Effect of chitin addition on water resistance properties of starch-based bioplastic properties

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Abstract. In this study, the fabrication of starch-based bioplastics and the addition of chitin have been prepared. Bioplastics were produced by mixing starch, glycerol and chitin at various concentrations (1 %, 2 %, 3 %, 4 % w/w) through the melting process at 130 °C. Chitin affected bioplastic characteristics especially on its water barrier property. Morphological structures of bioplastics showed that chitin flakes attached to bioplastics. Moreover, FTIR observation showed that interaction between starch and chitin marked by amide group appearances at 1656 cm⁻¹ and 1551 cm⁻¹. Then, DSC analysis revealed that chitin involved melting temperature insignificantly by raising chitin concentration from 90 °C (0 % chitin) up to 97 °C (4 % chitin). Although the addition of chitin derived slightly the tensile strength and elongation at break, it improved hydrophobicity of bioplastics from 37.54° (0 % chitin) up to 74.97° (4 % chitin). Permeability of bioplastics decreased from 0.0206 g/m²/2h/mmHg (0 % chitin) to 0.0173 g/m²/2h/mmHg (3 % chitin). Eventually, chitin improves the water barrier property of bioplastics.

Keywords: bioplastics; chitin; starch; water resistance

1. Introduction

Starch-based bioplastics have been studied recently with various additions to increase its properties [1,2,3]. Bioplastics from starch hold many advantages such as eco-friendly, renewed easily, biocompatible with human body, non-toxic and simply degraded in short time [4,5]. However, due to its hydrogen bond that easily absorbs water molecules, starch has hydrophilic properties. Therefore, starch-based bioplastics cannot resist toward humidity, of which plastics for packaging must be opposed against water [6].

To reinforce its water barrier properties, starch based bioplastics were blended with synthetic polymers such as PE, LDPE, HDPE, etc [7,8,9,10]. Nevertheless, the synthetic polymer reduces biodegradability of starch based bioplastics and it is not compatible with the environment [11]. One of biopolymers with hydrophobic property that can be used to optimize water resistance of starch-based bioplastics is chitin.

Chitin is biopolymer that can be found in shrimp and crab shell as a main component from exoskeleton of fungi, yeast, or sea plant and animal [12]. Chitin develops advantages such as stable to chemical reactions, low chemical selectivity, non-toxic, biodegradable and insoluble in water [13]. However, chitin structure is fragile and should be mixed with other materials to generate bioplastics.
Therefore, to improve its water resistance property, starch-based bioplastics can be combined with chitin. Fabrication of starch based bioplastics with the chitin addition had been studied [15,16,17]. Moreover, Bioplastic production by various techniques such as casting, extrusion, compression or injection moulding has been explored [18,19,20]. Rosa et al. produced starch-based bioplastics with the chitin addition using injection moulding process. After 30 days of retention, it showed that the bioplastic with the chitin addition improved its water resistance [15]. Moreover, Lopez et al. mixed the starch and chitin by using the melting-mix and thermo-compression method [21]. However, the temperature was high and energy consuming due to the transformation phase and the possibility of starch-based bioplastics destruction [22].

In this paper, bioplastics were obtained by mixing cassava starch and glycerol with the addition of chitin flakes at 140 °C to improve the water barrier property. The blends of starch and chitin were used by drying condition and applied chitin flakes on the bioplastics. Moreover, the effect of chitin addition on bioplastic properties was evaluated by using SEM, FTIR, DSC, tensile tester, water vapour permeability and contact angle measurements.

2. Experimental Method

2.1. Materials
Cassava starch was purchased from PT. Budi Starch & Sweetener, Tbk. (Central Lampung, Indonesia). Chitin was developed from local industry (Bandung city, Indonesia) and glycerol was purchased from EMD Millipore Corporation (Germany).

2.2. Preparation of bioplastics
Bioplastics were prepared by mixing starch and glycerol with mass ratio 3:1 and chitin was added with various concentrations (0 %, 1 %, 2 %, 3 %, and 4 % w/w) by drying condition. The components were blended using Phillips Blender HR211801 for 3 min. Afterward, samples were mixed by using Mixer Labo Plastomil 30R150 Toyoseiki at 130 °C. Bioplastics were compressed at 40 kgf/cm² to form film.

2.3. Characterization of bioplastics

2.3.1. Water Vapor Transmission Rate of bioplastics
Water Vapour Transmission Rate (WVTR) is one of methods that can be used to confirm the water barrier properties of bioplastics. WVTR was measured by using ASTM 96 with some adjustments. Bioplastic film was cut and sealed on holders which had been filled with water. Samples were then placed in desiccator by condition at relative humidity 50 % and temperature of ±25 °C. The bioplastic samples were evaluated every 2 h to know the transformation mass and the results were calculated by making permeability [17].

2.3.2. Contact angle
The hydrophobicity of bioplastics was determined by contact angle measurement with dropping water method. Water droplet pictures were measured its contact angle by Image-J application.

