Fabrication and Characterization Of Poly Lactic Acid (PLA)-Starch Based Bioplastic Composites

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Abstract. In this study, to make a good bioplastic composite, starch-based bioplastic is produced by adding poly(lactic acid) (PLA) to improve its properties. PLA was added into starch-based bioplastic with various concentrations of 0, 3, and 10 wt.%. The extrusion was performed at 90-150 °C and compression moulding process was conducted at 150 °C and pressured at 50 kgf/cm². Bioplastic composites have been characterized to know its properties. FTIR analysis indicated shifting and increasing spectra of interaction between PLA and starch-based bioplastic. Contact angle and solubility analysis revealed that adding PLA can increase the stability of hydrophobic characteristic and insoluble properties. The combination of PLA and starch-based bioplastic can improve the mechanical properties. In addition, thermal properties of bioplastic composites have a better thermal stability and produce a lower melting point thus the energy needed to melt for bioplastic composites becomes melt as raising PLA composition.

The density of bioplastics was in the range of 1.2 - 1.3 g/cm³ that would be good for light bioplastic. The results of this study showed that the combination of starch-based bioplastics and PLA at low concentration (10wt.%) potentially could enhance the properties of bioplastic composites for food packaging.

Keywords: Bioplastics, Starch, Poly Lactic Acid, Composites

1. Introduction

The use of conventional plastics (non-biodegradable polymer) as food packaging produced waste and threatens the environment because the decomposition process is so slow for decades. The accumulation of plastic waste can damage natural ecosystems thus needs an alternative to reduce the plastic waste used primarily for food packaging. Plastic also has health security deficiencies since plastic compounds are not friendly to body tissues. This has become one of the world's concerns in handling plastic waste in the environment and the influence of using plastic as a food packaging for health.

One alternative that can be used to deal with this problem is fabricating plastic from natural materials (bioplastic). Bioplastic research and manufacture has been completed by researchers with multiple material resources and techniques. In general, bioplastic can be fabricated from various types of natural polymers such as cellulose [1], protein [2], starch [3] etc. [4]. Starch is one of the basic ingredients that have been widely used to make bioplastics. Starch is a biopolymer that is abundant in
nature, biocompatible, biodegradable and easily renewed [5]. Starch generally contains amylose and amylopectin in different percentage of each source that would be affected on properties of bioplastics.

Research of starch-based bioplastics has been studied recently with various starch sources such as corn starch [6], potato starch [7], cassava starch, rice starch [8], canna starch [9], etc. However, the use of starch has disadvantages that its hydrophilic characteristic will decrease its properties as bioplastic [5]. Therefore, the addition of other ingredients is needed to improve typical starch-based bioplastic.

Poly Lactic Acid (PLA) is one of a synthetic polymer that can be degraded, renewable, eco-friendly, biocompatible and has hydrophobicity characteristic [10]. PLA has composed from lactic acid that synthesized from polysaccharide fermentation [3]. Blends of starch-based bioplastic and PLA have been investigated recently [11]. Several studies also add compatibilizers [12], modifying starch to be high crystallinity [13] and made layers to improve the hydrophobic properties of starch-based bioplastics with the addition of other materials such as chitosan [14], etc. Sanyang et al. (2016) conducted research of sugar palm starch-based bioplastics and PLA as layers, thus, the results showed that the addition of PLA improved the mechanical and hydrophobic properties of bioplastic [15]. Muller et al. (2016) also produced bioplastic from corn starch and PLA to identify interaction and miscibility of PLA and starch-based bioplastic with adding glycerol on PLA [16]. In this case, the addition of PLA in blending with starch-based bioplastic is above 10% which can affect the production cost of bioplastics for industrial scale. Besides, some solvents such as chloroform in the process of PLA dissolution is also dangerous since it ruins the health.

Researches of synthesis starch-based bioplastic and PLA addition at low concentration weren’t much performed, so we aim to produce PLA - starch-based bioplastic blend (bioplastic composites) at low percentages of PLA (0, 3, 10%) using extrusion method to know the effectiveness of the addition of PLA with small concentration. Bioplastic composites were characterized by physical, chemical, thermal, mechanical, hydrophobicity and morphological observations of bioplastic composites.

