The effect of clay nanoparticles as reinforcement on mechanical properties of bioplastic base on cassava starch

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Abstract. Plastics have been used widely for packaging material since long time ago. However, environmentally friendly plastics or plastics whose raw materials come from natural polymers are still very low in development. Efforts have been conducted to develop environmental friendly plastic from renewable resources such as biopolymer. The aim of this paper is to study the influence of clay nanoparticles as reinforcement on the mechanical properties of bioplastic were prepared by solution-casting method. The content of clay nanoparticles in the bioplastic was varied from 0.2%, 0.4%, 0.6%, 0.8% and 1.0% (w/w) by weight of starch. Structural characterization was done by Fourier Transform Infrared Spectroscopy. Surface morphologies of the plastic film were examined by scanning electron microscope. The result showed that the Tensile strength was improved significantly with the addition of clay nanoparticles. The maximum tensile strength obtained was 24.18 M.Pa on the addition of clay nanoparticles by 0.6% and plasticizer by 25%. Based on data of FTIR, the produced bioplastic did not change the group function and it can be concluded that the interaction in bioplastic produced was only a physical interaction. The bioplastic based on cassava starch-clay nanoparticles and plasticizer glycerin showed that interesting mechanical properties being transparent, clear, homogeneous, flexible and easy to be handled.

1. Introduction

Nowadays materials used for food packaging consists of a variety of petroleum-derived plastic polymer, metals, glass, paper and board, or combinations thereof. Among these packaging materials, plastic is found to be the best because of its long life properties. Thus, its utilization is increasing every day by day. However, plastics cannot be degraded by natural processes in a short period of time; therefore, they are left as plastic waste, causing environmental problems.

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 filler as reinforcement 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 biodegradable plastic film obtained by casting method; thermoplastic starch is reinforced by clay nanoparticles and thermoplastic starch was made from cassava starch by using glycerol as plasticizer. Morphology and physical properties of biodegradable plastic were determined by mechanical tensile tests and thermogravimetric analysis.

2. Materials And Method

2.1 Materials

Materials used for bioplastic film production were: cassava starch, polyvinyl alcohol (liquid), glycerin, water and clay nanoparticles as reinforcement. Starch was extracted from tree cassava tubers that purchased from the local market. 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. The polyvinyl alcohol and glycerin were all obtained from Merck, Germany. 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. 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. It is the plasticizer used in the bioplastic film production. A plasticizer is an additive that softens the material it is added to.

2.2 Bioplastic Film Preparation

The preparation of bioplastic packaging films and the casting was based on Alebooyeh et al [7] with some modifications. First, clay nanoparticles 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 ultrasonicated for 30 minutes. Then the solution was heated to 85 ± 5º, held for 15 minutes for gelatinization. Next, glycerin plasticized 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 oC for 5 hours. The dry bioplastic films were removed from the oven and stored at controlled conditions (25 ºC 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 bioplastic films were peeled and cut to have an average dimension of 7cm x 5cm. The thickness was also measured and samples were further used.

2.3 Analysis

a) Tensile Strength (TS)

In general, the physical and electrical properties of bioplastics 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 bioplastic film were conditioned prior to mechanical tests according to Standard method, ASTM- D638. Tensile Strength (TS) was conditioned at 75% relative humidity and 25 ºC 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 (MTS Criterion, Model-634).

b) 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.

c) Thermal Properties Analysis of the Film Plastics
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.

d) Fourier-Transform Infrared Spectroscopy (FT-IR)
The infrared analysis was carried out using Fourier-Transform Infrared Spectroscopy (FT-IR) model Mattson-Genssis, 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.

3. Results, Analyses and Discussions
3.1 Effect of concentration clay nanoparticles on tensile strength
Tensile strength is the maximum load large unity initial cross-sectional area of the sample. Tensile strength (TS) 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. 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 clay particles is added to the polymer matrix compared with composite materials. The result of tensile strength and elongation is given in Table 1 and Figure 1.

| Plastilizer Glycerin (%)| Tensile Strength (MPa) | Clay Nanoparticles Concentration (%) |
|-------------------------|------------------------|-------------------------------------|
|                         | 0.0    | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
| 25                      | 17.24  | 20.27 | 15.39 | 24.18 | 22.58 | 20.19 |
| 30                      | 13.48  | 9.23 | 20.74 | 18.90 | 23.88 | 18.34 |
| 35                      | 10.69  | 19.26 | 20.16 | 24.16 | 23.77 | 24.54 |

Table 1. Effect of concentration of clay particles on tensile strength
Figure 1 presented the influence of clay nanoparticles concentration reinforcement on tensile strength, where the increase of clay particles concentration indicates the tendency to increase tensile strength value and the further will be declined, in other words, the higher of the clay particles concentration, 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 clay particles. Figure 1 above illustrate the tensile strength properties that indicates the concentration addition tendency of glycerin as plasticizer could increase elongation percentage and reduce tensile strength. The maximum tensile strength obtained was 24.18 M.Pa on addition of clay nanoparticles concentration by 0.6 percent and plastilizer by 25%.

