

Synthesis and Characterization of PVA-Ether Starch Film from Alkoxylation of Fatty Acid Methyl Ester Epoxide of Candlenut Oils with Cassava Starch

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Abstract

The research focused on synthesis and characterization of PVA-ether starch film has been conducted. This study is divided into 4 steps, such as separation of unsaturated fatty acids of candlenut oils by urea complexation methods, epoxidation reactions of unsaturated fatty acid with a peracid acid, alkoxylation reactions of fatty acid methyl ester epoxide with cassava starch and preparation of PVA-ether starch film. The ether starch was obtained by alkoxylation reactions of fatty acid methyl ester epoxide of candlenut oils with cassava starch. The PVA-ether starch film was prepared by mixing polyvinyl alcohol and ether starch of the synthesis to obtained PVA-ether starch films which could applied as bioplastic. The tensile strength of PVA-ether starch films was higher than PVA-cassava starch films. The tensile strength, strain and modulus young's of PVA-ether starch films were 6,07 MPa; 18,41%; 32,97 MPa and PVA-cassava starch films were 4,23 Mpa ; 13,64% ; 31,01 MPa respectively. Furthermore, the hydrophobicity of the film was carried out by water-resistance test where the PVA-ether starch films has a higher water resistance than PVA-cassava starch with value were obtained 81,36% and 32,31%, respectively.

Keywords: Alkoxylation Candlenuts Oil, Epoxidation, Film and Urea Complexation

I. INTRODUCTION

Starch is an important natural source which can be obtained from renewable sources such as corn, potato, rice, wheat, peas or cassava at low cost. Its field of application is very broad from food, paper and pharmaceutical to plastic industries [1]. Among biopolymers, starch is one of the most promising candidates for preparing biodegradable films [2]. Nevertheless, some of the physical characteristics of the native starch (NS) limit some of its possible applications. Thus, the chemical modification of starch, as well as other polysaccharides, can be considered as an interesting alternative to expand these biopolymers applications and allow the development of environmentally friendly products from sources other than oil, such as these biodegradable polymers. Depending on the nature of the modifying agent or chemical modification, hydrophilic or hydrophobic starches can be synthesized increasing the potential industrial applications of starch [3].

The candlenut oils is a triglyceride which containing unsaturated fatty acids, ie oleic (C18: 1), linoleic (C18: 2), and linolenic (C18: 3) as well as saturated fatty acids such as palmitic acid. Based on previous research results candlenuts oil was containing of unsaturated fatty acids reached 90%. The unsaturated fatty acids of these candlenut oils had been heavily modified into a variety of products, as previous researchers had done to produce alkanolamide surfactants from the amine methyl ester of candlenuts oil fatty acids with ethanolamine followed by epoxidation with tert-butyl hydroperoxide and followed by hydrolysis [4].

Over the past decades, packaging industry generates an increasing interest for biopolymer films in order to reduce the environmental impact of plastic waste [5]. It has also been suggested that long-chain esters of starch may find application as substitutes for oil-based plastic materials especially in the packaging industries [6]. The etherification reaction had widely explored and the interaction of carboxymethyl reactions had frequently employed.

Chemical modifications of starches, cellulose and other materials were related to the insertion of alkyl chains had investigated for obtaining hydrophobic materials. Fatty acids were known to show good hydrophobic properties had inserted into the polymer matrix to improve the properties of water vapor barriers of starches [7]. The addition of lauric acid into biopolymer films decreased their water vapor permeability values compared with those of the pure films. have been reported [8].

Polyvinyl Alcohol (PVA) was one type of non-toxic hydrophilic polymer and dissolved in hot water. Polyvinyl alcohol was used as a plastic film packaging material. The function of the addition of PVA was to increase the strength, flexibility, and resistance of the film on starch-based material [9].

The aim of this study was to synthesis and characterization of PVA-ether starch film from alkoxylation of fatty acid methyl ester epoxide of candlenut oils and cassava starch. The tensile strength and hydrophobicity of PVA-ether starch film was higher than PVA-cassava starch film.

II. MATERIAL & METHODS

A. Materials

Sample of candlenuts and cassava were obtained from the traditional market of Pangururan, Samosir regency. The starch was obtained from cassava using conventional methods. The cassava was peeled and removed tuber then washed with clean water and blended. The result of the blender was filtered and precipitated, then washed. The starch was dried in an oven at $\pm 45^\circ\text{C}$ for 24 hours. The candlenut oils was extracted by modification previously methods [4,10].

