Mechanical properties of bioplastics cassava starch film with Zinc Oxide nanofiller as reinforcement

Harunsyah*, M Yunus and Reza Fauzan

Department of Chemical Engineering, Lhokseumawe State Polytechnic, Buketrata, Lhokseumawe 24300, Indonesia.

Email: *harunsyah@pnl.ac.id, mysri_son@yahoo.com, reza.fauzan@gmail.com

Abstract: This study focuses on investigating the influence of zinc oxide nanofiller on the mechanical properties of bioplastic cassava starch films. Bioplastic cassava starch film-based zinc oxide reinforced composite biopolymeric films were prepared by casting technique. The content of zinc oxide in the bioplastic films was varied from 0.2%, 0.4%, 0.6%, 0.8% and 1.0% (w/w) by weight of starch. Surface morphologies of the composites bioplastic films were examined by scanning electron microscope (SEM). The result showed that the Tensile strength (TS) was improved significantly with the additional of zinc oxide but the elongation at break (EB %) of the composites was decreased. The maximum tensile strength obtained was 22.30 kgf / mm on the additional of zinc oxide by 0.6% and plastilizer by 25%. Based on data of FTIR, the produced film plastic did not change the group function and it can be concluded that interaction in film plastic produced was only a physical interaction. Biodegradable plastic film based on cassava starch-zinc oxide and plasticizer glycerol showed that interesting mechanical properties being transparent, clear, homogeneous, flexible, and easily handled.

1. Introduction

Plastics have been used widely for packaging material since long time ago[1]. However, plastic wastes can pollute the environment because of its persistency to be biodegraded by microorganism. Efforts have been conducted to develop environmental friendly plastic from renewable resources. In recent years, a large progress has been achieved in the development of biodegradable products based on agricultural materials, due to a growing concern on the environmental impact and also the uncertainty of petroleum supply [1]. One of the most studied and promising raw materials for the production of biodegradable plastics is starch, which is a natural renewable carbohydrate polymer and an available low cost material. [2]. However, films formed from starch are brittle and difficult to handle; plasticizers are normally added to the film-forming solution before casting and drying procedures, as a way to overcome films brittleness [3]. To improve starch-based plastic characteristics and the mechanical resistance, many researchers have demonstrated the interest of using filler as reinforcement in thermoplastic matrixes and have shown that fibers incorporation can increase films tensile strength and elasticity modulus and decreases their elongation capacity [4]. Among the promising Nano fillers that have stirred much interest among researchers are including organo clay, nano silica, carbon Nano tube and Nano calcium carbonate. Studies have shown that the large surface area possessed by these Nano fillers promote better interfacial interactions with the polymer matrix compared to conventional micrometer sized particles, leading to better property enhancement [5]. There are number of inorganic mineral fillers used in polypropylene. The most common of these fillers are talc, calcium carbonate and barium...
sulphate; other mineral fillers used are wollastonite and mica. Mineral fillers are generally much cheaper than polypropylene resin itself. Mineral fillers reduce the costs of the compound formed with polypropylene and also increase the stiffness. Mineral fillers also provide reinforcement to the polymer matrix as well. Some mineral filler are surface treated to improve their handling and performance characteristics [6]. Silanes, glycols, and stearates are used commercially to improve dispersion and processing, as well as to react with impurities.

In the present work, we have investigated the fabrication of bioplastic film base on cassava starch (biopolymer) by using glycerol as plasticizer obtained by casting method. The bioplastic film is reinforced by zinc oxide nanofiller to enhance mechanical properties. The mechanical properties of bioplastic film were determined by tensile strength tests, surface morphology was examined by using scanning electron microscopy and thermo mechanical was examined by using thermogravimetric analysis.

2. Procedure

A. Starch Extraction
Starch was extracted from cassava and tree cassava tubers, grown in Indonesia and purchased from the local market. The cassava roots are ripe after 12 months. For each species, the tubers were washed, peeled and grated. The resulting paste was mixed with water and the solution was filtered on a clean cloth. The collected filtrate was then allowed to stand for 6 hours followed by the removal of the supernatant. The white precipitate (starch) was then recovered, sun-dried and stored in polyethylene bags at room temperature.

B. Preparation of ZnO Nanoparticle Bioplastic Film
ZnO nanoparticles was purchased from US Research Nanomaterials, Inc. The preparation of bioplastic packaging films and the casting was based on Alebooyeh et al. [7] with some modifications. First, zinc oxide nanoparticles were dispersed in distilled water solution at 0.2 to 1.0% (w/w) of the total starch and stirred for 1 hour and ultrasonicated for 30 minutes. Then the solution was heated to 85 ± 5°, held for 15 minutes for gelatization. Next, glycerol plasticizer addition is carried out with the concentration variation of 25, 30 and 35%, and it is agitated until homogeneous. Then, the homogeneous solution is casted above a plate with 2.0 mm thickness. Furthermore, drying is carried out in oven at temperature of 60 °C for 5 hours. The dry bioplastic films were removed from the oven and stored at controlled conditions (25 °C and 75% of relative humidity) for at least 48 hours before measurements. Control films were also prepared but without the additional of nanoparticles. The dried films were peeled and cut to have an average dimension of 7cm x 5cm. The thickness was also measured and samples were further used.

