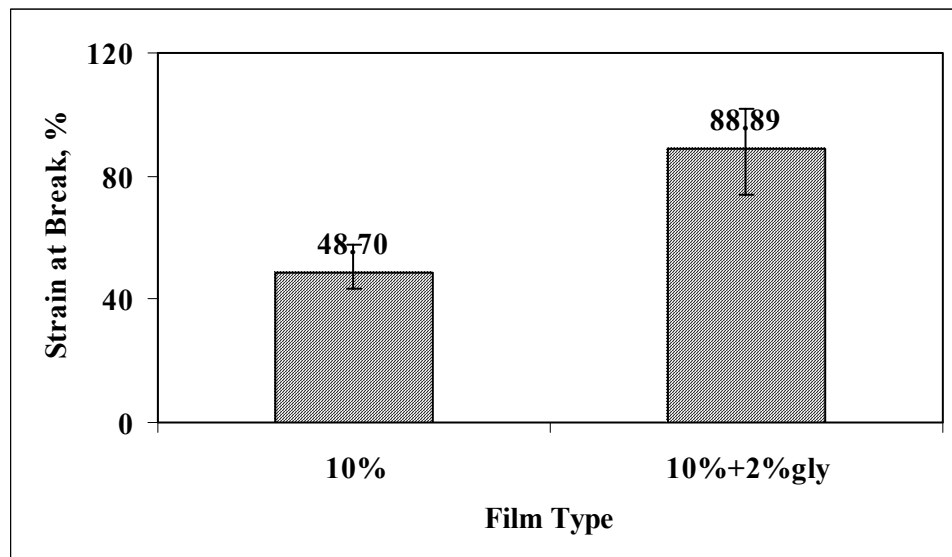


Figure 3.25 The effect of glycerol on strain at break values of cotton waste xylan films.

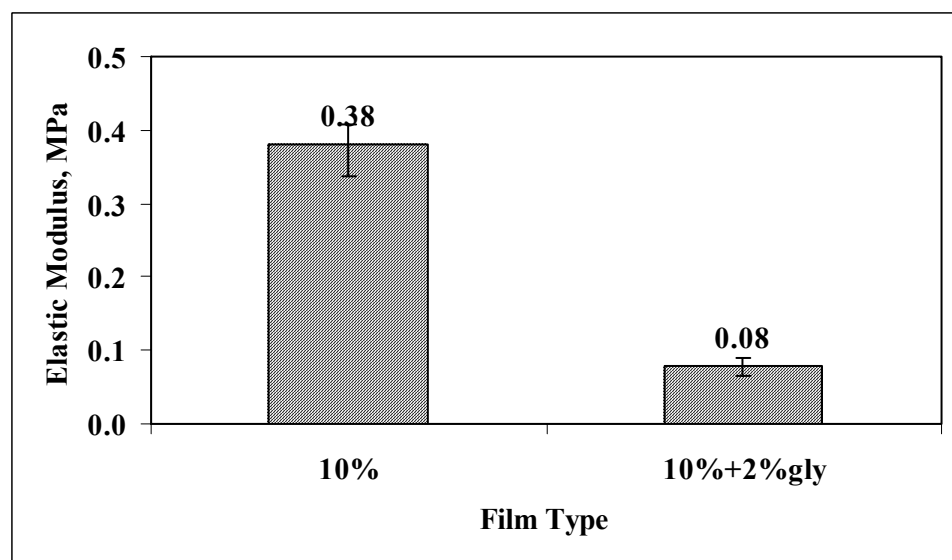


Figure 3.26 The effect of glycerol on elastic modulus of cotton waste xylan films.

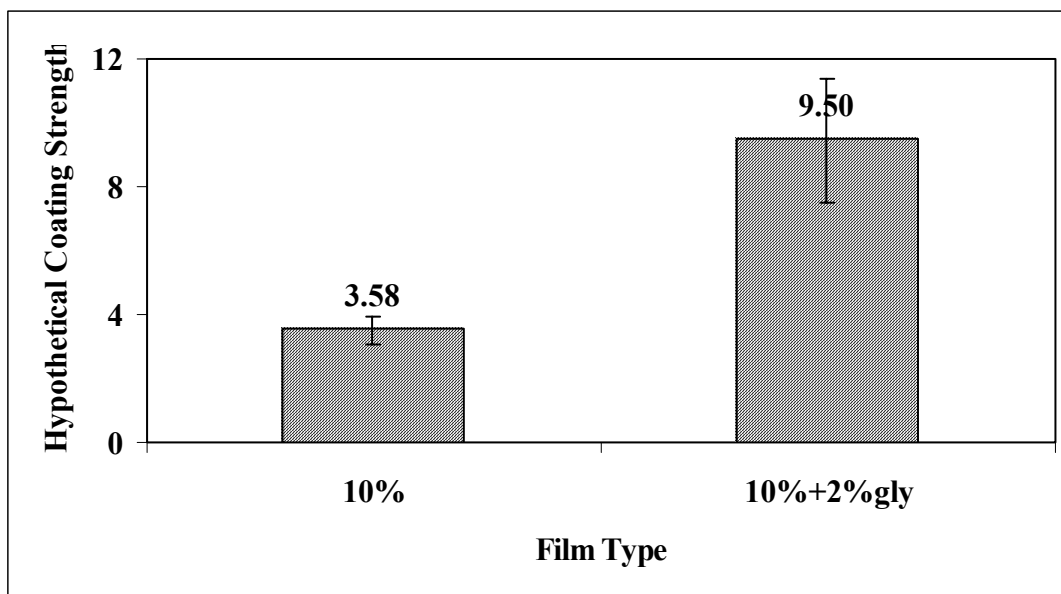


Figure 3.27 The effect of glycerol on hypothetical coating strength of cotton waste xylan films.

3.4.3 Film Solubility

Figure 3.28 shows the effect of plasticizer on the water solubility of the cotton waste xylan films. The solubility of the films decreased with the addition of the plasticizer. Nevertheless, the decrease is not pronounced to a great extent. The bond formation between the cotton waste xylan and the glycerol molecules may have decreased the water solubility of the films.

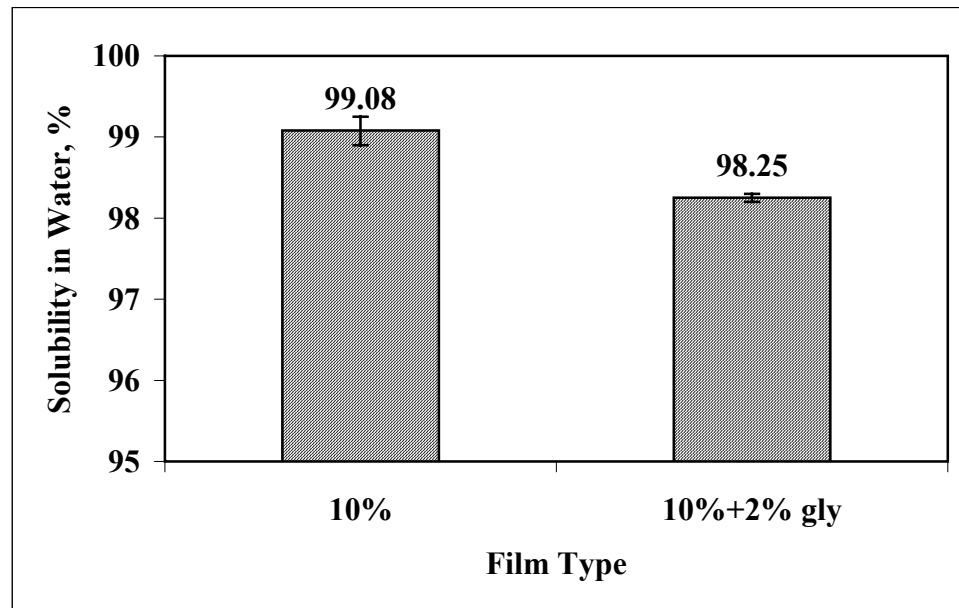


Figure 3.28 The effect of glycerol on water solubility of cotton waste xylan films.