B. Saponification of Candlenut Oils

The candlenut oils was saponificated used KOH, aquadest, and 95% ethanol to obtain the fatty acid mixture. The mixture was refluxed while stirring with a magnetic stirrer for 1 hour then cooled. Further added aquadest and extracted used n-hexane to separate the unsabbed compound then separated by separating funnel. The water phase was acidified with a 6 N HCl solution until pH 1 was then extracted used n-hexane. The water and oil phases were separated through a separating funnel. The oil phases was washed with distilled water and dried using anhydrous Na_2SO_4 was then filtered. The filtrate was evaporated with rotary evaporator to obtain free fatty acid [11].

C. Separation of Unsaturated Fatty Acids by Fractionation Method of Urea Complexation

Fatty acids of candlenut oils (10 g) were mixed with urea 50 g in 95% aqueous ethanol 200 ml and heated at $\pm 70^\circ\text{C}$ with stirring until the mixture turned into a clear homogeneous solution. The mixture were cooled at room temperature and then stored at $\pm 1^\circ\text{C}$ for 24 hours until crystals were formed and then filtered. The filtrate was evaporated with a rotary evaporator to remove ethanol. The residue was diluted with an equal volume of distilled water and acidified to pH 2–3 with 6 N HCl, an equal volume of n-hexane was subsequently added and the fatty acids were extracted. The non-aqueous phase (top phase), containing free fatty acids was separated from the aqueous layer containing urea by filtration. The n-hexane layer was washed with 5% NaCl solution to remove any remaining urea. The n-hexane fraction was dried over anhydrous Na_2SO_4 . The solvent was removed using a rotary evaporator to obtain an unsaturated fatty acids and the converted to fatty acid methyl ester for gas chromatography (GC) analysis [12].

D. Preparation of Methyl Ester Unsaturated Fatty Acids of Candlenut Oils

The unsaturated fatty acids of candlenut oils (50 g) were mixed with 100 ml of methanol and 25 ml of benzene while stirred with a magnetic stirrer. Furthermore, concentrated H_2SO_4 (2 ml) was added slowly through the dropper funnel. The mixture was refluxed while stirring for 3 hours. The mixture was cooled at room temperature and the solvent was removed using a rotary evaporator. The residue was extracted with 100 ml of n-hexane and washed with 10 ml of distilled water 2 times and then separated by separating funnel. The n-hexane fraction was dried over anhydrous Na_2SO_4 . The solvent was removed using a rotary evaporator to obtained unsaturated fatty acid methyl ester.

E. Preparation of Epoxide of Fatty Acid Methyl of Candlenut Oils

The 90% formic acid (60 ml) were added with 30 ml of 30% H_2O_2 slowly while stirring, was then added concentrated H_2SO_4 (2 ml) slowly through the dropper funnel and stirred with a magnetic stirrer at a temperature of $40 - 45^\circ\text{C}$ for an hour. Furthermore, unsaturated fatty acid methyl ester (50 ml) was added slowly through the dropper funnel. The mixture was stirred using a magnetic stirrer at $40 - 45^\circ\text{C}$ for 2 hours. The mixture was separated to obtained epoxide of fatty acid methyl ester of candlenut oils [13].

F. Preparation of Ether Starch by Alkoxylation Epoxide of Fatty Acid Methyl Ester of Candlenut Oils with Cassava Starch

The cassava starch (80 g, dry solids) was dispersed in distilled water (640 mL) containing anhydrous sodium sulfate (8%, w/w of starch), and pH adjusted to 11 using 1 M NaOH. The epoxide of fatty acid methyl ester of candlenut oils (25 g) was added dropwise to slurry with vigorous stirring at room temperature. The reaction bottle was sealed tightly and the mixture was stirred using magnetic stirrer (150 rpm, $\pm 45^\circ\text{C}$) for 20 h. Starch slurry was then neutralized to pH 5.5 by adding 1 M HCl. The recovered starch was washed with DMSO then washed distilled water (3x), and dried at $\pm 40^\circ\text{C}$ for 24 h to obtained ether starch. The ether starch was characterized by FT-IR, SEM, XRD and determined its degree of substitution [14].

