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DEVELOPMENT OF HEMICELLULOSES BIODEGRADABLE FILMS FROM OIL PALM FROND (*ELAIS GUINEENSIS*)

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ABSTRACT

Biodegradable films were developed from hemicelluloses of oil palm fronds (OPF) extracted using alkali extraction method. The effects of different alkali [Potassium Hydroxide (KOH)] concentrations (1.0, 2.0, 3.0M) on the film properties [Thickness, color, mechanical, solubility, and water vapor transfer rate (WVTR)] of the films were investigated. The hemicelluloses yields were found to be increased with the increase in concentration with all the extracts produced self-supporting films. Film thickness ranged from 0.13-0.14 mm. Measured data for the hemicelluloses films were 11–15 MPa tensile strength, 1–3 % elongation, 64-93% solubility in water, and 180-210 g m^{-2} d^{-1} water vapor transfer rate (WVTR). This study suggests that OPF has a good potential in obtaining hemicelluloses for production of biodegradable film for certain application.

Keywords
Biodegradable film, hemicelluloses, oil palm frond, alkali extraction

1. INTRODUCTION

Synthetic plastics derived from petrochemical have been used extensively in the packaging industry and this has contributed to environmental pollution due to its non-biodegradable properties [1]. Therefore, this has lead to intensification of research to develop biodegradable packaging materials from biological polymers. Polysaccharides have good natural barrier properties, which are necessary for packaging films, and in recent years, great interest has been shown in hemicelluloses as polymers for chemical and pharmaceutical applications. The film forming properties of pure hemicelluloses (xylan) isolated from birch wood and aspen wood has been studied but the results were not promising, as pure xylan did not form continuous and self-supporting films in its pure form [2]. On the contrary, hemicelluloses film produced from cotton wastes proved to be self-supporting film with good mechanical properties [3].

Oil palm frond (OPF) is one of the most abundant by-products of oil palm plantation in Malaysia. About 35 million tones of fronds are chipped and left to decompose in the plantation each year [4]. Instead of this practice, this large quantity of residue represents a low cost resource that can be exploited into valuable products. The objective of this study is to extract and develop a hemicellulosic biodegradable film from oil palm frond. Hemicelluloses were extracted using KOH of different concentrations in order to determine the effects of the difference concentration of KOH used on the film properties.

2. MATERIAL AND METHODS

Oil palm fronds (OPF) were supplied by Malaysia Palm Oil Board (MPOB), Bangi, Selangor. The raw material had been dried and ground to a particle size of 5 – 8 mm. The moisture content of the OPF is 7.1% (w/w).

2.1 Alkali Extraction

Alkali extraction using the method by Anis (2000) [5] had been used with some modifications to extract hemicelluloses from OPF. Extraction was done with 1:10 ratio OPF to solvent using 3.0, 2.0, and 1.0M KOH respectively. The mixtures were stirred at 40.0°C, 400 rpm for 4 hours. After filtration, the extracts were acidified to pH 4.8 ± 0.1 with acetic acid. The mixtures were kept at 4.0°C for 24 hours. Then, it was centrifuged (Kubota 5100, Tokyo, Japan) for 15 minutes at 3500 rpm. The supernatant was added with 4 volumes of 95 % technical ethanol to precipitate the hemicelluloses and was kept at 4.0°C for 24 hours. Hemicelluloses were recovered by centrifugation at 3500 rpm for 15 minutes. The pellet was dried in the oven at 40.0°C, and kept in a dessicator until further analysis. Klason lignin was determined using TAPPI test method T222 (1996) [6].

2.2 Molecular Weight

Molecular weights were estimated using an HPLC system comprising a Shodex column (KS-804) with Pullulans as standards (P1 to P8). A solution of hemicelluloses (4.0 mg/ml) was injected, the columns were eluted at 1.0 ml/min with deionized water, and Refractive Index was used for detection.

