Bio-plastic composite: Rice starch, and Organic clay as alternatives material cold food delivery box

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Abstract

There are various plants based on bio-plastic manufacturing technologies have been introduced in the world. Indonesia has many plants that contain starch as a base material for thermoplastics such as corn starch, cassava starch, rice starch and pine tree sap. In this study, the expired starch from rice will be used as a composite material. The expired starch from rice can be used as flour to make bioplastics. With the addition of glycerol and citric acid mixed with organic clay, the expired rice in the form of flour will be made into bioplastics by heating from 100 °C to 150 °C. A mixture of glycerol and citric acid can help the process of biodegradable composites while a mixture of clay can help the plastic matrix become stronger so that it is expected to increase its thermal resistance. The results of the measurement of the average value of thermal conductivity (TC) for 10% OC and the average measurement of polyurethane were 0.0296 (W/mK) and 0.0292 (W/mK) at different temperature measurement ranges of 8 to 14 K. The formed plastic is then molded into a tensile test specimen and for thermal resistance testing by making cold food box samples for cold food testing.

Keywords: Composite material; Rice starch; Bio-plastic; Cool box; Thermoplastic.

INTRODUCTION

Lately, the waste of conventional plastic become a serious problem throughout the world because of its decomposition time in nature is too long (Geyer, Jambeck and Law,
The latest effort is the use of technology for making bioplastics or biodegradable bioplastics that can be degraded by microorganisms from plant-derived compounds, natural raw materials, such as starch, cellulose, and lignin (Avérous, 2004). Various studies and tests have been carried out. Among them is the testing of various bioplastic mixtures using protein and albumen starch (potato and corn) as raw materials with high transparency and suitable mechanical properties (González-Gutiérrez et al., 2011). Tests on the use and effect of adding plasticizers glycerol and sorbitol on the manufacture of plastics from cassava starch (Lagos et al., 2015). The use of cassava starch in biodegradable and non-retro biodegradable research (Seligra et al., 2016). Starch is a natural polymer extracted from plants and proposed to invent biodegradable plastics because it is environmentally friendly and renewable (Kukhta, Vasilenko and Kostjuk, 2011). Apart from cassava starch, rice is the alternative that contains a large amount of starch, which is appropriately used for the production of bioplastics. This is a great opportunity to provide added value to rice, especially those that have decreased in quality due to being stored for too long or not stored properly, this rice can be used as raw material for making environmentally friendly plastics. Excess stock in the BULOG warehouse from rice that has been stored for a long time so that the quality of rice has decreased and is often released at low prices. Excess rice stock in the BULOG warehouse for a long time can reduce its quality so that it is finally sold at a very cheap price. At the beginning of the year (2021), it was reported that 20,000 tons of rice would be auctioned starting at Rp. 1800 to Rp. 5000/kg (Ihsanuddin, 2021). However, this starch generally has unstable thermal stability so chemical modification is needed to improve its mechanical properties by adding plasticizers.

Organic acids will produce cross-links that connect polymer chains and produce a less permeable film resistance that is useful for improving the properties of starch (Jiugao, Ning and Xiaofei, 2005). In addition, organic acids contribute to starch hydrolysis, facilitating the
crushing and breakdown of granules, lowering material viscosity, improving processing properties, and producing a more homogeneous matrix. High relative humidity can reduce the tensile strength and increase the elongation of the film due to the role of water as a plasticizer. So that it can produce biodegradable films with better properties. This biodegradable film is another option for synthetic packaging where its limitations are seen as an advantage (Olivato et al., 2012).

The purpose of this research is to make a composite material from bioplastic (biodegradable plastic) where rice starch is added with plasticizer glycerol, sorbitol, and citric acid, and mixed with the local material used, namely organic clay (OC). The material is added as a matrix to strengthen the composite and reduce its thermal conductivity. Find the method of manufacture and the appropriate composition are the exacted results to obtain a bioplastic composite material utilized as a thermal insulation material.