2.3.3. Morphology of bioplastics
The cross section of bioplastics was shattered by freezing it with liquid nitrogen. The fractures were coated and sputtered with gold ion. Morphology image of bioplastics was obtained by Scanning Electron Microscopy (SEM JEOL JSM-IT300) under the operating voltage of 20 kV at low vacuum.
2.3.4. Chemical interaction of bioplastics
Chemical interaction of bioplastics was determined using Thermo Scientific Nicolet iS5 ATR-FTIR Spectrometer (Madison, WI, USA) at range of wavenumber from 4000 to 400 cm\(^{-1}\), sensitivity of 60, and scanning resolution of 3.8 cm\(^{-1}\).

2.3.5. Thermal property of bioplastics
Thermal properties of bioplastics were characterized by using Differential Scanning Calorimetric (DSC Thermogram Netzsch 214 Polyma) to identify melting point of bioplastics. The process was obtained at temperature 40 – 150 °C with scan rate of 10 °C/min.

2.3.6. Mechanical properties of bioplastics
Mechanical characteristic of bioplastics was analysed by Universal Tensile-meter (Tensilon, Japan). Bioplastics were controlled with room temperature (23 ± 2 °C) and humidity 60 ± 1 %. Film of bioplastics was cropped using standard method JIS 7113-2-1/2 and load cell 40 % from 100 kgf. Then, samples were pulled with crosshead speed of 5 mm/min.

3. Results and Discussions

3.1. Water vapour transmission rate of bioplastics
To increase water resistance property of starch-based bioplastics, chitin was added and examined its characteristics. According to WVTR test of starch-based bioplastics which was combined with chitin showed water vapour percentage that transmitted through bioplastics on Figure 1. The existence of chitin on starch-based bioplastics will inhibit attraction between bioplastics and water; therefore it can prevent water vapour release through bioplastics. The percentage of the mass of water vapour shows that the higher the concentration of chitin, the lower the mass of water vapour coming out through bioplastics. So, overall bioplastics show an increase in the percentage of water that can be released. However, there is a difference in the value of the water percentage that can be released through five types of bioplastics. The percentage of water mass decreased is lowest shown on used bioplastic 3 % chitin (11 %). The highest percentage shown on bioplastic 2 % chitin (15.26 %) exceeded percentage which shown on bioplastic 0 % chitin (14.5 %). While the percentage of bioplastic 1 % chitin is 13.3 % and 13.4 % for bioplastic 4 % chitin, where both concentrations are lower than bioplastic 0 % chitin.

![Figure 1. Transformation of water vapour in the chamber](image-url)
Table 1. WVTR and permeability of bioplastics

| Samples  | WVTR (g/m²/2h) | Permeability (g/m²/2h/mmHg) |
|----------|----------------|-----------------------------|
| 0 % Chitin | 0.29785        | 0.020605                    |
| 1 % Chitin | 0.31405        | 0.020984                    |
| 2 % Chitin | 0.3178         | 0.020765                    |
| 3 % Chitin | 0.29025        | 0.017343                    |
| 4 % Chitin | 0.30445        | 0.019892                    |

According to Table 1, the evaluation was carried out to know the ability of sample permeability and WVTR. The permeability and WVTR of starch-based bioplastics decreased as chitin concentration increase. Although the concentration of 4 % chitin is higher slightly than 3 % chitin, this still shows that the addition of chitin affects the bioplastics on water barrier property compared to bioplastics without chitin. This is due to the unevenly chitin distribution. Moreover, the existence of chitin on starch-based bioplastics inhibited the hydrogen interaction between starch and water vapour molecules to establish hygroscopic integration [3]. This circumstance avoids the release of water vapour through bioplastics films. This result is in line with Lopez et al. that the addition of chitin showed more prominent impact than chitosan due to the higher quantity of acetyl group in the chitin structures [21].

3.2. Contact angle of bioplastics

Contact angle measurement is used to know the hydrophobicity of bioplastics. Based on Figure 2, chitin content increased the hydrophobicity of bioplastics. Contact angle of bioplastics without chitin absorbed water rapidly because the hydrophilic of starch and glycerol interacted with water molecules [23]. Then, bioplastics with chitin addition had a barrier that resisted water molecules and some authorities such as physical roughness, surface configuration, temperature, humidity and adsorbed substance [24]. The role of chitin in bioplastics is as an inhibitor of attractive interaction among polar molecules; therefore avoid the interaction between starch and water. The result is aligned with Rosa et al. and Rebecca et al. that the addition of chitin on bioplastics enhance hydrophobic properties of bioplastics of which it is used for food packaging and medical technology [15].

