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Characterization of Degradable Plastics from Sago and Breadfruit Starch-Based with Addition of Zinc Oxide (ZnO) Catalyst and Polyvinyl Alcohol (PVA)

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Abstract

Degradable plastic can be used as a substitute for commercial plastic. Degradable plastic made from starch with zinc oxide (ZnO) catalyst and polyvinyl alcohol (PVA) has biodegradable properties. This research used sago starch, breadfruit starch, ZnO catalyst, and PVA as additives to strengthen the mechanical properties of degradable plastic. The research methodology encompassed several stages, including the preparation of sago and breadfruit starch, the synthesis of degradable plastic, and the subsequent evaluation of its characteristics. Various concentrations of ZnO and PVA catalysts (10%, 20%, 30%, and 40%) were employed in this study. Mechanical characteristic test for degradable plastic showed that the tensile strength test for sago starch-based plastic with 40% ZnO catalyst and PVA was 2.31–3.96 MPa, while for breadfruit starch-based degradable plastic was 2.88–3.20 MPa. FTIR analysis revealed that the compound constituents of degradable plastics exhibit hydrophilic properties and readily interact with water, making them susceptible to natural degradation in soil. Furthermore, the thermal characteristics were examined using DSC, which indicated that sago starch-based degradable plastic (with ZnO 40% and PVA 40%) exhibited a thermogram peak at a temperature of 137.15°C, while the breadfruit starch-based plastic displayed a peak at 136.97°C. In terms of water absorption, the swelling index for sago starch-based plastic ranged from 18.35% to 65.26%, whereas for breadfruit starch-based plastic, it ranged from 19.91% to 64.06%. Notably, the lowest water absorption levels were observed at a ZnO concentration of 40% and a PVA concentration of 10%. The higher the PVA concentration, the more water was absorbed due to the hydrophilic nature of PVA, but the higher the ZnO concentration, the lower the water absorption. Degradation of plastics sago and breadfruit starch occurred for 20-28 days and by ASTM D-20.96 (degradable plastics should be decomposed before 180 days). The higher the concentration of ZnO catalyst added to bioplastics, the longer the degradation time, while the higher the PVA content, the faster the degradation time.

1. Introduction

Commercial plastics today produce much waste and harm health and the environment because they cannot decompose naturally for thousands of years. The issue of recycled plastics remains controversial due to its safety and health concerns and high processing costs. Today, the world needs a solution to the growing plastic waste problem. Conventional plastics like PET take about 23 to 48 years to break down in the environment [1]. Some ways of dealing with plastic waste are recycling, incineration, and burial. However, burning plastic waste can produce toxic substances harmful to living things and the environment. Meanwhile, planting waste is ineffective because plastic is difficult to degrade [2].

The right solution is to make plastic products with materials easily decomposed by bacteria, namely environmentally friendly plastics (degradable plastics), using starch sources as a basic material for manufacturing. Starch has been used from various plastic bases to develop biodegradable plastics and as an alternative to petroleum-based plastics. One of the disadvantages of biodegradable plastics is that their mechanical properties are not yet comparable to conventional plastics, so technology is needed to improve their performance.

Starches are used as thickeners, emulsifiers, and binding agents in the food and non-food sectors. Since starch is biodegradable, low cost, renewable, and abundant, it is considered a "green line" as a raw material to produce porous substances such as aerogels, biofoams, and bioplastics [3]. Sago contains starch, fiber, protein, fat, and ash. Sago starch contains cellulose as a macromolecular material [4]. Sago starch can be used as a base material for developing biodegradable plastics. Sago is abundant in Southeast Asia and has a low cost compared to other starches [5]. Breadfruit (*Artocarpus communis*) is a plant that grows in the tropics. This plant has long been cultivated by the people of Indonesia and even in several countries such as Fiji, Tahiti, Samoa Islands, and Hawaii. Breadfruit has been utilized as a traditional staple food. However, for Indonesians, the consumption of breadfruit is generally still limited to snacks and vegetables. Both types of starch have the potential to be used as raw materials for making bioplastics.

Alebooyeh *et al.* [6] made degradable plastics from sago starch with the addition of ZnOnanorodson. In this study, adding ZnOnanorod showed antimicrobial properties against *E. coli*. Sago starch-based degradable plastics supported with ZnOnanarod can be used in the medical field, pharmaceutical industry, and potential food packaging. Sapei *et al.* [7] conducted a study on the effect of ZnO addition on the properties of banana starch-based bioplastics with chitosan mixture. In this study, banana chitosan-starch bioplastics were made in a ratio of 70:30 in the presence of 30% glycerol as a plasticizer. ZnO with 1, 3, and 5% concentrations was added into the biopolymer blend to improve its mechanical properties. At 3%, ZnO significantly increased the tensile strength of bioplastics up to 36 MPa. Bioplastics with 3% ZnO degrade relatively quickly within 90 minutes. The addition of ZnO can improve the mechanical properties and biodegradability of bioplastics [7].

Mahardika *et al.* [8] successfully produced plastic biocomposites with PVA matrix with durian skin cellulose fibers as fillers, with a tensile strength of 24 MPa. Research by Saputra *et al.* [9] stated that adding zinc oxide and glycerol significantly affected tensile strength, elongation at break, elasticity, and development. However, it did not significantly affect the Water Vapor Transmission Rate (WVTR) and the degradation rate of bioplastics. PVA is a very strong polymer with flexible properties and the ability to form hydrogen bonds with cover molecules. In addition, this PVA can also be easily degredated in soil. ZnO is an inorganic compound with a white powdery form that is very difficult to dissolve in water. ZnO is very widely used as an addictive substance for various additions to materials and products such as plastics, glass, ceramics, rubber cement, and lubricants [10].