2. Experimental method

2.1 Materials and chemicals
The native corn starch was obtained from PT. TEREOS (Indonesia) and moisture analyzer showed that water content of starch was around 15% and density measurement using pycnometer (PYREX) was around 1.45 g/cm³, PLA was purchased from NatureWorks (U.S.A), and glycerol was obtained from PT Wilmar Nabati Indonesia.

2.2 Preparation of Starch-based Bioplastic
Starch-based bioplastic was prepared by dry-blending of corn starch and glycerol with ratios 3:1 (w/w based on starch) by using Philips Blender HR2116 through 600 W power for 3 minutes. Then, forming pellets of starch-based bioplastics were extruded by using a single screw extruder from Labo Plastomill, (Toyoseki, Japan). The heating sections were 80-130 ºC and the screw speed was 35-50 rpm. Starch-based bioplastic also will be called as J-PLA 0%.

2.3 Fabrication of Bioplastic Composites
Pellet of starch-based bioplastics and PLA were combined with various concentrations of PLA at 3wt.% and 10 wt.% (J-PLA 3% and J-PLA 10%). Extrusion process was performed at heating temperature 90-150 ºC. and samples were formed to be plates by compression moulding machine (Toyoseki, Japan) conducted in temperature 150 ºC and pressured at 50 kgf.cm² for 5 min for J-PLA 0%, J-PLA 3% and J-PLA 10%.

2.4 FTIR Analysis
To identify the chemical interaction of bioplastic composites, samples were analyzed by Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR) using Thermo
Scientific Nicolet iS5. Samples were determined by using air as background, recording 64 scans and resolution from 4000 – 400 cm\(^{-1}\).

2.5 Density Analysis
The density of composites was measured by calibrated pycnometer (10 ml volume, PYREX) and distilled water was used as the immersing liquid with three repetitions. The sample was weighed before putting into pycnometer that contains liquid. After that, the sample in the pycnometer was weighed (m) and the density (\(\rho\)) was calculated by the equation:

\[
\rho = \frac{m}{V}
\]  

(1)

2.6 Contact Angle Analysis
The contact angle of samples was captured triplicate for each sample manually and imageJ software was used to analyze hydrophobicity degree of composites.

2.7 Solubility Analysis
The samples were dried at 105 °C and weighed as \(W_i\). Then, samples were immersed at 50 mL of distilled water for 24 h at room temperature. After that, samples were dried at 105 °C and weighed as \(W_o\). Water solubility of samples was calculated with the equation:

\[
\text{Solubility (\%)} = \left(\frac{W_i - W_o}{W_i}\right) \times 100
\]  

(2)

2.8 Mechanical Analysis
Mechanical properties of samples were measured by Universal Tensile-meter (Tensilon, Japan) with three repetitions of each sample. It was controlled with room temperature and (23 ± 2 °C) and 60 ± 1% RH. The samples were analyzed using standard method JIS 7113-2-1/2 and load cell 40% from 100 kgf. The samples was pulled with crosshead speed 5 mm/min.

2.9 Morphological Analysis
Morphology image of composites was obtained by SEM (JEOL JSM-IT300) under the operating voltage of 20 kV at low vacuum. Samples were coated with gold and strip by adhesive tape (carbon tape).

2.10 Thermal Analysis
Thermal properties of the sample were carried out using TGA-DSC thermogram (Netzsch 214 Polyma) to analyze decomposition stability and melting point of the samples. The TGA test was measured at temperature 40 – 450 °C and scan rate 10 °C/min. then, DSC test was obtained at temperature 40 – 200 °C with scan rate 10 °C/min.

