Production and Characterization of Films from Cotton Stalk Xylan

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Composite film production based on cotton stalk xylan was studied, and the mechanical and physical properties of the films formed were investigated. Xylan and lignin were separated from cellulose by alkali extraction and, then, lignin was removed using ethanol washing. Self-supporting continuous films could not be produced using pure cotton stalk xylan. However, film formation was achieved using 8–14% (w/w) xylan without complete removal of lignin during xylan isolation. Keeping about 1% lignin in xylan (w/w) was determined to be sufficient for film formation. Films were produced by casting the film-forming solutions, followed by solvent evaporation in a temperature (20 °C) and relative humidity (40%) controlled environment. The elastic modulus and hypothetical coating strength of the films obtained by using 8% xylan were significantly different from the ones containing 10–14% xylan. The water vapor transfer rates (WVTR) decreased with increasing xylan concentration, which made the films thicker. The glycerol addition as an additional plasticizer resulting in more stretchable films having higher WVTR and lower water solubility values. As a result, film production was successfully achieved from xylan, which was extracted from an agricultural waste (cotton stalk), and the film-forming effect of lignin on pure xylan has been demonstrated.

KEYWORDS: Hemicellulose; xylan; lignin; cotton stalk; film; birchwood xylan

INTRODUCTION

Properties of food-packaging films are important for the preservation of food substances. Commonly used food-packaging materials are petrochemical-based plastics having many beneficial properties such as good mechanical strength and high elasticity. However, they are totally non-biodegradable, leading to serious environmental problems. Consequently, there is a shift to the production of biodegradable packaging materials from renewable biomass such as various biopolymers isolated from plant-based biomass, for example, agricultural waste materials (*1*).

Annual cotton (*Gossypium hirsutum*) production in the world is about 19 million tons, which makes up approximately half of all fiber sold in the world, and 0.7 million tons of it is produced in Turkey (*2*). Therefore, a considerable amount of cotton stalk, that is, >1.5 million tons per year (*2*), is generated as waste biomass. Cotton stalk contains mainly three macro-molecules: cellulose (36%), hemicellulose (21%), and lignin (28%) (*3*). Cellulose, the most abundant biopolymer on earth, is a homogeneous polysaccharide composed of β- (*1, 4*)-linked D-glucose units. Hemicellulose, on the other hand, is not a single homogeneous polymer like cellulose but contains different heterogeneous polymers such as xylan, galactan, and mannan. The most common hemicellulosic biopolymer is xylan, which is considered to be the second most abundant polysaccharide in nature after cellulose (*4–6*), accounting for one-third of all renewable biomass available on earth (*7*). The third macromolecule, lignin, is a complex polyphenolic compound that cross-links to hemicelluloses and, together with them, fills the space between the cellulose fibrils, which are formed by cellulose–polymer interactions (*8*).

After separation of these three main polymers, cellulose can be used in mainly paper production besides many other applications. Lignin has also some utilization areas such as glue, board, and cement productions. However, hemicellulose, and more specifically xylan, do not have any application area due to its source-dependent composition, high heterogeneity, and low water solubility. Therefore, researchers have been working on the conversion of xylan into value-added products such as xylose, xylitol, ethanol, xylooligosaccharides, and xylan-based biodegradable films (*3, 9*).

There are various studies on the biodegradable packaging film made of naturally occurring biopolymers such as cellulose, chitosan, and gluten. However, literature on xylan films is limited. Film-forming properties of xylan extracted from aspen, birchwood, corncob, and grass were studied (*7, 10, 11*). In all of these studies, pure xylans from these various plant sources

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were determined as non-film-forming polymers. However, they were utilized as additives to other film-forming biopolymers, without disturbing the film formation property of those polymers. Mixtures of xylan and various amounts of chitosan were prepared, and it was observed that at as low as 5% chitosan content, the solutions started to form films upon drying. At 10%, continuous, self-supporting films were achieved. Films with 5–30% chitosan formed hydrogels when immersed into water with a degree of swelling increasing with the increase in the chitosan content. Films with >20–30% chitosan content dissolved in water (*7*). Kayserilioglu et al. (*10*) worked on the incorporation of xylan into wheat gluten films. It was found that up to 40% (w/w) xylan could be added to wheat gluten films without altering the gluten film properties significantly. Birchwood, corncob, and grass xylan were added into gluten film-forming solutions in various quantities. Tensile strength, strain at break, and elastic modulus of the films were found to be range between 1 and 8 MPa, 20 and 650%, and 5 and 140 MPa, respectively, depending on the type of the xylan used. The film solubility was between 40 and 60% depending on xylan content, and the water vapor transfer rate was not affected by the xylan additions.