3.4.4 Water Vapor Transfer Rates

Figure 3.29 represents the effect of glycerol incorporation into the film forming solution on the water vapor transfer rate of the films. The use of plasticizer increased the water vapor transfer rate of the films from about 263 g/(m²xday) to 271 g/(m²xday). As mentioned previously, the plasticizer interferes with the bonds among the molecules and increases the free volume. Moreover, the discontinuity of the surface and the cross-sectional areas of the plasticized films compared with the unplasticized ones corroborate this phenomenon.

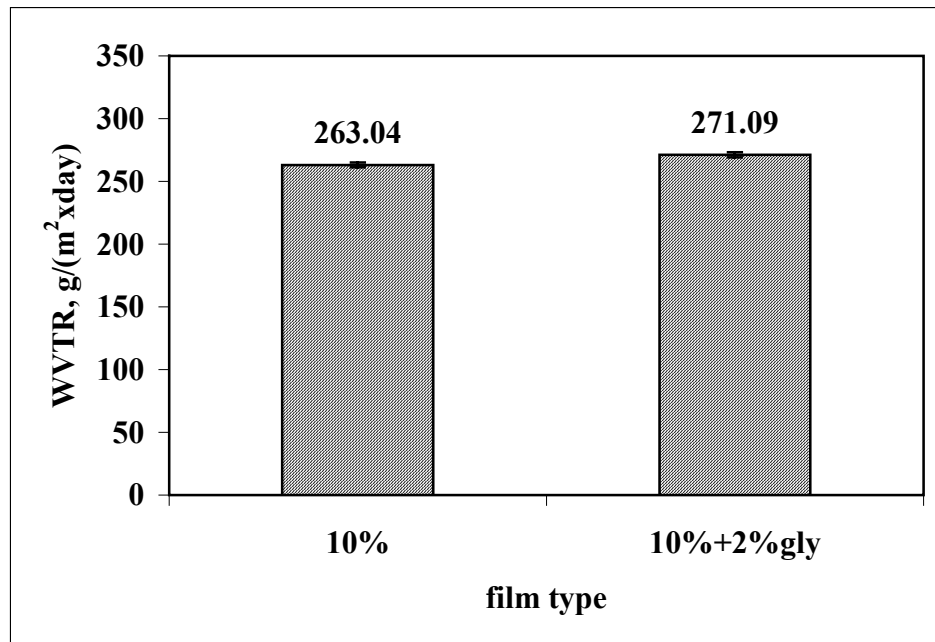


Figure 3.29 The effect of glycerol on the water vapor transfer rate of cotton waste xylan films.

This result is in conjunction with the result of Gontard et al. (1993) stating that the water vapor transmission rate of the wheat gluten films increased as the glycerol is introduced into the medium and as its concentration was increased. In another study, the water vapor transmission rate of the cellulose based films increased with increasing plasticizer level (Park and Chinnan, 1995). Similar to the unplasticized cotton waste xylan films, the water vapor transfer rates of the plasticized cotton waste xylan films are much higher than the plasticized gluten films prepared by following the same procedure which is about 0.07 g/(m²xday) (Kayserilioğlu et al., 2003b).

3.4.5 Color of the films

The effect of the plasticizer addition into the film forming solution on color is given in Figure 3.30. Only the data for the total color change is given here, since the detailed information for the specific color ranges was given mentioned previously. The total color change increased as the glycerol was introduced into the medium.

There found to be no significant difference between the a^* and b^* values with the addition of the plasticizer. The basic responsible reason is the deviation of the lightness of the films from the reference color.

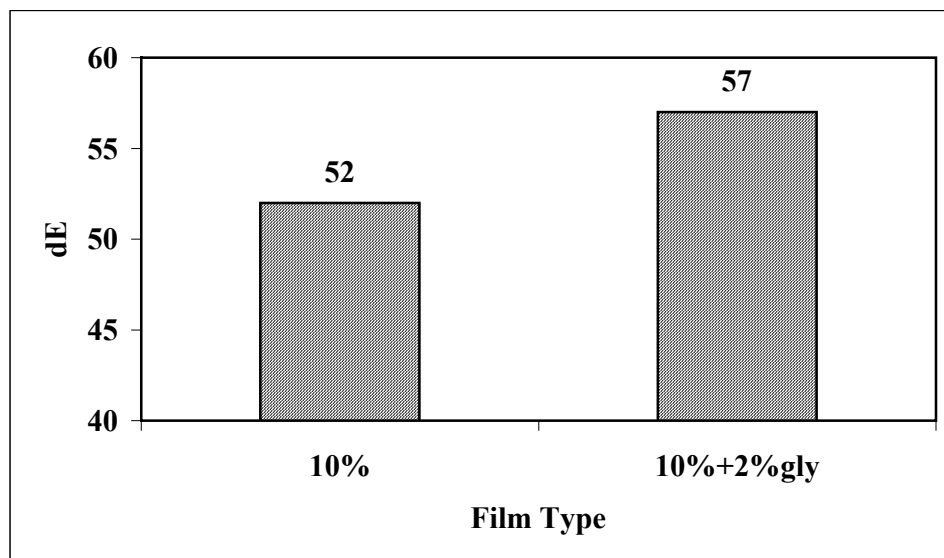


Figure 3.30 The effect of glycerol on the total color change (ΔE) of the cotton waste xylan films with respect to white paper.

3.5 Incorporation of Wheat Gluten

The studies on the use of composite films have received great attention in the recent years. Those composite films may be utilized in food industry, grafts biosynthesis and suture and wound dressing production. The properties of the composite materials may sometimes be better than the properties of the individual materials alone (Schmitt et al., 1998).

Kayserilioğlu and coworkers (2003a) worked on the incorporation of the xylan into the wheat gluten films. They have used three different types of xylan, namely, birchwood, corncob and grass and reported that xylan type and wheat gluten to xylan ratio affected the mechanical and solubility of the films. However, water vapor transfer rates were not significantly affected.

In this study, the possibility of the incorporation of the wheat gluten into cotton waste xylan films was investigated. Three different xylan to gluten ratios were used, namely, 8:2, 5:5 and 2:8. The photographs of those films are given in Figure 3.31.

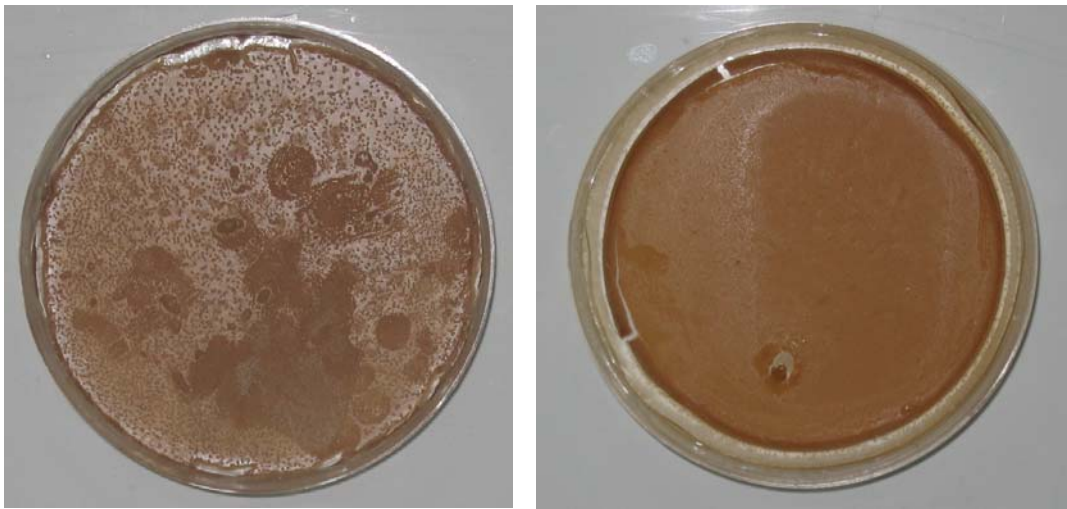
Although continuous films were obtained at all compositions, the films were not self-supporting, i.e., they could not be peeled from the petri plates since they were broken into pieces. In addition, the use of 5:5 xylan to gluten ratio resulted in phase separation.

