

Mechanical Physical Properties of Chlorella-PVA based Bioplastic with Ultrasonic Homogenizer

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Abstract. Public demand for environmentally friendly packaging material especially in food industry is increasing. One of the many solutions invented for this problem is the development of biodegradable plastic. Biopolymer can be mixed with synthetic polymer to produce biodegradable films with properties suitable for varying applications. This study examines the mechanical physical properties of Chlorella-polyvinyl alcohol (PVA) based bioplastic by pre-treating the Chlorella powder with ultrasonic homogenizer. Variation of Chlorella concentration and temperature was done during the ultrasonication. Before being used as bioplastic base, pre-treated Chlorella with different concentrations were equated. Bioplastic films were then prepared with the pre-treated Chlorella powder and PVA using solvent casting method. Mechanical physical properties of the pre-treated Chlorella films then compared with non pre-treated Chlorella film as control. Mechanical test shows the increasing of bioplastic tensile strength up to 15,3 kgf/cm² and elongation percentage up to 99,63%. Field emission scanning electron microscopy test shows the increasing of bioplastic homogeneity and smoother surface with less pores. Fourier transform infrared analysis shows that there are crosslinkages between Chlorella and PVA. Thermal analysis by thermogravimetric analysis shows ultrasonication creates a more compact linkages. The performance of the film could suggest its potential as an eco-sustainable food packaging plastic material.

1 Introduction

Food packaging with sufficient mechanical strength and thermal stability is substantial in food products for food quality protection and safety. Majority of the food packaging nowadays are petroleum based plastic. Unfortunately, petroleum based plastic has chemical building blocks that might harm people and the environment, and its production and disposal contribute to an array of environmental problems [1]. Several precautions were developed such as the development of biodegradable plastic (bioplastic). Bioplastic is made from natural polymer materials (biopolymer) and is designed to accelerate the natural degradation of plastic by microorganisms. Generally, biopolymers are used to blend with synthetic polymers to improve bioplastic characteristics and extend its applications. It is desired to use other biomass as a source of bioplastic production that improves bioplastic characteristics and to avoid food source competition.

On the other hand, microalgae have been attracted as the most promisingly renewable resource for bioplastic production because of their faster growth rate, higher photosynthetic efficiency and biopolymer source. Microalgae perform oxygenic photosynthesis and are capable of taking up a large amount of CO₂ [2]. The cultivation of microalgae can be enhanced by alteration of illumination during growth [3]. However, microalgae has relatively thick cell wall and large particles [4].

Ultrasonic technologies have been used as pre-treatment methods in various industrial fields for decades [5]. It is

used to reduce small particles in a liquid so that they become uniformly small and evenly distributed.

In this work, microalgae pre-treatment and its conversion to bioplastic with addition of polyvinyl alcohol (PVA) as synthetic polymer were attempted. The effect of ultrasonication treatment on bioplastic characteristics such as elongation, tensile strength, thermal properties, Field emission scanning electron microscopy, and Fourier transform infrared (FTIR) was clarified.

2 Materials and Methods

2.1 Materials

Chlorella; polyvinyl alcohol; glycerol, analytical pure; citric acid; distilled water, (laboratory homemade). C-MAG HS 7 IKA Hotplate Stirrer; BSA2245-CW sartorius analytical balance; glass plate, (laboratory homemade); SK7210HP Kudos ultrasonic; Universal Testing Machine - Shimadzu; Scanning Electron Microscope - JEOL JSM-6510 LA; Thermal Gravimetry Analyzer - Mettler Toledo; Fourier Transform Infrared spectroscopy.

2.2 Methods

2.2.1 Biomass Pre-treatment

Chlorella: distilled water (C/W) solutions were treated with ultrasonic homogenizer. Dry 2,8 g of *Chlorella* powder was added into distilled water and then mixed with magnetic stirrer followed by ultrasonic treatment using a homogenizer (Merk) 53 kHz for 40

minutes. The treatment was done by the extraction method of starch from microalgae as described by Asada

et al [5]. The test design of composition of this pre-treatment is presented in Table 1.

Table 1. Test design of composition.

