Study of the Effect of Glycerol Plasticizer on the Properties of PLA/Wheat Bran Polymer Blends

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Abstract. Polylactic Acid (PLA) is a natural polymer that can be used as a raw material for making plastics. PLA plastic manufacturing has developed rapidly since the crude oil supply is getting lower, besides PLA plastic is environmentally friendly. In this research, the development of PLA from starch and wheat bran was developed by using glycerol as a plasticizer. PLA film is made by lactic acid fermentation. After fermentation, PLA mixed with wheat bran with a ratio of 20:80 (w/w) and a variety of glycerol concentration of 0%; 1%; 3%; 5%; and 7%, then heating at 200 °C for 5 minutes. The film later printed in plastic size dimension of 15cm × 20cm and incubated at 50 °C for 5 hours, then dried in room temperature of ± 27 °C. The effect of glycerol addition as a plasticizer on PLA is analyzed using mechanical tests, swelling, solubility, and chemical resistance. Film with 1 wt% of glycerol composition is optimal composition of tensile strength value of 1.22 MPa, 0.014% elongation, swelling of 0.4, solubility of 0.0207%.

1. Introduction
The increasing of carbon dioxide due to fossil fuels combustion has focused the development of polymeric materials based on natural materials. PLA (Polylactic acid) is a nature-based polymer material that has the potential to be a petroleum-based polymer substituent. PLA is a polymer that is biocompatible, biodegradable, and comes from renewable resources [1]. This material can be obtained from lactic acid which comes from sugar, starch, cellulose, and glycerin [2]. L-lactic acid and D-lactic acid are lactic acid stereoisomers that can be used to form PLLA (poly (L-lactic acid)) and PDLA (poly (D-lactic acid)) [3].

Besides its good properties, PLA also has the weaknesses, such as low ductility, brittleness, and high hydrophobicity [4], [5]. To improve the mechanical properties, PLA can be modified by blending methods with other polymers. This method is classified as effective, simple, and versatile for developing new materials without synthesizing new polymers [6]. Several polymers are used, such as polyethylene glycol (PEG), polyhydroxybutyrate (PHB), polycaprolactone (PCL), polybutylene adipate coterephthalate (PBAT), chitosan, and starch [7]. The choice of polymer blending is very important because it greatly affects the thermal and mechanical stability during processing.

Wheat bran (WB) is produced by separating flour and the embryo from milled wheat. A total of quarter ton of WB is produced from one million tonnes of wheat. The current application of WB is classified as low value, because it is only used as animal feed [8]. The component distribution of WB consists of (dry-basis), 55-60% non-starch carbohydrate, 14-25% starch, 13-18% protein, 3-8%
minerals, and 3-4% fat [9]. The total fraction of non-starch carbohydrates is 52-70% is arabinoxylan. Arabinoxylan is a polysaccharide group that can be made into films with high strength and good lubrication [10]. Besides that, arabinoxylan is also a good hemicellulose for film formation with addition of plasticizers [11].

PLA and WB are biodegradable polymers from renewable resources. The mixture of PLA with WB can be one of the promising efforts because WB is an abundant and cheap biomaterial. The WB in the PLA/WB blend is used to increase the flexibility, hydrophilicity and strength of PLA. PLA/WB blend polymers can be produced by solution blending and melt-blending [4]. The blending of PLA and WB will improve the mechanical characteristics of the polymer blend indicated by a decrease in tensile strength and an increase in elongation so that the polymer has a greater stretch [12].

In this study, polymer blend PLA/WB plasticized with glycerol is made to obtain biomaterials that are safe to use for biomedical applications and food packaging. Glycerol is known to be a good plasticizer for PLA polymer blends, studied by some previous researchers [13], [14]. The purpose of this study is to determine the effect of plasticized glycerol on the polymer blend PLA/WB on its mechanical properties and chemical resistance.

2. Experimental

2.1. Materials
The materials used in this study consist of lactic acid (90%, technical grade), distilled water, nitrogen gas, wheat bran (obtained from local farm), and glycerol (Merck). The glycerol concentration was varied from 0 to 5 wt%.

2.2. Preparation of Lactic Acid
The lactic acid used in this study is prepared based on the method by Rahmayetty et al. (2017) [5]. Lactic acid of 85%-wt aqueous solution was added to the four-necked flask with hotplate magnetic stirrer and condenser. The reaction was held at 120 °C for 1 hour with a continuous flow of nitrogen gas. After that, polycondensation was carried out at 150 °C for 2 hours followed by 180 °C for 2 hours. The product in the form of solid PLA was cooled to room temperature for one day.