G. Preparation of PVA-Ether Starch Film

The polyvinyl alcohol (10 g) was dissolved with 100 ml of distilled water and heated at $\pm 75^{\circ}\text{C}$ while stirring using magnetic stirrer for 1 hour and was added ether starch (2 g). The mixture was stirred at $\pm 75^{\circ}\text{C}$ with a speed of 8000 rpm for 4 hours. Furthermore, the mixture of PVA and ether starch were poured into an acrylic mold then dried in an oven at 50°C for 24 hours. The film obtained was characterized by tensile strength test and water resistance test.

H. Analysis of Results

FT-IR analysis was performed on the candlenut oils, the ester compound of candlenut oils, the epoxide compound of candlenut oils, the cassava starch and the ether starch with infrared spectrophotometer Shimadzu IR 470. Infrared spectra were recorded on a Shimadzu IR 470 instrument from KBr discs samples prepared. All the spectra were performed with 32 scans and spectral resolution of ± 4 .

Morphological analysis with SEM was conducted to see the surface topographic structure of cassava starch and ether starch. Microstructural analysis of the starch was carried out using a Supra 55 (ZEISS, Jena, Germany) electron microscope at an accelerating voltage of 5 kV. The starches were adhered to a conductive carbon tape, and a sputter coated with Au/Pd

The crystal structure of the starch was analyzed using an X-ray diffraction (XRD). Cu-K β radiation was used to observe samples from 2.8° to 80° with a scan rate of $6.1424^{\circ}\text{ min}^{-1}$, a voltage of 40 kV, and a current of 100 mA.

The degree of substitution of the ether starch can be evaluated by the FT-IR method of the absorbance ratio at 1080 cm^{-1} wave numbers (C-O-C bands) and absorbance at 3348 cm^{-1} wave numbers (hydroxyl group), calculated using the equation:

$$\text{DS (\%)} = \left[\frac{A_{C-OC}}{A_{OH}} - 0,10 \right] \times 100$$

DS is degree of substitution and the value of 0.10 represents the specific hydroxyl group in the original starch [15].

The film was cut with size 1 cm x 1 cm and then weighed with an analytical balance. The film was dipped into distilled water (5 ml in 10 ml beaker glass). Every minute, the film was taken, the water on the film surface was wiped with a tissue, then weighed. This step was done repeatedly until obtained constant weight [16]. Based on the measurement of the weight, the calculation was as follows:

$$\text{Water absorbed} = \left[\frac{W - W_0}{W_0} \right] \times 100\%$$

Water resistance film = 100% - % Water absorbed

W_0 = dry sample weight and W = sample weight after being conditioned in distilled water.

III. RESULTS & DISCUSSION

A. Extraction of Candlenut Oils

The result of fatty acids composition by analysis of GC-FID was obtained unsaturated fatty acids was 89.51% which consist of $C_{18:1} = 21,61\%$, $C_{18:2} = 39,33\%$ and $C_{18:3} = 28,54\%$ indicating that the candlenut oils was sufficiently potential to be oxidized as a source of hydrophobic material that could improve the nature of starch. This result showed that the candlenut used has a higher unsaturated fatty acids content than the previous research of 87.5 % [10].

Table - 3.1

Fatty Acid Composition of Candlenut Oils

Fatty Acids	Amount (%)
Lauric Acid ($C_{12:0}$)	0.05
Palmitic Acid ($C_{16:0}$)	6.87
Stearic Acid ($C_{18:0}$)	2.73
Oleic Acid ($C_{18:1}$)	21.64
Linoleic Acid ($C_{18:2}$)	39.33
Linolenic Acid ($C_{18:3}$)	28.54

B. Separation of Unsaturated Fatty Acids by Complexation Fractionation Urea

The free fatty acids of candlenut oils containing saturated fatty acids and unsaturated fatty acids were further separated by fractionation of urea complexation.