3. Results and discussion

3.1 FTIR analysis
Chemical interaction of bioplastic composites can be identified using FTIR spectrum analysis as shown in Figure 1. The addition of PLA into starch-based bioplastic produces functional groups formed in J-PLA 3% and J-PLA 10%. The functional group of –C=O stretching produced shifting peak from 1721 cm\(^{-1}\) (PLA) to 1750 cm\(^{-1}\) (J-PLA 3% and J-PLA 10%). The functional group of –C-O stretching also generates a shifting area from 1198 cm\(^{-1}\) to 1180 cm\(^{-1}\). Then, the functional group of –CH\(_3\) stretching was also developed at wavenumbers 1450 and 1370 cm\(^{-1}\).
-C-O stretching was also grown from PLA and starch-based bioplastics in the wavenumber area of 1080 cm\(^{-1}\) that created a constructive peak, thus the absorbance values of J-PLA 3% and J-PLA 10% is higher than J-PLA 0%. The -OH bending in the wavenumber area of 1020 cm\(^{-1}\) is developed from starch-based bioplastic. Shifting and constructing peaks indicate the interaction between PLA and starch-based bioplastic developed on J-PLA 3% and J-PLA 10%. However, molecular bonds on FTIR spectra is not sufficient to justify the miscibility of PLA and starch-based bioplastic. Some functional groups were not strong enough to make changes in typical vibration in composite of PLA and starch-based bioplastic. Sanyang et al. (2016) confirmed that PLA and bioplastic from sugar palm starch produced the physical interaction only between PLA and bioplastic. In addition, Gonzales at al. (2013) verified that PLA and bioplastic from soy protein could not mix each other because the chemical carriage of them is appeared and not established a new chemical bond [2]. Muller et al. (2016) recognized the interaction between PLA and starch-based bioplastic by thermomechanical analysis and thermodynamic modeling indicate that interaction between PLA and thermoplastic starch (bioplastic) give poor miscibility and heterogeneous structures [16].

### 3.2 Density Analysis

![Figure 2](image-url)  
**Figure 2.** The density of bioplastic composites.
Physical properties of PLA – starch-based bioplastic composites were exhibited from density measurement in Figure 2. Based on that, J-PLA 0% had the highest density (1.3 g/cm³) than others. Then, J-PLA 3% and J-PLA 10% produced density derivation related to the raising of PLA content. Starch and glycerol were included in J-PLA 0% in which the density values of starch and glycerol are 1.45 g/cm³ and 1.21 g/cm³ (based on experiment). While PLA density is around 1.24 g/cm³[17] that mean PLA would decrease the density value of composites. It designates that increasing of PLA content can improve the density of composites to be light bioplastics.

3.3 Thermal Analysis

![TGA thermogram of bioplastic composites.](image1)

**Figure 3.** TGA thermogram of bioplastic composites.

![DTG thermogram of bioplastic composites.](image2)

**Figure 4.** DTG thermogram of bioplastic composites.

Thermal properties of bioplastic composite were analyzed by TGA-DTG Thermogram as shown in Figure 3 and Figure 4. The thermal degradation of PLA – starch-based bioplastic was observed in the TGA curve (Figure 3). The samples has losing the weight at a temperature under 200 °C which is water molecules according to previous literature [2]. Furthermore, the DTG curve (Figure 4) shows decomposition at 290.6 °C with 20.86% weight loss in J-PLA 0% that indicated the evaporation of glycerol, which concurs with the literature [15]. J-PLA 3% and J-PLA 10% didn’t present the peak of glycerol loss directly since the processes were heated twice. Then, decomposition process significantly
established at temperature 317.9 °C with 52.4 % weight loss for J-PLA 0% indicating where the starch was degraded. And sharp peaks of J-PLA 3% and J-PLA 10% were established at temperature 311.9 °C and 319.9 °C related with 62.64% and 76.28% weight loss. Also, thermal degradation process records a residual mass until temperature 450 °C, where J-PLA 0% produced the lowest residual mass (7.96 %) than J-PLA 3% and J-PLA 10% which leaves 12.51% and 10.77% residue. The addition of PLA wasn’t changed the thermal stability of bioplastic composites significantly and by adding PLA content can maintain the temperature so that the material mass is not easily decreased. This concurs with the literature that mass loss of PLA/starch blend increased as raising PLA content [15].

Figure 5. DSC thermogram of bioplastic composites.

Figure 6. Contact angle measurements of bioplastic composites.

Melting point temperature of bioplastic composites was carried out by DSC thermogram analysis as shown in Figure 5. The results showed that the addition of PLA decreased melting temperature and energy requirements. J-PLA 0% had a melting temperature 107.6 °C and ΔH at 182 J/g. Thus, J-PLA 3% held melting temperature 96.7 °C with ΔH of 53.28 J/g and J-PLA 10% develop a melting point at 94.3 °C with ΔH of 54.71 J/g. Combination of PLA and starch-based bioplastic reduced melting point temperature and energy. This indicated that PLA addition increasing its free volume[18]. It is comparable with the density measurements that PLA addition can lessen the density value. It is good for the industry to minimalize the use of energy in the processing materials.
3.4 Contact Angle Analysis
The wettability and hydrophobicity properties of composites were analyzed by contact angle measurement as seen in Figure 6. The results indicated that J-PLA 0% had the highest degree, but also decreased significantly after a few minutes. J-PLA 0% contains materials that can absorb water such as starch. It has –OH bond so that bioplastics can bind H₂O molecules. The –OH bending also appears in FTIR spectra that is parallel with the literature [19].

