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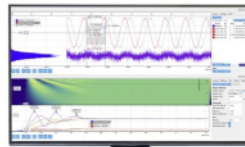


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Effect of L-Lactic Acid Oligomer (OLLA) to Cassava Starch Ratio on Characteristics and Mechanical Properties of Blend Film

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Abstract. L-Lactic acid oligomers (OLLA) which are produced from polycondensation without catalysts is safe to use as food packaging. However the nature of the brittle oligomer is an obstacle in its application. The oligomer is then blended with other materials to solve the problem. Modification of OLLA with the addition of cassava starch and glycerol plasticizer is a way to improve the mechanical properties of OLLA. The aim of this study is to obtain the best characteristics of the blending film of OLLA/cassava starch. OLLA was synthesized with L-lactic acid by direct polycondensation at 180°C for 4 hours. The synthesized glycerol-coated cassava starch was carried out by mixing cassava starch (3% w/v) and glycerol (1% v/v) at 65°C. The blending polymer was conducted at 80°C, then formed to be thin films and dried at 60°C for 24 hours. The results showed that the best OLLA/ cassava starch ratio were obtained at 40/60 with tensile strength was 2.78 MPa and elongation at break was 20.5% While the degree of crystallinity of OLLA films, cassava starch film and OLLA/cassava starch blend film were 30.1; 15.7 and 19.2% respectively.

INTRODUCTION

The depletion of fossil resources and the raising atmosphere concentrations of carbon dioxide have focused attention on the development of bio-based plastics. These efforts are carried out by utilizing biological materials to be converted into biodegradable polymers that are environmentally friendly and can replace conventional plastics made from petroleum. One of the polymers that have great potential to be developed as a substitute for conventional plastics is polylactic acid (PLA).

PLA is a polymer that is biocompatible, biodegradable, and derived from renewable resources [1]. PLA can be obtained from lactic acid derived from sugar, starch, cellulose and the remaining glycerin of biodiesel [2]. PLA is a non-toxic and non-carcinogenic polymer for human so it is good material for biomedical and food packaging applications. Besides its advantages, PLA has some shortcomings, such as brittle, low gas-barrier and hydrophobic character [3]. Rahmayetty reported that the synthesis of PLA in form oligomer (OLLA) from lactic acid with polycondensation method without using catalyst produced PLA was brittle and hydrophobic [4]. The fragile nature of PLA with elongation at break of less than 10% will limit the polymer processing conditions [5]. The hydrophobic nature of PLA and OLLA causes the rate of degradation through hydrolysis of ester to require a long time, this become an obstacle in biomedical applications and food packaging. PLA films for biomedical applications and food packaging must have high elasticity at room temperature, transparency and low crystallinity [6][7].

Modification of OLLA by blending with other natural polymers can improve their mechanical strength including tensile strength, elongation at break, and degradation rate of film. Blending polymers are an effective, simple and versatile method for developing new materials with certain properties without synthesizing new polymers [8]. The selection of the right blending polymer greatly affects the change in polymer property, because it relates to thermal and mechanical stability during polymer processing.

Starch is a natural polymer with advantages that are produced from renewable sources, cheap and biodegradable. Cassava starch is abundant material in Indonesia with its hydrophilic properties and biodegradable character. The mixing of OLLA with cassava starch will provide some benefits, such as : reducing raw material, cost and maintain polymer biodegradability. PLA/starch mixing in a pure manner will improve the degradation properties but does not

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reduce the level of fragility [9][3]. Decreasing brittle properties can be overcome by adding plasticizers. One of the safe and non-toxic plasticizers is glycerol. The mechanical properties and toughness of PLA/gelatinized starch are far superior to PLA/pure starch blends, the addition of glycerol enhances the interfacial. Gelatinization of starch is also a good method to enhance the interfacial affinity between the distinct phases [10]. Based on the description above, the research on making OLLA/gelatinized cassava starch blend film is necessary to obtain biomaterials that are safe to use for biomedical applications and food packaging with good characteristics.

MATERIALS AND METHODS

Materials details

L-lactic acid (90%) and glycerol were obtained from Merck (Indonesia). Cassava starch was produced from Bumi waras Group Company, Indonesia.