The aim of this study was film production mainly from cotton stalk xylan using lignin as an additive to enhance film formation. This is the first study demonstrating the film-forming ability of lignin and continuous self-supporting film formation from xylan.

MATERIALS AND METHODS

Materials. Ground dry cotton stalk was obtained from a local cotton producer in Urfa, Turkey. Potassium hydroxide, sodium hydroxide, sodium borohydride, acetic acid, sodium bromide, potassium bromide, ethanol, and silica gel were purchased from Merck. The other chemicals used were of analytical grade from either Sigma or Merck.

Xylan Extraction. The method used by Zilliox and Debeire (*12*) was followed for the xylan extraction. One hundred milliliters of distilled water was added to 2 g of milled cotton stalk (particle size = 2.5 mm), and the sample was swelled at 60 °C for 16 h in an incubator (Nüve). The swollen sample was filtered by means of a filter paper (Whatman no. 41), and the pellet was mixed with solution containing 17 mL of 24% (w/v) KOH + 1% (w/v) NaBH₄ solution and stirred for 3 h at room temperature. Afterward, the suspension was filtered and the supernatant was mixed with 5 mL of cold ethanol solution containing 10% acetic acid and shaken for several minutes to keep some of the lignin in the xylan fraction (xylan–lignin mixture). On the other hand, to remove the lignin completely, lignin removal solution volume was increased to 85 mL. After a centrifugation step performed at 8300*g* for 20 min, the pellet was dried at 60 °C for 24 h and used as xylan source with and without lignin.

Film Production. *Cotton Stalk Xylan–Lignin Films.* Film-forming solutions with concentrations of 8, 10, 12, and 14% (w/w) were prepared by dissolving cotton stalk xylan–lignin mixture in distilled water. After 8 h of stirring on a magnetic stirrer (Heidolph, MR3001), the beakers were placed into a water bath at 70 °C for 10 min to prevent bubble formation in the films upon casting. Then, 20 g of the solution was cast into Petri dishes with a 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% to a condition so that they could be peeled from the Petri plates. Glycerol-containing films were prepared with the addition of 2% glycerol to film-forming solutions.

Birchwood Xylan–Lignin Films. Film-forming solutions (10% xylan) were prepared with the addition of different quantities of cotton stalk lignin removal solution. After preparation of the films using the same protocol, their appearances were investigated and their lignin concentrations were measured as explained below.

Film Characterization. Films were conditioned in the presence of a saturated NaBr solution at 20 °C and 60% relative humidity for at least 48 h prior to all measurements.
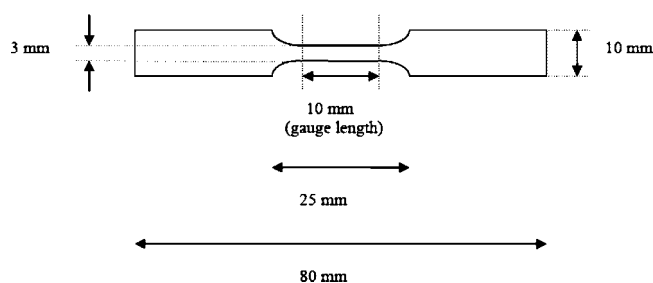

Figure 1. Shape and dimensions of the specimen used in mechanical testing procedures.

Thickness. Film thickness was measured by using a digital micrometer (accuracy = 0.01 mm) (Pass). Film strips 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.

Tensile Tests. Test specimens having the shape and dimensions given in **Figure 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.) 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. 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 the linear part of the stress–strain curves. 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 (*13, 14*).

Solubility. Films were cut, and 0.2 g of film was put into 20 g of distilled water and swollen for 24 h. Afterward, the piece of film was taken out and dried in an environment at a temperature of 20 ± 2 °C and a relative humidity of 40 ± 4% for 48 h and weighed. The solubility (%) values were calculated as follows:

$$\text{solubility (\%)} = [(\text{initial wt} - \text{final wt})/\text{initial wt}] \times 100$$

Water Vapor Transfer Rate (WVTR). Glass bottles were completely filled with dry silica particles to maintain 0% realtive humidity within the bottles. Films were clamped on top of the bottles, and bottles were placed in an environmental chamber at 20 °C and 80% relative humidity in the presence of saturated KBr solution. After incubation for 24 h, the increase in the weight of the bottles was monitored in time up to 3 days to assess the WVTR of the films (*15*). Two measurements were performed on each day. Net weight (grams) versus time (hours) plots were obtained. Net weight of the water was the difference between the measured weight of the bottle and the weight of the bottle at the first day. The WVTR values of the films were calculated as follows, and the normalized values with respect to film thickness were reported to eliminate the possible effect of film thickness on permeability (*16*):

$$\text{WVTR} = \text{slope (g/h)} \times (24\ \text{h /day})]/\text{area of the film (m}^2)$$