Solution	<i>Chlorella</i> (g)	Distilled water (mL)	Temperature (°C)	Time (min)
C/W ^{1:3}	2,8	8,4	25	40
C/W ^{1:5}	2,8	14	25	40
C/W ^{1:10}	2,8	28	25	40
C/W ^{1:3}	2,8	8,4	50	40
C/W ^{1:5}	2,8	14	50	40
C/W ^{1:10}	2,8	28	50	40

The solutions were taken and added with distilled water until *Chlorella*: distilled water of each solutions equals 1:10 for usage in the next method.

2.2.2 Preparation of films

Chlorella/Polyvinyl alcohol (PVA) blend films were prepared using the solvent casting method as described by Wang et al. [1] with modification of solution temperature, and all the bioplastic have the same

composition. First, 2,8 g of PVA was dissolved in 10 mL of distilled water at 80 °C while *Chlorella* solution was added with 2,11 g of glycerol and heated at 90 °C. Thereafter, 1 g of citric acid was added to the PVA solution at 80 °C alongside with the addition of *Chlorella* and glycerol solution and were stirred for 30 minutes. All the solutions were cast onto glass plate (15 cm x 15 cm) and were dried for 24 h at room temperature and peeled off from the plate to obtain a dried film.

Table 2. Blend films composition.

<i>Chlorella</i> Solution	Polyvinyl Alcohol (g)	Distilled Water (mL)	Glycerol (g)	Citric Acid (g)
C/W ^{1:3}	2,8	10	2,11	1
C/W ^{1:5}	2,8	10	2,11	1
C/W ^{1:10}	2,8	10	2,11	1
C/W ^{1:3}	2,8	10	2,11	1
C/W ^{1:5}	2,8	10	2,11	1
C/W ^{1:10}	2,8	10	2,11	1

2.2.3 Mechanical Properties

The mechanical properties of the films were analyzed by measuring the tensile strength (TS) and elongation at break (E) according to the standard ASTM method D882-12 using an Shimadzu Universal Testing Machine.

2.2.4 Thermal Properties

The thermal stability of film samples was evaluated according to the standard ASTM method D1131-14 using a Mettler Toledo thermogravimetric analyzer.

2.2.5 Surface Morphology and FTIR Analysis

The surfaces of the films were fixed with conductive adhesive and were sprayed with platina. The composite films were observed using a field JEOL JSM-6510 LA Scanning Electron Microscope. By using Spectrum 100 Fourier transform infrared spectroscopy (FT-IR), spectroscopy analysis was performed.

3 Results and Discussion

3.1. Mechanical Properties

Mechanical properties such as tensile strength and elongation of the *Chlorella*/PVA blend films are shown in Table 3. Tensile test result shows that C/W^{1:5:25} doubles the tensile strength and elongation percentage of *Chlorella* based bioplastic film (control). Optimum composition of solvent in a sonication process depends on the cell particle size and thickness [6]. Asada et al. (2012) [5] research shows that microalgae concentration of 1 g/mL in sonication treatment resulting in starch extraction ratio of 93,8%. Optimum condition of sonication resulting in higher amount of cell disruption and more dispersed particles which allows water molecule to intervene the polymer chain thus resulting in more flexible bioplastic film. Temperature also takes a big role in this reaction [5]. The higher the temperature, the weaker polymer bond will be, thus the easier water molecule to intervene the polymer chain. The tensile

strength properties peak is at the *Chlorella*:water ratio of 1:5 because the amount of polymer-polymer bonds is equivalent to the amount of polymer-plasticizer bonds, while ratio of 1:3 has a higher amount of polymer-polymer bonds than the polymer-plasticizer bonds, and the ratio of 1:10 has higher amount of polymer-plasticizer bonds than the amount of polymer-polymer bonds. As a result, the optimum condition of *Chlorella* sonication is *Chlorella*:water ratio of 1:5 with the temperature of 25 °C.

The result of comparing *Chlorella*-PVA based bioplastic film with ultrasonic pre-treatment with *Chlorella*-PVA based bioplastic film without ultrasonic pre-treatment shows that ultrasonication increases the tensile strength of the film up to 1,8x and increases the elongation percentage up to 2,5x. This shows that ultrasonication improves the mechanical characteristic of *Chlorella*-PVA based bioplastic film.

Table 3. Tensile properties of *Chlorella*/polyvinyl alcohol blend films.