The SEM images of the films with xylan to gluten ratios of 8:2 and 2:8 are given in Figure 3.32 and 3.33, respectively. The addition of a small amount of wheat gluten into the cotton waste xylan films made the surface and the cross-sectional areas more heterogeneous and discontinuous as in Figure 3.32 compared with the Figure 3.2. The films with the xylan to gluten ratio of 8:2 had the smoothest surface areas that have been obtained throughout this study as in Figure 3.33. However, the globularity that was observed in the cross-sectional areas of the films made the films non-self-supporting. The size of the globules was smaller compared with Figure 3.2.

Additionally, the possibility of incorporation of extra washed cotton waste xylan into wheat gluten films was investigated. Films with a xylan to gluten ratio of 2:8 were prepared. The films had continuous structures as given in Figure 3.34. However, the surface areas were heterogeneous and the films could not be peeled from the petri plates. The reason is probably the decrease in xylan solubility in water after extra washing treatment so that a homogeneous film forming solution could not be obtained which affected the film quality.

Therefore, incorporation of cotton waste xylan extracted by using both of the methods used into wheat gluten films was found not suitable. Kayserilioğlu and coworkers (2003a) used commercial birchwood xylan throughout their studies. In this study, xylan was extracted with the extraction procedure that was mentioned before. The difference between the film formation behavior of cotton waste and

birchwood xylan with wheat gluten may be due to the procedures that were followed to extract xylan.



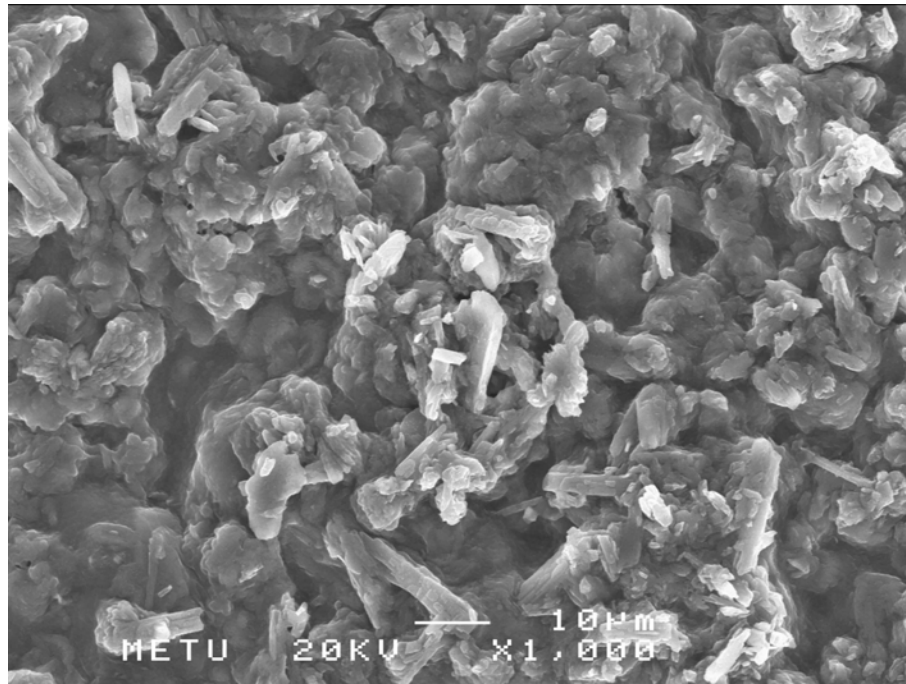
A

B

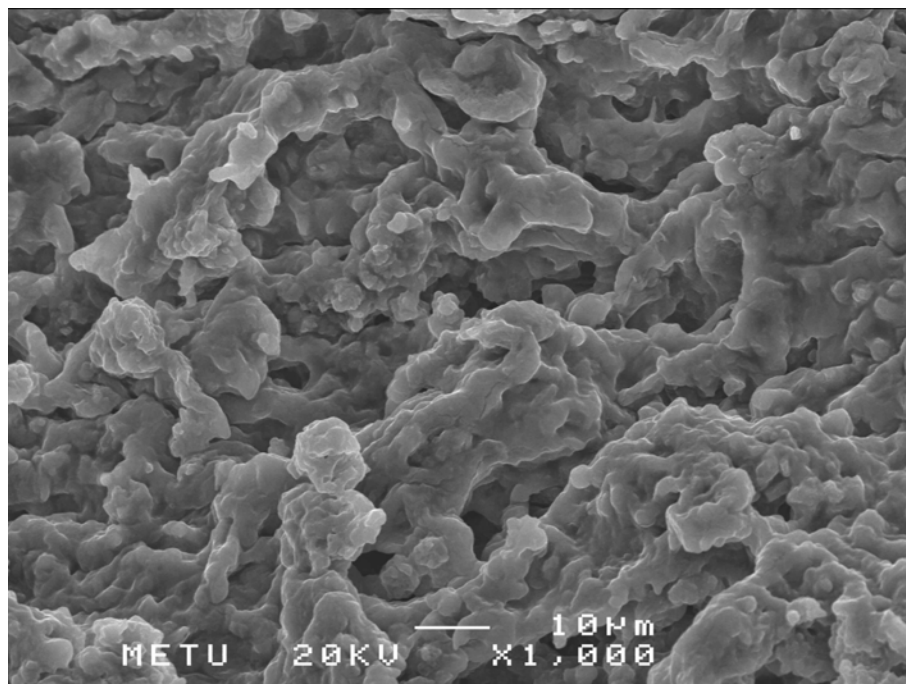


C

Figure 3.31 Photographs of cotton waste xylan and wheat gluten composite film with different xylan to gluten ratios of (A) 8:2 (B) 5:5 (C) 2:8.

