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Effect of Clove Essential Oil Addition on Characteristics of Cassava Starch Bioplastic Film Incorporated Zinc Oxide-organoclay as Reinforcement

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Effect of Clove Essential Oil Addition on Characteristics of Cassava Starch Bioplastic Film Incorporated Zinc Oxide-organoclay as Reinforcement

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Abstract. The main objective of this study is to improve mechanical properties of bioplastic film and resistant to bacteria by the addition of percent ratio Zinc Oxide/Organoclay (ZnO/Clay) nanoparticles as enforcement and clove essential oil. All bioplastic film was formed by casting method. The addition of clay nanoparticles in the plastic films was varied from 1:9%, 2:8%, 3:7%, 4:6%, and 5:5% (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 20.87 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 glycerin showed that interesting mechanical properties being transparent and clear.

1. Introduction

Plastics have been used widely for packaging material since long time ago. However, plastic wastes can pollute 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 increases films tensile strength and elasticity modulus and decreases their elongation capacity [4].



Among the promising nanofillers that have stirred much interest among researchers include organo clay, nano silica, carbon nano tube and nano calcium carbonate. Studies have shown that the large surface area possessed by these nano fillers promotes better interfacial interactions with the polymer matrix compared to conventional micrometer sized particles, leading to better property enhancement [5].

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 are generally much less expensive 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 is 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 obtained by casting method; thermoplastic starch is reinforced by zinc oxide nanofiller 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. Preparation of bioplastic film

Starch was extracted from cassava and tree cassava tubers, grown in Indonesia and was 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.

The preparation of bioplastic films and the casting was based on Alebooyeh et al [7] with some modifications. First, zinc oxide/organoclay nanoparticles were dispersed in distilled water solution for 1 hour and ultra-sonicated for 30 minutes. Then the solution was heated to $85 \pm 5^\circ$, and mixed with starch and then held for 15 minutes for gelatinization. Next, glycerol plasticized addition is carried out with concentration variation of 25%, and it is agitated until homogeneous. Then, the homogeneous solution is casted above 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 addition 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.

2.2. Tensile Strength (TS) and Elongation (E)

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 bioplastic films were conditioned prior to subjecting 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 desiccator over a saturated solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 accordance with ASTM standard D638 for tensile tests and the creep specimen was prepared as dumbbells by compression molding in accordance to ASTM D2990 for tensile creep tests.

2.3. Scanning Electron Microscopy Analysis (SEM)

Scanning electron microscopy film plastic surface morphology was examined 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 Å) 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.

2.4. Thermal Properties Analysis of the Film Plastics

The thermo mechanical (TM) test of the films plastic was taken 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 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. 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-organoclay is added to the polymer matrix compared with composite materials. The result of tensile strength and elongation at break is given in Figure 1 and Table 1.

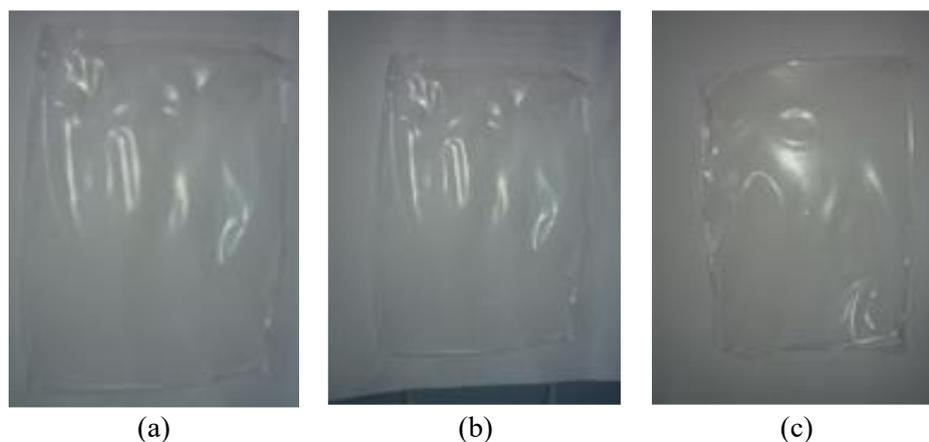


Figure 1. Bioplastic film (a) unmixing clove oil (b, c) mixed clove oil
Table 1. Effect of ratio zinc oxide-clay concentration on tensile strength