2.3. Preparation of polymer blend PLA/WB
The procedure of making PLA/WB plasticized with glycerol solution was carried out based on study by Kanani et al. (2017) [15]. As much as 1 wt% WB was dissolved in distilled water and stirred at room temperature for 20 minutes. Glycerol was added to the solution and stirred continuously for 15 minutes at 70 °C. A total of 100 g of PLA was heated at 80 °C until it melted homogeneously. WB and glycerol solution were added and mixed for 20 minutes. Glycerol was varied as the composition of each material is shown in Table 1. The PLA/WB blend is cast by the casting method. Drying process was carried out for 6 hours at 70 °C.

2.4. Characterization
Mechanical tests were carried out in this study using a tool called the Texture Analyzer. Tensile strength (σ) can be measured based on the maximum load (F) used to break the material divided by the initial

| Variation   | PLA (%-wt) | Wheat Bran (%-wt) | Glycerol (%-wt) |
|-------------|------------|-------------------|-----------------|
| PLA/WB-G1   | 80         | 20                | 0               |
| PLA/WB-G2   | 80         | 19                | 1               |
| PLA/WB-G3   | 80         | 17                | 3               |
| PLA/WB-G4   | 80         | 15                | 5               |
| PLA/WB-G5   | 80         | 13                | 7               |
cross-sectional area ($A_0$) shown in Eq 1. The elongation of a material ($\varepsilon$) can be determined by the ratio between the increase in length and the original length as in Eq. 2.

$$\sigma = \frac{F}{A}$$  \hspace{1cm} (1)

$$\varepsilon (\%) = \frac{L_1 - L_0}{L_0} \times 100\%$$  \hspace{1cm} (2)

Samples were also tested for swelling power and solubility in distilled water. The swelling power calculation is done based on the difference in the weight of the paste from the centrifuged supernatant from the water bath to the dry basis (Eq 3). Meanwhile, water solubility is calculated by dividing the weight of dry precipitate with the weight of the supernatant (Eq 4).

$$Swelling (\%) = \frac{Paste\ Weight}{Dry\ Weight} \times 100\%$$  \hspace{1cm} (3)

$$Solubility (\%) = \frac{Dry\ Weight}{Supernatant\ Weight} \times 100\%$$  \hspace{1cm} (4)

Chemical resistance test was carried out according to ASTM D1647-89 with the principle of damage, cracking, and loss of coating adhesion to the substrate by qualitative observation. The test was carried out for 3 days at room temperature. The sample was immersed in HCl solution (pH = 3) and NaOH solution (pH = 10). Sample assessment indicators are based on time (days).

3. Results and Discussion

3.1. Mechanical behavior of PLA/WB

Tensile strength is the maximum stress a material can withstand when it is stretched prior to fracture. The effect of adding glycerol to PLA/WB on tensile strength and elongation is shown in Fig. 1. Based on the figure, it can be seen that the addition of glycerol plasticizer can reduce tensile strength, with the optimum value on PLA/WB-G1 of 1.22 MPa. While the optimum elongation value is found in the PLA/WB-G4 variable with a value of 0.017. elongation values below 15% indicate the material is brittle [7]. The addition of WB plasticized with glycerol can change the characteristics of the material. These results are consistent with research conducted by Yu et al. (2006), mixing PLA with wheat-derived products can increase tensile strength [12].

![Figure 1. Effect of glycerol plasticizer with mechanical properties of PLA/WB.](image)
3.3. **Swelling ratio of PLA/WB**

The addition of glycerol plasticizer to PLA/WB can reduce the water absorption properties of the material, as shown in Fig. 2. Based on these results, it can be seen that the increase in glycerol concentration is directly proportional to the decrease in the swelling ratio. This decrease indicates the greater water resistance of polymer blends. The addition of glycerol as a plasticizer can cause flexibility, softening, and increase in resin elongation [16]. Besides that, glycerol is also known to keep polymer blends compact and there are no significant physical changes. The combination of hydrophilic and hydrophobic polymers is an effective way to improve degradation properties but does not reduce brittleness.

![Figure 2. Effect of glycerol plasticizer with swelling ratio of PLA/WB.](image)

3.4. **Chemical resistance of PLA/WB**

Chemical resistance is a test used to evaluate the resistance of a material. Chemical resistance testing is carried out based on ASTM D1647-89. The test medium was an acid (HCl pH 3) and alkaline (NaOH pH 10) solution for 3 days. Failure to test indicated that the coating surface had lost its adhesion to the substrate and appeared to be peeling off. The test results are tabulated in Table 2.

| Conditions | PLA/WB-G1 | PLA/WB-G2 | PLA/WB-G3 | PLA/WB-G4 | PLA/WB-G5 |
|------------|-----------|-----------|-----------|-----------|-----------|
| Acid (pH 4)| Soluble   | Soluble   | Insoluble | Insoluble | Soluble   |
| Neutral (pH 7)| Soluble   | Insoluble | Insoluble | Soluble   | Soluble   |
| Base (pH 10)| Soluble   | Insoluble | Insoluble | Soluble   | Soluble   |

Based on the chemical resistance test results, it can be concluded that PLA/WB-G3 is the best layer. This can be seen from the presence of WB and glycerol which are strongly bonded to PLA so that they have good chemical resistance compared to other variations.