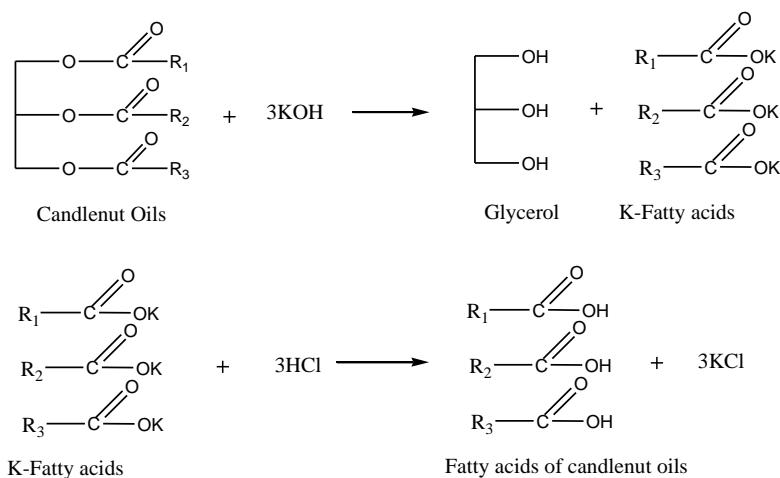


Fig. 3.1: Saponification Reactions of Candlenut Oils

The GC-FID analysis of fatty acids showed the composition of unsaturated fatty acids (Table 3.2) as followed $C_{18:1} = 5.22\%$, $C_{18:2} = 57.71\%$ and $C_{18:3} = 36.70\%$. In this study, not all unsaturated fatty acids could separate from saturated fatty acids and this result was consistent with previous research [17]. The reason was that mono-unsaturated fatty acids ($C_{18:1}$) would form complex with urea readily after saturated fatty acids had been complexed to a certain extent

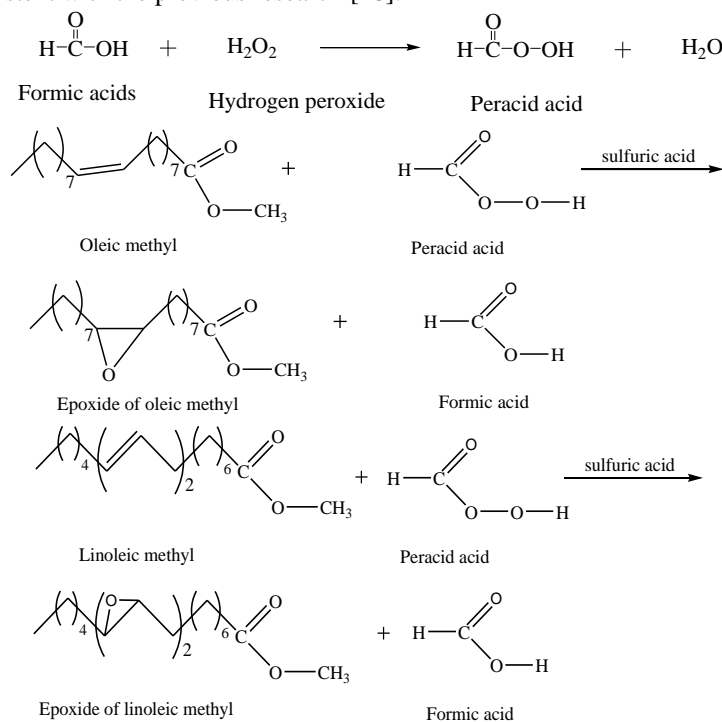
Table - 3.2

Fatty Acid Composition of Separation Result by Urea Complexation

Fatty Acids	Amount (%)
Palmitic Acid ($C_{16:0}$)	0.36
Oleic Acid ($C_{18:1}$)	5.22
Linoleic Acid ($C_{18:2}$)	57.71
Linolenic Acid ($C_{18:3}$)	36.70

C. Epoxide of Fatty Acid Methyl Ester of Candlenut Oils

The esterification reaction of unsaturated fatty acids of candlenut oils was done in order to avoid saponification reaction of alkoxylation reaction of fatty acid epoxide with starch because of using NaOH catalyst. The epoxide compounds was obtained by reaction between the unsaturated fatty acid methyl ester of the candlenut oils with the peracid acid with sulfuric acid as catalyst (Fig. 3.2). The oxygen ring on the epoxide compound was highly reactive, where in this study the heating was carried out for 2 hours and this result was consistent with the previous research [18].



