Synthesis and Characterization of Biodegradable Blend based on LDPE/cassava stem nanofiber cellulose

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Abstract.
Conventional plastics becomes trend topic due to its long degradation time and needs attention related to environmental problem. One type of plastic that is difficult to be degraded is LDPE. Some of the efforts were done to synthesize biodegradable plastic based on organic material to accelerate the degradation process. Cellulose is an organic material that is abundant in nature and can be used as filler. This research aims to synthesis the biodegradable plastic films composted by the nanocellulose cassava stems and recycled LDPE. Mechanical (UTM), water resistance and degradation test has been done. The properties of the biodegradable composites still meet the commercial LDPE. Even though the biocomposite based on LDPE-nanofiber cellulose do not degradable totally but it is can be used as a solution to reduce the degradation time of a plastic waste.

Key Words: Biocomposite, cassava stem, nanocellulose, commercial.

INTRODUCTION
Present in the amount of 10% of the total 100 million tons of waste volume annually, the plastics waste cannot easily decomposed by decomposer organisms which make the environment is getting worse. This plastic requires 300-500 years to be fully decomposed or degraded [1]. Various attempts have been made, one of them through plastic synthesis with organic materials to accelerate the degradation process. In 2015 Lampung Province was the largest cassava producer in Indonesia with a total production of 7,387,084 tons [2]. Based on these data, the amount of cassava produced will also produce a lot of waste i.e. cassava stems. Cassava stems containing cellulose, hemicellulose, and lignin, respectively 39.29, 24.34 and 13.42% [3]. With a large cellulose content, the availability of abundant cassava stems in Indonesia, especially in Lampung Province, make it...
has a great potential to be used as a filler in the form of nanocellulose which is a cellulose particle that changes in size. This change aims to increase crystallinity, surface area, increase dispersion and biodegradation.[4].

Previous research has been carried out on the Making of Biodegradable Plastic Films from Durian Seed Cellulose Waste [5]. The result showed that variations in the temperature of the stirring process affect the ability of tensile strength and elongation, and resulted in the start of degradation on the 15th day [5].

In this research a biodegradable plastic was made with nanocellulose variations of cassava stems - LDPE and mixing temperature. The composition used was 5%; 10% (w/w) and mixing temperature 160 °C; 180 °C; 200 °C. The analysis used are a mechanical test, water resistance test, and degradation test. From these methods, its expected that biodegradable plastic formed from cassava stems nanocellulose - LDPE has good physical properties and can be applied as packaging plastics that can be degraded environmentally well.

**RESEARCH METHODOLOGY**

**Tools and Materials**

The tools used in this study are; milling (hammer mill and disk mill), 60 mesh sifter, digital balance sheet, hotplate, magnetic stirrer, three neck flask, pH meter, measuring cup, erlenmeyer, petri dish, thermometer, oven. The materials used in this research were cassava waste, aquadest, formic acid (80%), hydrogen peroxide (5%), low density polyethylene (LDPE) plastic, xylene, NaOH, VCO, and EM4- bacteria.

**Delignification Process**

The delignification process uses a mixture of formic acid solution, hydrogen peroxide, and distilled water with cassava ratio and a solution of 1: 15 v / v for 2 hours at 100 °C. Then the cellulose obtained was separated from the acid solvent and washed with distilled water until neutral. After washing, the wet cellulose is then dried at 100 °C for 3 hours [6].

**Nanocellulose Synthesis**

5 grams of cellulose solid from the delignification process was dissolved with distilled water as much as 300 ml. Then put into an ultrasonification with a wave treatment that is used 80 Hz, with a temperature of 70 °C within 90 minutes. The output cellulose from ultrasonification was dried in an oven at 100 °C to remove moisture within 3 hours [7].

**Biodegradable Plastics Synthesis**

The composition of 5% (w / w) of nanocellulose is dissolved with 10 ml of NaOH and heated at 100 °C within 30 minutes. Then the LDPE 9gr based plastic was dissolved using 100ml xylene at 140 °C for 30 minutes before nanocellulose was mixed. After each ingredient is mixed then added 3 ml of virgin coconut oil (VCO). Mixing temperatures vary by 160 °C; 180 °C; and 200 °C with a time of 2 hours each. The composition of 10% (w / w) nanocellulose was mixed with LDPE using the same parameters as the previous composition. The mixture that has been obtained is printed on the glass which is then in the oven for 15 minutes at 200 °C [8].