3.5. **Solubility of PLA/WB**

The results of the solubility test on PLA/WB plasticized with glycerol showed quite varied results, as shown in Fig. 3. The results showed that the highest solubility value was found in PLA/WB-G5. This is due to the glycerol content, which in the preparation of plastics is very necessary for its function as plasticizers. Masutani (2014) reported that plastic is an organic solvent with a high boiling point which when added to a hard or stiff resin causes the accumulation of intermolecular forces on long chains to decrease [17]. Therefore, plasticization will affect the physical properties and mechanism of the film, including tensile strength, hardness elasticity and resistance to water.
Figure 3. Effect of glycerol plasticizer with solubility properties of PLA/WB.

4. Conclusion
The addition of glycerol can improve the mechanical properties of the PLA/WB blend. The PLA/WB composition that has optimum tensile strength is found in PLA/WB-G2 with a value of 1.22 MPa and the highest elongation at break is found in PLA/WB-G3. The PLA/WB-G5 variable has the highest solubility and the lowest swelling compared to other variations. This research will further project the production of polymer packaging materials or biomedical applications with environmentally friendly biomaterials.

References
[1] Mofokeng J P and Luyt A S 2015 Morphology and thermal degradation studies of melt-mixed poly(lactic acid) (PLA)/poly(ε-caprolactone) (PCL) biodegradable polymer blend nanocomposites with TiO₂ as filler Polym. Test. 45 93–100
[2] Lasprilla A J R, Martinez G A R, Lunelli B H, Jardini A L, and Filho R M 2012 Poly-lactic acid synthesis for application in biomedical devices — A review Biotechnol. Adv. 30 (1) 321–328
[3] Lopes M S, Jardini A L, and Filho R M 2012 Poly (Lactic Acid) Production for Tissue Engineering Applications Procedia Eng. 42 1402–1413
[4] Zuo Y, Gu J, Yang L, Qiao Z, Tan H, and Zhang Y 2014 Preparation and characterization of dry method esterified starch/polylactic acid composite materials Int. J. Biol. Macromol. 64 174–180
[5] Rahmayetty, Sukirno, Prasetya B, and Gozan M 2017 Synthesis and characterization of L-lactide and polyactic acid (PLA) from L-lactic acid for biomedical applications
[6] Peesam M, Supaphol P, and Rujiravanit R 2005 Preparation and characterization of hexanoyl chitosan/polylactide blend films Carbohydr. Polym. 60 (3) 343–350
[7] El-hadi A M 2017 Increase the elongation at break of poly (lactic acid) composites for use in food packaging films Sci. Rep. 7 (1) 46767
[8] Prückler M et al. 2014 Wheat bran-based biorefinery I: Composition of wheat bran and strategies of functionalization LWT - Food Sci. Technol. 56 (2) 211–221
[9] Hell J, Kneifel W, Rosenau T, and Böhmdorfer S 2014 Analytical techniques for the elucidation of wheat bran constituents and their structural features with emphasis on dietary fiber – A review Trends Food Sci. Technol. 35 (2) 102–113
[10] Whistler R O Y L 1993 Chapter 1 - Introduction To Industrial Gums R. O. Y. L. Whistler And J. N. B. T.-I. G. (Third E. Bemiller, Eds. London: Academic Press, 1993, pp. 1–19.
[11] Holloway W D, Tasman-Jones C, and Bell E 1980 The hemicellulose component of dietary fiber
Am. J. Clin. Nutr. 33 (2) 260–263
[12] Yu L, Dean K, and Li L 2006 Polymer blends and composites from renewable resources Prog.
Polym. Sci. 31 (6) 576–602
[13] Finkenstadt V L, Liu C-K, Cooke P H, Liu L S, and Willett J L 2008 Mechanical Property
Characterization of Plasticized Sugar Beet Pulp and Poly(Lactic Acid) Green Composites
Using Acoustic Emission and Confocal Microscopy J. Polym. Environ. 16 (1) 19–26
[14] Clarizio S C and Tatara R A 2012 Tensile Strength, Elongation, Hardness, and Tensile and
Flexural Moduli of PLA Filled with Glycerol-Plasticized DDGS J. Polym. Environ. 20 (3)
638–646
[15] Kanani N, Wardalia W, Wardhono E, and Rusdi R 2017 Pengaruh Temperatur Pengeringan
Terhadap Swelling dan Tensile Strength Edible Film Hasil Pemanfaatan Pati Limbah Kulit
Singkong J. Konversi 6 (2) 75
[16] Koh J J, Zhang X, and He C 2018 Fully biodegradable Poly(lactic acid)/Starch blends: A review
of toughening strategies Int. J. Biol. Macromol. 109 99–113
[17] Masutani K and Kimura Y 2014 Chapter 1. PLA Synthesis. From the Monomer to the Polymer
1–36.