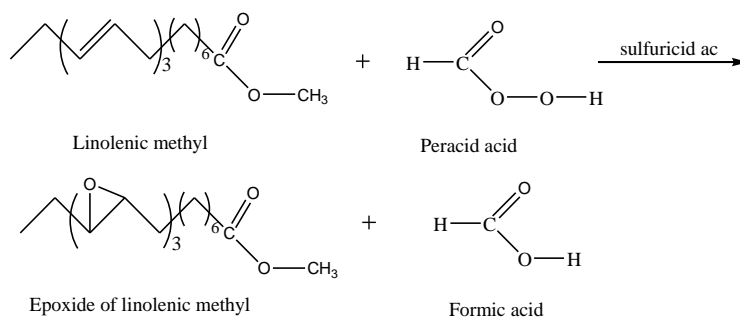


Fig. 3.2: Epoxidation Reactions of Unsaturated fatty acid methyl ester of Candlenut Oils

D. Starch Ether by Alkoxylation Epoxide of Fatty Acid Methyl Ester of Candlenut Oils with Cassava Starch

The alkoxylation reactions of epoxide fatty acid methyl ester of candlenut oils with cassava starch occurred the termination of the oxiran ring (epoxide) resulting in the starch ether compounds (Fig 3.3). The ether starch was analyzed by FT-IR spectroscopy, XRD analysis and surface morphological analysis with SEM.

Substitution degrees of the ether starch was 48.44 %, indicating that only 48.44% of the epoxide fatty acid methyl ester of the candlenut oils was substituted to the primary OH group of starch.

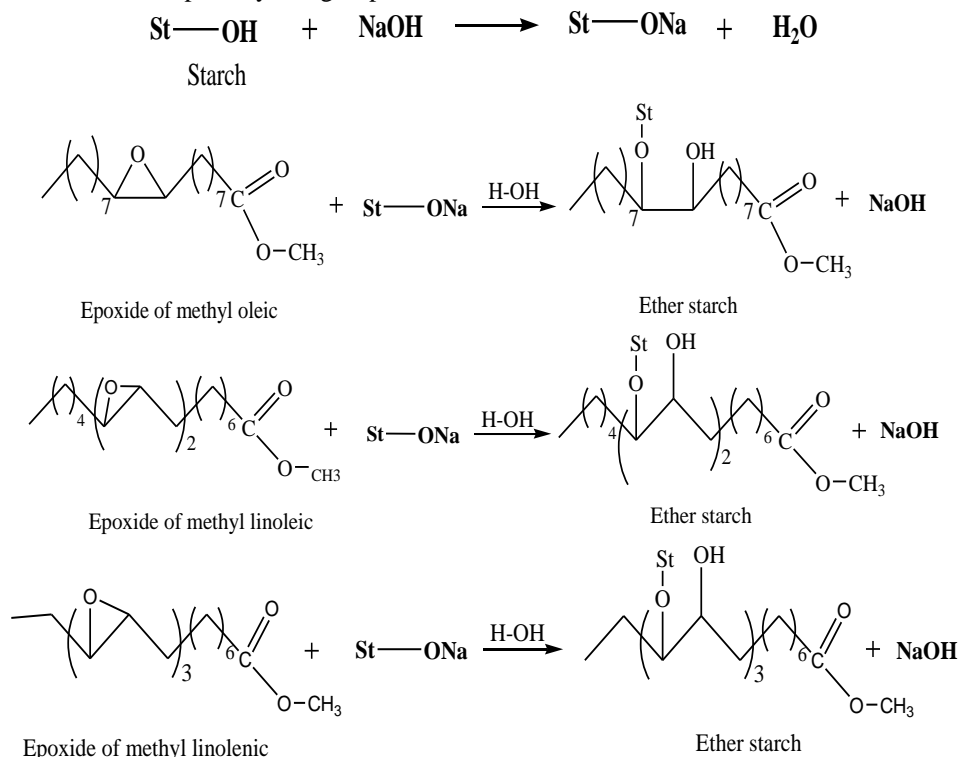


Fig. 3.3: Reaction of Alkoxylation Epoxide fatty acid methyl ester of candlenut oils with Cassava Starch

E. Analysis of Functional Groups used FT-IR

The result of FT-IR analysis showed that the candlenut oils contains unsaturated hydrocarbon where with the appearance of the vibration peak at wavelength (ν) = 3008 cm^{-1} (CH sp^2) and ν = 1651 cm^{-1} (C=C), ν = 1743 cm^{-1} (C = O group of the ester), ν = 1234-1095 cm^{-1} (C-O-C ester bond), ν = 725 cm^{-1} ($(\text{CH}_2)_n$ where $n \geq 4$).