Furthermore, J-PLA 3% and J-PLA 10% have the stability degree after a few minutes. It shows that the addition of PLA can be improving the hydrophobicity of composites. Nonetheless, appending PLA doesn’t influence hydrophobicity degree at the beginning of measurement that is similar to the statement of literature [2].

3.5 Solubility Analysis
The solubility of composites is shown in Figure 7. J-PLA 0% has the highest solubility percentage at 48%. Then, J-PLA 3% and J-PLA 10% have lower solubility than J-PLA 0% where the solubility percentage is 27% and 25% respectively. This indicates that the addition of PLA can reduce the solubility of composite bioplastic and perform better water barrier properties. This is matched with the results of the contact angle measurement and literature [2].

3.6 Mechanical Analysis
The mechanical properties of PLA - starch-based bioplastic composites are presented in Figure 9. It can be seen that J-PLA 0% has the lowest tensile strength, thus, with PLA addition in J-PLA 3% and J-PLA 10% increase the tensile strength values completely. On the other hand, the elongation at break of J-PLA 3% and J-PLA 10% are lower in the proportion of increasing PLA. It proved that adding PLA can raise tensile strength and decrease elongation at break. Mechanical properties of PLA is brittle and have high tensile strength values (55.4 MPa [11]) capable of enhancing tensile strength properties from bioplastic composites. This consists with previous studies that starch-based bioplastics have higher bending properties than PLA because starch-based bioplastic has amylose/amylopectin bonds which produce flexural properties and the addition of glycerol to starch-based bioplastic also improve the flexibility of bioplastic. Meanwhile, PLA has a very low elongation at break (<10% [11]) since PLA has strong bonds between lactic acid monomers which make PLA more rigid and have no flexibility like starch [5].
Figure 8. Mechanical properties of bioplastic composites.

3.7 Morphological Analysis

Figure 9. SEM image cross section of bioplastic composites J-PLA 0 % (a), J-PLA 3 % (b), and J-PLA 10 % (c).

Figure 10 shows a cross-sectional image of a morphological PLA – starch-based bioplastic composites. It can be considered that the fracture of J-PLA 0% (Figure 10a) has emerged. It means that J-PLA 0% arranges ductility characteristic on mechanical properties. However, J-PLA 3% and J-PLA 10% have a mixed fracture that requires the transition properties between ductile and brittle characteristics to have formed. J-PLA 3% exhibits PLA existence on wrinkle sheet structure that sticks on starch-based bioplastic. Furthermore, J-PLA 10% presents agglomeration structures and PLA content at wrinkle sheet structures, it appears much more than on J-PLA 3%. Besides, J-PLA 10% has a crack considering tensile strength between J-PLA 3% and J-PLA increase insignificantly. On the other hand, the solubility of J-PLA 10% and J-PLA 3% consume more than 20%. It means that crack on the samples influences water barrier solubility and mechanical properties. Also, the crack affected higher free volume in the samples that cause decreasing melting point temperature on thermal properties.

4. Conclusion

Bioplastic composites were produced successfully by extrusion and compression molding of starch-based bioplastic and PLA at low matter to determine its properties. The FTIR analysis indicated shifting wavenumbers and increasing spectra that means the interaction between starch-based bioplastic and PLA were happened in bioplastic composites. Nevertheless, raising PLA concentration can decrease bioplastic composite density to be light bioplastic that would be a good point for bioplastic. Afterwards, the contact angle measurement revealed hydrophobic properties of bioplastic.
composites by increasing PLA contents. The Solubility analysis also observed that adding PLA can resist water molecules up to 20% compared with bioplastic without PLA, so that bioplastic composites have a good resistance of water soluble. Furthermore, adding PLA can improve mechanical properties of bioplastic composites up to 5 MPa (10wt.% of PLA). The combination of PLA 10wt.% and starch-based bioplastic showed the best possession than the others based on its properties especially mechanical and water barrier properties. Despite adding PLA in low matter, these results affirmed that bioplastic composites had suitable properties and potentially could be developed as food packaging.

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