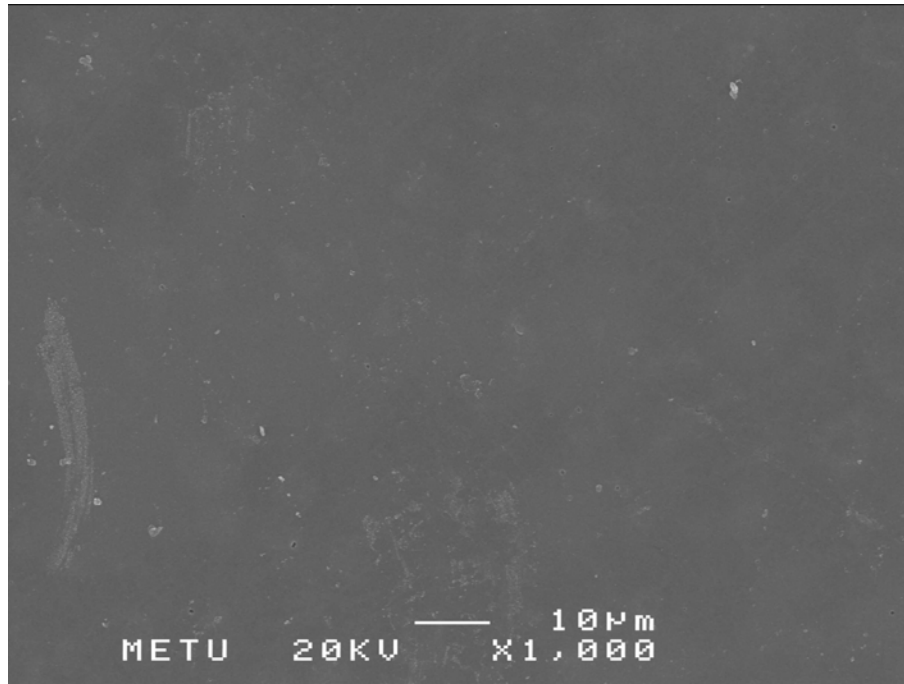


A

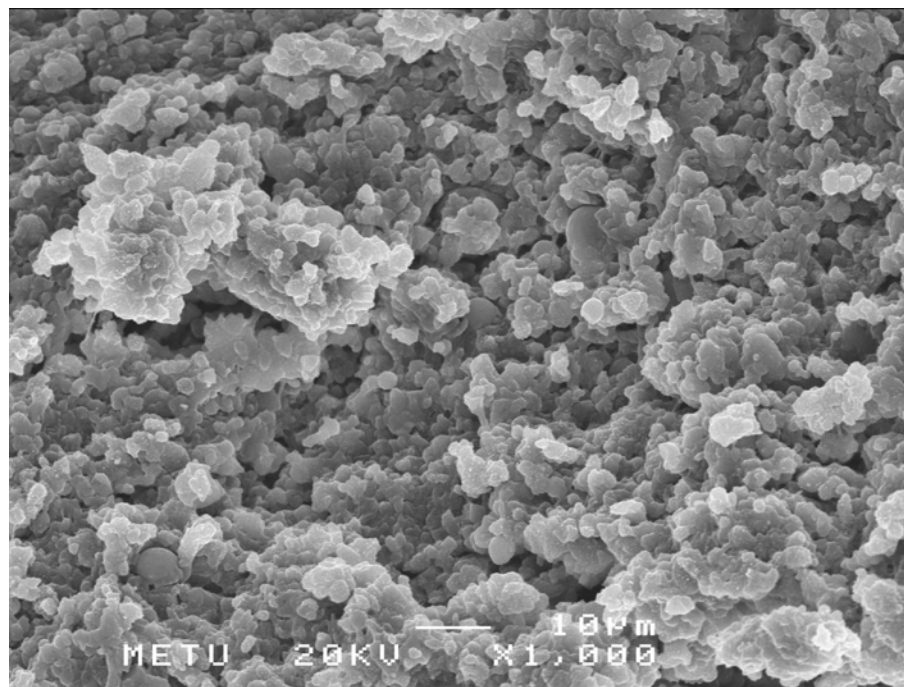


B

Figure 3.32 SEM images of cotton waste xylan and wheat gluten composite films with xylan to gluten ratio of 8:2 (A) surface area (B) cross-sectional area.



A



B

Figure 3.33 SEM images of cotton waste xylan and wheat gluten composite films with xylan to gluten ratio of 2:8 (A) surface area (B) cross-sectional area.



Figure 3.34 Photograph of extra washed cotton waste xylan and wheat gluten composite film with xylan to gluten ratio of 2:8.

CHAPTER 4

CONCLUSION AND RECOMMENDATIONS

Cotton waste xylan was used to produce biodegradable films. Pure xylan did not form films. The presence of an unknown compound, probably lignin, enhanced the film formation. The mechanical properties of the produced films were comparable to the other biodegradable films in the literature. The water solubility and water vapor transfer rate of the films were found to be quite high. The effect of glycerol and wheat gluten addition was investigated. The cotton waste xylan-wheat gluten films were not self-supporting.

For the future studies, the verification of the presence of lignin may be performed. The properties of the cotton waste xylan films may be improved by changing the lignin content or adding other biological or synthetic polymers depending on the application purposes. The degradability of the synthetic polymers might be increased as the cotton waste xylan is incorporated. The effect of the drying conditions on the film properties may be investigated. The lignin-xylan composite films from different sources may be prepared and characterized at different compositions.

REFERENCES

- Biely, P., 1993. Biochemical aspects of the production of microbial hemicellulases *in* Hemicellulose and Hemicellulases. pp.29-52. M. P. Coughlan and G. Hazlewood (Eds). Portland Press Ltd, NC, U.S.A.
- Brink, D. L., 1981. Making alcohol from cotton gin waste and stalks. Proceedings of the symposium on: Cotton gin trash utilization alternatives. University of California Cooperative Extension, Hanford, CA, 20-27.
- Beck, R. S. and Clements, D. L., 1982. Ethanol production from cotton gin trash. Proceedings of the symposium on: Cotton gin trash utilization alternatives. Texas Agricultural Experiment Service, Lubock, TX, 163-181.
- Chandra, R. and Rustgi, R., 1998. Biodegradable polymers. Progress in Polymer Science, 23:1273-1335.
- Chauvelon, G., Gergaud, N., Saulnier, L., Lourdin, D., Buleon, A., Thibault, J. F. and Krausz, P., 2000. Esterification of cellulose-enriched agricultural by-products and characterization of mechanical properties of cellulosic films. Carbohydrate Polymers, 42:385-392.
- Chen, H., 1995. Functional properties and applications of edible films made of milk proteins. Journal of Dairy Science, 78:2563-2583.

Coughlan, M. P., Tuohy, M. G., Filho, E. X. F., Puls, J., Claeysens, M., Vrsanska, M., and Hughes, M. M., 1993. Enzymological aspects of microbial hemicellulases with emphasis on fungal systems *in* Hemicellulose and Hemicellulases. pp.53-85. M. P. Coughlan and G. Hazlewood (Eds). Portland Press Ltd, NC, U.S.A.

Cuq, B., Gontard, N. and Guilbert, S., 1997. Thermal properties of fish myofibrillar protein-based films as affected by moisture content. *Polymer*, 38:2399-2405.

Donavan, J. W., 1967. Spectrophotometric observation of the alkaline hydrolysis of protein disulfide bonds. *Biochemistry Biophysics Research Communication*, 29:234.

DPT, Devlet Planlama Teşkilatı, Annual Report, 2004.

Ebringerová, A. and Heinze, T., 2000. Xylan and xylan derivatives – biopolymers with valuable properties, 1 Naturally occurring xylan structures, isolation procedures and properties. *Macromolecular Rapid Communications*, 21:542-556.

Fuller, S., Gillis, M., Parnell, C., Ramaiyer A. and Childers, R., 1997. Effect of air pollution abatement on financial performance of Texas cotton gins. *Agribusiness*, 13(5):521-532.

Gabriellii, I. and Gatenholm, P., 1998. Preparation and properties of hydrogels based on hemicellulose. *Journal of Applied Polymer Science*, 69:1661-1667.

Gabrielli, I. and Gatenholm, P., Glaser, W. G., Jain, R. K. and Kenne, L., 2000. Separation, characterization and hydrogel-forming of hemicellulose from aspen wood, *Carbohydrate Polymers*, 43:367-374.

Garcia, M. A., Pinotti, A., Martino, M. N. and Zaritzky, N. E., 2004. Characterization of composite hydrocolloid films, *Carbohydrate Polymers*, 56:339-345.

Gennadios, A., Weller, C. L. and Park, H. J., 1993. Relative humidity and temperature effects on tensile strength of edible protein and cellulose ether films. *Trans. ASAE* 36, 1867-1872.

Gontard, N., Guilbert, S. and Cuq, J.L., 1993. Water and glycerol as plasticizer affect mechanical and water vapor barrier properties of an edible wheat gluten film. *Journal of Food Science*, 58:206-211.

Griffin, A. C., 1974. Fuel value and ash content of ginning wastes. Winter Meeting of American Society of Agricultural Engineers, Oklahoma State University, Stillwater OK, 23-26.

Guilbert, S., Cuq, B. and Gontard, N., 1997. Innovations in edible and/or biodegradable packaging. *Food Additives & Contaminants*, 14: 741 –751.

Hazlewood, G. P. and Gilbert, H. J., 1993. Molecular biology of hemicellulases *in* *Hemicellulose and Hemicellulases*. pp.103-127. M. P. Coughlan and G. Hazlewood (Eds). Portland Press Ltd, NC, U.S.A.

Holton, E. E., Asp, E. H. and Zottola, E. A., 1994. Corn-starch-containing polyethylene film used as food packaging. *Cereal Foods World*, 39: 237-241.

Jeoh, T. and Agblevor, F. A., 2001. Characterization and fermentation of steam exploded cotton gin waste. *Biomass and Bioenergy*, 21:109-120.

Joshi, H. N., Kral, M. A., and Topp, E. M., 1989. Microwave drying of aqueous tablet film coatings: A study on free films. *International Journal of Pharmaceutics*, 51:19-25.

Kasarda, D. D., Bernardin, J. E. and Kohler, G. O., 1976. Wheat proteins *in* *Advances in Cereal Science and Technology*. pp: 158-236. Y. Pomeranz (Ed). St Paul, MN: American Association of Cereal Chemists, Inc., U.S.A.