The rest of the paper is structured as follows: Section 2, briefly presents an overview of the related work and application. Section 3, explains the method. Section 4, provides the experimental settings and discusses the experimental results. Section 5, elaborates on the conclusions.

Related Work

The integrated mixing, heating, and molding techniques are a combination technology in the manufacture of bioplastics. There are three effective ways to use starch as a raw material for making biodegradable plastics:

1. Starch is used as a filler for petroleum-based plastics, the amount is relatively small, ranging from 6-15% and only the starch is biodegradable.

2. Starch is mixed with biodegradable polymers such as PLA. The amount of starch used reaches 85%.
3. Thermoplastic starch, with the help of plasticizers (water, glycerin, and sorbitol), and high-temperature heating (90-160°C), in the manufacturing process then flows like thermoplastics (Solovyev, Rabotkin and Kovsharov, 2015).

Making biodegradable plastic with this mixing technique is quite simple. However, the implementation of production technology on a larger scale has not been widely reported. In some countries, the technology for producing biodegradable plastics on a large scale not only produces film sheets but also in other forms.

Biodegradable plastics of various shapes can be made from starch with the help of additives. A mixture of natural starch, gelatinized starch, thermoplastic starch, and modified starch, polymers, or monomers (lactic acid, hydroxy alkanoate) can be added with plasticizers, bleaching or dyes carried out through an extrusion process using an extruder at a temperature of 100-160°C. Plasticization is a thermoplastic starch process with the help of plasticizers such as (water, glycerin, and sorbitol) at a high temperature (90-160°C). Reports on Plasticization using corn starch by adding a little distilled water adjusted to 10% by weight (wet) have been done (Jiugao, Ning and Xiaofei, 2005). The techniques used are; mix glycerol and water first, add cornstarch then blend (3000 rpm, 2 minutes) using a high-speed. The mixture is covered and stored overnight. The ratio of glycerol to corn starch water (w/w weight basis) is 30:100. The mixture is manually fed into a single screw plastic extruder SJ-25(s) (screw ratio L/D = 25:1, made in China). The thread speed is 20 rpm. The temperature profiles along the extruder barrel are 130°C, 140°C, 150°C, 130°C (from feed zone to end). The results of extrusion after going through the drying and pelleting process produce biodegradable plastic pellets.

Bioplastic pellets or seeds can be processed into various forms of plastic by using a plastic converter in the form of blowing film to produce plastic bags. The use of thermoforming and injection molding will produce products such as keyboards and
telephones. Meanwhile, blow molding is used to produce products in the form of plastic bottles, and extrusion coating produces laminated films for snack packaging.

The manufacture of bioplastic composite materials refers to the general adhesive properties of plastics that can be used to make composites of used plastic mixtures of the HDPE type. Experimental testing shows that polymer tile composites are reported to show the best quality for compositions containing 70% HDPE with 30% desert sand (Seghiri et al., 2017). Other materials as reported (Senoro, Grino, and Chan, 2018) adding 5-10% clay filler (OC), have the potential for thermal insulation materials. The use of ordinary clay materials is also used for ceramic materials which affect the strength of ceramics.

**Method**

The method used in this research is qualitative experimental. Data collection was obtained based on direct observations and measurements by testing the composition of bioplastics. Based on the literature review, bioplastics with composition (1) in table 1 consist of 250 grams of rice flour, 150 ml of glycerol plasticizer, 150 ml of citric acid, 150 grams of pure water, and 150 grams of chitosan, then stirred slowly with a mixer for 5 minutes while adding 50 grams of organic clay. The next process is heated with stirring at 150 °C for 15 minutes, after which it is removed and molded, and finally cooled to room temperature. This cooling process takes eight days. After the cooling process, several tests were carried out as material requirements for the application of making cold food delivery boxes. For the proposed test composition, see table 1. (Composite sample 1 with added by 5% OC, and Composite sample 2 with added 10% OC).
Table 1. Bio-plastic composite composition