C. Tensile Strength (TS) and Elongation at Break (%E) Analysis
In general, the physical and electrical properties of plastics are influenced by temperature and relative humidity in a manner that materially affects test results. In order to make reliable comparisons between different materials and between different laboratories, it is necessary to standardize the humidity conditions, as well as the temperature, to which specimens of these materials are subjected prior to and during testing. Therefore, all films plastic were conditioned prior to subject them to permeability and mechanical tests according to Standard method, ASTM-D618-61. Films used for testing Water Vapor Permeability (WVP), Tensile Strength (TS) and Elongation (E) were conditioned at 75% relative humidity and 25 °C by placing them in a desiccators over a saturated solution of Mg (NO3)2.6H2O for 24 hours or more. For other tests, film samples were transferred to plastic bags after peeling and placed in desiccators. The tensile strength and elongation at break of the films were measured using a computer type universal testing
machine (HUNG TA, TH-8503). The tensile samples were cast in a collapsible aluminum mold in based on ASTM standard D638 for tensile tests and the creep specimen was prepared as dumbbells by compression molding based on ASTM D2990 for tensile creep tests.

D. Scanning Electron Microscopy Analysis (SEM)
Scanning electron microscopy film plastic surface morphology was examined by using scanning electron microscopy. The samples were mounted on stub with double-sided adhesive tape (5x5 mm) and coated with a thin layer (150-180 A) of gold (JEOL JFC-1600 auto fine coater). Images were taken using a JEOL JSM-6510-LA Japan with an accelerating voltage of 0.5 to 30 kV. TEM images were recorded with a JEOL model transmission electron microscope, operating at 200 kV, with a point-to-point resolution of 0.3 nm.

E. Thermal Properties Analysis
The thermo mechanical (TM) test of the films plastic was taken by using computer controlled Thermogravimetric analysis (TGA) (Model: DSC-60 Supplier: Shimadzu Corp.). The temperature range was maintained at 30°C to 600°C and the temperature was increased at a rate of 10°C/min. The flow rate of nitrogen gas was 20 ml/min. Sample weights were 5.0 mg.

3. Results
In order to know the quality of resulted bioplastic film, several parameters which usually used to analyse resulted bioplastic are measured such as tensile strength, elongation at break. Mostly, bioplastic materials are used because they have desirable mechanical properties such as tensile strength and elongation at break. For this reason, the mechanical properties may be considered as the most important of all the physical properties of bioplastic for most applications.

| Plastilizer (Glycein) | Tensile Strength (kgf/mm²) | ZnO nanofiller (%) |
|-----------------------|---------------------------|-------------------|
|                       | 0.0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
| 25 %                  | 20.90 | 17.30 | 20.50 | 22.30 | 18.60 | 12.90 |
| 30 %                  | 17.00 | 19.20 | 20.00 | 20.60 | 18.80 | 14.30 |
| 35 %                  | 12.60 | 20.10 | 19.30 | 20.20 | 20.50 | 12.40 |

| Plastilizer (Glycein) | Elongation at Break (%) | ZnO nanofiller (%) |
|-----------------------|-------------------------|-------------------|
|                       | 0.0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
| 25 %                  | 266.20 | 332.20 | 252.00 | 198.40 | 153.20 | 236.80 |
| ZnO nanofiller (%) | 25 % Glycerol | 30 % Glycerol | 35 % Glycerol |
|-------------------|---------------|---------------|---------------|
| 0.00              | 250.80        | 234.80        | 213.20        |
| 0.20              | 182.40        | 162.80        | 141.70        |
| 0.40              | 123.40        | 105.80        | 83.80         |
| 0.60              | 122.80        | 107.60        | 84.00         |
| 0.80              | 139.60        | 117.00        | 90.80         |
| 1.00              | 123.20        | 105.20        | 82.40         |

**Figure 1.** Effect of ZnO filler concentration on tensile strength

**Figure 2.** Effect of ZnO filler concentration on elongation at break
4. Discussion

4.1 Effect of Zinc Oxide Filler Concentration on Tensile Strength and Elongation

Tensile strength is the maximum load large unity initial cross-sectional area of the sample. Tensile strength indicates the ability to accept load or tension without damaging the composite or broken which is stated with a maximum tension before breaking namely ultimate tensile strength. Tensile strength of composite material can be affected by several factors, including the relative comparison between the matrix and the reinforcement materials in composite materials, namely how many zinc oxide is added to the polymer matrix compared with composite materials. Elongation at Break indicates the quantity of the change of maximum film length while obtaining tensile strength until the film breaks, compared to the initial length. The result of tensile strength and elongation at break is given in Table 1 and table 2.