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

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

Color. Color of the films was measured using a Minolta color reader (CR-10) 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, whereas the *b** value represents "yellowness" or "blueness" ranging from +60 to –60. Total color

Xylan–Lignin Composite Films

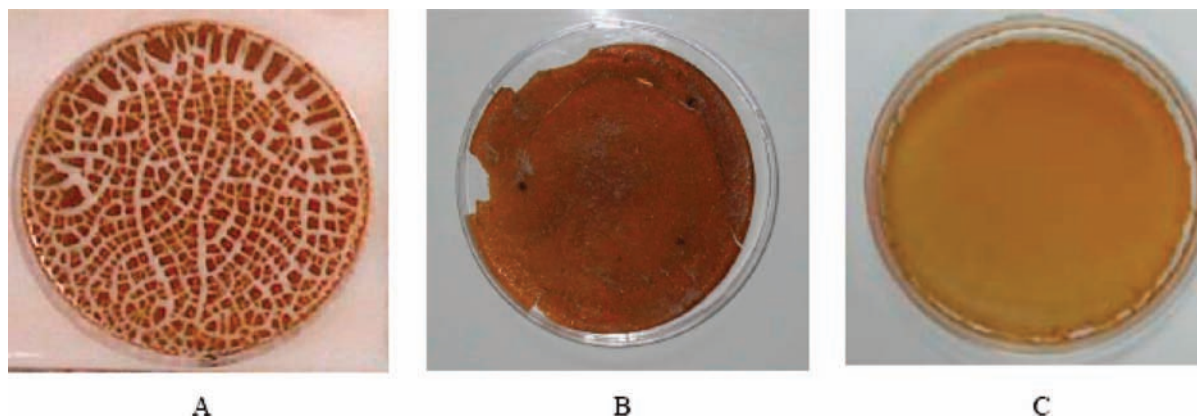*J. Agric. Food Chem.*, Vol. 55, No. 26, 2007   **10687**

Figure 2. Effect of lignin on film formation; structures obtained by using the solutions of (**A**) commercial birchwood xylan, (**B**) commercial birchwood xylan with the addition of lignin removal solution, and (**C**) cotton stalk xylan without complete removal of lignin.

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:

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

Moisture Content. The sample was cut into pieces, and the weights of the pieces were measured. The pieces were placed in an incubator at 105 °C and stored for 24 h. The final weight of the sample was measured. The moisture content of the films was calculated as follows:

$$\text{moisture content } (\%) = [(\text{initial wt} - \text{final wt})/\text{initial wt}] \times 100$$

Thermal Analysis of Xylan. Differential scanning calorimetry (DSC) analysis was carried out using DSC Gold Plus (Thermal Instruments Inc., New Castle, DE). DSC was calibrated using sapphire, indium, and tin, the first one being used for baseline calibration and the other two for temperature calibration. For accurate measurement of the glass transition temperature, DSC was also calibrated at subambient temperatures using sapphire and mercury. Nearly 2–3 mg of sample was used for each experiment, and nitrogen gas was purged at a flow rate of 20 mL/min.

Scanning Electron Microscopy (SEM) Analysis. Differences in surface film morphology were investigated using a scanning electron microscope (JEOL JSM-6400, Noran Instruments). The samples were sputter-coated with gold prior to examination.

Determination of Lignin Content. Film sample, which was dissolved in 72% H_2SO_4, was diluted to 3% H_2SO_4 by adding distilled water and boiled for 4 h under a reflux condenser. After the insoluble material had been allowed to settle, the material was filtered into the tared filtering crucible and the residue was washed with hot water. Finally, the crucible and contents were dried in an oven at 105 °C until a constant dry weight was obtained (*17*).

RESULTS AND DISCUSSION

Film Formation. In this study, xylan was extracted from cotton stalk, and a novel xylan-based self-supporting continuous film production was achieved when a minor amount of lignin was left in cotton stalk xylan. To date, film formation had not been achieved from pure xylan even with the addition of glycerol as plasticizer, as reported in the literature (*7, 10, 11*). Instead, other film-forming polymers, such as chitosan and gluten, had been added to xylan in different proportions to achieve film formation. In the case of chitosan addition, only 5% chitosan was reported to be sufficient for film formation (*7*). However, as high as 60% gluten should be added to xylan to form films having acceptable properties (*10*).

