Effect of Addition of Chitosan-ZnO as an Antibacterial on The Thermal Stability of PLA-Based Nanocomposites for Biofilm Packaging

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Abstract. This research is about Composite Polylactic Acid with chitosan and zinc oxide reinforcement (ZnO) in the manufacture of packaging biofilms. The purpose of this study is to produce biofilms with good characteristics that can be applied to food packaging. The method used is heating by varying the concentration of chitosan (1, 3 and 6%) and the concentration of ZnO at (1, 2, 3 and 4%). The resulting biofilm was analyzed by tensile test, thermal gravimetric, and FTIR. The results showed that the optimum tensile strength value obtained at the addition of Chitosan 6% - ZnO 3%, amounting to 1.22 MPa. The functional groups contained with the addition of ZnO and chitosan are functional groups C-H, C = O, O-H, and N-H. Biofilm samples underwent single decomposition with biofilm degradation temperatures ranging from 220-300 °C, the highest On Set temperature was 238.24°C, while the highest End Set was 295.16 °C. ZnO reinforcement added to the resulting composite can increase the tensile strength.

1. Introduction
The development of technology that accelerated this century pushed the industry to include food. Currently available food packaging that is practical and durable in a long time. Unfortunately, this food packaging is made from ingredients that cannot be degraded in nature, thus encouraging environmental pollution. These non-degradable materials are generally material from petroleum products that are harmful to the environment. The solution to this is to use biopolymer materials that can be degraded naturally by nature. Many researchers have improved the material from the biopolymer, one of which is to use it the concept of nanocomposites [1]. Nanocomposites are promising solutions for biopolymer problems.

Bio-composite is an environmentally friendly and biodegradable material, this material consists of two or more materials, the matrix of which is a Polylactic Acid (PLA) biopolymer and nanofiller used as chitosan and zinc oxide (ZnO). Because several materials used can increase the durability of the packaging.

The PLA matrix is synthesized by the fermentation of renewable agricultural sources, including corn, cellulose, and other polysaccharides. Although some of its characteristics are unfavorable (for example poor melting properties, mechanical fragility, low heat resistance, and slow crystallization), there are routes potential to overcome this deficiency. Then the PLA matrix can be included in the
copolymerization, mixing, modification of the plasticization, or the addition of the reinforcing phase for example, chitosan (Cs), cellulose, and starch) [2] and is well applied for food security.

In a study conducted by Lin et al [3], which mixed PLA and Chitosan with variations in the concentration of 0.2; 0.4; 0.8% by weight after 2 hours of incubation in 10 times simulated body fluid (10 × SBF). X-ray diffraction results show that it can increase more nucleation and growth calcium phosphate in the condition of chitosan concentration of 0.4%. These results indicate that this composite can mimic the structural, composition and biological functions of the original bone and can function as a good candidate for bone tissue engineering (BTE).

Silva et al [4], conducted research between PLA and ZnO having great potential for antimicrobial activity, but poor interface interactions between PLA and ZnO caused poor mechanical and thermal properties. The ZnO / PLA film selects the mechanical properties of the inferior by proving that 5% of the mass of ZnO-PLA increases the tensile strength and modulus of elasticity of each 30% and 65%, respectively. PLA nanocomposite films with ZnO exhibit exceptional antimicrobial properties against E. coli and S. aureus, where bacterial counts are greater than 98% in a day and there are no dead bacterial colonies in high fillers.

Based on the reference of the composite merge research above, the focus of this research is on mixing PLA, chitosan and ZnO to be able to improve the mechanical and thermal properties. Because in this case, chitosan used in this research as an amplifier of the film produced and the addition of ZnO here is very influential, because ZnO has properties such as an antibacterial effect or intensive ultraviolet absorption. ZnO is also a multifunctional and active ingredient for packaging (to increase the shelf life of food products) as well as textile applications with exceptional antimicrobial properties.