| Sample | Composition in /100 ml solution | | Tensile Strength (MPa) | | | | |
|----------|---------------------------------|----------|-------------------------------|-------|-------|-------|-------|
| | Glycerin (%) | Oil (ml) | ZnO : Organoclay Ratio (gram) | | | | |
| | | | 1:9 | 2:8 | 3:7 | 4:6 | 5:5 |
| Sample-1 | 25 | 0.2 | 42.63 | 45.68 | 31.51 | 33.94 | 39.44 |
| Sample-2 | 25 | 0.4 | 31.39 | 34.82 | 34.29 | 50.69 | 44.24 |
| Sample-3 | 25 | 0.6 | 42.02 | 51.05 | 34.25 | 22.13 | 34.78 |
| Sample-4 | 25 | 0.8 | 23.69 | 51.17 | 49.55 | 34.01 | 48.57 |
| Sample-5 | 25 | 1.0 | 32.7 | 29.19 | 44.41 | 47.56 | 26.44 |

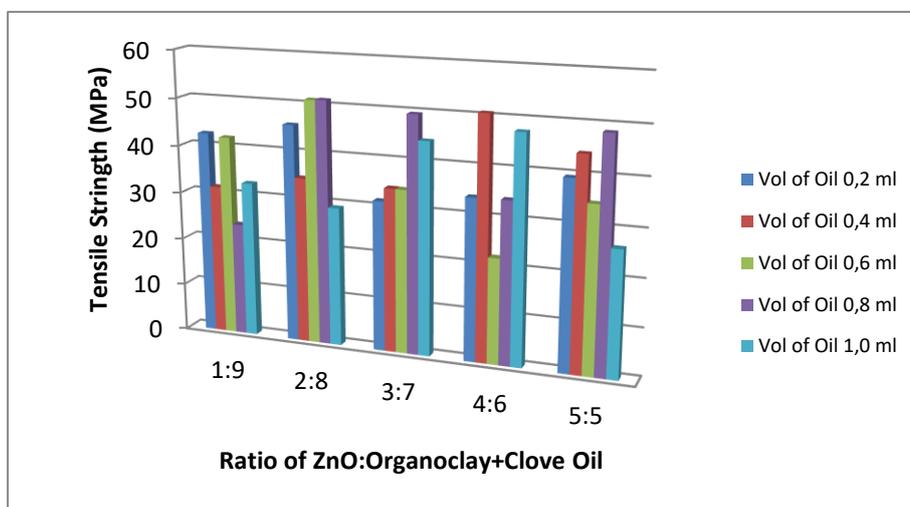


Figure 2. Effect of variation ZnO-Organoclay concentration on tensile strength

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 decline or in other words, the higher the concentration of nano zinc oxide, 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 et al [8] and Waryat et al [9].

While for the percentage elongation value will decrease with increasing concentration of zinc oxide. The Table 1 and table 2 above illustrates the tensile strength properties indicates that 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/mm on addition of zinc oxide by 0.6 percent and plastilizer by 25%.

3.2. Thermal Properties Analysis of the Bioplastic Films

Thermogravimetric analysis (TGA) was used to investigate experimentally the thermal stability of ZnO/Organoclay blends. Figures 3 show the initial TGA thermograms and the corresponding rate of reaction curves of different ratios of ZnO/Organoclay 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).