Cotton stalk, which is a renewable agricultural biomass generated in huge quantities each year in cotton-producing countries, contains three major components, namely, cellulose, xylan, and lignin. In an attempt to separate these components

and use the least utilizable component, xylan, for a value-added product formation, an alkaline extraction method was used (*12*). In this method, at first, both xylan and lignin were solved in an alkaline solution to separate alkaline-insoluble cellulose, and then lignin was removed from xylan by ethanol washing (*11*). For complete removal of lignin from ethanol-insoluble xylan, the volume of ethanol washing solution is important, so that it is possible to keep a part of the lignin by reducing the volume of the washing solution.

In this study, at first, two film-forming solutions were prepared using 10% commercial birchwood and cotton stalk xylan in distilled water; continuous films could not be produced using either birchwood or cotton stalk xylan, as reported previously (*7, 10, 11*). Afterward, some of the lignin was kept in the xylan fraction by reducing the ethanol washing solution volume during xylan extraction from cotton stalk. In addition, the washing solution containing lignin from cotton stalk was concentrated by evaporating ethanol and added to commercial birchwood film-forming solution. As observed in **Figure 2**, the addition and keeping lignin in the cases of birchwood and cotton stalk xylan, respectively, resulted in continuous and self-supporting film formation.

Three xylan samples, namely, cotton stalk xylan, commercial birchwood xylan, and lignin-containing cotton stalk xylan, were compared via DSC analysis. One can note the high resemblances of the DSC diagrams of commercial birchwood and cotton stalk xylan samples (**Figure 3A,B**), verifying both complete removal of the lignin and their structural similarity. However, the DSC diagram of the cotton stalk xylan containing lignin that results in film formation was quite different from the other two diagrams verifying the existence of a crystalline compound with a major peak around 155 °C (**Figure 3C**).

To determine the lignin concentration necessary for continuous film formation, a set of experiments was designed with commercial birchwood xylan and concentrated lignin solution produced from cotton stalk. As shown in **Figure 4**, the number of cracks decreased and the size of the film patches increased with increasing lignin concentration, and about 1% (w/w lignin/xylan) was determined to be sufficient for continuous film formation.

Effect of Cotton Stalk Xylan Concentration of the Film-Forming Solution on Film Properties. Film-forming solutions in the range of 8–14% (w/w) xylan concentrations were prepared because the addition of xylan at > 14% (w/w) caused dense and viscous film-forming solutions, which in turn brought some practical problems such as inefficient mixing, whereas decreasing the xylan concentration to 5% inhibited continuous and self-
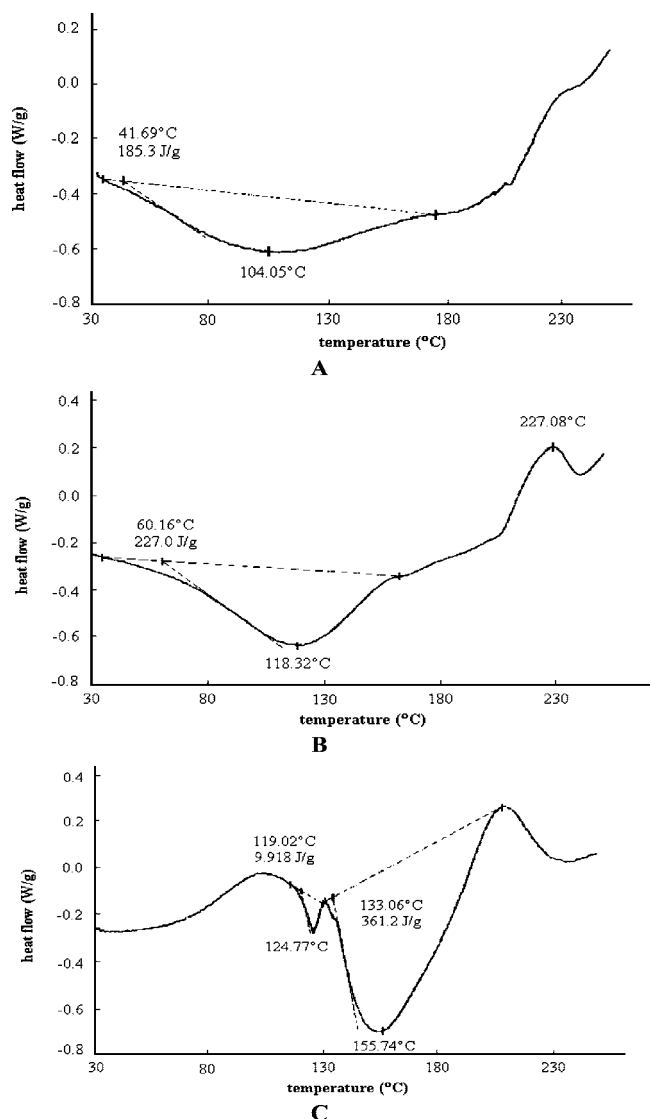
Figure 3. DSC diagrams of (**A**) pure cotton stalk xylan, (**B**) commercial birchwood xylan, and (**C**) cotton stalk xylan without removal of complete lignin.