<table>
<thead>
<tr>
<th>Komponen</th>
<th>Composite sample 1</th>
<th>Composite sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(gram)</td>
<td>(%)</td>
<td>(gram)</td>
</tr>
<tr>
<td>Rice starch</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Pure water</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>Gliserol</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Citric acid</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Chitosan</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Organic clay</td>
<td>50</td>
<td>100</td>
</tr>
</tbody>
</table>

Tensile test specimens are molded using factory standard press machines. Tensile strength testing will be carried out to determine the strength of the material with a tensile test tool type RAMT 0-100 Kgf as shown in Figure 1. The results of this test are recorded on control data acquisition, and displayed on a PC.

The solubility test in water is shown in Figure 2. The test sample used in this test is a square with a size of 2 cm². The mass of the dry sample was accurately weighed and recorded. The sample which was still immersed in 100 mL of tap water was stirred constantly at 180 rpm with 25 °C for 6 hours (Zhang et al., 2017). The surviving part of the sample was filtered and then dried in a hot air oven at 110 °C until a final constant weight was obtained. Glycerol has good water solubility ranging from 18% to 25% (Suriyatem, Auras and Rachthanapun, 2018). The percentage of total solute (% solubility) is calculated as:

\[
WS (\%) = \frac{(W_0 - W_f)}{W_0} \times 100
\]

Where; WS is solubility in water, W₀ is the last weight of bioplastic, W_f is the initial weight of the bio-plastic. The analysis is then carried out by comparing the test results from the existing literature so that the results can be concluded.

The effective composite conductivity may vary significantly depending on the thermal resistance (Han and Fina, 2011). The thermal resistance test is carried out by making a box as shown in Figure 3. Boxes are made of several units of the same size. The walls of box 1 are...
made of polyurethane coated with aluminum sheet and the other box is made of bioplastic which is also coated with aluminum sheet. The test was carried out with PCM ice cream and the cooler was placed in an insulated sealed box. Temperature measurements were carried out using a thermocouple and data acquisition (Datascan 7320 Measurement System Limited). This measuring instrument consists of 16 analog and digital channels that can be used to record temperature, pressure and flow rate data as needed. The controller and recorder are connected using a PC.

Thermal conductivity testing conducting by using two thin film heat flux sensors (HFS-4) serial no 10034586 manufactured by omega engineering (4-wire sensor with Thermocouple has a sensitivity rating of 6.51). This sensor is a differential thermocouple sensor which is suitable for measurement of heat transfer in any material. It can be mounted on a flat or curved surface and has a lower thermal profile for efficient reading. A thin foil, 50 plus thermopile junctions is bonded to both sides of the Kapton barrier where the thermal characteristics are known. Since the heat transfer rate is directly proportional to the temperature difference across the thermal barrier, it is necessary to measure the difference and the heat transfer rate can be calculated by measuring this difference. The copper/constant-on junction is formed and connected in series on the alternating side of the Kapton core. The copper output cable is attached to the cable where the first cable connection is on the top surface and the last cable connection is on the bottom surface.

The installed HFS sensor has a sensitivity of 6.37 microvolts per BTU/ft2 hour. An OMEGA CN3000 controller is available to provide display and control capabilities. It will take Input 0 to 100mV and has a range of 31,565 engineering counts. When generating a voltage level of 100mV, the sensor measures:

\[
(100 \times 10^{-3})/(6.37 \times 10^{-6}) = 15,699 \text{ BTU/ft}^2\text{-Hr} \]

(2)
Since 15,699 is well within the maximum display reading of 31,565 available on the CN3000, the controller can then be programmed to display zero at 0 mV and 15,699 at 100mV. In addition, HFS sensors are often connected to chart recorders, data loggers or totalizers in order to record a running tally of total heat transfer through a given surface.

**Experimen Results**

Figure 1 shows the results of the tensile test of bioplastic composites with the average load and elongation of 28.02 N and 1.77%, respectively. When compared with the results of the rice and corn bioplastic tensile tests from the literature (Wu, Sung and Chuu, 1999), the average load and elongation values are 9.578 N and 5.35%, respectively.