**RESULT AND DISCUSSION**

**Delignification**

The delignification process will dissolve the lignin content in material so that make the process of separating lignin with fiber/cellulose easier [9]. This research are using formic acid as the solvent, because formic acid can be used to decompose lignin at low pressure and temperature and the price is relatively cheaper than other solvents. The delignification process uses formic acid (80% -weight) and hydrogen peroxide (5%-weight) as a catalyst with a reaction time of 120 minutes at a temperature of 100 °C to get 78.54% cellulose, 9.11% hemicellulose and 1.25% lignin from the total ingredients used [10]. Addition of hydrogen peroxide to formic acid will form peroxiformic acid so that it can accelerate the delignification process and protect cellulose from hydrolysis of formic acid (Azam et al 2002 and Kham 2005). From a fairly high percentage value, the delignification process using formic acid + hydrogen peroxide was considered more effective in getting cellulose from cassava stems used as LDPE plastic fillers.
Nanocellulose Synthesis

The formation process of nanofiber cellulose is carried out at the ultrasonification process. Ultrasonification is one method to degrade micromolecules to nano size, this is influenced by the time and frequency control used. In this study, the delignification process uses the optimum parameters that have been investigated by Lismerti et al., Hoping to get the best nanocellulose size. The optimum conditions for making nanocellulose using ultrasonification with 80Hz waves in 90 minutes using a temperature of 70 °C [10].

Manufacture of Biodegradable Plastics

The blending process was chosen in method of making LDPE-based biodegradable plastic films. The blending method is the process of mixing two or more polymers in a solution phase. Nanocellulose is dissolved with NaOH and heated at 100 °C. Non-polar LDPE is dissolved by using xylene before adding nanocellulose. Xylene is an organic non-polar solvent with a boiling point of 137 - 143oC. However, the synthesis of LDPE-nanocellulose with xylene solvents has not been homogeneously dispersed, coupling agents must be added to improve the level of homogeneity [10]. So, in this study coupling agent was added in the form of virgin coconut oil (VCO). Coupling agent can increase the bond between filler (nanocellulose) and matrix [11].

In this study, varying the composition of nanocellulose and temperature in the blending process. The composition is 5% -weight and 10% -weight, while the processing temperatures are 160 °C, 180 °C and 200 °C. Each variation was processed with fixed LDPE, xylene, and VCO values. Furthermore, the composite film is made by compression molding method with a hotpress tool. The results of making LDPE-based composite films can be seen below.

Figure 4.1 The results of the delignification process of cassava stems into cellulose

Figure 4.2 5% nanocellulose – 160°C, 180°C, and 200°C
From each sample that has been made with different parameters, testing is carried out to determine the best value and conditions that are equal to the standard of LDPE plastic. The tests used include a mechanical test (UTM), a water resistance test, and a Scanning Electron Microscopy (SEM) test. After that, to find out the effectiveness value of LDPE-based biodegradable plastic film, a degradation test is carried out to determine the minimum time of decomposition.

**Mechanical Test**

Tests are carried out using Universal Testing Machine (UTM). The mechanical properties of plastics is one of the main characteristics and plays an important role. Mechanical properties tested in this study include Tensile Strength, Elongation, and Young Modulus.

**Table 4.1 Mechanical Properties of Plastics in Accordance with SNI [13]**

| Number | Characteristic            | Value     |
|--------|---------------------------|-----------|
| 1      | Tensile strength (Mpa)    | 24.7-302  |
| 2      | Elongation (%)            | 21-220    |
| 3      | Hydrophobicity (%)        | 99        |

The results of the analysis of the mechanical characteristics of nanocellulose and LDPE in this study are explained in the following table:

**Biodegradable Plastic Testing**

**Table 4.2 Test Results for the UTM Nanocellulose and LDPE**

| Plastic      | Nanocellulose Composition (%) | Temp. (°C) | Tensile Strength (Mpa) | Elongation (%) | Young Modulus (Mpa) |
|--------------|-------------------------------|------------|------------------------|----------------|---------------------|
| LDPE Murni   |                               | 160        | 81.41                  | 76.1           | 1.07                |
| 5            |                               | 160        | 50.38                  | 8.83           | 5                   |
| 10           |                               | 160        | 30.16                  | 4.51           | 10                  |
| 5            |                               | 180        | 56.33                  | 11.04          | 5                   |
| 10           |                               | 180        | 31.18                  | 4.86           | 10                  |
| 5            |                               | 200        | 82.53                  | 41.06          | 5                   |
| 10           |                               | 200        | 35.90                  | 16.71          | 10                  |
Tensile Strength

Tensile strength is the maximum stretch strength that the material can accept before breaking up[14].