supporting film formation. The lignin to xylan ratio in the film-forming solutions was kept constant (1% w/w, lignin/xylan). The films were tested in terms of their thickness, water solubility, water vapor transfer rate, color, and mechanical properties, and the results are given in **Table 1**.

Film Thickness. Thickness is an important parameter for packaging films in terms of mechanical properties and gas transfer rates. In this study, the film thicknesses were in the range of 0.29–0.38 mm, which increased as the xylan concentration of the film-forming solution increased. With the increasing xylan concentration of the films, the number of the xylan layers and the amount of the entrapped water within the films were increased, which resulted in an increase in the film thickness. Moisture contents of the 8 and 10% films were determined as 17 and 20%, respectively, validating the former argument.

Mechanical Properties. The films were characterized in terms of their mechanical properties obtained from the tensile tests (**Table 1**). 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 (*18*). The tensile strength values of the films having a xylan concentration of 14% were significantly higher than those of the 8% films.

The reduced amount of xylan may be the major factor of this decrease with decreasing xylan concentration. Moreover, the 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 h, whereas the drying period for the others was around 48 h. The increase in the drying period might have caused a decrease in the tensile strength of the films.

The tensile strength of the cotton stalk xylan films were in the range of 1.08–1.39 MPa. This value was comparable with the tensile strengths of the corncob xylan–gluten and grass xylan–gluten composite films having gluten to xylan ratios of 8:2 (*10*), wheat gluten films (*16*), and cellulose films prepared by using wheat bran and maize (*19*). However, it was much lower than the tensile strengths obtained for low-density polyethylene, hydroxypropyl cellulose, and methyl cellulose films, which ranged between approximately 15 and 60 MPa (*1*).

Strain at break is quantitative representation of the film's ability to stretch (*18*). As the xylan concentration in the film-forming solution increased, the strain at break values increased. This was probably due to the increase in the amount of the entrapped water amount. The strain at break values were ranged between approximately 45 and 57%, which was higher than values for the birchwood xylan–wheat gluten, grass xylan–wheat gluten, (*10*), hydroxypropyl cellulose, and methyl cellulose films (*1*), which ranged from 20 to 35%.

Elastic modulus is the ratio of stress to strain over the linear range and measures the intrinsic stiffness of the film (*20*). The increase in 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 bonds between the molecules increased, the flexibility of the films decreased. The increase in elastic modulus with increasing xylan concentration was not linear; there was a jump between the films having 8 and 10% xylan concentrations, probably due to the aforementioned reasons, that is, very low quantity of xylan or the length of the drying period of the films. The elastic modulus value for films was found to be in the range of 0.11–0.49 MPa, which was quite lower than the values obtained for other types of packaging films, indicating that the cotton stalk xylan films were not as stiff as the gluten, gluten–xylan, and chitosan–methylcellulose composite films.

HCS values for 10, 12, and 14% films were close to each other and lower than that of the 8% films, probably due to the increase in the drying time for the solution with 8% xylan concentration. The average HCS value for the films was found to be approximately 4.7. This value was smaller than the value obtained for the plasticized wheat gluten films, which was approximately 7.3. However, the value for the 8% films was compatible with the gluten films having a value of approximately 9.5.