Kasarda, D. D., Nimmo, C. C. and Kohler, G. O., 1978. Proteins and amino acids composition of wheat fractions *in* *Wheat Chemistry and Technology*, 3rd ed. pp: 227-299. Y. Pomeranz (Ed). St Paul, MN: American Association of Cereal Chemists, Inc., U.S.A.

Kayserilioğlu, B. Ş., Bakır, U., Yılmaz, L., and Akkaş, N., 2003a. Use of xylan, an agricultural by-product, in wheat gluten based biodegradable films: mechanical, solubility and water vapor transfer rate properties. *Bioresource Technology*, 87:239-246.

Kayserilioğlu, B. Ş., Bakır, U., Yılmaz, L., and Akkaş, N., 2003b. Drying temperature and relative humidity effects of wheat gluten film properties. *Journal of Agricultural and Food Chemistry*, 51:964-968.

Kersting, H. J., Lindhauer, M. G. and Bergthaller, W., 1994. Application of wheat gluten in non-food industry – wheat gluten as a natural co-binder in paper coating. *Industrial Crops and Products*, 3:121-128.

Kim, M., and Pometto III, A. L., 1994. Food packaging potential of some novel degradable starch-polyethylene plastics. *Journal of Food Protection*, 57:1007-1012.

Lim, S. W., Jung, I. K., Lee, K. H. and Jin, B. S, 1999. Structure and properties of biodegradable gluten / aliphatic polyester blends. *European Polymer Journal*, 35:1875-1881.

Makino, Y. and Hirata, T., 1997. Modified atmosphere packaging of fresh produce with a biodegradable laminate of chitosan-cellulose and polycaprolactone. *Postharvest Biology and Technology*, 10: 247-254.

Park, H. J. and Chinnan, M. S., 1995. Gas and water vapor barrier properties of edible films from protein and cellulosic materials. *Journal of Food Engineering*, 25: 497-507.

Parnell, C. B., Lepori W. A. and Capareda, S. C., 1991. Converting cotton gin trash into useable energy-technical and economic considerations. Proceedings Beltwide Cotton Conference, National Cotton Council of America, Memphis, TN, 969-972.

Perez-Gago, M. B. and Krochta, J. M., 2000. Drying temperature effect on water vapor permeability and mechanical properties of whey protein-lipid emulsion films, *Journal of Agricultural Food Chemistry*, 48:2687-2692.

Petersen, K., Nielsen, P. V., Bertelsen, G., Lawther, M., Olsen, M. B., Nilsson, N. H. and Mortensen, G., 1999. Potential of biobased materials for food packaging. *Food Science & Technology*, 10:52-68.

Puls, J. and Schuseil, J., 1993. Chemistry of hemicelluloses: relationship between hemicellulose structure and enzymes required for hydrolysis *in* Hemicellulose and Hemicellulases. pp.1-28. M. P. Coughlan and G. Hazlewood (Eds). Portland Press Ltd, NC, U.S.A.

Rowe, R. C., 1983. Correlations between the in situ performance of tablet film coating formulations based on hydroxypropylmethylcellulose and data obtained from tensile testing of free films. *Pharmaceutical Technology*, 29:205-207.

Schacht, O. B. And Lepori, W. A., 1978. Analysis of cotton gin waste for energy. Winter Meeting of American Society of Agricultural Engineers, Chicago, IL, 18-20.

Schmitt, C., Sanchez, C., Desobry-Banon, S. and Hardy, J., 1998. Structure and technofunctional properties of protein-polysaccharide complexes: A review. *Critical Reviews in Food Science and Nutrition*, 38:689-753.

Tharanathan, R. N., 2003. Biodegradable films and composite coatings: past, present and future. *Food Science & Technology*, 14:71-78.

Tharanathan, R. N. and Saroja, N., 2001. Hydrocolloid-based packaging films-alternate to synthetic plastics. *Journal of Scientific and Industrial Research*, 60:547-559.

Thomasson, J. A., 1990. A review of cotton gin trash disposal and utilization. *Proceedings Beltwide Cotton Production and Research Conference*, National Cotton Council of America, Memphis, TN, 689-705.

Weber, C., 2001. Properties of biobased packaging materials *in* *Biobased Packaging Materials*. pp 13-39. C. Weber (Ed). KVL Department of Dairy Food Science, Copenhagen, Denmark.

Wrigley, C. W., 1968a. Gel electrofocusing – a technique for analysing multiple protein samples by isoelectric focusing. *Science Tools*, 15:17.

Wrigley, C. W., 1968b. Analytical fractionation of plant and animal proteins by gel electrofocusing. *Journal of Chromatography*, 36362.

Zilliox, C. and Debeire, P., 1998. Hydrolysis of wheat straw by a thermostable endoxylanase: Adsorption and kinetic studies. *Enzyme and Microbial Technology*, 22:58-63.

APPENDIX A

Table A.1. Data for xylan concentration in film forming solution.

Xylan Concentration in film forming solution %, (w/w)	Actual Xylan Concentration in film forming solution %, (w/w)
8	5.965
10	7.455
12	8.945
14	10.435

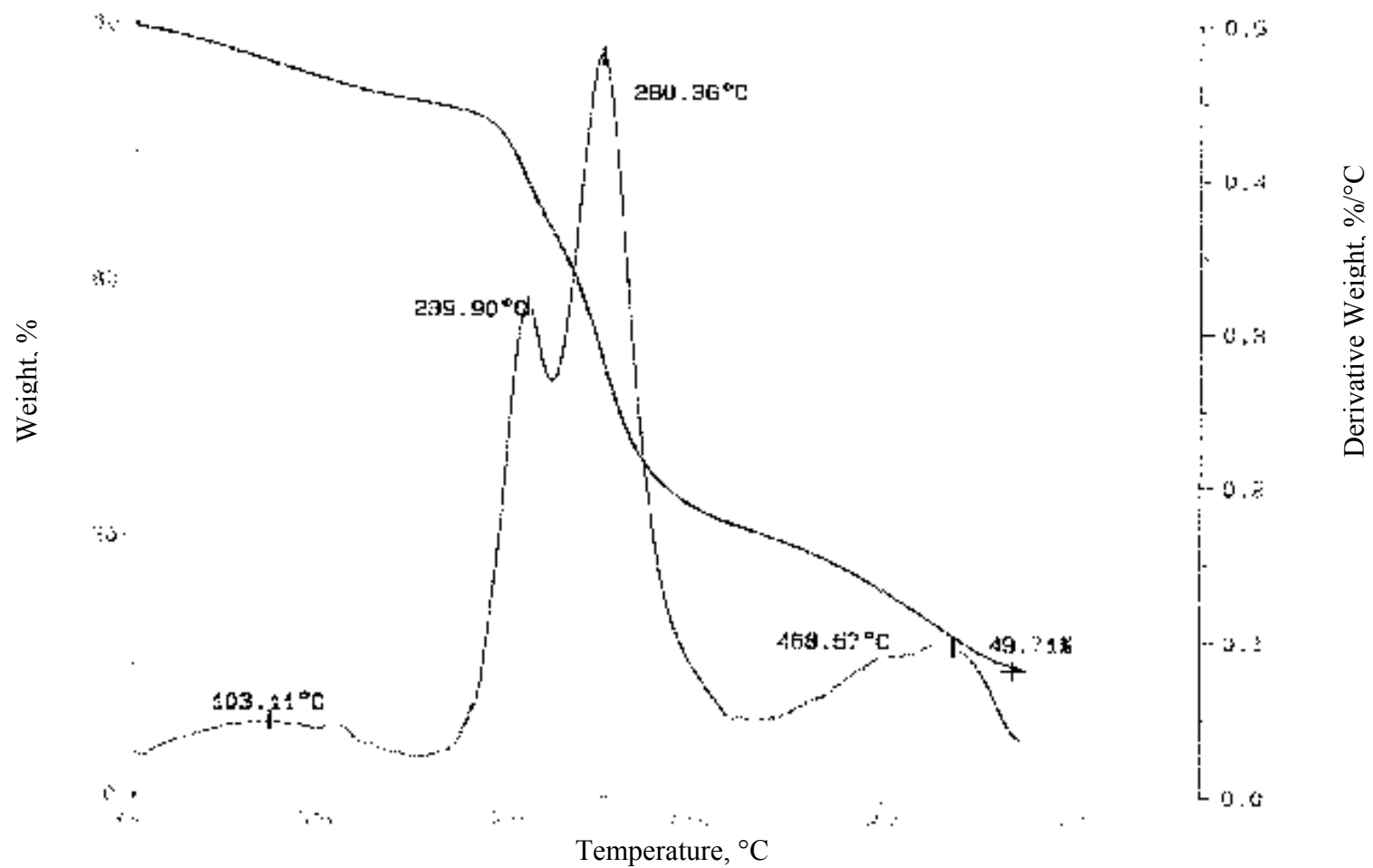


Figure A.1 TGA diagram of extra washed cotton waste xylan.