The results of the analysis of tensile strength can be seen as follows:

![Tensile Strength](image)

**Figure 4. Tensile Strength**

From the table above, samples of LDPE-based biodegradable plastic films that have been made meet SNI LDPE plastic standards. The data shows that the tensile strength value decreases with increasing filler content used. This result was reinforced by Marpaung, N.D., (2011) in his study which stated that the yield of the tensile strength of the composite material decreased with increasing content of the filler. The decrease in tensile strength is due to the low adhesion properties between the LDPE matrix material and the nanocellulose filling material. In addition, the nature of polarity between the matrix material and filler material which is still different prevents the interaction between the two. According to Hariadi (2000), another thing that can affect the tensile strength of composites is the spread of the filler material in the matrix has not been completely evenly distributed or the mixture of matrix particles with filler particles is less homogeneous.

From the graph, only 5% nanocellulose mixed film samples with processing temperatures of 200 °C have increased. In biodegradable plastic films with a composition of 5% temperature of 200 °C, the tensile strength value is 82.53MPa. Its value is better than the tensile strength of commercial LDPE at 81.47 MPa. This happens because of good homogeneity in both materials (nanocellulose and LDPE) so that the distribution of nanocellulose is more evenly distributed on the surface (Iriani, et al. 2015). The results show that temperature changes affect the tensile strength of composites, because the increased temperature of plastic film processing causes nanocellulose to decompose further. This is supported by research by Marpaung, N.D., (2011) which states that the maximum temperature of cellulose processing is 2000°C[15]

Elongation

Measurement of tensile strength is generally followed by measurement of elongation (elongation), which is the change in the maximum length experienced by a material when pulled up to break. The% extension determines the elasticity of a material. The higher the value of the% extension, the more elastic the material is so that the material can be stretched out more[16]

The analysis of tensile strength can be seen as follows:

![% Extension Value](image)

**Figure 5. % Extension Valve**

Plastic film test results show that elongation properties decrease with increasing filler content. This is because, with the increase in the filler content in the plastic film, it reduces the deformation on the matrix surface, thereby reducing the elongation properties of the composite[15]. However, the percentage of elongation is the effect of deformation, the greater the tensile strength the percentage of elongation is also greater[17]

Oksman and Clemons (1998) stated that fillers which have higher stiffness properties compared to the matrix will cause a decrease in the elongation%. Decreasing the elongation properties of plastic films with increasing cellulose filler material is also caused by changes in the composite properties of soft elastic to brittle strength.

From the diagram above it can also be seen that temperature changes affect the% plastic film extension, because at each nanocellulose: LDPE ratio
with different temperatures, the elongation of the composite increases. From the data, the value of the% extension that meets SNI standards is only at the composition of 5% nanocellulose with a processing temperature of 200 ° C, with a value of 41.06%. This is due to the temperature of 200 ° C, LDPE is completely fused and the nanocellulose is at the maximum processing temperature so that the mixture is homogeneous.

**Young Modulus**

Young modulus is often said to be a measure of the rigidity of a material. Young modulus is obtained from a comparison between tensile strength and percent elongation at break. The higher the modulus young value means that the material is more rigid[18]. Young modulus will be greater if the tensile stress is greater with the elongation getting smaller.

The results of the modulus young sample analysis can be seen as follows:

![Figure 6. Young Modulus Value](image)

From this graph it can be seen that Young's modulus is increasing with increasing filler content and decreasing with increasing processing temperatures in plastic films. The increase in young modulus in plastic films is due to an increase in the nature of the stiffness of the composite formed[15]. The lowest modulus value of young and the closest to the modulus value of commercial LDPE plastic is in the composition of 5% nanocellulose with a processing temperature of 200 ° C of 2.01 MPa.

From the data from the addition of composition and temperature in the tensile strength test, % extension, and modulus young test, it can be seen that the composition of 5% and temperature of 200 ° C is relatively better and close to commercial LDPE plastic specifications compared with other parameters. This can be explained that in the 5% composition and 200 ° C temperature is the optimal temperature for plastic film processing.

**Water Resistance Test**

Water resistance test is a test conducted to find out how much the absorbability of the material to water[19]. It is expected that in this study plastic films have a low absorption so that they have good resistance to water. The nature of biodegradable plastic film resistance to water is determined by swelling test, ie the percentage of film distention by the presence of water[20].

The results can be seen in the following graph:

![Figure 7. Absorption Value](image)

From the graph shows the absorption value of pure water is 0%, while the absorption value of plastic films with nanocellulose composition is 5% with a temperature of 160°C; 180°C; and 200°C is 1.2%; 2%; 1.7. Whereas in the composition of 10% the absorption rate experienced an increase to 3.3%; 4.4%; and 2.4 with the same temperature parameters.