The FT-IR spectrum of the unsaturated fatty acid methyl ester provided spectral where with the appearance of the vibration peak at the area (ν) = 3008 cm^{-1} (CH₂) and ν = 1651 cm^{-1} (C=C), ν = 1165-1026 cm^{-1} (C-O-C ester), ν = 1743 cm^{-1} (C=O group of esters) and at ν = 717 cm^{-1} ($(\text{CH}_2)_n$ where $n \geq 4$).

The spectrum of epoxide compounds found the vibration peak at area ν = 2931-2854 cm^{-1} showed vibration of bonding C-H sp^3 , ν = 1720 cm^{-1} (C = O bonds of ester), ν = 1442-1381 cm^{-1} (C-H sp^3), ν = 1180 cm^{-1} (C-O-C ester), ν = 1072 cm^{-1} (C-O-C bonds of the epoxide) and at ν = 725 cm^{-1} ($(\text{CH}_2)_n$ chain $n \geq 4$), the loss of the vibration peak at the area ν = 1651 cm^{-1} showing the C=C bonds of the unsaturated fatty acid proved that epoxidation reaction had occurred in π bonds of unsaturated fatty acids.

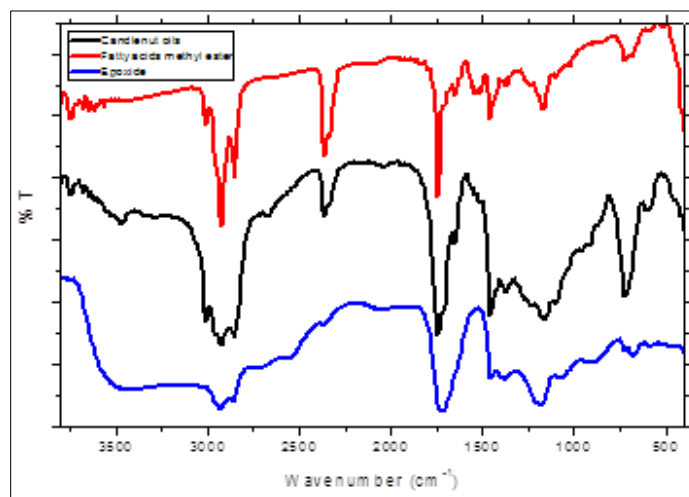


Fig. 3.4: The FT-IR spectrum of candlenut Oils, Fatty acid methyl ester and Epoxide compounds

The FT-IR spectrum of cassava starch found the vibration peak at area $\nu = 3417 \text{ cm}^{-1}$ showed (-OH) group, $\nu = 1018 \text{ cm}^{-1}$ (primary OH group), $\nu = 1157 \text{ cm}^{-1}$ (C-O-C) bonds, $\nu = 1635 \text{ cm}^{-1}$ (C=O of aldehyde groups).

The result of FT-IR spectroscopic analysis of ether starch gave spectrum with vibration peak at area $\nu = 3348\text{-}3278 \text{ cm}^{-1}$ (OH group), $\nu = 2924\text{-}2854 \text{ cm}^{-1}$ (C-H sp^3), $\nu = 1080 \text{ cm}^{-1}$ (C-O-C ether), $\nu = 1172 \text{ cm}^{-1}$ C-O of ester bonds), $\nu = 1743 \text{ cm}^{-1}$ (C=O ester bonds). Vibration at area $\nu = 1041 \text{ cm}^{-1}$ shows the presence of primary -OH groups, where it could see that the transmittance increased compared with cassava starch. This indicates that there was an alkoxylation reaction epoxide compounds with starch at the position of C₆ (primary OH). Then on the IR spectrum was found vibration in the area $\nu = 725 \text{ cm}^{-1}$ indicating the presence of hydrocarbon chain (CH₂)_n, n \geq 4, which not found on cassava starch but found in epoxide methyl ester of fatty acid.

