Effect of ZnO / Clay Nanoparticles Concentration Ratios to Improve the Mechanical Properties of Cassava Starch Bioplastics Film for Food Packaging Applications

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Abstract. Nowadays, conventional plastics are extensively used in almost daily activities such as the plastic packaging bags produced from polyethylene and polypropylene. However, the products from these polymers cause the environmental problem. To solve this problem the conventional plastic can replace with biodegradable plastic. The main objective of this study is to improve mechanical properties of biodegradable plastic by the addition of percent ratio ZnO/Clay nanoparticles as enforcement. All biodegradable plastic was formed by casting method. The addition of ZnO/clay nanoparticles in the plastic films was varied from 0:1%, 0.1:0.9%, 0.2:0.8%, 0.3:0.7%, 0.4:0.6%, 0.5:0.5%, 0.6:0.4%, 0.7:0.3%, 0.8:0.2% 0.9:0.1% and 1:0% (w/w) by weight of starch. Structural characterization was done by Fourier Transform Infrared Spectroscopy (FTIR). Surface morphologies of the plastic film were examined by scanning electron microscope (SEM). The result showed that the tensile strength (TS) was improved significantly with the addition of ZnO/Clay nanoparticles. The optimum tensile strength obtained was 10.87 M.Pa on the additional of ZnO/Clay nanoparticles by 0.3:0.7% and plasticizer by 25%. Based on data of FTIR, the produced film plastic does not change the group function and it can be concluded that the interaction in biodegradable plastic produced was only a physical interaction. The biodegradable plastic based on cassava starch-ZnO/Clay nanoparticles and plasticizer glycerine showed that interesting mechanical properties being transparent and clear.

1. Introduction
Over the last decades, the use of conventional plastics as food packaging material has increased considerably. Conventional plastics are widely used for packaging and other applications because of their several advantages compared to other materials. For example, plastics are inexpensive, light weight and chemically inert. Moreover, they are heat-sealable, easy to print on and offer the flexibility of fabricating into various shapes. Unfortunately, conventional plastics have their origin in petrochemical industry making them non-biodegradable and non-renewable [1,2]. The non-biodegradable and non-renewable nature of plastics has been a serious disadvantage to their application leading to huge municipal wastes and environmental degradation.
So, the use of conventional plastic as food packaging material facing various environmental problems, which cannot be recycled and cannot decompose naturally by microbes in the soil, resulting in the accumulation of plastic waste that causes pollution and damage to the environment. Therefore, to replace the conventional plastics with biodegradable plastic base on starch can solve this problem. Cassava starch is one which starch is a natural polymer, inexpensive, readily available, and often used as a filler for the replacement of petroleum-derived synthetic polymers to decrease environmental pollution. However, cassava starch has severe limitations because of its solubility and poor water-resistance, making starch products very sensitive to the relative humidity at which they are stored and used.

Cassava starch has been considered as the most promising raw material to develop new environmentally friendly materials especially for packaging disposable applications because of its low density, its renewable character and its complete biodegradability, and its availability worldwide under different shapes at relatively low cost [3-6].

The main disadvantages of biodegradable plastic base on cassava starch, compared to conventional plastics, are their hydrophilic character and their poor mechanical properties which lead to low stability [7,8]. In order to replace conventional polymer by biopolymers, these drawbacks have to be circumvented. Indeed, depending on the targeted applications, may need specific properties such as stiffness, flexibility, and strength.

And also, there are some strong limitations for developing starch based products, since they present poor tensile properties and high-water vapour permeability when compared to conventional films derived from crude oil on account of their hydrophilic nature and their sensitivity to moisture content, a factor that is difficult to control [9].

Numerous studies have been conducted to optimize the properties of biodegradable plastic base on starch. The most important properties in bioplastic materials include mechanical and thermoforming properties, gas and water vapour permeability, and its transparency [1]. To improve characteristics of the biodegradable plastic base on starch, many researchers have demonstrated the interest of using filler as reinforcement and have shown that certain compounds such as inorganic mineral incorporation can increase films tensile strength and elasticity modulus and decreases their elongation capacity.

There are a 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 also provide reinforcement to the polymer matrix as well. Some mineral filler is surface treated to improve their handling and performance characteristics.

In the present work, we have investigated the fabrication of biodegradable plastic base on cassava starch obtained by casting method. Thermoplastic starch is reinforced by zinc oxide-clay nanofiller and thermoplastic starch was made from cassava starch by using glycerol as plasticizer.