Film Solubility. One of the important properties of packaging films is its solubility in aqueous solutions. 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 (*21*). There was no significant difference between the solubilities of the films in water with respect to xylan concentration. The solubility of the films was about 99%, indicating that the films were almost totally soluble in water. This value was much higher than the values obtained for other types of the packaging materials and might be lowered with the addition of some hydrophobic molecules with low solubility in water.
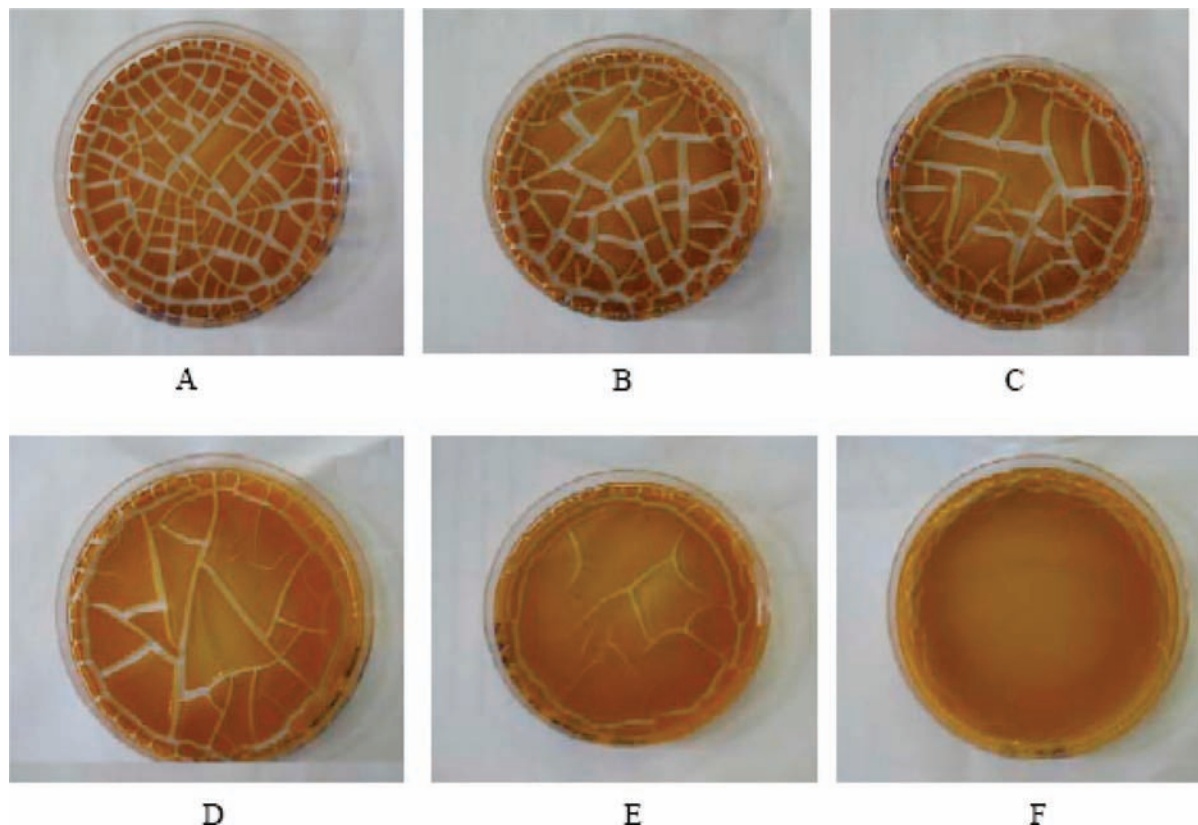
Figure 4. Effect of lignin concentration on film formation of birchwood xylan [lignin % (w/w)]: (**A**) 0.867 ± 0.005,; (**B**) 0.938 ± 0.004; (**C**) 0.999 ± 0.001; (**D**) 1.061 ± 0.001; (**E**) 1.122 ± 0.001; (**F**) 1.132 ± 0.003.

Table 1. Effect of Xylan Concentration on Film Properties[a]

	xylan concentration			
	8% (w/w)	10% (w/w)	12% (w/w)	14% (w/w)
thickness, mm	0.29 ± 0.02 a	0.32 ± 0.02 a	0.37 ± 0.02 b	0.38 ± 0.03 b
tensile strength, MPa	1.08 ± 0.15 c	1.34 ± 0.13 cd	1.27 ± 0.12 cd	1.39 ± 0.25 d
strain at break, %	45.56 ± 6.13 e	48.70 ± 5.43 ef	52.45 ± 3.46 ef	56.76 ± 5.17 f
elastic modulus, MPa	0.11 ± 0.01 g	0.37 ± 0.03 h	0.44 ± 0.06 hi	0.49 ± 0.08 i
hypothetical coating strength	9.45 ± 1.45 j	3.58 ± 0.37 k	2.86 ± 0.29 k	2.87 ± 0.11 k
solubility in water, %	99.12 ± 0.16 l	99.08 ± 0.18 l	98.92 ± 0.06 l	99.03 ± 0.03 l
normalized water vapor transfer rate, (g/m^2·day)/mm thickness	917.4 ± 7.2 m	832.4 ± 8.6 n	699.1 ± 14.8 o	574.3 ± 8.4 p
total color change	55.6 ± 1.0 r	52.4 ± 0.3 s	54.0 ± 0.2 t	56.4 ± 0.4 r

[a] Values are in terms of means ± standard deviations. Effect of xylan concentration on each property was analyzed by one-way analysis of variance (ANOVA), and the values were compared by multiple-comparison test. Different letters in each row represent a significant difference ($p \leq 0.05$).