2.3 Film Preparation

Films were prepared using method by Goksu (2005) [3] with some modification. The film forming solution with concentrations of 10.0% (w/v) was prepared by dissolving hemicelluloses from all extracts in distilled water and continuous stirring at room temperature for 8 hours with magnetic stirrer. The film solution was then casted and dried in controlled environment at 40.0°C for 24 hours. Films were conditioned at 52.9% RH using saturated Mg $(NO_3)_2$ at 25.0°C for 48 hours prior to all analysis.

2.4 Thickness Measurement

Film thickness was measured using a thickness gauge (Mitutoyo, Kawasaki, Japan). Measurements were taken at 5 different places on the films, and the average value was calculated.

2.5 Solubility

Films were cut into pieces of 12.0 mm x 12.0 mm, and dried in an oven at 70.0°C to constant weight and then weighed to obtain the initial film dry weight. About 0.2 g of the films was put into 20.0 g of distilled water for 1 hour. The remaining pieces of films were then taken out and dried at 70.0°C for 24 hours and weighed. The solubility (%) values were calculated as follows:

$$\text{Solubility (\%)} = \frac{\text{Initial weight} - \text{Final weight}}{\text{Initial weight}} \times 100$$

2.6 Color Measurement

Film color was determined by a colorimeter (CM-3500D Minolta spectrophotometer, Minolta, Japan) calibrated with CM-A124 zero calibration box and CM-A124 white calibration plate. The HunterLab color scale was used, lightness = 0 to 100 (Black and white) and chromaticity parameters, +a is the red direction, –a is green direction, +b is the yellow direction and –b is the blue direction. Samples were analyzed in triplicates, recording five measurements for each sample.

2.7 Water Vapor Transfer Rate (WVTR)

WVTR tests were determined using the method by Kayserilioğlu, *et al.* (2001) [7] with some modifications. The films were prepared in triplicates and tested at 25.0 ± 2°C. The test films were sealed to a glass permeation cell containing silica gel with a 1.5 cm headspace and placed in a dessicator maintained at 52.9% using saturated salt solution of $Mg(NO_3)_2$. The dull sides of the films were oriented towards the higher RH compartment. The cups were weighed to the nearest 0.001 g at 24 hours intervals for 6 days. The water vapor transmission rate through the films was determined from weight loss of the cup over time.

2.8 Mechanical Properties

Tensile strength and breaking elongation of films were measured using a TA.XT2TM Texture Analyzer (Stable Micro System, Surrey, UK) according to ASTM Standard Method D882-88 (ASTM, 1989a) [8]. Films strips (each measuring 14.0cm x 2.0 cm) were stretched at 0.3 mm s^{-1}. Eight replicates were tested.

2.9 Statistical Analysis

Statistical analysis was performed using the SPSS 10.0 software. Comparisons were performed by Duncan's test with a significance level of 0.05. All experiments were done in triplicate, and repeated 3 times.

3. RESULTS AND DISCUSSION

3.1 Hemicelluloses Yield and Lignin Content

The effect of different KOH concentrations on the hemicelluloses yield is shown in figure 1. As expected, increasing the alkali concentration resulted in an increment of the solubilized hemicelluloses. The successive increase of KOH concentrations from 1.0 to 2.0 and 3.0 M, were observed to increase the yields of each fraction, 17.53% ± 0.41, 21.10% ± 0.22, and 26.66 % ±0.39, respectively. Lower yield of 1.0M KOH hemicellulose extract compared to 2.0 and 3.0M was probably due to weak concentration of alkali used in releasing the hemicelluloses from the carbohydrate–lignin complex structure [9]. In addition, the lignin content for each extract also displayed similar trend. According to Sun, et al., [10] this increasing tendency was probably because more lignin-hemicellulosic complex was co-extracted with hemicelluloses at higher alkali concentration. This phenomenon indicated that increasing the KOH concentration favored the release of hemicelluloses and lignin.