2. Materials, Method and Analysis

2.1. Materials

Materials used for bioplastic film production were: cassava starch, polyvinyl alcohol (liquid), glycerin, water and clay nanoparticles. Starch was extracted from cassava tubers and purchased from the local market. 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. The polyvinyl alcohol and glycerin were all obtained from Merck, Germany. Zinc Oxide and clay nanoparticles was obtained from Aldrich Chemistry, Germany. Polyvinyl alcohol (PVA) is a water-soluble polymer made by hydrolysis of a polyvinyl ester (such as polyvinyl acetate). It is used in adhesives, as textile and paper size, and for emulsifying, suspending, and thickening of solutions. A glycerin is an additive that softens the
material. It's function as plasticizer used in the bioplastic film production. Glycerin is a simple polyol compound. It is a colorless, odorless, viscous liquid and has a high boiling point and freezes to form a paste.

2.2. Method

The preparation of bioplastic film and the casting was based on Alebooyeh [10] with some modifications. First, clay nanoparticles were dispersed in distilled water solution at 0.2 to 1.0% (w/w) of the total starch (based on starch weight) and stirred for 1 hour and ultra-sonicated for 30 minutes. Then the solution was heated to 85 ± 5º, held for 15 minutes for gelatinization. Next, glycerin 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 O C for 5 hours. The dry bioplastic films were removed from the oven and stored at controlled conditions (25 O C and 75% of relative humidity) for at least 48 hours before measurements. Control bioplastic films were also prepared but without the additional of nanoparticles. The dried films were peeled and cut to have an average dimension of 7 x 5 cm. The thickness was also measured and samples were further used.

2.3. Analysis

In general, the physical properties of bioplastics are influenced by temperature and relative humidity, it can affect test results. Therefore, 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. All bioplastic films were conditioned prior to subject them to permeability and mechanical tests according to Standard method. Films used for testing Oxygen Permeability (OTR) [11,12], Tensile Strength (TS) [13] was conditioned at 75% relative humidity and 25 O C by placing them in a desiccator 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 (MTS Criterion, Model-634). 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. Morphology and physical properties of biodegradable plastic were determined by Scanning Electron Microscopy Analysis (SEM), thermogravimetric analysis (TGA) was used to investigate experimentally the thermal stability of ZnO/Clay blends.

3. Results and Discussion

3.1. Effect of ZnO/Clay Concentration on Tensile Strength

The most 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 the most important of all the physical properties of bioplastic for most applications. Tensile strength is the maximum load large unity initial cross-sectional area of the sample. Tensile strength indicates the ability to accept a load or tension without causing the composite becomes damaged or broken 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-clay nanoparticles 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 bioplastic and tensile strength is given in Figure 1 and Table 1.

![Bioplastic (a) without reinforcement (b) with reinforcement](image)

Figure 1. Bioplastic (a) without reinforcement (b) with reinforcement

| Gliserol (%) | 0:1 | 0.1:0.9 | 0.2:0.8 | 0.3:0.7 | 0.4:0.6 | 0.5:0.5 | 0.6:0.4 | 0.7:0.3 | 0.8:0.2 | 0.9:0.1 | 1:0 |
|--------------|-----|---------|---------|---------|---------|---------|---------|---------|---------|---------|-----|
| 25           | 3.93| 9.34    | 4.16    | 10.87   | 9.27    | 7.75    | 5.8     | 5.46    | 10.03   | 4.71    | 7.41 |
| 30           | 7.93| 5.48    | 7.79    | 4.54    | 5.18    | 5.99    | 5.2     | 6.3     | 4.68    | 6.72    | 4.79 |
| 35           | 4.28| 4.12    | 3.55    | 4.47    | 4.66    | 4.46    | 4.78    | 4.74    | 5.38    | 5.58    | 3.61 |

Table 1. Effect of ratio zinc oxide-clay concentration on tensile strength

From Table 1 and Figure 2 presented the influence of ratio zinc oxide-clay reinforcement on tensile strength and, where the increase of ratio zinc oxide-clay composition quantity indicates the tendency to increase tensile strength value and the further will be decline or in other words, the higher the concentration of nano zinc oxide-clay, it will generate a tensile strength diminishing. This is because the particles more space in the matrix (starch), thus affecting the tensile strength of the bioplastic film, as obtained in the study of Wang [14,15]. The maximum tensile strength obtained was 10.87 M.Pa on addition of ratio ZnO/Clay by 0.3:0.7 percent and plastilizer by 25%.