Preparation of OLLA

OLLA was synthesized from L-lactic acid by using direct polycondensation process without catalyst. L-lactic acid by volume of 50 ml was poured into a four neck flask equipped with a magnetic stirrer, a temperature controller, and a condenser, which was connected to a collector distilled. The reaction was carried out at 120°C for 1 hour with continuous nitrogen flowed to push evaporative water into the condenser. Afterwards, the oligomerization stage held gradually at 180°C for 4 hours without nitrogen flowed.

Gelatinization of starch with glycerol plasticized

Cassava starch dispersed in distilled water with a concentration of 3% (w/v) was stirred with a magnetic stirrer for 5 minutes. Glycerol 1% (v/v) was added in starch suspension. The starch suspension was heated at 65°C under continued stirring at 150 rpm until it is gelatinized.

Blending OLLA and gelatinization of starch

OLLA was melted at 80°C and mixed with gelatinization of starch. The solution was stirred with a magnetic stirrer and heated to 80°C for 20 minutes. Polymer blend solution was poured into petri dishes with an internal diameter of 15 cm. Blend film were obtained after drying at 60°C for 24 hours.

Analytical methods

Mechanical characteristics of blend film with tensile strength, elongation and swelling tests. Molecular bonding was analysis by using FT-IR (Agilent Technologies type Cary 630). The degree of crystallinity of blend film was measured by X-ray diffraction (XRD; Panalytical type Empyrean).

RESULTS AND DISCUSSION

Visual Form of OLLA/Starch Blend Film

Blending of OLLA and gelatinization of starch by varying the ratio (100/0; 80/20; 60/40; 50/50; 40/60; 20/80; 0/100) were carried out at 80°C. The blend film that produced have different visual shape as shown in Fig. 1. The higher OLLA content caused an increase in the yellow color of film and the film surface is rough. This shows the dispersion of starch into the OLLA matrix is not perfect. Imperfect dispersion or inhomogeneity is caused by the

hydrophobic property of OLLA and starch hydrophilic so that the interface adhesion of these two components is imperfect.

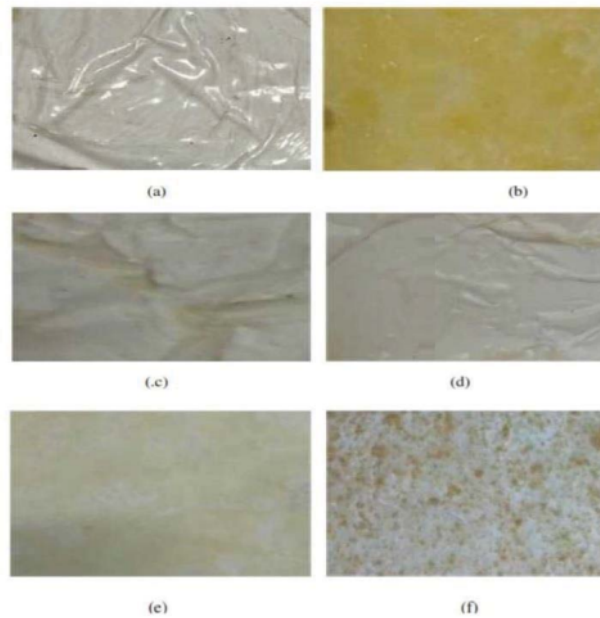


FIGURE 1. Visual form of blend film with OLLA/starch ratio (a) 0/100; (b) 100/0; (c) 20/80; (d) 40/60; (e) 60/40; (f) 80/20

Mechanical Properties of Blend Film

Tensile strength is the maximum stress that can be held by a material when stretched or pulled before the material breaks. The extension of edible film or elongation is the ability to extend the material when it is given a tensile force. The value of the edible film elongation shows its range ability. Addition of starch to OLLA affects the mechanical properties of the film blend as shown in Fig. 2.