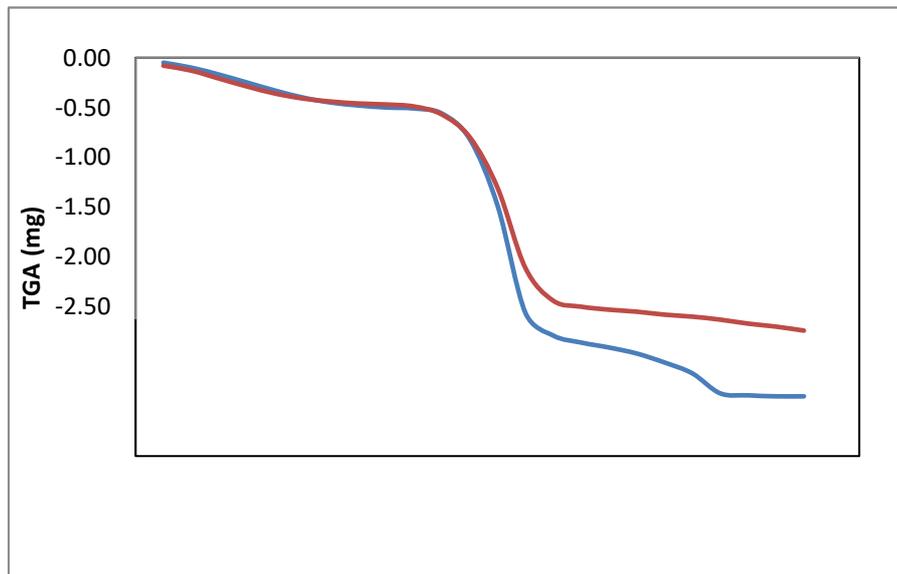


Figure 3. Thermogram of bioplastic without and with Zn

3.3. Scanning Electron Microscopy Analysis (SEM)

Morphology, hygroscopic and mechanical characteristics of the film plastic produced is closely related to the concentration of glycerol and ZnO/Organoclay that were added in synthesizing of the film plastic produced. Effect of ZnO/Organoclay was added to the on-morphology films can be seen in Figure 4 and Figure 5. Visually one of the results of scanning electron microscopy film plastic produced for optimum conduction is not porous and its looks smoother, no cracks or air bubbles and in general, the film appearance was 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.

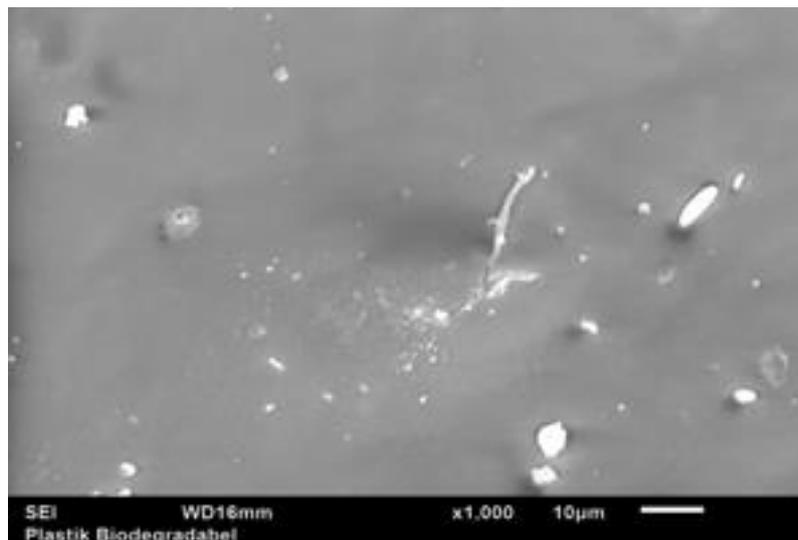


Figure 4. SEM analysis bioplastic film unmixed with ZnO/Organoclay

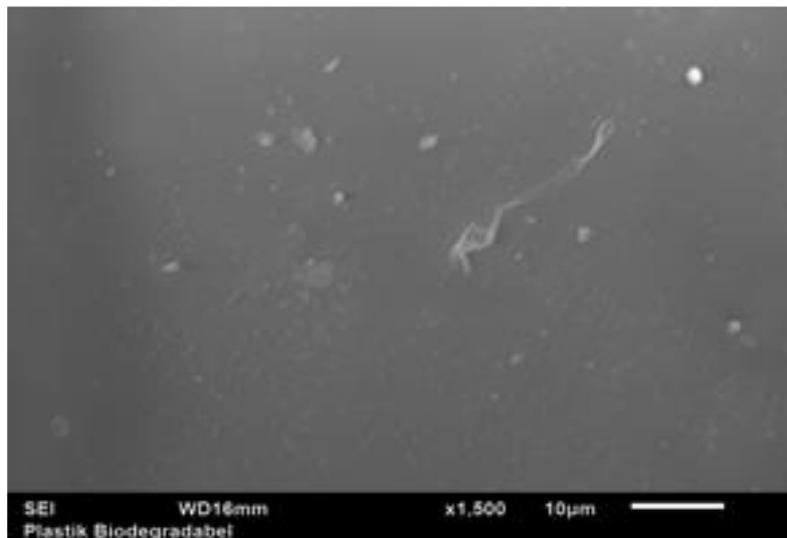


Figure 5. SEM analysis bioplastic film mixed with ZnO/Organoclay and oil

3.4. Biodegradation properties of bioplastic film

Analysis biodegradable bioplastic films aimed to determine the extent of degradation of polymers contained in bioplastic films. Degradation of polymers can be done using enzyme microorganism and can be also using hydrolysis process. Factors affecting the degradation process by hydrolysis is a type of chemical bond, pH, temperature and composition of the polymer, whereas factors affecting degradation using microorganisms is a type of polymer chemistry, methods of manufacture of polymers and polymer properties (biodegradable or not).