This article discussed the effect of the ZnO catalyst on the characteristics of biodegradable plastics derived from sago starch and breadfruit starch. The concentrations of ZnO and PVA catalysts used were 10%, 20%, 30% and 40%. Sago has a composition of 7.48% moisture content, 0.062% ash content, 0.04% crude fiber, and 88.31% starch content [5]. Meanwhile, breadfruit contains 4% protein, 1% fat on a dry basis, 68% phosphorus, and starch [11]. The variation of different concentrations of ZnO and PVA catalysts was used to determine the best characteristics of the degradable plastics produced in terms of mechanical properties, thermal properties, functional groups, water resistance, and biodegradation rate.

2. Experimental

The research method consisted of several stages: the preparation of starch from sago and breadfruit, the synthesis of degradable plastics, and the testing stage of the plastic produced.

2.1. Materials

The materials used in this research were sago starch, breadfruit starch, zinc oxide (ZnO) Pro Analysis Merck, polyvinyl alcohol (PVA) with 88% purity, distilled water, and glycerol 85% Pro Analyst Merck.

2.2. Degradable Plastic Synthesis

The starches from sago and breadfruit were made by chopping the sago stems and breadfruit, washing them thoroughly, pulverizing them using a blender, and then adding water. After becoming sago pulp and breadfruit pulp, they were filtered using a cloth, and the filtrates were deposited for 24 hours. The precipitates were separated from the water part and then dried using an oven to become starch. Furthermore, the process of making biodegradable plastic was done by adding a ZnO catalyst and PVA. Each sago and breadfruit starches were weighed 10 grams, put into a beaker glass, and added with 200 mL of distilled water. Then, the mixture was heated to 70°C, added with ZnO and PVA (10, 20, 30, 40%) from the determined starch weight, and added with glycerol 40% from the starch weight. The solution was stirred until it became a gel with a time range of 40 minutes and a temperature not exceeding 85°C. Then, the molding stage used glass casting and was dried in the oven for 6 hours at 60°C.

2.3. Study of the Effect of ZnO Catalyst and PVA Addition to Degradable Plastics

The mechanical properties of starch-based biodegradable plastics are currently still low. One of the ways to increase the mechanical strength of biodegradable plastics is the addition of ZnO and PVA. The addition of ZnO also helps accelerate the biodegradability process of degradable plastics. This study used ZnO and PVA catalysts to compare the effects on mechanical properties, thermal properties, water resistance, and optimal biodegradability of degradable plastics derived from sago and breadfruit starch. ZnO was chosen for its biocompatibility, non-toxicity, and chemical stability under elevated temperatures and exposure to UV light.

Furthermore, the United States Food and Drug Administration (FDA) has affirmed the safety of using ZnO in such applications [12]. PVA can be used as a synthetic degradable polymer because it has excellent mechanical properties and water solubility that can be adjusted by changing the degree of polymerization. In addition, PVA can also be completely degraded in the presence of bacteria in wet environmental conditions such as river water [13]. Jiménez-Rosado *et al.* [14] studied how to incorporate ZnO nanoparticles into soy protein-based bioplastics processed using injection molding. The results showed that mechanical (flexural and tensile properties, morphological characterization, microstructure, and nanoparticle distribution) and functional (water uptake capacity, micronutrient release, and biodegradability) properties significantly influence the final characteristics of bioplastics. Soy protein-based bioplastics have demonstrated their great capacity to hold ZnO nanoparticles and release them in a controlled manner [14].

Sapei *et al.* [7] made banana chitosan-starch bioplastics, utilizing a 70:30 ratio, and incorporated 30% glycerol as a plasticizer. ZnO with different concentrations of 1%, 3%, and 5% was each added to the biopolymer blend before casting to improve its mechanical properties. It was found that 3% ZnO significantly increased the tensile strength of bioplastics up to ~36 MPa. In the reverse, the percentage of elongation and swelling decreased with increased ZnO concentration. Bioplastics made with 3% ZnO degraded in a relatively short time of 90 minutes. This banana chitosan starch bioplastic reinforced by ZnO seems promising enough to replace some conventional plastic commercial bioplastics.

Shang *et al.* [15] studied starch and cellulose, two typical natural polymers from plants with similar chemical structures. This research investigated the rheological properties of cellulose/starch/$ZnCl_2$ solution, and the structure and properties of cellulose-starch hybrid films were characterized. Rheological studies show that compared with starch (which contains mainly amylose), cellulose contributes more to the viscosity of the solution and has a stronger thinning behavior. For starch-rich hybrid films, less than 7% by weight of cellulose can improve mechanical properties despite the reduced crystallinity of starch. A higher starch content reduces the material properties of cellulose-rich hybrid films, although the chemical interactions are not affected. The mechanical properties of biopolymer films are influenced by the structural conformation, as shown by the rheology results [15].

2.4. Characterization and Analysis

The mechanical characteristics of sago starch-based and breadfruit starch-based degradable plastics with ZnO and PVA catalysts were carried out by tensile, elongation, and Young's Modulus tests. The tensile strength test used the ASTM D-638 (American Standard Testing and Material) standard. This test method uses dumbbell-shaped specimens with either a 50 mm gauge length. The tensile strength and elongation of samples cut to a size of 165 mm were analyzed using a Mechanical Universal Testing Machine. The tensile strength and elongation can be determined by Equations (1) and (2).

$$\sigma = \frac{F_{max}}{A} \tag{1}$$

where, σ is the tensile strength (MPa), F_{max} is the maximum stress (N), and A is the cross-sectional area of the film subjected to stress (mm^2).

$$\varepsilon = \frac{\triangle l}{l_0} \tag{2}$$

where, ε is the strain (MPa), l is the gauge length, the gauge length of the test sample after elongation (mm^2), and l_0 is the gauge length of the pre-sample (mm^2).