3.2. Thermal Properties Analysis of the Bioplastic Films

The thermo mechanical (TM) test of the films bioplastic 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.

Thermogravimetric analysis (TGA) was used to investigate experimentally the thermal stability of ZnO/Clay blends. Figures 2 show the initial TGA thermograms and the corresponding rate of reaction curves of different ratios of ZnO/Clay blends, before and after melting process at optimum condition.
Based on the TGA study, few points may be concluded, the onset of degradation temperatures for the ZnO and clay reinforcement was generally in the range 270–300 °C. The addition of mineral ZnO and Clay reinforcement generally increased the degradation temperature (Figure 3).

3.3. 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.

Effect of ZnO/Clay nanoparticles was added to the on morphologic bio plasma films can be seen in Figure 3.4a.b. Visually one of the results of scanning electron microscopy film plastic produced for optimum condition 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

3.4. Oxygen Permeability

An important characteristic of food packaging, especially in the case of modified atmosphere packaging, is the oxygen permeability. The food and packaging industry has a strong interest in the specification of the barrier properties of the thermoformed tray, based on the oxygen transmission rate (OTR) and thickness of the sheet or film. The oxygen transmission rate is the amount of oxygen passing a material during a specified time at a given temperature and partial pressure of oxygen. The common unit of OTR is cc O₂/m²/24 hr or (cm²/cm².s.cm H₂O) (at 0.21 atm, 23°C, 50% RH). The currently used method for measuring the oxygen transmission rate uses an instrument from Mocon Inc. Packages are mounted on the equipment, with pure nitrogen flowing through the package. Oxygen molecules entering the package are transported by the nitrogen flow to a sensor detecting the number of molecules. When a steady flow of oxygen molecules entering the package have been achieved the OTR value is determined. The result of the oxygen permeability bioplastic film is given in Table 2.

| Bioplastic | Volume cm (STP) | Film Thickness (cm) | Film Area (cm²) | ΔP (cm H₂O) | Time (s) | Permeability Rate (cm O²/m².day) |
|------------|----------------|--------------------|----------------|-------------|---------|-------------------------------|
| Blangko    | 19.7           | 0.026              | 19.64          | 14.5        | 160     | 1.12411x10⁻⁵                  |
| ZnO        | 19.5           | 0.026              | 19.64          | 15.1        | 160     | 1.06849x10⁻⁵                  |
| Clay       | 19.3           | 0.028              | 19.64          | 15.3        | 160     | 1.08385x10⁻⁵                  |

Data in table 2 is showed that the permeability rate for bioplastic without reinforcement is greater than that of bioplastics with reinforcement. It means that ZnO/clay nanoparticles not only as reinforcement but also can be a retarder of permeability because ZnO and clay nanoparticles fill in empty space on starch.

The oxygen permeability value is affected by the thickness of the bioplastic. The thicker the bioplastics are tested the more difficult the bioplastic is translucent by oxygen, this leads to the lower the resulting oxygen permeability value. In this analysis, the best value can be in the Nanoclay sample.

4. Conclusion

Production biodegradable of cassava starch-ZnO/Clay nanoparticles plastic films were prepared by via casting processing techniques. From the obtained the results the following conclusions can be drawn as: i) the results establish that films bioplastic based on cassava starch mixture with ZnO/clay nanoparticles as reinforcement and plasticized with glycerol can be considered as an interesting biodegradable alternative packaging material; ii) the addition of ZnO/Clay nanoparticles was able to increase the tensile strength of the bioplastics value because of increases in hydrogen bonding between ZnO/Clay amylose- amylopectin chains; iii) bioplastic film made from cassava starch by using glycerol and the addition of ZnO/clay nanoparticles as reinforcement has mechanical properties such as transparent white, clean, and homogeneous; iv) a reinforcing effect of the clay nanoparticles on the tensile strength of the cassava starch was observed, showed the increasing addition of the plasticizer seems to negatively affect the reinforcing effect of the ZnO/clay nanoparticles; v) the optimum formulation composition has tensile strength value of 24.18 M.Pa at clay nanoparticle concentration of 0.6% and plasticizer concentration of 25%; vi) bioplastic film produced has hydrophilic properties or not resistant to water; vii) the morphology structure of bioplastic, both top and cross section, has not
given homogeneous morphology structure, and viii) the permeability rate for bioplastic with reinforcement is lower than that of bioplastics without reinforcement. It means that ZnO/clay nanoparticles not only as reinforcement but also can be a retarder of permeability because ZnO and clay nanoparticles fill in empty space on starch.

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