Methods of polymer degradation can be done in various ways, including the method of soil burial test. In the soil burial method, degradation which is influenced by the environment and microorganisms, the burial method there will be an aerobic process as much as 50% - 60% the rest is another factor, namely the sunshine, rain, macro-organism and soil (texture, structure, composition, organic content, acids / bases, water). Biodegradation method used in this research is the method of soil burial, is because the bioplastic film used has a water-soluble nature and it can be degraded by microorganisms.

The test results biodegradation by soil burial method is carried out for four (4) weeks with the rest of the weight percentage of bioplastics which are shown in Table 4.

In Figure 6 shows that the weight of the rest of bioplastics without the addition of ZnO/Organoclay nanoparticles decreases very significant versus degradation time and otherwise with the additional of ZnO/Organoclay nanoparticles only decreased slightly. This shows that with the addition of ZnO/Organoclay nanoparticles, bioplastic film will have a longer time decompose by organism. In this case due to addition of ZnO/Organoclay nanoparticles dispersed in a polymer matrix, these particles act as a barrier to the diffusion rate of water into the polymer.

From the analysis of the biodegradation of bioplastic films were tested in soil degradation has increased exponentially with time due to that the plastic film that is formed containing hydroxyl groups (OH), and carbonyl (CO) and ester (COOH) group indicates that the bioplastic that is produced can be degraded properly in the ground in the not too long.

4. Conclusion

Results of the study showed that the addition of ZnO nano filler resulted in some changes in the mechanical behavior of bioplastic film as the results establish that bioplastic films based on cassava starch mixture with ZnO/Organoclay and plasticized with glycerol can be considered as an interesting biodegradable film alternative packaging material. Bioplastic film made from cassava starch by using

glycerol and the addition of ZnO/Organoclay add essential oil has mechanical properties such as transparent white, clean, homogeneous, easily bent and easily handled. The optimum formulation composition has tensile strength value of 51.17 Mpa at ZnO/Organoclay ratio concentration of 2:8 and plasticizer concentration of 25%. Plastic 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 is happening is the process of blending physics and the group C = O and CO ester carbonyl make environmentally friendly plastic. The morphology structure of bioplastic, both top and cross section, has not given homogeneous morphology structure.

5. Acknowledgment

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Table 4. Residue of Bioplastic film for four weeks

| No | Residue (%) | | | | | | |
|----|--------------|----------------------------|--------|--------|--------|--------|--------|
| | Time (weeks) | ZnO/Organoclay + oil ratio | | | | | |
| | | 0:0 | 1:9 | 2:8 | 3:7 | 4:6 | 5:5 |
| 1 | 0 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2 | 1 | 92.685 | 98.399 | 98.528 | 98.978 | 97.424 | 98.289 |
| 3 | 2 | 91.763 | 96.889 | 97.223 | 97.653 | 95.455 | 97.186 |
| 4 | 3 | 86.476 | 92.745 | 93.365 | 94.885 | 88.243 | 90.982 |
| 5 | 4 | 81.578 | 82.462 | 84.658 | 85.362 | 83.274 | 80.838 |

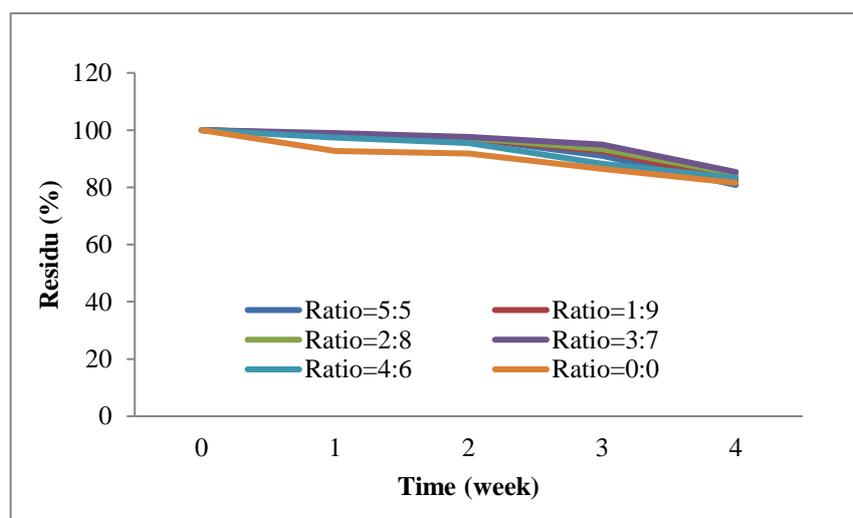


Figure 6. Effect of different concentration ratio on degradation time

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