To identify chemical bonds in organic materials, polymers, metals, and various materials, Fourier Transform Infrared Spectroscopy (FTIR) can be used. The FTIR analysis method uses infrared light to scan the test sample and observe chemical properties. When a material is irradiated with infrared radiation, the absorbed IR radiation usually keeps the molecules at a higher vibrational state. The wavelength absorbed by the sample is characteristic of its molecular structure. In this study, FTIR analysis was carried out at wave numbers 550-4000 cm^{-1}. The thermal properties of degradable plastics were tested using Differential Scanning Calorimetry (DSC) analysis to determine the energy absorbed. Differential Scanning Calorimetry (DSC) is used to analyze the effects of polymer heating during physical changes (glass transition and melting). The DSC test equipment used in this study is DSC 8000 Perkin Elmer using ASTM D3418-15 test standards. The resistance of degradable plastics to water was analyzed by swelling test (water absorption). The degree of swelling was determined using ASTM D2765. Samples were weighed, placed in the solvent for 24 hours, weighed again while swell, then dried and weighed the final weight. The swelling degree is calculated using the Equation (3).

$$\text{Swelling degree} = \frac{\text{weight of expanded sample} - \text{weight of pre sample}}{\text{pre} - \text{weight sample}} \times 100\% \tag{3}$$

The microbial decomposition rate was analyzed by burial in the soil (biodegradability). Biodegradability analysis followed the ASTM G-21-70 reference with the direct contact of bioplastics with soil. Degradable plastic samples were cut into 5 × 2 cm and weighed the sample as the pre-mass. Subsequently, these samples were placed in soil excavated to a depth of 30 cm, and evaluations were conducted every 4 days. After each assessment, the samples were removed from the soil, thoroughly cleaned of any remaining soil, and then reweighed as the final mass (M_1). The biodegradability of degradable plastics is calculated by Equation (4).

$$\text{Biodegradability (\%)} = \frac{M_0 - M_1}{M_0} \times 100\% \tag{4}$$

where, M_0 is the pre-mass (gram), and M_1 is the last mass (gram).

3. Results and Discussion

3.1. Mechanical Properties Analysis of Tensile Strength

Mechanical properties (tensile strength, elongation, and Young's modulus) were measured using a texture analyzer. Tensile strength is the maximum ability of a degradable plastic to withstand external forces before the degradable plastic is damaged or broken. Damage can be caused by rupture due to excessive pressure or possibly by deformation of the structure. Elongation is employed to ascertain the ratio of the increase in length of degradable plastics to their initial length, while Young's Modulus is used to quantify the elasticity of degradable plastics. The tensile strength value is inversely proportional to the elongation value, and Young's Modulus is proportional to the elongation value. The outcomes of the tensile strength, elongation, and Young's Modulus examinations for degradable plastics derived from sago starch and breadfruit starch, with differing proportions of ZnO catalyst (10%, 20%, 30%, and 40%) and a consistent PVA 40% content, are presented in Tables 1 and 2.

Table 1. Tensile strength values of sago starch-based degradable plastic

ZnO catalyst (%)	PVA (%)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
10	40	3.23	113.5	2.85
20	40	2.99	107.5	2.78
30	40	3.96	107.0	3.70
40	40	2.31	86.5	2.67

Table 2. The tensile strength value of breadfruit starch-based degradable plastic

ZnO catalyst (%)	PVA (%)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
10	40	2.85	32.9	8.67
20	40	2.97	32.4	9.17
30	40	3.14	31.5	9.96
40	40	3.20	31.2	10.25

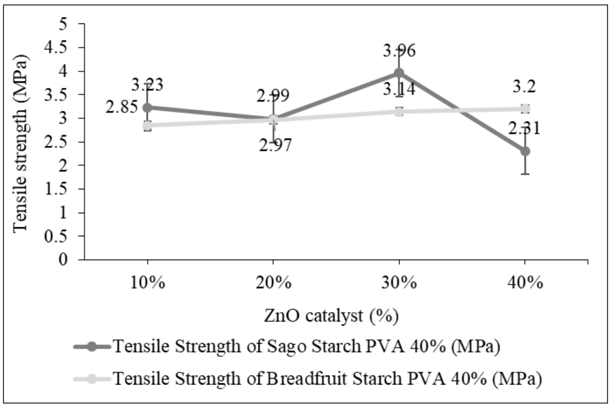


Figure 1. Effect of ZnO catalyst on tensile strength of sago starch and breadfruit starch-based degradable plastics

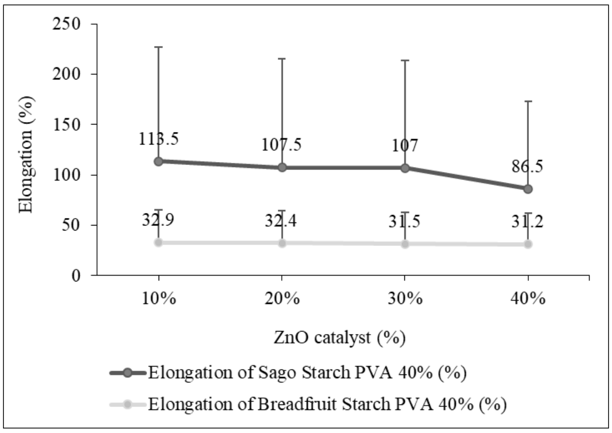


Figure 2. Effect of ZnO catalyst on elongation of sago starch-based and breadfruit starch-based degradable plastics