2. Material and Method

2.1. Manufacture of PLA-Chitosan-ZnO nanocomposites
PLA pellets are dissolved in 30 ml of chloroform solution at 60 °C for 2 hours. After the PLA dissolved, chitosan and zinc oxide (ZnO) were added with variations in the concentration of zinc oxide (ZnO) 1%, 2%, 3%, and 4% and variations in the concentration of chitosan 1%, 3%, and 6%. Then it is heated at 80 °C and stirred constantly so that the mixture is homogeneous for 15 minutes. After all homogeneous, added 2 ml of glycerol. The composite solution is put into a mold, then dried in the oven at 40 °C for 24 hours to dry. Then the composite formed is tested by tensile strength and FTIR tests.

2.2. Characterization of PLA-Chitosan-ZnO nanocomposites

2.2.1. Tensile Strength Test (ASTM. D 638-02 type 4)
Testing of mechanical properties is carried out by tensile strength testing of composite materials using ASTM D 638 carried out by cutting dumbbell-shaped samples using typical cuts following specified dimensions: 1. Samples that have been printed according to size are placed at both ends of the stapler that are positioned on the pulling tool, 2. The pull engine switch and the chart recording switch are turned on together, according to the engine pull speed, 3. From the results of testing the test machine will be obtained by the relationship between the tensile force to the length increase. And here is a picture of a tensile strength test specimen [5] as in figure 1.
2.2.2. FTIR analysis
Infrared Fourier Transform (FTIR) analysis is the spectra determined in the spectral range from 600 cm$^{-1}$ to 3600 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Data were analyzed with FTIR Spectrum (Perkin Elmer) software.

2.2.3. XRD analysis (Thermogravimetric Analyzer)
The thermal stability of the sample is determined using a thermogravimetric analyzer, using the Perkin Elmer Thermogravimetric analysis at a heating rate of 10 °C/min under atmospheric nitrogen, from 50 °C to 700 °C. About the weight of each sample is analyzed and consequently, the weight loss of the sample is determined.

3. Result and Discussion

3.1. Effect of Chitosan and Zinc Oxide Concentration Variations on Mechanical Characteristics of PLA-Chitosan-ZnO Composites
The mechanical characteristics of PLA-Chitosan-ZnO composites were analyzed through testing the tensile strength of the sample using a UTM (Universal Testing Machine). The specimen dimensions used follow the specimen dimensions in ASTM D 638-99 type IV where each composite to be tested is given a tensile load of 200 kgf, with the test specimen being pulled parallel until the composite material is broken. According to Farah [6], the value of the tensile strength of a material is shown based on the value of UTS (Ultimate Tensile Strength) which is the maximum stress value that can be received by the material before the test material is damaged or broken.

The result of the high tensile strength (mechanical properties) is related to research conducted by Wafiroh [7], on biofilms that have high mechanical properties will increase the ability and strength of biofilms to improve the quality of the products it provides. This tensile strength test was made by the biofilm constituent components published by PLA, chitosan and Zinc Oxide (ZnO), the homogeneous level of the dissolution of this biofilm and the relationship of tensile strength with the concentration of Chitosan and ZnO are presented in Figure 2.
The variation in the tensile strength of PLA-Chitosan-ZnO composites is a function of optimal dispersion and good inter-component interactions between PLA, Ks and ZnO. This shows that uniform dispersion in the presence of fillers causes good interaction with the matrix. The polymer then causes an increase in mechanical integrity and thermal stability of the composite. It is recognized that the tensile strength of the PLA matrix shows improvement with the addition of ZnO and chitosan in composites with a certain charge.

From the picture, it can be seen that the tensile strength value produced during testing is not constant, this result is not in accordance with research conducted by Amni [8], where the results produced are increasingly added to ZnO reinforcement, then the tensile strength value produced by biofilms will be the higher, because more ZnO amplifiers will affect the structure of the biofilm. This is caused by the effect of the addition of plasticizer Glycerol as plasticity, this is reinforced by research conducted by Yuniarti [9], which obtained an unstable tensile strength test value of starch-based bioplastics with the addition of glycerol resulting from. Glycerol causes a tendency to unite between atoms and molecules in stretchable bioplastics, where this is one of the important factors that affect the mechanical properties of bioplastic materials is activity between its constituent components which is a phenomenon where atoms or molecules tend to unite and bind [10].