3.2. Thermogravimetric Analysis (TGA)
Thermal degradation can be studied through TGA. The thermal decomposition of the bioplastic under nitrogen atmosphere comprises a three-step process. Figure 2 presents the TG curve of the bioplastic with and without clay nanoparticles as reinforcement. The first step of the process, at temperatures from 30°C to 270°C, showed a weight loss of around 10%. Previous studies have revealed that the loss of weight at this stage was due to the evaporation of moisture from the material [10]. The second stage of weight loss occurred at 278°C to 360°C with 55% weight loss and the third stage of the thermal decomposition of the bioplastic was from 360°C to 500°C. The overall results of the physical and thermal properties analysis of the bioplastic with clay nanoparticles as reinforcement can be concluded that the major loss in weight (10-65%) for without clay or with clay nanoparticle occurs within the range of 270-500°C, in which with clay nanoparticles blends possess higher thermal stability than without clay nanoparticles. Base on this study, the thermal properties of the bioplastic with clay nanoparticles as reinforcement are around 160°C for the melting temperature and around 180°C as the degradation temperature.
3.3 Fourier Transform Infra-Red Analysis of Bioplastic Films (FT-IR)
Fourier-Transform Infrared Spectroscopy (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.

Figure 2. TGA analysis of bioplastik film without and with clay nanoparticles

Figure 3: Fourier Transform Infra-Red Spectral bands of bioplastic film without and with clay nanoparticles
The interaction of polymer starch with clay nanoparticle could be identified with FT-IR spectra shown in Figure 3. The FTIR spectra of blend substances should show no appreciable changes in the spectral band positions. However, if the two blend substances were compatible, a distinct interaction existed between the chains of one polymer and the co-added substances, causing FTIR spectrum change by band shifting and broadening. Results of this study suggested that addition of clay nanoparticles on starch-based bioplastics interact strongly on fabricated films. FTIR data showed that clay nanoparticles incorporated films detected OH (hydrogen) bond interaction between 3300-3200 cm\(^{-1}\), C-O bond at about 1400 cm\(^{-1}\) - 1000 cm\(^{-1}\), C-H band between 3000-2850 cm\(^{-1}\), C= C bond at around 1680-1600 cm\(^{-1}\), CH\(_3\) group at around 1450-1375 cm\(^{-1}\), and alkanes group with out of the plane bending at around 1000-650 cm\(^{-1}\).

### 3.4 Scanning Electron Microscopy Analysis (SEM)

Morphology, hygroscopicity 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 morpholetic bioplastics can be seen in Figure 4.

![Figure 4. SEM analysis bioplastik film with clay nanoparticles](image)

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.

### 4. Conclusion

Production biodegradable of cassava starch/clay nanoparticles plastic films were prepared by homogeneously dispersing montmorillonite nanoparticles via polymer melt processing techniques. From the obtained results the following conclusions can be drawn:

a) The results establish that films bioplastic based on cassava starch mixture with clay nanoparticles as reinforcement and plasticized with glycerol can be considered as an interesting biodegradable alternative packaging material.

b) Bioplastic film made from cassava starch by using glycerol and the addition of clay nanoparticles as reinforcement has mechanical properties such as transparent white, clean, and homogeneous.
c) A reinforcing effect of the clay nanoparticles on the tensile strength of the cassava starch that was observed, showed the increasing addition of the plastilizer seems to negatively affect the reinforcing effect of the clay particles.
d) Based on the result of the tensile strength, it showed that the addition of clay as an amplifier to the bioplastic manufacture gives a significant effect of increase.
e) 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%.
f) In this bioplastic synthesis that occurs is the process of mixing physics and functional groups C = O, CO and carbonyl occur similar to the components of this starch design show this bioplastic is environmentally friendly.
g) The morphology structure of bioplastic, both top and cross section, has not given homogeneous morphology structure.

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