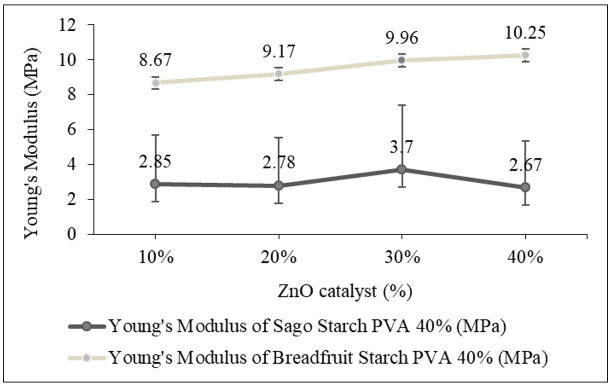


Figure 3. Effect of ZnO catalyst on Young's modulus of sago starch-based and breadfruit starch-based degradable plastics

The tensile strength values of sago starch-based degradable plastic with ZnO and PVA catalysts obtained in this study ranged from 2.31–3.96 MPa, while that of breadfruit starch-based degradable plastic ranged from 2.88–3.20 MPa. Figure 1 shows that the tensile strength of sago starch-based degradable plastic is slightly lower than that of plastic made from breadfruit starch. Notably, the sago starch-based plastic reached its maximum ZnO addition level at 30%. The addition of ZnO catalyst and the concentration of PVA used affect the mechanical properties of degradable plastics. It is observed that higher ZnO concentrations correspond to improved tensile strength.

Amni *et al.* [16] produced cassava starch-based bioplastics with the addition of ZnO 3% and obtained a tensile strength of 36 MPa, which was higher than the tensile strength of ZnO 9% (32 MPa). Maryam *et al.* [17] studied the effect of adding sago starch nanoparticles with PVA, resulting in a standardized bioplastic with a tensile strength of 15.08 MPa. A higher tensile strength value in the bioplastic indicates an enhanced ability to protect the product from various mechanical factors, including physical pressures such as drops and friction and vibrations and impacts between materials. The tensile strength value obtained in the present study remains below those reported in the two studies mentioned earlier. The criteria for the Moderate Properties group set a range of 10-100 MPa for tensile strength, whereas, according to SNI standards, the tensile strength of plastic should fall within the range of 24.7-302 MPa.

Moreover, the stirring factor might be one factor affected during degradable plastic synthesis. Incorporating PVA at a specific concentration has the potential to enhance tensile strength; however, an excessive amount of PVA may result in a decrease in this property. The tensile strength value in this study was not comparable to the tensile strength obtained by synthetic plastics, such as LDPE (10-12 MPa), PET (55-79 MPa), and PP (100-600 MPa) [18].

Elongation is a measure of a material's ability to stretch when pulled and determines the elasticity of a material. A higher elongation percentage signifies increased elasticity in degradable plastic, indicating that the material can undergo substantial stretching. Figure 2 shows that the highest elongation test value was found in sago starch-based biodegradable plastic with a percent elongation of 86.5–113.5%. The concentration of the ZnO catalyst affects the elongation value; the higher the ZnO concentration, the lower the elongation percentage. Meanwhile, the elongation value obtained in breadfruit starch-based degradable plastic was 31.2-32.9%. Percent elongation on breadfruit starch also decreased with increasing ZnO concentration, but the value was insignificantly different. The SNI value for bioplastic elongation is 21-220%. The elongation values obtained in this study for both starches are in accordance with SNI standards. The elongation value obtained is also almost comparable to the elongation value of PET (15-165%) [19].

If the force or stress is discontinued, the object has the ability to revert to its initial state. The consistency in the ratio of stress to strain and the magnitude of this constant is referred to as the modulus of elasticity, commonly known as Young's modulus. The elastic modulus of the material is proportional to the elongation value, where the elastic modulus is a measure of the stiffness of the elastic material and is a quantity used to characterize the material, which is related to the size of the stress and strain of an object.

The modulus of elasticity for sago starch-based degradable plastic, utilizing a ZnO catalyst, ranged from 2.67 to 2.85 MPa. In contrast, the modulus of elasticity for breadfruit starch-based degradable plastic fell within the range of 8.67 to 10.5 MPa. A higher modulus of elasticity indicates a stiffer and less deformable material. However, it is essential to note that the modulus of elasticity values obtained in this study are not comparable to those of Polyethylene Bralen RA 2-63 foils, which typically range from 222.73 MPa to 298.24 MPa. The observed differences suggest distinct mechanical properties between the degradable plastics and Polyethylene Bralen RA 2-63 foils [20].

3.2. Functional Group Analysis with Fourier-Transform Infrared Spectroscopy (FTIR)

Functional group analysis using FTIR is employed to identify the functional groups present in degradable materials. The samples are positioned in a holder, and their spectra are recorded. The result is a diffractogram that depicts the relationship between wavenumber and intensity. FTIR analysis of sago starch-based and breadfruit starch-based degradable plastics samples (with ZnO catalyst 40% and PVA 40%) can be seen in Figures 4 and 5.