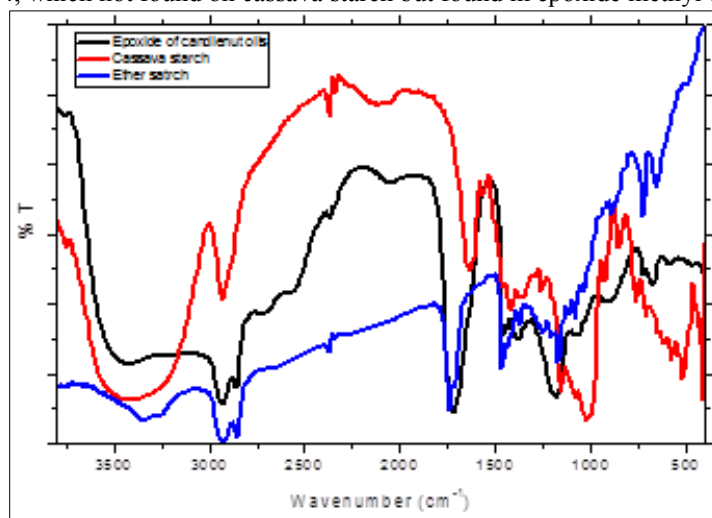


Fig. 3.5: FT-IR spectrum of Epoxide of Candlenuts Oil, Cassava Starch and Ether Starch

F. Crystal Starch Structure Analysis used XRD

Cassava starch powder had a sharp diffraction peak at 38.03° with d-spacing 2.3639 \AA , the sharpness of the peak showed high crystallinity properties. However, after the alkoxylation reaction of cassava starch with the epoxide compounds of candlenut oils, the diffraction peak shifted to 20.12° with the 4.410 \AA d spacing indicating ether starch had formed. In accordance with previous research [19] that the addition of fatty acids caused crystallinity to decrease due to the double helical dissociation of amylopectin and the formation of the amylose-fatty acid complex. Curve of intensity change to 2θ (deg) could see in Figure 3.6.

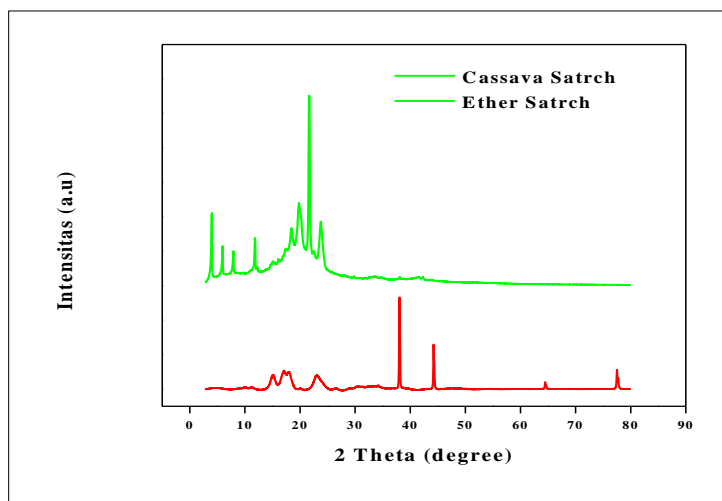


Fig. 3.6: Diffraction of Cassava Starch and Ether Starch

G. Morphological Analysis by SEM

Analysis of surface morphology on cassava starch is shown in Figure 3.7 the pictures appeared that the surface of cassava starch was granule-shaped.

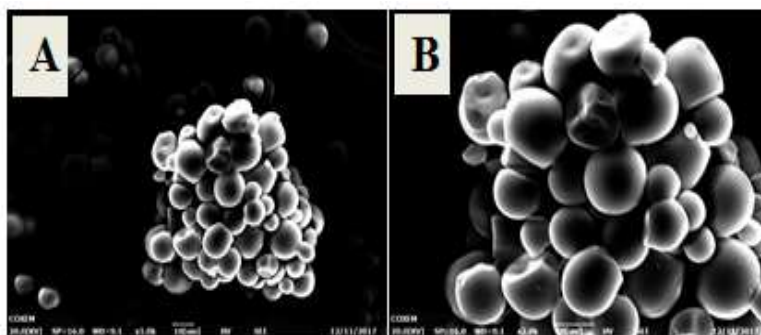


Fig. 3.7: Photo of SEM on Cassava Starch Surfaces with magnification 1000 times; (B) 2000 times

Analysis of surface morphology on ether starch (Figure 3.8) shows that had occurred change in surface morphology, in which the surface of ether starch was only partially granule-shaped. This morphological alteration proves that had occurred reaction between the hydroxyl groups of starch and the oxyran groups of the epoxide compounds of candlenut oils.