![Figure 1. Tensile Test Results](image)

**Composite Water Absorption Rate Test**

This test is needed to determine the solubility level of the composite so that it can help the process of biodegradable bio-plastics in nature (Wu, Sung and Chuu, 1999). (Thakur et al., 2016). It is also used to provide technical specifications in the application. Figure 2 shows...
a comparison of the solubility levels of rice and clay composites with rice-corn bioplastics. The test results show that the percentage value of water absorption from rice-starch bioplastic is an average of 15% (blue line) while the average value of rice-corn bioplastic is 11.98% (red line from the literature). With these results it can be stated that the composite of rice and clay has a higher water absorption capacity. Water absorption is obtained due to the presence of a glycerol component which has good water solubility with values ranging from 18% to 25% (Ghasemlou et al., 2013). The presence of clay matrix in the composite is also an additional factor to increase it.

![Image of rice and clay composites](image_url)

Figure 2. Comparison of the solubility bio plastic

This shows that the tensile strength of rice-clay bioplastics is three times greater than that of rice-corn bioplastics (Marichelvam, Jawaid and Asim, 2019). This comparison also shows that the plasticity has decreased almost threefold. The above properties are sufficient to make a candidate for bioplastic board filling material that can be used for food cooler boxes.
Figure 3 (insertion view) informs about the bioplastic box made of rice clay which is covered with an aluminum sheet on the outside so that it is the same as the comparison box made of polyurethane - covered with aluminum sheet of the same thickness. The position of the ice cream and PCM is in the box. The installation of the temperature sensor for the measuring instrument is at the measuring point. The figure also shows how the test is carried out.

Data collection was organized by Msi data acquisition with MSL 7000 series data scanning for 6 hours. Repeated several times, the average results are plotted as shown in Figure 4. The light blue line on the graph shows the ambient temperature (TL) of the measured results ranging from 28-30 °C with an average of 29.5 °C in each test. In this case, the ambient temperature is assumed to be constant. The line (T1 K1) is the room temperature on the inner box of the polyurethane material while the line (T1 K2) is the temperature on the inside of the bioplastic material box. Both show a similarity in terms of temperature rise with slight differences.
Figure 4. Temperature plot of the test of thermal resistance.

The lines (T2 K1), K1 are indicated on the polyurethane box, and T2 is the PCM temperature. The lines (T2 K2), T2 shown on the temperature box (K2) of the bioplastic material, both indicate that PCM performs well in storing and releasing latent heat in both test boxes.

The temperature of the ice cream has increased, this is shown in Figure 4. The value of the initial temperature of the ice cream tested in both boxes is the same, namely at a temperature of -11°C. The green line (T3 K1) shows the temperature rise of the ice cream in a box made of polyurethane.

The orange line (T3 K2) is a graphic line that shows the temperature rise of the ice cream in the bioplastic box. This line intersects the 0°C temperature line from the PCM at 2 hours 24 minutes. While the ice cream temperature line in the second inbox of polyurethane intersects the 0°C temperature line from PCM at 3 hours 54 minutes. This shows that the second box has better resistance to maintain the cold temperature of the ice cream. With a time difference of 1 hour 25 minutes, it can be said that the addition of 5% clay to bioplastics can increase the density of the material.

Figure 5. shows the results of the thermal resistance test of bioplastic material with the composition of two samples (Table 1) with the addition of 10% organic clay. It is similar
to Figure 4. The line (T1 K1) is the room temperature on the inner box of the polyurethane material while the line (T1 K2) is the temperature on the inside of the bioplastic material box. Both of them show a corresponding increase in temperature with little difference. The lines (T2 K1), K1 are indicated on the polyurethane box, and T2 is the PCM temperature. The lines (T2 K2), T2 shown on the temperature box (K2) of bioplastic materials with 10% OC, both indicate that PCM performs well in storing and releasing latent heat in both test boxes.