Figure 4 shows the FTIR test on the sago starch-based degradable plastic sample with ZnO catalyst 40% and PVA 40%. Based on Figure 4, the presence of the -OH group is evident at a wavenumber of 3267.41 cm^{-1}. This indicates that thermoplastic starch from sago contains free hydroxyl groups (-OH) resulting from the reduction of atoms binding with hydrogen atoms. Another absorption peak at a wavenumber of 2939.52 cm^{-1} reveals the -CH stretching of the alkyl group, while 1710.86 cm^{-1} shows the -C-O stretching of the acetyl group in PVA. Absorption in the range of 1261.45 cm^{-1} points to C-O vibrations in PVA. Other absorptions in the range of wavenumbers 921.97 cm^{-1}, 1375.25 cm^{-1}, and 1415.75 cm^{-1} indicate the presence of alkane C-H vibrations.

According to Ramadhani *et al.* [21], the wavenumber of 1083 cm^{-1} represents the C-O stretching functional group of acetyl groups, which is within the scope of PVA. A wavenumber of 1250 cm^{-1} is associated with the C-H wagging functional group, a characteristic group of PVA. The absorption peak at wavenumber 2939.52 cm^{-1} is characterized as C-H stretching vibrations on the methyl group in sago starch. Meanwhile, wavenumbers 999.13 cm^{-1}, 921.97 cm^{-1}, and 840.96 cm^{-1} are characterized as C-H stretching vibrations, specifically the alkene group contained in ZnO [21].

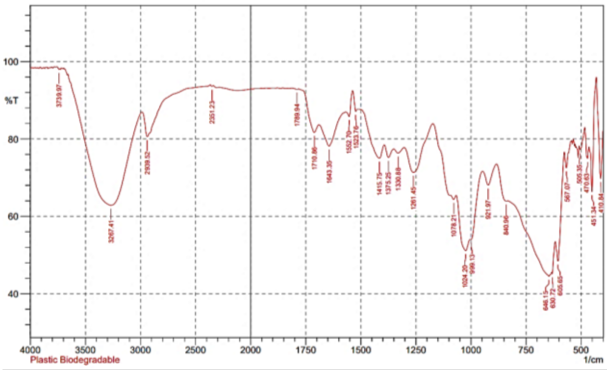


Figure 4. FTIR analysis of sago starch-based degradable plastic

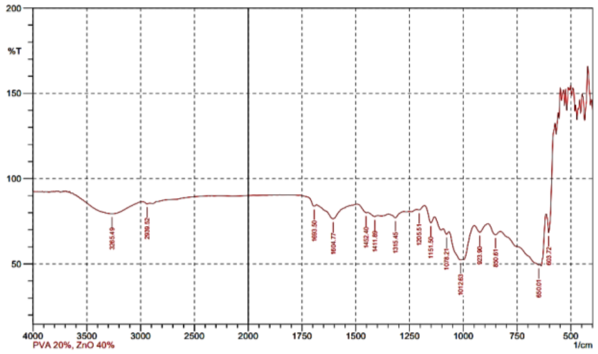


Figure 5. FTIR analysis of breadfruit starch-based degradable plastic

According to Yunita *et al.* [22], the presence of a broad band in the wavenumber range of 3200-3600 cm^{-1} in the FTIR spectrum indicates starch. This observation suggests that no new functional groups were formed. Starch has a spectrum similar to its constituent material. Based on the interpretation of the FTIR spectra of the produced bioplastics, there is no evidence of the addition of new functional groups. However, shifts in several wavelength numbers and changes in the intensity of the absorption bands have been observed. These findings suggest that the interaction between starch and the ZnO catalyst is only a physical interaction.

In Figure 5, the presence of the -OH group is evident at an approximate wavenumber of 3265.49 cm^{-1}. This indicates that thermoplastic starch from breadfruit possesses a free hydroxyl group (-OH) resulting from reduced atoms that bind with hydrogen atoms. Another absorption peak at a wavenumber of 2939.52 cm^{-1} represents the -CH stretching of the alkyl group, while 1315.45 cm^{-1} shows the -C-O stretching of the acetyl group in PVA. C-O vibrations in PVA are observed at 1012.63 cm^{-1}. Additionally, absorptions at 923.90 cm^{-1}, 1452.40 cm^{-1}, and 1411.89 cm^{-1} indicate alkane C-H vibrations. The absorption peak at 2939.52 cm^{-1} represents the C-H stretching vibration specific to breadfruit starch. Furthermore, C-H stretching vibrations at 923.90 cm^{-1} and 850.61 cm^{-1} are associated with alkene groups in ZnO.

The FTIR analysis of sago starch-based and breadfruit starch-based degradable plastics with ZnO and PVA catalysts indicates the presence of an organic compound. The biodegradable plastic is characterized as hydrophilic, meaning it has an affinity for water, facilitating its degradation by soil. This also indicates that the degradable plastics have more free hydroxyl groups - OH caused by fewer atoms binding to hydrogen bonds. The -OH groups are derived from PVA or other extractive substances. Tan *et al.* [23] stated that the hydrogen bond between the OH group of starch and the COOH group of cellulose nanocrystals (CNC) has a high tensile strength value and a low elongation value.

3.3. Energy Absorption Analysis by Differential Scanning Calorimetry (DSC)

The basic principle of the DSC analysis technique is that when a sample undergoes a physical transformation, such as a phase transition, heat changes will be required to flow from the reference and the sample to maintain both at the same temperature. Whether less or more heat is required to flow to the sample depends on whether the process is exothermic (heat loss) or endothermic (heat absorption). In this study, DSC analysis was conducted to determine how much energy was absorbed by the degradable plastic. The results of DSC testing on sago starch-based and breadfruit starch-based degradable plastics (with ZnO 40%, PVA 40%) can be seen in Table 3 and Figures 6 (a) and 6 (b).