The results of the data show that the more cellulose is added the water absorption increases on the plastic film, but the increase in temperature with the same nanocellulose composition does not affect the absorption rate. When compared with the LDPE plastic water absorption value, the composite water absorption is still relatively high. This is due to a change in the nature of its constituents. Associated with the statement of Darni & Utami (2010) that the nature of water resistance of a molecule is related to the basic properties of its constituents. When viewed from the nature of the chemical structure, cellulose has a strong hydrogen bond making it difficult to join with water (Septiosari, A., 2014). However, the addition of excess cellulose can increase cellulose absorption. This happens because hydrogen bonds in cellulose molecules tend to form intramolecular hydrogen bonds including water molecules[22]. So it...
can be said that the plastic film produced is hydrophilic.

**Degradation Test**

Degradation test is carried out to find out whether a material can be degraded well in the environment. Biodegradable plastic films that have been made are tested for their biodegradability with the help of Effective Microorganism or EM4 bacteria, which are compostable bacteria[23]. In this test immersion of the sample is carried out into the EM4 solution. But before that, EM4 which is still in a state of sleep (dormant) is activated by providing food (molasses) and water (Tyasning, D. S., 2012). The EM4 bacteria used are bacteria that are used to ferment soil organic matter. EM4 contains fermented bacteria, from the genus Lactobacillus, fermented mushrooms, photosynthetic bacterial actinomycetes, phosphate solvent bacteria, and yeast[24].

Testing biodegradable plastic films is done through visual film observation by observing changes that occur every day. Biodegradable plastic films cut into 2cmx3cm size are then weighed and then immersed in EM4 bacteria and observed.

- **Before Research**

1. Pure LDPE
2. 10% - 180 °C

- **After Research (20 day)**

1. Pure LDPE
2. 10% - 180°C
3. 10% - 200°C

**Figure 8.** Results of sample degradation testing
Table 4.3 Degradation Test Results

| Nanocellulose Composition (%) | Temp. (°C) | Initial Mass (g) | Mass Test (g)/20 Days | Degradation Time (Day) |
|-------------------------------|------------|------------------|-----------------------|------------------------|
| Pure LDPE                     | 160        | 0.046            | 0.046                 | >109,500               |
| 5                             | 160        | 0.165            | 0.160                 | 667                    |
| 10                            | 160        | 0.163            | 0.155                 | 408                    |
| 5                             | 180        | 0.119            | 0.114                 | 477                    |
| 10                            | 180        | 0.093            | 0.088                 | 370                    |
| 5                             | 200        | 0.175            | 0.165                 | 351                    |
| 10                            | 200        | 0.178            | 0.158                 | 179                    |

Figure 9. Degradation Value

The results obtained that biodegradable plastic films began to degrade on the 20th day. This is marked by the physical changes on the surface of the film that begins to erode. The data also showed that on the 20th day all plastic films had experienced mass degradation. Furthermore, from the mass degradation data obtained, the calculation is done using the soil burial test method to predict the period of time the sample can be completely degraded. Where the soil burial test method is a test to show that the plastic is completely degraded within a certain period, in terms of the percent loss of plastic weight (% weight loss) that reaches 100%.

From the above data obtained the fastest degradation time in samples with 10% nanocellulose composition and 200 °C processing temperature with 179 days. Based on European Union standards on plastic biodegradation, biodegradable plastics must be decomposed into carbon dioxide, water, and humus substances within a maximum of 6 to 9 months or 180 to 270 days[25]. From the graph above, it can be concluded that the composition and processing time have an effect on the duration of a sample's degrading process. This is also supported by research conducted Behjat, et al. (2009), states that the more cellulose contained in a plastic, the faster the plastic is to be degraded. So that plays a role in the degradation factor of a plastic is cellulose. Because cellulose is a natural material that can be degraded in nature due to microbial activity (Septiosari, A., 2014) then increased by the use of optimal cellulose processing temperatures, so that the fastest degradation time on biodegradable plastic films with a composition of 10% and a processing temperature of 200°C.

CONCLUSIONS

Synthesis of nanocellulose with LDPE-based plastic affects the mechanical and degradation properties. From all samples made, biodegradable plastic film samples with 5% nanocellulose parameters with a processing temperature of 200 °C have the best mechanical properties compared to other samples, with tensile strength values of 82.3 Mpa, elongation value of 41.06%; and young modulus of 2.01 Mpa. Increasing the composition of nanocellulose decreases the value of tensile strength and elongation but increases the value of young modulus. Whereas the increase in processing temperature increases the mechanical property value of biodegradable plastic films.

Increasing the composition of nanocellulose and processing temperature increases the value of resistance to water. The best value is at parameter 5% and the temperature is 160 °C with a value of 1.2, and the fastest degradation time is at the 10% parameter with a temperature of 200 °C in 179 days.
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