Sample	Chlorella Ultrasonication Condition		Tensile Strength (kgf/cm ²)	Elongation (%)
	<i>Chlorella</i> :water ratio	Temperature (°C)		
C/W ^{1:3:25}	1:3	25	32,9 ± 3,5	92,20 ± 13,77
C/W ^{1:5:25}	1:5	25	35,1 ± 4,3	127,50 ± 18,99
C/W ^{1:10:25}	1:10	25	20,8 ± 1,5	159,60 ± 35,75
C/W ^{1:3:50}	1:3	50	23,8 ± 1,1	132,90 ± 32,27
C/W ^{1:5:50}	1:5	50	28,8 ± 1,5	149,90 ± 54,19
C/W ^{1:10:50}	1:10	50	15,2 ± 2,7	210,90 ± 73,41
Chlorella Control	No sonication	No sonication	19,8 ± 3,0	27,87 ± 3,16

3.2 Thermal Properties

TGA thermograms of *Chlorella* based bioplastic film with ultrasonic pre-treatment shows that the initial thermal decomposition at 80 – 140 °C was due to evaporation of water accounting for weight loss of 7,74% of the total mass of the sample, and then the main thermal decomposition was at 200 – 440 °C due to chemical degradation by polymer chain scission accounting for weight loss of 75,4% of the total mass of the sample. Final residue after final heating of 600 °C of *Chlorella*-PVA based bioplastic film with ultrasonic pre-treatment and *Chlorella*-PVA based bioplastic film without ultrasonic pre-treatment respectively are 5,03% and 1,32%. The heat application makes the *Chlorella* and PVA molecules through hydrogen bonding form more new structure thermal decomposition [7]. The same phenomenon was observed by Asada et al. (2012) where the modification of bioplastic mixture improves the compactness of the crosslinkages within the material proven by the increase of residuals left after heating. The *Chlorella*-PVA based bioplastic film with ultrasonic pre-treatment has more residuals which shows that ultrasonication improves the bioplastic film by creating a more compact crosslinkages between *Chlorella* and PVA.

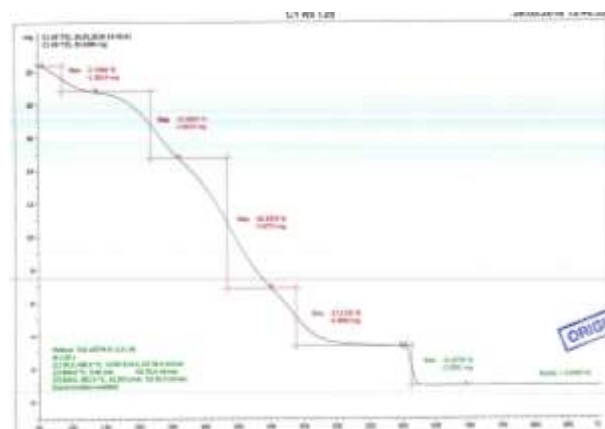


Fig. 1. TGA thermograms of *Chlorella*/polyvinyl alcohol blend films with ultrasonic pre-treatment.

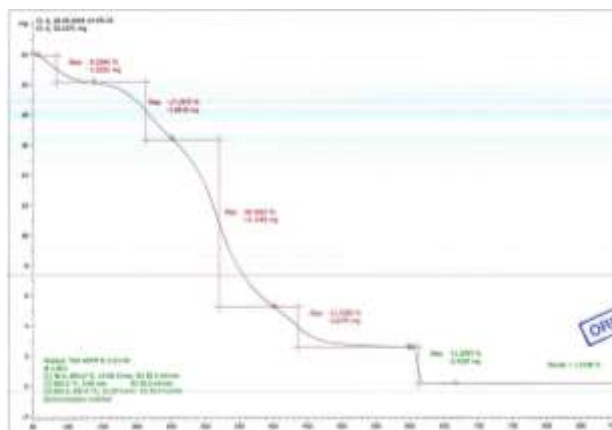


Fig. 2. TGA thermograms of *Chlorella*/polyvinyl alcohol blend films without ultrasonic pre-treatment.

3.3 Surface Morphology and FTIR Analysis

Micromolecular structure of the bioplastic film was evaluated using SEM and the resulting images are shown in Fig. 3 dan Fig. 4. The images shows that ultrasonic pre-treated *Chlorella* resulting in more homogenized and less pores bioplastic film, creating a smoother film surface compared with the untreated *Chlorella* based bioplastic film. Ultrasonication also reduces the particle size of *Chlorella*. This indicates that ultrasonication can significantly improve the binding of *Chlorella* and PVA an enhance the dense homogeneity of the film.