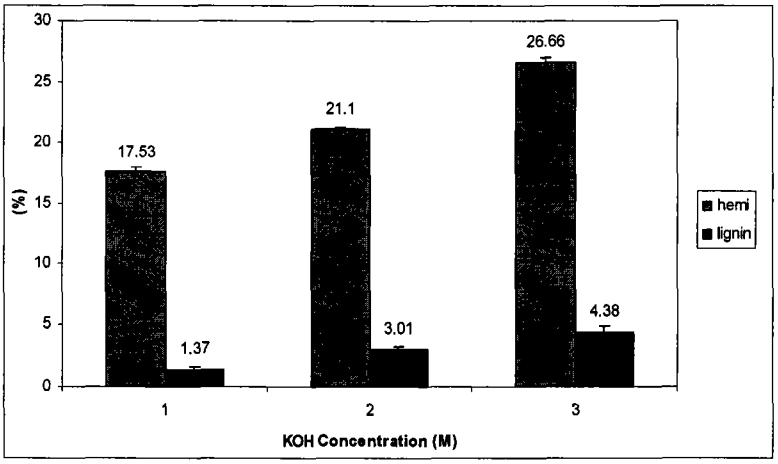

Figure 1: Hemicelluloses Yield (%) and Klason Ligin (%) for 1.0, 2.0 and 3.0M KOH extracts

3.2 Molecular Weight

All of the samples have high molecular weights ranging from 400 000 to 621 000 Da. The calculated molecular weights are shown in table 1. Data showed that molecular weights of hemicelluloses decreased from 621 693 to 409 833 Da with increase in KOH concentration (1.0M to 3.0M). This result is inline with Sun *et al.*[11] that shows the average molecular weights of hemicelluloses decreased with increased of extraction concentration of KOH, mainly due to fragmentation at higher KOH concentrations.

Table 1 : Molecular weight determined by GPC

Hemicelluloses	Mn	Mw	Polydispersity
1.0M	443 219	621 693	1.4027
2.0M	400 981	453 948	1.1321
3.0M	344 853	409 833	1.1884

3.3 Film Thickness, Solubility and Color

Hemicelluloses extracted were used to prepare 10.0 % film forming solutions. All extracts produced self-supporting films, easily peeled and showed smooth surfaces. Film thickness prepared by hemicelluloses 1.0, 2.0 and 3.0M KOH extracts showed no significant difference, with an average thickness of 0.13 mm, 0.14mm, and 0.13 mm respectively. With regard to solubility, 1.0M hemicellulose film showed the highest solubility in distilled water at room temperature 1 hour (92.2 %), where as, 2.0 and 3.0 M films has moderate solubility which is 65.4 % and 64.4 % respectively. The low solubility by 3.0M and 2.0M films were probably to due to their high percentage of lignin content as compared to 1.0M film, since lignin has low solubility in water. The color of the films prepared from all extracts was dark and it may be desired if the packaged material is light sensitive. Table 2.0 shows the result of color parameters for studied films. Although there were significant results in Lightness (L*Value), redness (+a values) and yellowness (+b values), but the value are not far apart. Therefore, different concentration of KOH used to extract hemicelluloses did not affect the color of the films produced.

Table 2 : Color analysis

Hemicelluloses Film	L*Value	a*	b*
1.0M	23.36 ± 0.24^a	0.34 ± 0.22^a	-0.32 ± 0.14^a
2.0M	22.39 ± 0.20^b	0.60 ± 0.09^b	0.62 ± 0.06^b
3.0M	23.22 ± 0.54^a	0.60 ± 0.19^b	0.25 ± 0.08^c

- Values having the same superscript within columns are not significantly different ($P > 0.05$)