One of the indicators of plastic quality is its properties or resistance to heat. Figure 6 illustrates the reversible change starting with hydrated material, dehydration being the first process to occur upon heating and shown by an endotherm. Dehydrated materials undergo a polymorphic transition, which is also endothermic at higher temperatures. Finally, the sample melts, giving a second endotherm. On cooling, the melt crystallizes, as pointed out by the exothermic peak, and polymorphic changes also take place exothermally, but rehydration did not occur. For this type of process, if heating is endothermic, then cooling must be exothermic [24].

The DSC thermogram of the biodegradable plastic from sago starch in Figure 6 (a) shows some artifacts at 137.15°C; the thermogram reveals a very sharp peak. This peak corresponds to the physical alterations resulting from the residual water group in the synthesized product. Since water begins to evaporate at 100°C, this dehydration corresponds to the loss of H_2O molecules from the sample physically bound to its surface. At 305.89°C, an endothermic peak occurred, indicating a glass transition state. This point is important for preparing the compound lattice of biodegradable plastics.

Table 3. DSC data summary of sago starch-based and breadfruit starch-based degradable plastics

Sago starch-based degradable plastic		Breadfruit starch-based degradable plastic	
Peak	137.15°C	Peak	136.97°C
Onset	124.87°C	Onset	117.68°C
Endset	175.89°C	Endset	168.40°C
Heat	-1.57 J	Heat	-1.00 J
	-392.77 J/g		-200.42 J/g
	-375.32 mcal		-239.39 mcal
	-93.83 cal/g		-47.88 cal/g
Peak	305.89°C	Peak	292.58°C
Onset	283.29°C	Onset	275.65°C
Endset	322.96°C	Endset	302.65°C
Heat	-458.28 mJ	Heat	-146.27 J
	-114.57 J/g		-29.25 J/g
	-109.48 mcal		-34.94 mcal
	-27.37 cal/g		-6.99 cal/g

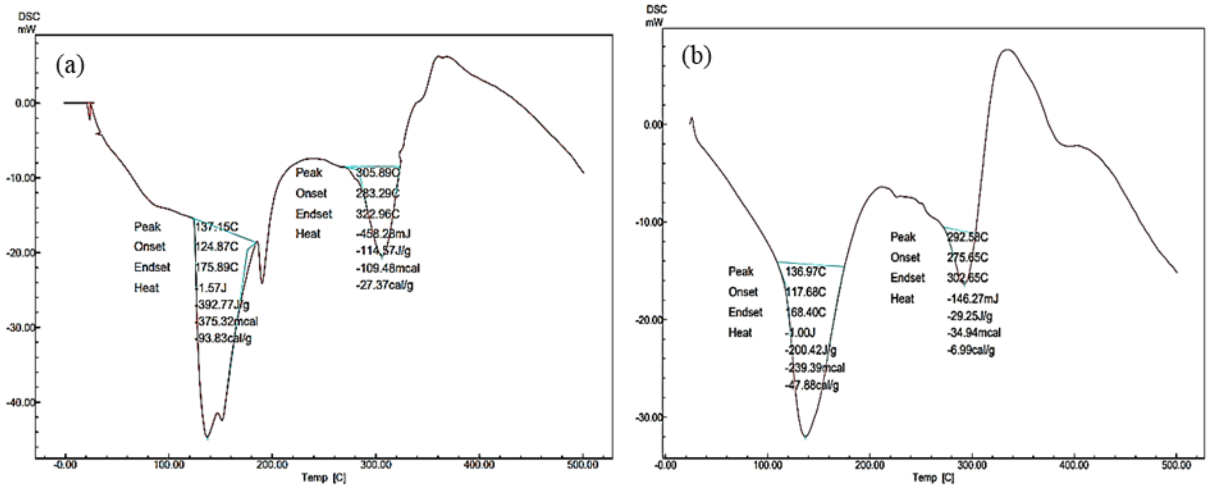


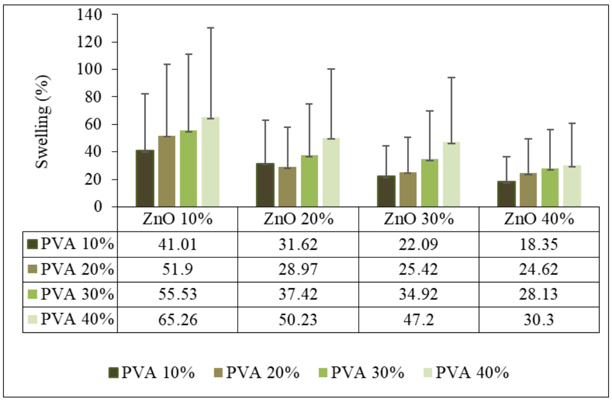
Figure 6. DSC thermograms of degradable plastic with ZnO 40%: PVA 40%: (a) Sago starch-based, (b) Breadfruit starch-based

For the thermogram of breadfruit starch-based biodegradable plastic, Figure 6 (b) denotes dehydration occurred at 136.97°C, which is a little higher than the sago starch biodegradable plastic. At 292.58°C, a sloping peak with characteristic endothermic enthalpy was observed, indicating a glass transition. The nearly identical melting points of the sago starch-based and breadfruit starch-based biodegradable plastics imply a homogenized structure formed among starch, ZnO filler, and PVA. In comparison to the relatively low melting points of standalone sago starch and breadfruit starch at around 70°C, the melting point of biodegradable plastic was significantly increased.