The temperature of the ice cream increased, as shown in Figure 5. The initial temperature of the ice cream tested was the same in both boxes, namely at -11°C. The green line (T3 K1) indicates the temperature rise of the ice cream in a polyurethane box. The orange line (T3 K2) is a graphic line that shows the temperature rise of ice cream in the bioplastic box and intersects the 0°C temperature line from PCM at 3 hours 44 minutes, while the temperature line inbox two of polyurethane ice cream intersects the 0°C temperature line from PCM at 3 hours 54 minutes. It shows that the second box has the durability to maintain the cold temperature of the ice cream which is almost close to box 1. With this time difference of 10 minutes, it can be said that it can increase the additional OC by 10%. This is an indication that rice-clay composite bioplastics can be candidates for polyurethane substitutes.

Figure 5. Temperature plot of the test of thermal resistance.
Figure 6. A schematic of the test of thermal conductivity.

The two thin film heat flux sensors HFS-4 serial no 10034586 from omega engineering are 4 wire sensors with Thermocouples with a sensitivity rating of 6.51. This sensor can be directly connected to a standard microvolt meter with no cold connection compensation required. Due to its thin profile and overall flexibility, we install this sensor on almost any flat or curved surface and glue it in place using an epoxy or conventional adhesive. The instrumentation for using the HFS heat flow sensor is a self-generating device and does not require external voltage or current stimulation. The voltage output from the device can be read with a commercially available voltmeter that has a microvolt resolution. As an alternative, we can also use Datascan 7320 (Measurement System Limited). This device consists of 16 analog and digital channels that can be used to record temperature, pressure and discharge data as needed. The controller and recording are connected using a PC. The test is used to obtain the k(TC) value of the thermal conductivity of bioplastics.
Figure 7. Thermal conductivity of sample 1 with a composition of 5% Organic clay

The test of thermal conductivity for box composite (sample 1) with 5% clay shown in Figure 7. The average measurement result is 0.036 (W/m. K). The mean thermal conductivity value obtained from the polyurethane box measurements was 0.0292 (W/m. K) and the value was in accordance with the range obtained from the literature. Typical thermal conductivity values for polyurethane foams are between 0.02 and 0.03 W/m. K (Wu, Sung and Chuu, 1999), (Jelle, 2011), (Zhang et al., 2017).

Figure 9. a)Thermal conductivity of sample 2 with a composition of 10% Organic clay, b) Polyurethane
While the composite box with 10% clay, the measurement result is 0.0296 (W/m.K) with a measurement temperature of 8 to 14 °C or 281.15 to 287.15 degrees K. In this case, the criteria for a thermal insulating material with a conductivity lower than 0.07 (W/m.K) have been met (Asdrubali, D’Alessandro and Schiavoni, 2015).

**Conclusion**

Mechanical testing of rice starch and clay bioplastic composites with compositions such as table 1 is the subject of this paper. With a mixture of 5% clay, the resulting material with an average tensile test result of 28.02 N and has a solubility in water of 15%. When compared with rice-corn bioplastics from the literature, the average is 11.98%. This material is stronger than rice-corn bioplastic and its solubility in water makes this material have better prospects for biodegradability than plastics in general.

The results of the thermal resistance test of the rice-organic clay composite box material with 5% clay able to withstand the temperature of ice cream at an initial temperature of -11°C for 2 hours 24 minutes until the temperature is reached with a PCM working temperature of 0°C faster 1 hours 20 minutes from the rice-organic clay with 10% clay concentration, and 1 hour 30 minutes from the polyurethane box.

The results of the measurement of the average value of thermal conductivity (TC) for 10% OC and the average measurement of polyurethane were 0.0296 (W/m. K) and 0.0292 (W/m. K) at different temperature measurement ranges of 8 to 14 K. This corresponds to the typical thermal conductivity values for polyurethane foams (0.022 and 0.035 W/m. K) and meets the criteria for thermal insulating materials lower than 0.07 (W/m. K) as well.

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References