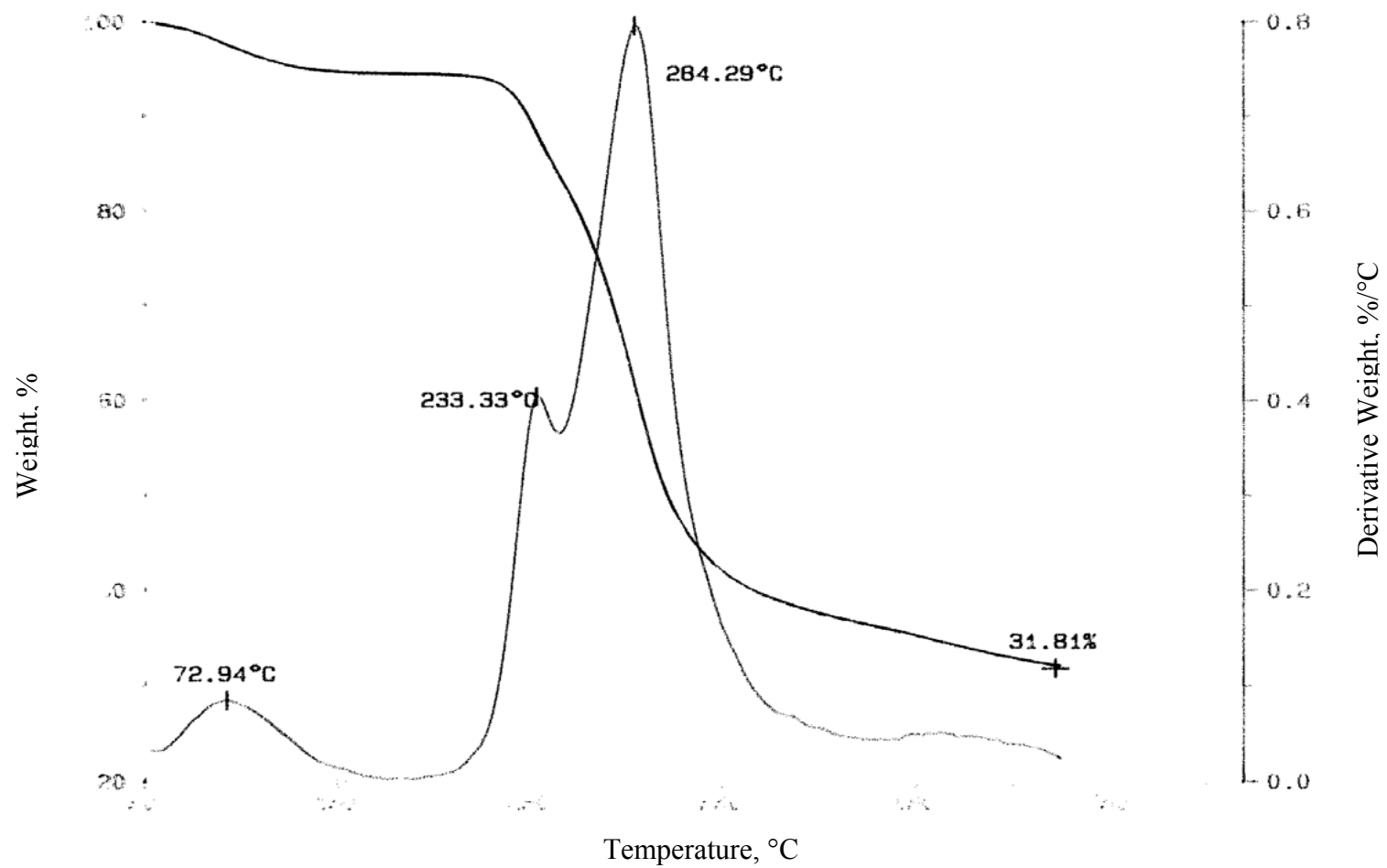


Figure A.2 TGA diagram of birchwood xylan.

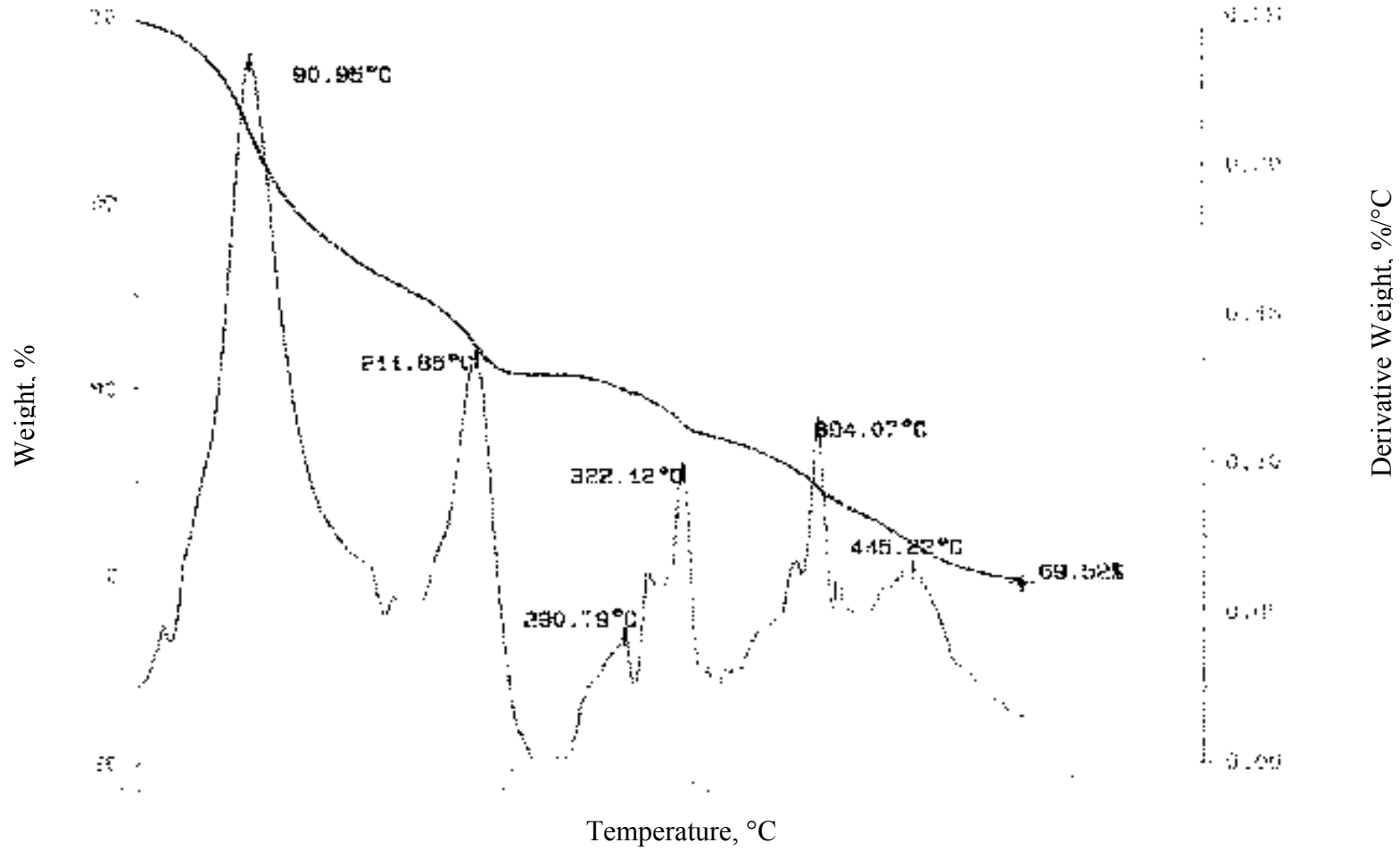


Figure A.3 TGA diagram of cotton waste xylan.