Adding fillers to the matrix has increased the melting point of the biodegradable plastic, proving that cross-linking has occurred. The higher the melting point, the more cross-linking that occurs. The melting point is affected by the hydrogen bonds contained in the plastic. The greater the number of hydrogen bonds present in the plastic, the higher its melting point, as the increased energy required to disrupt these bonds contributes to heightened thermal stability. DSC analysis shows that biodegradable plastics based on sago starch and breadfruit starch using ZnO catalyst and PVA as filler and starch as matrix has good thermal characteristics and stability. The greater the number of hydrogen bonds in plastic, the higher its melting point, as breaking these bonds necessitates a higher amount of energy [25]. This has also been proven in research conducted by Dewi *et al.* [24], where the addition of polyurethane causes an increase in the melting point of bioplastics because the melting point of the added polyurethane is higher than the melting point of starch [26].

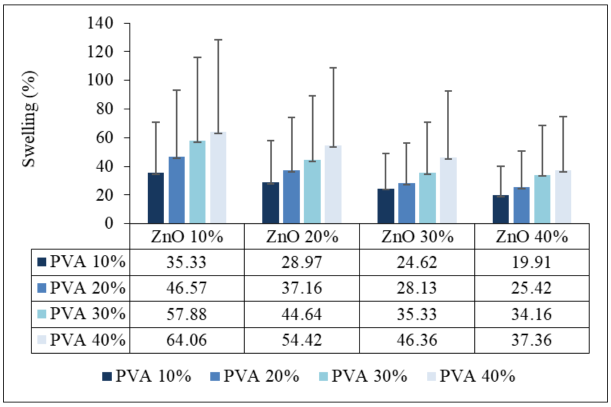
3.4. Analysis of Water Resistance Through Swelling Degree

The water resistance of degradable plastic is determined by the swelling test, indicated by the percentage of biodegradable plastic expansion in the presence of water. Percent swelling analysis is conducted to assess the amount of liquid absorbed, leading to the expansion of the degradable plastic. Figures 7 and 8 show the water resistance test results of sago starch-based and breadfruit-based degradable plastics with ZnO (10, 20, 30, and 40%) and PVA (10, 20, 30, and 40%) catalyst by swelling test.



	ZnO 10%	ZnO 20%	ZnO 30%	ZnO 40%
■PVA 10%	41.01	31.62	22.09	18.35
■PVA 20%	51.9	28.97	25.42	24.62
■PVA 30%	55.53	37.42	34.92	28.13
■PVA 40%	65.26	50.23	47.2	30.3

Figure 7. Water resistance analysis on sago starch-based degradable plastic with ZnO catalyst and PVA variations



	ZnO 10%	ZnO 20%	ZnO 30%	ZnO 40%
■PVA 10%	35.33	28.97	24.62	19.91
■PVA 20%	46.57	37.16	28.13	25.42
■PVA 30%	57.88	44.64	35.33	34.16
■PVA 40%	64.06	54.42	46.36	37.36

Figure 8. Water resistance analysis on breadfruit starch-based degradable plastics with ZnO catalyst and PVA variations

Table 4. Results of standard deviation on sago starch-based and breadfruit-based degradable plastics by swelling

ZnO (%)	PVA (%)	Sago starch-based degradable plastic (%)	Breadfruit starch-based degradable plastic (%)
10	10	41.01	35.33
10	20	51.90	46.57
10	30	55.53	57.88
10	40	65.26	64.06
20	10	31.62	28.97
20	20	28.97	37.16
20	30	37.42	44.64
20	40	50.23	54.42
30	10	22.09	24.62
30	20	25.42	28.13
30	30	34.92	35.33
30	40	47.20	46.36
40	10	18.35	19.91
40	20	24.62	25.42
40	30	28.13	34.16
40	40	30.30	37.36
Standard Deviation		13.51	12.63

Figures 7 and 8 illustrate the swelling values obtained for sago starch-based degradable plastic, ranging from 18.35% to 65.26%, and for breadfruit starch-based degradable plastic, ranging from 19.91% to 64.06%. The swelling values obtained for sago starch-based and breadfruit starch-based plastics did not differ significantly. However, utilizing ZnO and PVA catalysts had a considerable impact on the water resistance properties of the degradable plastic. The highest swelling percentages were observed in sago starch-based plastic and breadfruit starch-based plastic with ZnO 10% catalyst and PVA 40%, reaching 65.26% and 64.06%, respectively. PVA, characterized by a hydroxyl group, has the ability to retain a substantial amount of water molecules through hydrogen bonds. Consequently, PVA can absorb water almost equivalent to its weight. The hydrophilic nature of PVA results in increased water absorption with higher PVA concentrations, thereby influencing the overall water absorption (swelling) behavior, which is inherently dependent on the hydrophilic characteristics of PVA [21].

Research by Agustin and Padmawijaya [26] stated that the more ZnO added, the less water absorption in the sample because the nature of ZnO is hydrophobic. The main function of ZnO was to act as a catalyst to cover the cavities or pores on the surface of bioplastic. This can cause bioplastic to experience a decrease in water absorption. This study also obtained the same results, where the higher the ZnO content, the lower the expansion percent obtained. The smallest expansion development value was obtained at ZnO 40% and PVA 10%, 18.35% for sago starch-based plastic, and 19.91% for breadfruit starch-based plastic. Meanwhile, according to the Indonesian National Standard (SNI) for conventional plastic types, such as polypropylene, it has a water resistance value of only 0.01%. The water absorption rate of plastic is highly dependent on the application of the plastic, especially food packaging, which requires a low water absorption rate to maintain food quality.