Water Vapor Transfer Rate. The WVTR is a critical parameter for food-packaging films and depends on the type of the material to be packaged and the storage conditions. If the packaging material is used for vegetable or fruit packaging purposes, a high water transfer rate is beneficial 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 to protect the food material from bacterial or other types of spoilage. The WVTR values of the films decreased as the concentration of the xylan in the film-forming solution increased. The increased xylan quantity most probably enhanced the packing of the xylan molecules, and the films became better barriers to water vapor than the films having low xylan concentrations in the film-forming solution.

Color. The color of the packaging film is important not only from the consumer's point of view but also for the packaging of light-sensitive materials. Investigation of the color of the packaging films in the literature is limited. Total color change of the cotton waste xylan films was calculated in comparison with reference values of 86, 2.9, and 4.5 for *L*, *a**, and *b** values, respectively. The values for the 8 and 14% films were close to each other, and the values for 10 and 12% films were lower than the others. The main reason for the higher values was the high redness of 8% films and the low lightness of the 14% films.

Effect of Plasticizer on Film Properties. The addition of the plasticizers in polymeric materials leads to modifications in the molecular three-dimensional organization and therefore in functional properties (*22*). 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, and the results are given in **Table 2**. Although the effect of glycerol addition into the film-forming solution on the film properties can be estimated, the magnitude of the contribution is important in order to be used in industrial applications.

Table 2. Effect of Glycerol on Film Properties[a]

film type	10% xylan	10% xylan + 2% glycerol
thickness, mm	0.32 ± 0.02	0.30 ± 0.01
tensile strength, MPa	1.34 ± 0.13	0.76 ± 0.05
strain at break, %	48.70 ± 5.43	88.89 ± 10.09
elastic modulus, MPa	0.37 ± 0.03	0.08 ± 0.01
hypothetical coating strength	3.58 ± 0.36	9.50 ± 1.32
solubility in water, %	99.08 ± 0.18	98.25 ± 0.05
normalized water vapor transfer rate, $(g/m^2 \cdot day)/$ mm thickness	832.4 ± 8.6	904.7 ± 10.4
total color change	52.4 ± 0.3	56.4 ± 0.0

[a] Values are in terms of means ± standard deviations. Effect of glycerol addition on each property was compared by *t* test. All values for glycerol-added films were found to be significantly different from the films that include no glycerol ($p \leq 0.05$).

The SEM images of the surface and the cross-sectional areas of plasticized xylan films given in **Figures 5C,D** indicate that the outer surface of the plasticized films was rougher than the surface area of the unplasticized xylan films, and the cross-sectional area of the films (**Figures 5A,B**) looks similar to the unplasticized films; however, the layers were more globular.

The thickness values decreased with the addition of plasticizer. This decrease of the thickness may be due 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, as well as the average drying temperature and humidity changes during the drying step.

The tensile strength of the films decreased to approximately 0.8 MPa with the introduction of plasticizer into the film-forming solutions. On the contrary, the strain at break values increased up to 90% and became comparable with those of the plasticized gluten films. Plasticizers increase the free volume and molecular mobility; thus, in general, they decrease the tensile strength and elastic modulus, but increase the strain at break. The SEM images show that the surface and cross section of the plasticized films were not as uniform as those of the unplasticized films. In addition, the continuity of the structure decreased. These effects may also cause tensile strength to decrease and strain at break values to increase. The elastic modulus values of the films decreased from 0.38 to 0.08 MPa, indicating a decrease in the stiffness of the films. Another point was that the addition of the plasticizer increased the HCS value from approximately 4 to 10; that is, plasticized films were more suitable for coating purposes than unplasticized films.

Although not very pronounced, the solubility of the films decreased with the addition of the plasticizer. The presence of glycerol and the bond formation between the cotton stalk xylan and the glycerol molecules may have decreased the water solubility of the films.

The use of plasticizer increased the WVTR of the films. One of the possible reasons may be the fact that plasticizer interferes with the bonds among the molecules and increases the free volume, as mentioned previously. In addition, the discontinuity of the surface and the cross-sectional areas of the plasticized films compared with the unplasticized ones corroborates this phenomenon. This result agrees with the results of Gontard et al. (*23*) who showed that the WVTR of the wheat gluten films increased as the glycerol was introduced into the medium and as its concentration increased. Moreover, WVTR values of the cellulose-based films increased with increasing plasticizer level (*24*). Similar to the unplasticized cotton stalk xylan films, WVTR values of the plasticized cotton stalk xylan films were much higher than that of the plasticized gluten films prepared by following the same procedure, which was about 0.07 $g/(m^2 \cdot day)$ (*16*).