![Figure 2. Contact angle of bioplastics](image-url)
3.3. Morphology of bioplastics
The cross section image of starch based bioplastics with the chitin addition is shown in Figure 3. Bioplastics without the chitin addition (Figure 3a) presents the clear agglomeration of starch granules caused by imperfect gelatinization of starch molecules. Moreover, the water barrier property of bioplastics without chitin hold hydrophilic characteristic because of the pores on the surface. Besides, the interaction between starch and water molecules can be easier without chitin as a shield. The bioplastics with chitin addition from 1–4 % (Figure 3b-3e) also shows rough structures. Gelatinization process was improved by the addition of chitin into bioplastics and decreased starch granules entrance. There were no pores or cracks found in the surface of bioplastics and the addition of chitin has increased the water resistance of bioplastics. Figure 3f shows magnification of bioplastics to see chitin arrangement in starch based bioplastics. Chitin flakes were seen attached to the fully melted starch and physical interactions were formed between starch and chitin. The process of mixing starch and chitin plays an important role in homogeneity which affects the morphology of bioplastics.

![Figure 3](image-url)

3.4. FTIR analysis of bioplastics
FTIR spectra show in Figure 4. The spectra of starch based bioplastics without chitin shows –OH functional group at wavenumber 3000-3500 cm\(^{-1}\), C-H stretching at 2924 cm\(^{-1}\), C=O at 1644 cm\(^{-1}\), and C-O at 1366 cm\(^{-1}\). On the other hand, the addition of chitin in bioplastics increased the peak intensity of –OH group at 3000 to 3500 cm\(^{-1}\) and C-O group at 1366 cm\(^{-1}\). Furthermore, amide I and amide II appear at 1656 cm\(^{-1}\) and 1551 cm\(^{-1}\) indicating the interaction between starch and chitin [25]. Although the addition of chitin does not provide a significant change in each spectrum, it can improve the bioplastic water barrier properties. This shows that there is a chemical and physical interaction between starch-glycerol and chitin where the adhesive attachment is made.
Figure 4. FTIR spectra of bioplastics at wave number of (a) 4000-500 cm\(^{-1}\) and (b) 2000-1250 cm\(^{-1}\)

3.5. Thermal properties of bioplastics

Figure 5 shows DSC thermogram of bioplastics with chitin addition. The result exhibits that bioplastics without chitin developed melting point temperature at 90.3 °C and enthalpy 78.44 J/g. Then, bioplastics with chitin concentration from 1 % up to 3 % had no pronounced different melting point at temperature 90.7 to 88.6 °C while the addition of chitin at 4 % increased the melting point temperature up to 97 °C as described in Table 1.

However, the enthalpy of chitin content in the range 1 % up to 4 % had decreased from 72.38 J/g (3 % chitin) up to 71.77 J/g (4 % chitin). This indicated that the increase of chitin concentration on bioplastics improve the melting point insignificantly and decreased the enthalpy of bioplastics. This achievement is similar with the report from Rosa et al. indicated that chitin established the movement of amylose molecules slower and reduced the retrogradation process [15]. Therefore, the heat flow of bioplastic is decreased by increasing chitin percentage.

Figure 5. Thermal properties of bioplastics
Table 2. Melting point and enthalpy of bioplastics

| Samples | Tm (°C) | ΔH (J/g) |
|---------|---------|----------|
| 0% Chitin | 90.3    | 78.44    |
| 1% Chitin | 90.7    | 67.26    |
| 2% Chitin | 88.6    | 69.02    |
| 3% Chitin | 89      | 72.38    |
| 4% Chitin | 97      | 71.77    |

3.6. Mechanical properties of bioplastics

Mechanical property of bioplastics with chitin addition is shown in Figure 6. The addition of chitin decreased the tensile strength and elongation at break slightly. Tensile strength of bioplastics without chitin addition is 7.8 MPa and elongation at break of 58.5%. Bioplastics with 1-4% chitin decreased tensile strength from 6.7 to 6.3 MPa. On the other hand, the elongation at break of chitin addition in bioplastics exhibits the reduction from 55.5 to 40.8%. These results show a difference from previous achievements where chitin increases tensile strength and reduces elongation when corn starch and 30% chitin are mixed using injection molding [15]. These indicated that chitin has strong inter-molecular hydrogen bond and difficult to melt [26]. In other words, the weak interaction between chitin and starch molecules has affected the mechanical properties of bioplastics.

![Image of tensile properties of bioplastics](image)

Figure 6. Tensile properties of bioplastics

4. Conclusion

The SEM image shows that chitin flakes are attached to gelatine starch and there are no pores or cracks on the bioplastic surface with the addition of chitin. FTIR analysis also shows that the interaction between starch and chitin is formed by the emergence of an amide group from the chitin molecule. In addition, the thermal properties of bioplastics show a reduction in enthalpy by increasing chitin and involving unstable melting temperatures. Although increased levels of chitin result in decreased tensile strength and elongation at break, water resistance is improved. The contact angle property is improved and the permeability of bioplastics vapour decreases while chitin is added. The results showed that chitin improved the water barrier properties of starch-based bioplastics, especially their permeability and hydrophobicity.

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