Figure 1 and figure 2 presented the influence of zinc oxide reinforcement on tensile strength and elongation at break, where the increase of zinc oxide composition quantity indicates the tendency to increase tensile strength value and the further will be declined, in other words, the higher the concentration of nano zinc oxide, it will generate a tensile strength diminishing. This is because the particles have more space in the matrix (starch), thus affects the tensile strength of the bioplastic film, as obtained in the study of Wang et al [8] and Waryat et al [9]. While for the percentage elongation, the value will decrease with increasing concentration of zinc oxide. Table 1 and table 2 above illustrate the tensile strength properties that indicates the concentration addition tendency of glycerol as plasticizer could increase elongation percentage and reduce tensile strength. The maximum tensile strength obtained was 22.30 kgf/mm² on addition of zinc oxide by 0.6 percent and plasticizer by 25%.

4.2 Scanning Electron Microscopy Analysis (SEM)

Morphology, hygroscopcity and mechanical characteristics of the bioplastic film produced is closely related to the concentration of glycerol and ZnO that were added in synthesizing of the film plastic produced. Effect of ZnO nanofiller was added to the on morphologytic bioplafilms can be seen in Figure 3.

![Figure 3. SEM analysis bioplastic film with ZnO nanofiller at optimum condition](image-url)
Visually one of the results of scanning electron microscopy film plastic produced for optimum condition (plastilizer glycerol 25\% and ZnO 0.6\%) is not porous and it looks smoother, no cracks or air bubbles and in general, the film appearance is transparent. By using SEM, the morphology of the resulting film packaging there are a number of starches that this clumping occurs because starch insoluble depleted due to the effects of complaining and temperature conditions are not uniform when the plastic film is made.

4.3 Thermogravimetric analysis (TGA)
Thermogravimetric analysis (TGA) was used to investigate experimentally the thermal stability of cassava starch-ZnO blends. The thermal stability of any polymeric material is largely determined by the strength of the covalent bonds between the atoms forming the polymer molecules. Figures 4 show the initial TGA thermograms (without ZnO) and the corresponding rate of reaction curves of with concentration of ZnO blends. Based on the TGA study in figure 4 and figure 5, few points may be concluded that the major loss in weight (20-70\%) for without ZnO or with ZnO blends occurs within the range of 200-350 \^\circ C, in which with ZnO blends possess higher thermal stability than without ZnO blends.

4.4 Fourier Transform Infra-Red Analysis of Bioplastic Films (FT-IR)
The infrared analysis was carried out using Fourier-Transform Infrared Spectroscopy (FT-IR) model Mattson-Genesis, made by Unicam, England, over the range 400- 4000 cm\(^{-1}\). FT-IR spectroscopic analysis can give useful information about chemical changes occurring in polymer systems due to blending process, casting process. However, the detection of such changes may be restricted because often different polymer compounds in the polymer blends are chemically similar, so their absorption peaks are masked. To facilitate the detection of changes, a comparison between the characteristic bands of the compounds is investigated.

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because often different polymer compounds in the polymer blends are chemically similar, so their absorption peaks are masked. To facilitate the detection of changes, a comparison between the characteristic bands of the compounds is investigated. The interaction of polymer starch with ZnO nanoparticle could be identified with FT-IR spectra shown in Figure 5, the FTIR spectra of blend substances should show no appreciable changes in the spectral band positions.

![Figure 5. FTIR spectra analysis of bioplastik film with ZnO nanofiller on optimum condition](image)

Results of this study suggested that addition of ZnO nanofiller on starch-based bioplastics interact strongly on fabricated films. Data revealed that the increasing concentration of ZnO nanoparticles in bioplastic films involved stronger alkane bond, C-O bond, C=C bond, and C-C bond formations. This suggests a stronger attachment and stronger material strength as shown in films mechanical properties.

5. Conclusion
This study described the effect of ZnO nanofiller on optimum mechanical properties of bioplastic film based on cassava strach. The goal of the research was to obtain an early identification of formulation composition to further design on a complete experimental study. Results of the study showed that the addition of ZnO nanofiller resulted in some changes in the mechanical behaviour of bioplastic film as outlined below:

1) Cassava starch based films plasticized with glycerol showed interesting mechanical properties such as being transparent, clear, homogeneous, flexible, and easily handled.

2) The results establish that films plastic based on cassava starch and plasticized with glycerol can be considered as an interesting biodegradable alternative packaging material.

3) Bioplastic film made from cassava starch by using glycerol and the addition of Zinc Oxide filler has mechanical properties such as white transparent, clean, homogeneous, easily bent and handled.
The optimum formulation composition has tensile strength value of 22.30 kgf/mm² at ZnO concentration of 0.6% and plasticizer concentration of 25%.

5) The best value of Elongation at Break is as large as 122.80% ZnO concentration of 0.6% and plasticizer concentration of 30%.

6) Bioplastic film hydrophilic or not resistant to water and the resulting functional groups together with the constituent components of starch. In the synthesis of plastic film that happening is the process of blending physics and the group C=O and CO Ester carbonyl makes environmentally friendly plastic. The morphology structure of bioplastic, both top and cross section, has not given the homogeneous morphology structure.

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