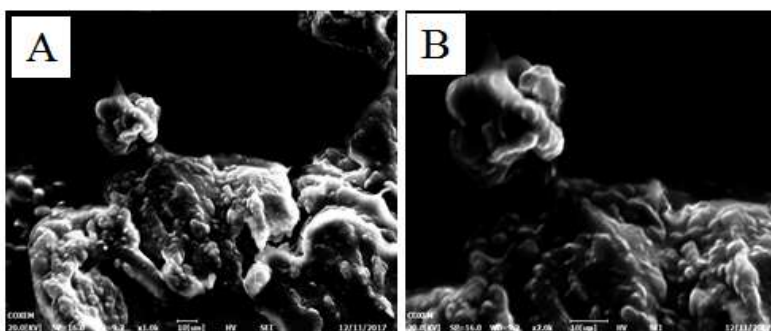


Fig. 3.8: Photo of SEM on Ether Starch Surfaces with magnification 1000 times; (B) 2000 times

H. Analysis of Mechanical Properties of Film

Analysis of the mechanical properties of the film was carried out for the purpose of bioplastic applications, where the analysis was performed by tensile test. The result of test of mechanical properties in table 3.3 showed that tensile strength for starch ether was higher than cassava starch. This result was consistent with previous research [20] which suggested that fatty acids might affected the mechanical properties of the polymer matrix. In the presence of saturated fatty acids would produce a higher tensile strength than the original starch due to the formation of amylose-fatty acids complexes during the process of film formation.

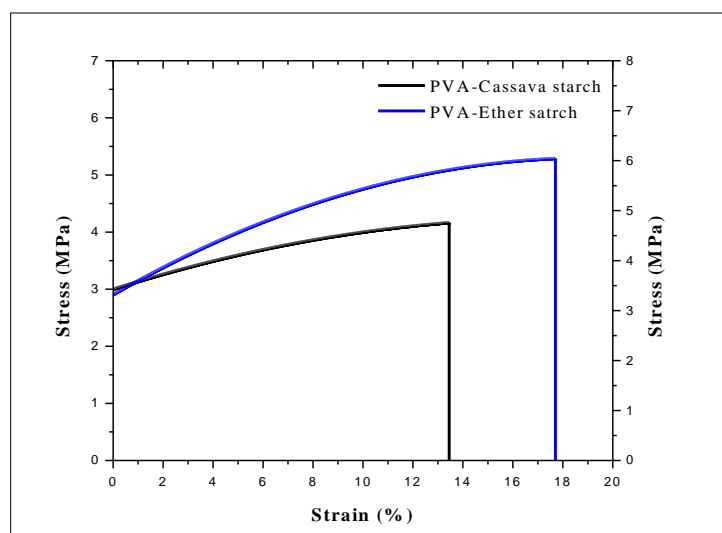


Fig. 3.9: Stress-Strain Curve of PVA-Cassava Starch Film and PVA-Ether Starch

Table - 3.3
Mechanical Properties of PVA-Cassava Starch Film and PVA-Ether Starch Film

No	Sample	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
1	PVA-Cassava Starch	4,23	13,64	31,01
2	PVA-Ether Starch	6,07	18,41	32,97

I. Water Resistance Test

The water resistance test resulted that the film of ether starch had higher water resistance than cassava starch. This was indicated that long chain hydrocarbon groups of the fatty acids of the candlenut oils improved the hydrophobic properties of the film.

Table 3.4 Water Resistance Film of PVA-Cassava Starch and PVA-Ether Starch

No	Samples	Water Resistance (%)
1	PVA-Cassava Starch Film	32,31
2	PVA-Ether Starch Film	81,36

IV. CONCLUSION

The ether starch was obtained by alkoxylation reactions of fatty acid methyl ester epoxide of candlenut oils with cassava starch. The PVA-ether starch film was prepared by mixing polyvinyl alcohol and ether starch of the synthesis to obtained PVA-ether starch films. The mechanical properties showed that tensile strength for starch ether was higher than cassava starch. The tensile strength, strain and modulus young's of PVA-ether starch were 6,07 MPa ; 18,41% ; 32,97 MPa and PVA-cassava starch were 4,23 Mpa ; 13,64% ; 31,01 MPa respectively. Furthermore, the hydrophobicity of the film was carried out by water-resistance test where the PVA-ether starch had a higher water resistance than PVA-cassava starch with value were obtained 81,36% and 32,31%, respectively.

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