3.4 Tensile Properties

Mechanical property data [Tensile strength (TS), and percentage (%) elongation] of hemicelluloses films analyzed and hemicelluloses films from other researchers are shown in Table 3.0. All the films are moderately strong, with a stress at break above 10.0 MPa, and have an elongation less than 3.0%. Tensile strength for hemicelluloses films from OPF are lower compared to hemicelluloses films prepared from Barley Husk [12] (50 MPa) and Corn Hull [13] (53.8 MPa), but higher than cotton waste [3] (1.3 MPa) hemicelluloses film. The differences in tensile strength for each film were probably attributed by different sources and method of hemicelluloses extracted. Kayserilioğlu, *et al.* (2001) [7] study showed that mechanical properties changed not only due to different process conditions like pH and drying, but also due to type and composition of hemicelluloses.

Table 3 : Mechanical Properties of Hemicelluloses Films

Hemicelluloses Film	Tensile Strength (MPa)	Elongation (%)
1.0M	13.10 ± 1.15^a	1.53 ± 0.44^a
2.0M	14.65 ± 2.21^b	1.77 ± 0.32^b
3.0M	11.22 ± 0.88^c	2.21 ± 0.21^c

3.5 Water Vapor Transfer Rate (WVTR)

As shown in figure 3, WVTR for 3.0M hemicelluloses films is the highest which is 210 g/(m^2xday) whereas WVTR for 1.0M is the lowest, 184.7 g/(m^2xday). 1.0M film has the lowest permeability probably because is high molecular weight value compared to 2.0 and 3.0M films. According to Erol, *et al.* [14], decrease in permeability with increasing molecular weight may be explained by the possibility that the mobility of the molecule decreases with increasing molecular weight and thus its contribution to water vapor transfer becomes less. The water vapor transfer rate (WVTR) for all films prepared were higher compared to

gluten-xylan composite film (0.07 g/(m^2xday) studied by Kayserilioğlu, *et al.* [7] but lower than hemicellulose films prepared from cotton wastes which is 250 g/(m^2xday) [3]. High WVTR values were expected as the films demonstrated high solubility in water. A lower water vapor transfer rate can be obtained by coating the film surface with hydrophobic molecules such as lipids [3].

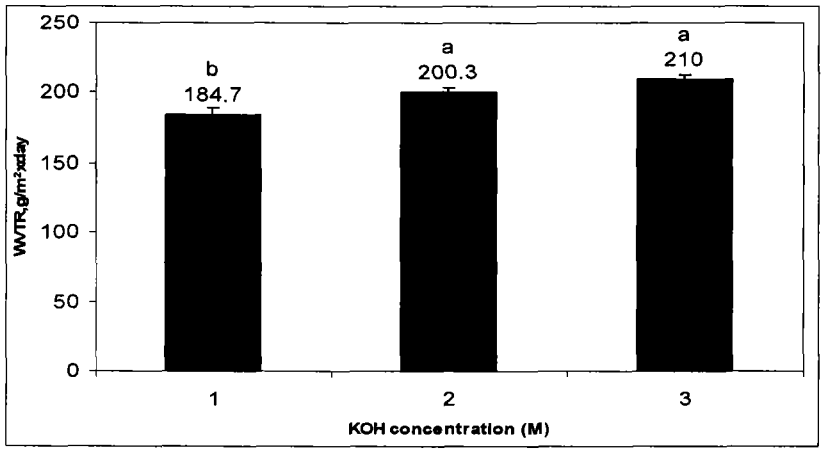

Figure 3 : Water Vapor Transfer Rate (WVTR) Value for Films Stored for 6 Days, at 25^{0}C, at 52.9% RH.

4. CONCLUSION

This study showed that alkali concentration played an important role in properties of hemicelluloses yields and films. All hemicelluloses extracted from 1.0, 2.0 and 3.0M KOH produced a self-supporting film with different properties. Variations in the films properties could be explained by difference in hemicelluloses composition. As a conclusion, OPF has a good potential in obtaining hemicelluloses for production of biodegradable films.

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