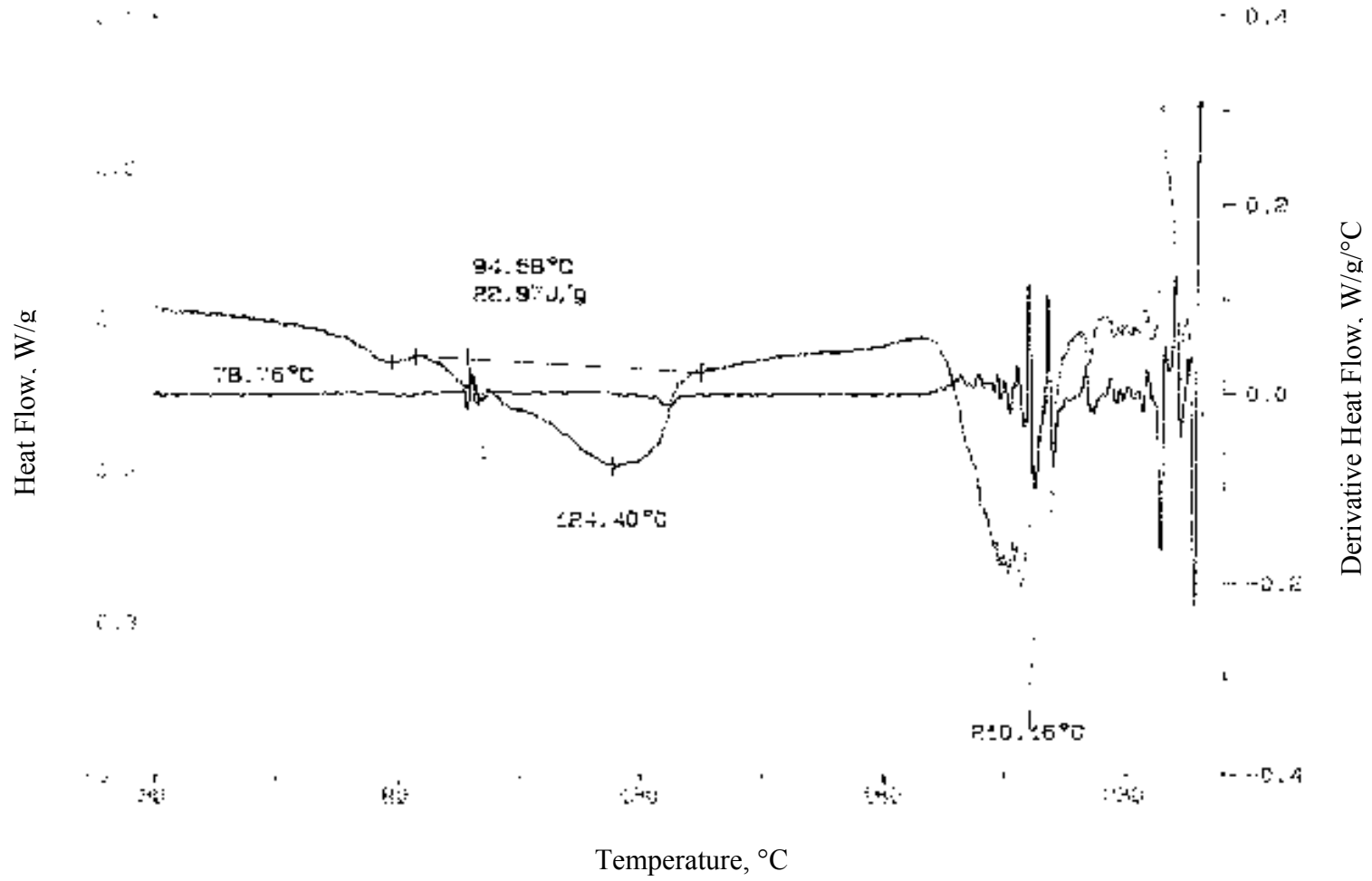


Figure A.4 DSC diagram of tannic acid.

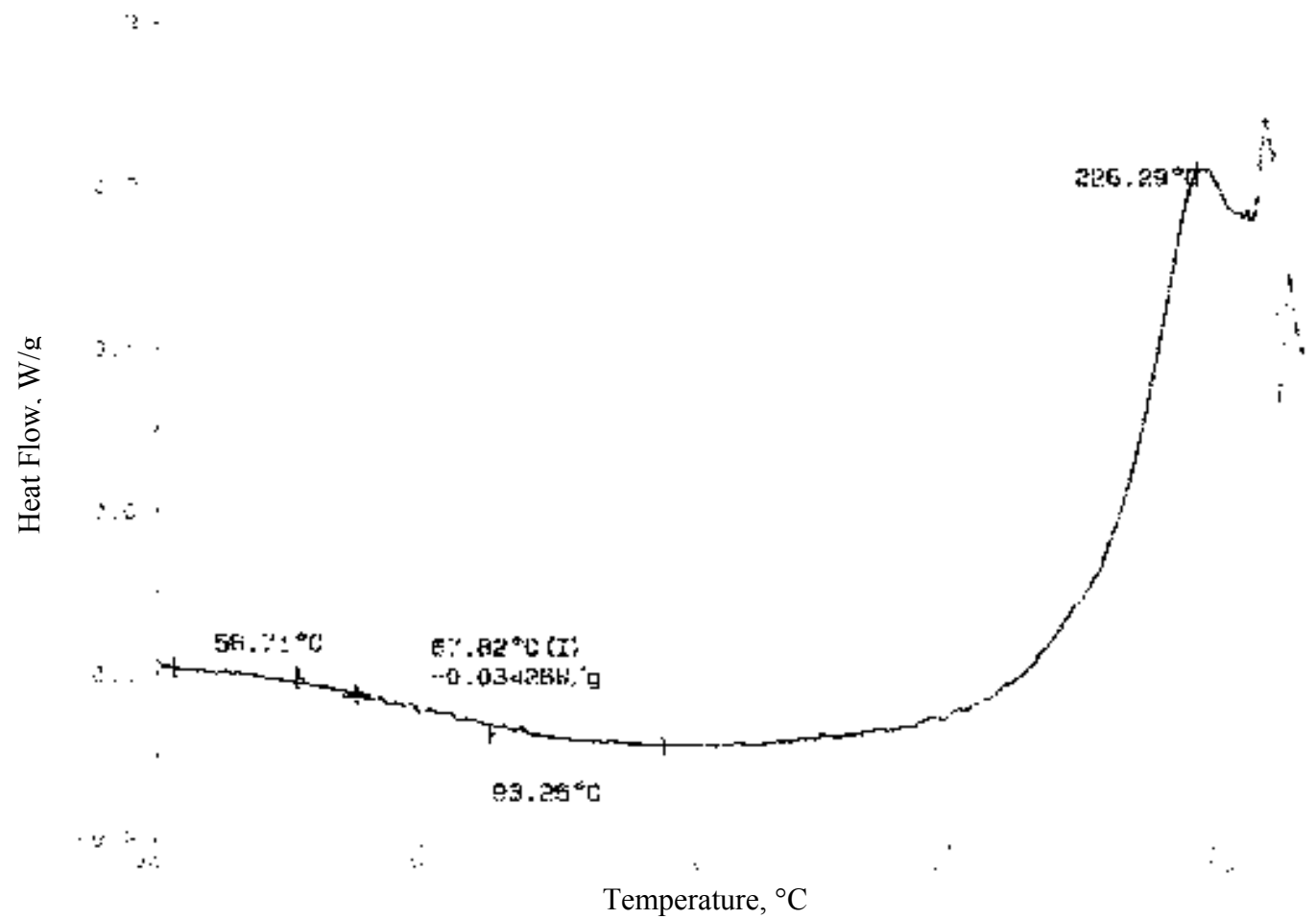


Figure A.5 DSC diagram of extra washed cotton waste xylan dried at 90°C.