The total color change increased as glycerol was introduced into the solution. There was no significant difference between a^* and b^* values with the addition of the plasticizer. The basic
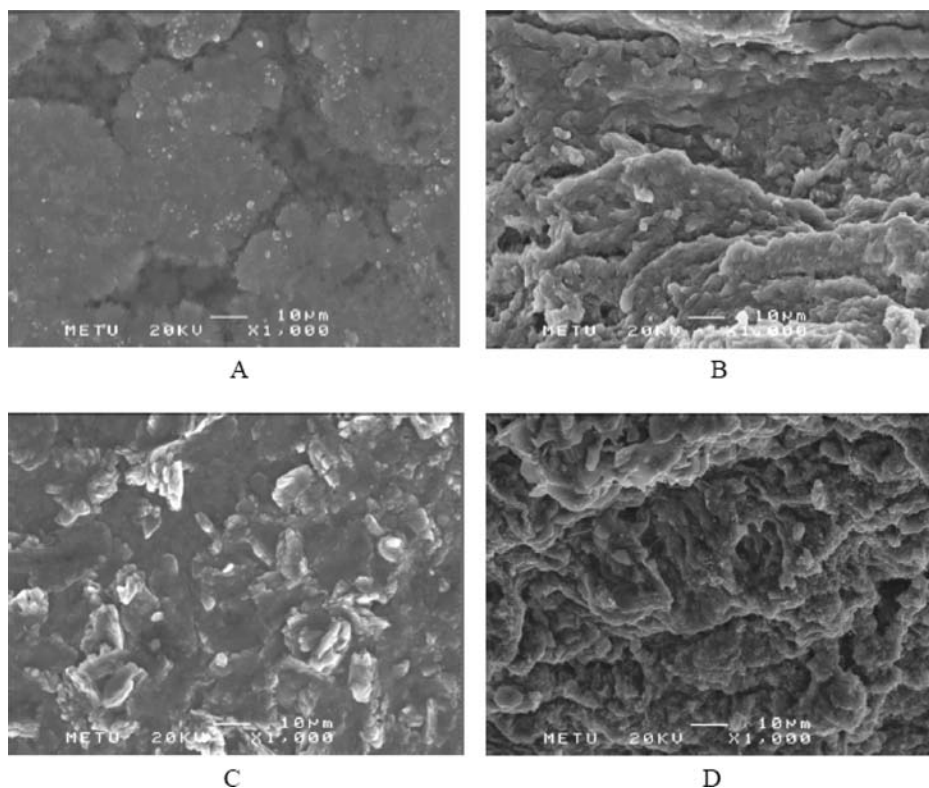

Figure 5. SEM images of the cotton waste xylan films: (**A**) unplasticized, surface area; (**B**) unplasticized, cross-sectional area; (**C**) plasticized, surface area; (**D**) plasticized, cross-sectional area.

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reason was the deviation of the lightness of the films from the reference color.

Upon investigation of **Table 1** to observe the effect of xylan concentration on the film properties from a statistical point of view, one can note that the thickness, tensile strength, strain at break, and elastic modulus values increased significantly, whereas hypothetical coating strength and normalized water vapor transmission rates decreased significantly as the concentration of the xylan increased from 8 to 14% (w/w). For the intermediate values (10 and 12%), on the other hand, some of the results were comparable to each other and 8 and 14% values. The solubility of films in water was found to be not affected by the xylan concentration significantly. Total color change of the films for 8 and 14% were not significantly different from each other, but higher than those for 10 and 12%. As for the effect of the glycerol addition of film properties, all of the film properties changed significantly with the inclusion of glycerol in the structure.

Conclusions. Self-supporting film production was achieved from cotton waste xylan with the introduction of small quantities of lignin. The necessary quantity of lignin on xylan-based film formation was determined as about 1% (w/w lignin/xylan) for both cotton stalk and birchwood xylan. The mechanical properties of the films obtained by using 8% xylan were lower in comparison with the ones containing 14% xylan. The water vapor transfer rates decreased with increasing xylan concentration, which made the films thicker. The addition of glycerol as an additional plasticizer resulted in more stretchable films having higher WVTR and lower water solubility values. In addition, glycerol-containing films were more suitable for coating purposes. Overall, films having characteristics similar to those of many other biopolymer-based films were obtained from xylan with the introduction of lignin.

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