3.5. Biodegradability Rate Analysis with Soil Burial

The biodegradability test aims to ascertain the degradation rate of degradable plastic, allowing us to determine the duration required for these plastics to decompose in the soil. The biodegradability rate was conducted by burial test in soil using ASTM D5338 (Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions). Figures 9 and 10 present the biodegradability rate of sago starch-based and breadfruit starch-based degradable plastics with variations of ZnO catalyst and PVA (10, 20, 30, and 40%).

The degradation time of sago starch-based and breadfruit starch-based degradable plastics with ZnO and PVA catalysts (10, 20, 30, and 40%) ranged from 20-28 days, as shown in Figures 9 and 10. Sago starch-based plastic with 10% ZnO catalyst and 10% PVA by weight of starch tends to decompose faster on day 16. In contrast, breadfruit starch-based degradable plastic decomposed completely on day 20. Incorporating a ZnO catalyst has a notable impact on the biodegradation rate, where an increased quantity of ZnO catalysts corresponds to an extended time for plastic degradation. This effect is attributed to the antibacterial properties of ZnO, which inhibit the growth of microorganisms within the sample, consequently diminishing its biodegradability. This contrasts with PVA, which exhibits higher susceptibility to soil degradation due to its hydrophilic nature, facilitating microbial degradation. A higher concentration of PVA accelerates the decomposition process in the soil. Additionally, the glycerol plasticizer, possessing hydrophilic properties, contributes to a higher water absorption rate, creating a conducive environment for developing microorganisms [27].

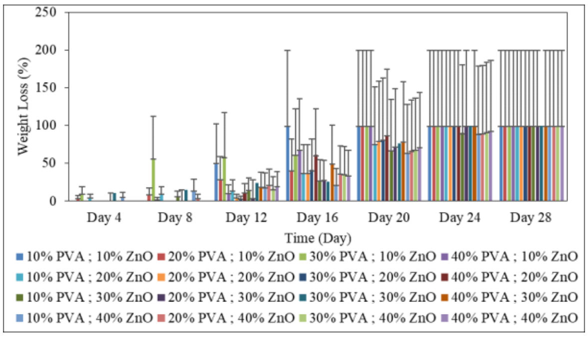


Figure 9. Relation of weight loss rate (%) with time in sago starch-based degradable plastic

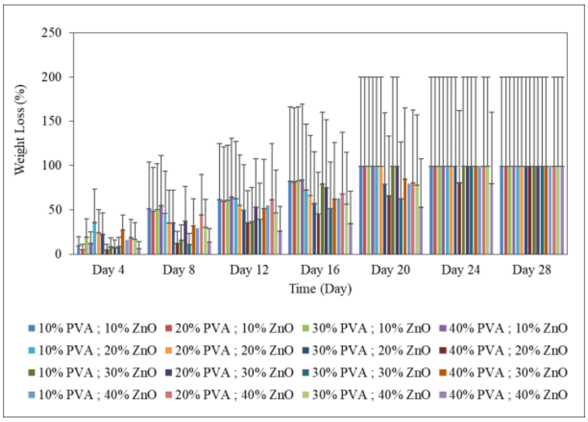


Figure 10. Relation of weight loss rate (%) with time in breadfruit starch-based degradable plastic

Biodegradable plastic standards (ASTM D-6002: Guide for Assessing the Compostability of Environmentally Degradable Plastics and ASTM D-20.96 on Environmentally Degradable Plastic), which states for products consisting of a single polymer (homopolymer or random copolymer), 60% of the organic carbon must be converted to carbon dioxide by the end of the test period which is a maximum of 180 days. Hence, the duration of decomposition of sago starch-based and breadfruit starch-based plastics has met the standard [28]. Starch blended with the synthetic polymer PVA has been studied as a potential biodegradable polymer [29].

4. Conclusion

The mechanical properties of biodegradable plastic derived from sago starch and breadfruit starch, incorporating ZnO and PVA catalysts, exhibit favorable tensile strength, elongation, and Young's Modulus. In the conducted mechanical tests, the tensile strength for sago starch-based degradable plastic with a ZnO catalyst and 40% PVA ranged from 2.31 MPa to 3.96 MPa. Similarly, the tensile strength of breadfruit starch-based degradable plastic fell from 2.88 MPa to 3.20 MPa. The compound composition test conducted using FTIR revealed that the material is hydrophilic. This characteristic implies that the material can readily bind to water molecules, making it susceptible to degradation by soil. The thermal characteristics determined through DSC thermogram testing indicated that the sago starch-based degradable plastic (ZnO 40%; PVA 40%) had a thermogram peak at 137.15°C, while the thermogram peak for the breadfruit starch-based degradable plastic was at 136.97°C. The swelling values obtained for the sago starch-based degradable plastic ranged from 18.35% to 65.26%, whereas for the breadfruit starch-based degradable plastic, it fell from 19.91% to 64.06%. The lowest water absorption rate occurred at ZnO 40% and PVA 10% concentrations. The degradation of sago starch-based and breadfruit starch-based degradable plastics, incorporating ZnO and PVA catalysts at varying concentrations (10%, 20%, 30%, and 40%), resulted in complete decomposition within the range of 20 to 28 days. This degradation time aligns with the specifications outlined in ASTM D-20.96 for degradable plastics. Notably, an increase in the percentage of ZnO catalyst added to the bioplastic corresponds to an extended degradation time in the soil. In contrast, a higher PVA content accelerates the degradation process, leading to shorter degradation times.

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