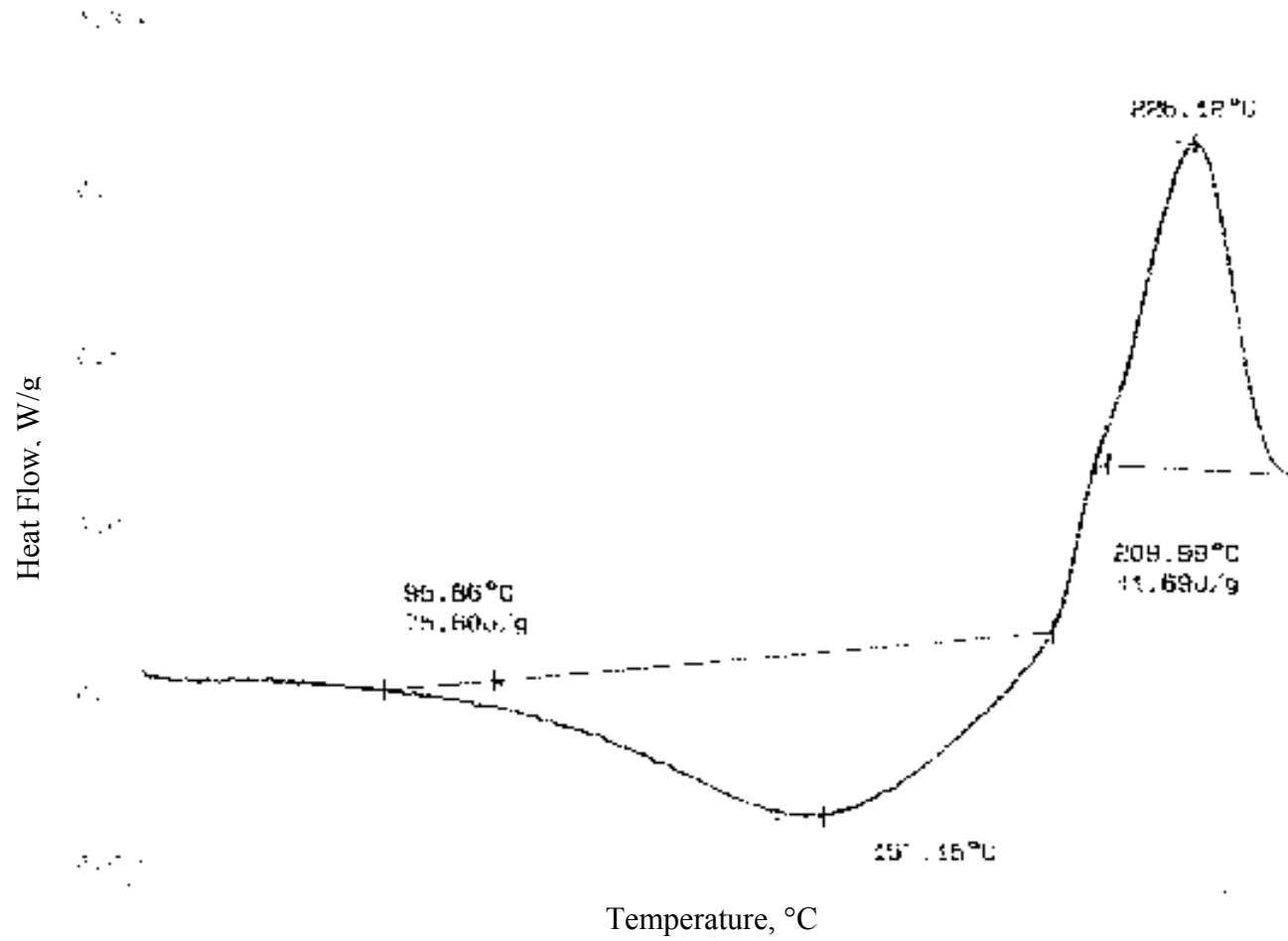


Figure A.6 DSC diagram of birchwood xylan dried at 90°C.

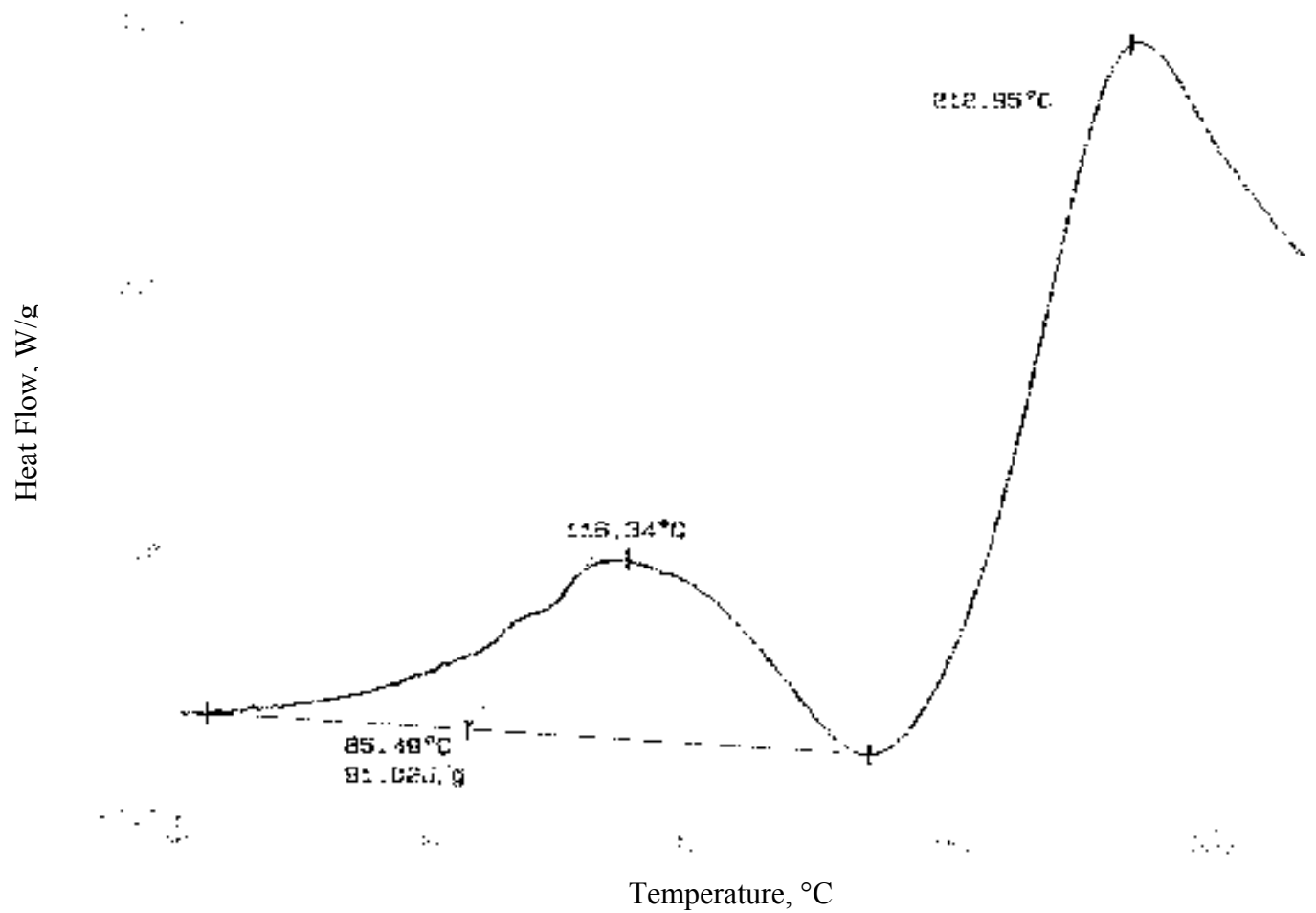


Figure A.7 DSC diagram of cotton waste xylan dried at 90°C.