ZnO and Chitosan were put into the PLA matrix, the composite tensile strength was obtained well, so that the optimal tensile strength value was obtained from the highest value obtained in the composition with a ratio of 6% chitosan and 3% ZnO.

### 3.2. FTIR analysis of PLA-Chitosan-ZnO nanocomposites

FT-IR analysis was carried out to identify the functional groups contained in the PLA-Chitosan-ZnO Composite sample by using a Shimadzu IR Prestige - 21 Fourier Transform Infrared Spectrophotometer (Serial No. A210048 02519). This analysis also aims to determine whether the addition of chitosan and ZnO concentrations affect existing functional groups and to observe the possibility of reactions occurring at the processing stage marked by the emergence of new functional groups that were not previously detected or vice versa.
Figure 3. Graph analysis of PLA-Chitosan-ZnO Composite functional groups

Table 1. Wave Number with Alleged Compounds

| Functional Groups | Wave Number cm⁻¹ |
|-------------------|------------------|
| N-H               | 3336.85          |
| O-H               | 3630.03          |
| C-H               | 3294.42          |
| C-O               | 1793.80          |

In figure 3, a graph of the PLA-Chitosan-ZnO composite functional group analysis graph is displayed. The graph shows the FTIR test results that from the optimum sample the tensile strength at PLA-Ks 6% -ZnO 3% contained N-H, C-H, O-H, and C = O. Where the NH group is in the wavenumber 3336.85 cm⁻¹ with a wavelength range 3300-3400 cm⁻¹, the OH group is in the number 3630.03 cm⁻¹ in the wave range 3584 - 3700 cm⁻¹, the CH group is in the number 3294.42 cm⁻¹ with a wave range of 3267-3333 cm⁻¹, and the C = O group is found at number 1793.80 cm⁻¹ with a wave range 1540-1870 cm⁻¹. This means that no new functional groups have been found so that this PLA biofilm has properties such as its constituent components.

3.3. TGA analysis (Gravimetric Thermal) of PLA-Chitosan-ZnO nanocomposites

Thermogravimetric analysis is a method used to measure the overall temperature and weight loss due to the influence of temperature on the composite material when the material is heated there will be a structural change resulting in a change in heat capacity or the thermal energy of the material. TGA testing aims to determine qualitatively the thermal stability of biocomposite PLA-Chitosan with ZnO amplifier. Effect of addition of chitosan and zinc oxide on resistance properties thermal composite materials can be seen in the following image.
Figure 4. TGA composite PLA-Ks-ZnO test

From the figure 4. above it can be seen that the decrease in mass on the y-axis and increase in temperature on the x-axis. The graph shows that biofilm samples undergo a single decomposition because on set and end set only occur once, where on set is the temperature at which the sample begins to be degraded thermally and the end set is the temperature at which the sample temperature holds its mass during the thermal combustion reaction process. Biofilm degradation temperature at this research ranges in the range 220 - 300 °C. Based on the picture of 4 biofilms that experienced on set the highest thermal degradation is a biofilm with the addition of ZnO of 238.24 °C, this shows that the thermal resistance of biofilms has higher thermal stability to temperature. As for figure 4, the oldest degradation process (End Set) is obtained biofilm namely the degradation process ends at 295.16 °C. End Set is the end of the degradation process which is the stage where the process of evaporation of a substance or termination of group chain fish will cause the release of these compounds in biofilms. And at the stage after the End Set sample will undergo a carbonization process (ashing) because there are no more compounds and water in the evaporated biofilm.

4. Conclusion
From the result of this study some conclusion can be drawn : (1) The optimum tensile strength value obtained on the addition of Chitosan 6% - ZnO 3%, which is equal to 1.22 MPa. (2) The FT-IR test results contained C-H, O-H, N-H and C = O groups and showed no new functional groups. (3) Biofilm samples underwent single decomposition with biofilm degradation temperatures ranging from 220 - 300 °C, the highest On Set temperature was 238.24 °C, while the highest End Set was 295.16 °C. (4) ZnO reinforcement added to the resulting composite can increase the tensile strength.

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