FTIR analysis of the films resulting FTIR spectra that are shown in Fig. 5 and Fig. 6. The peak in 3650 – 3200 cm^{-1} wavenumber shows that there are free hydroxyl group which causes the films to be soluble in water. The peak in 2200 – 1800 cm^{-1} wavenumber shows that there are C—H bonds which are hydrogen bonds between amylose and amylopectin in *Chlorella* [8]. The peak in 1640 – 1320 cm^{-1} wavenumber shows that there are amide group and indicates the protein in *Chlorella* that was not fully bonded with PVA [9]. The peak in 1320 – 1140 cm^{-1} wavenumber shows that there are ether group (C-O) and acetal ring (C-O-C) which are the bond of PVA and *Chlorella* [9].

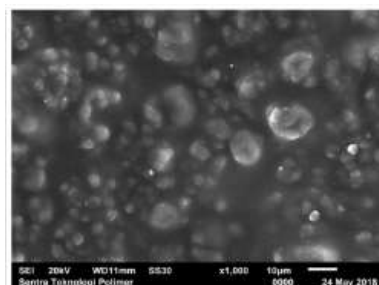


Fig. 3. SEM images of *Chlorella*/polyvinyl alcohol blend films with ultrasonic pre-treatment.

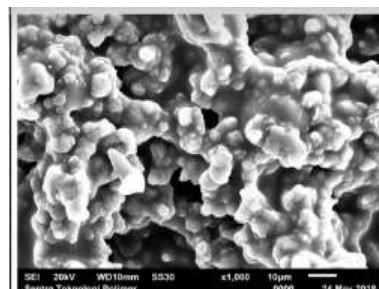


Fig. 4. SEM images of *Chlorella*/polyvinyl alcohol blend films without ultrasonic pre-treatment.

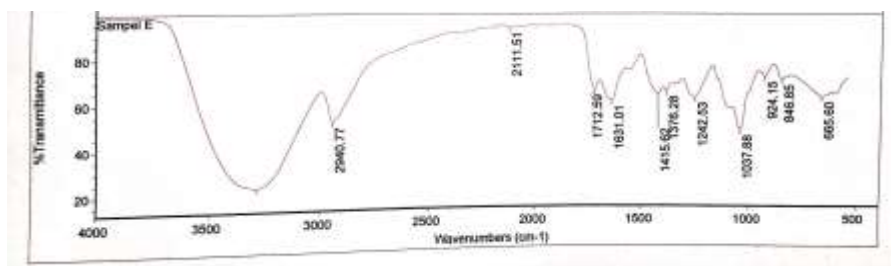


Fig. 5. FTIR spectra of *Chlorella*/polyvinyl alcohol blend films with ultrasonic pre-treatment.

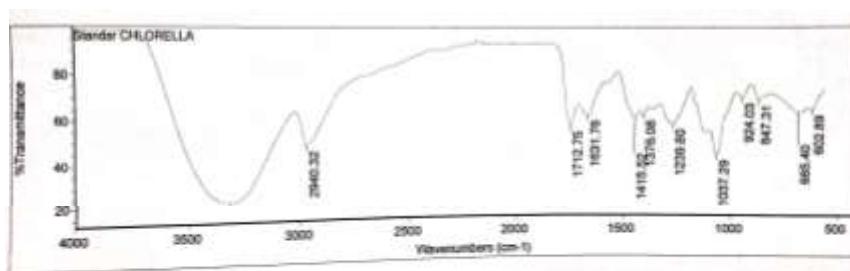


Fig. 6. FTIR spectra of *Chlorella*/polyvinyl alcohol blend films without ultrasonic pre-treatment.

4 Conclusions

In this study, the ultrasonication pre-treatment of *Chlorella* to produce films with PVA mixture enhances performance of the film and could suggest its potential as a eco-sustainable food packaging plastic material. Mechanical test shows the increasing of bioplastic tensile strength up to 15,3 kgf/cm^2 and elongation percentage up to 99,63%. Field emission scanning electron microscopy test shows the increasing of

bioplastic homogeneity and smoother surface with less pores. Fourier transform infrared analysis shows that there are crosslinkages between *Chlorella* and PVA. Thermal analysis by thermogravimetric analysis shows ultrasonication creates a more compact linkages.

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