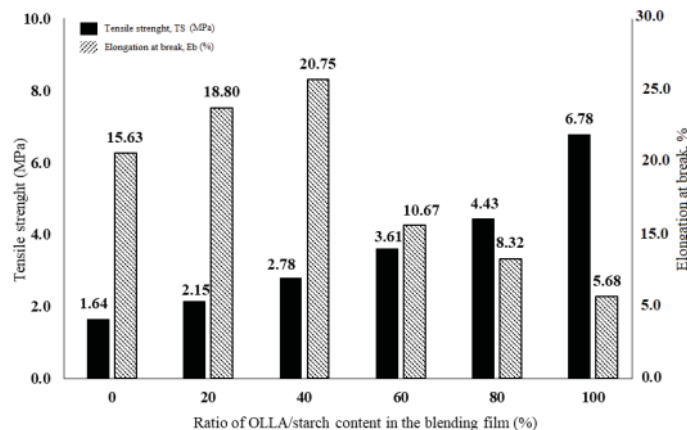


FIGURE 2. Effect of ratio OLLA/starch to mechanical property blending film

In Fig. 2, revealed that the higher the amount of starch in the blend film, the tensile strength value decreased. Conversely, the high the amount of OLLA in the blend film, the value of tensile strength increase and elongation at break decrease. The decrease in elongation at break was caused by the brittle nature of the OLLA. The best mechanical properties of the blend film were obtained at an OLLA/starch ratio of 40:60 with tensile strength and elongation at break values of 2.78 MPa and 20.75%, respectively. Tensile strength and elongation at break values in this study were still very low. This was caused by mixing OLLA and starch without using compatibilizer to improve the compatibility of OLLA/gelatinization of cassava starch blends.

Chemical Property Characterization of Blend Film

The blend film function group was analyzed using FT-IR spectrometry. The result is shown in Fig. 3. The peak of cassava starch-glycerol at 2930 cm^{-1} indicated the C-H function which was at a weak intensity. The peak at 2974 cm^{-1} indicated the presence of O-H carbohydrate groups, $3500\text{-}3200\text{ cm}^{-1}$ indicated the H bond of O-H. The peak at 1050 ; 1150 ; $1640\text{-}1550$; $1640\text{-}670$ and $3100\text{-}3500\text{ cm}^{-1}$ sequentially indicated the C-O functional group of C-O-C; C-O from C-H-O; N-H (amide); C = O (amide) and N-H (amine).

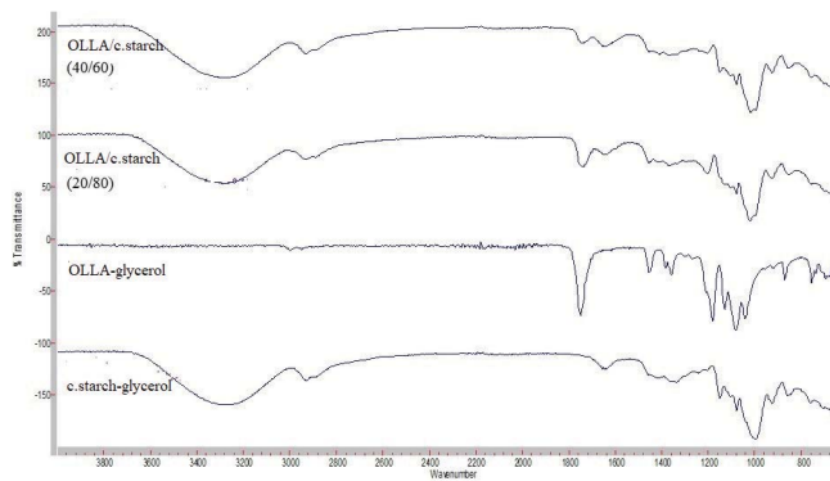


FIGURE 3. The FT-IR spectra of OLLA, cassava starch, OLLA/cassava starch film

In the FT-IR of OLLA-glycerol spectrum, the peak at 1749 cm^{-1} indicated a carbonyl stretch $\text{-C}=\text{O}$ and $\text{-C}=\text{O}$ carbonyl bending at 1181 cm^{-1} . In the spectrum, there were 2 bonding -C-H stretching which were at 2996 cm^{-1} (asymmetric) and 2940 cm^{-1} (symmetric). The -OH stretching was seen at 3550 cm^{-1} which was characteristic of carboxylic acid. Clusters $\text{-C}=\text{O}$ and -OH were found at 1220 cm^{-1} and 1064 cm^{-1} respectively.

In Fig. 3, the infrared spectrum for blend film with a ratio OLLA/starch of 20/80 and 40/60 were shown by the peaks at 1749 cm^{-1} with weak intensity, which was not possessed in the infrared spectrum of blend film, but was owned by OLLA film with sharp intensity. Based on the analysis of this infrared spectrum, it can be ascertained that a blend film of OLLA and cassava starch had been formed.

The degree of crystallinity of cassava starch film, OLLA and blend film (OLLA/starch) produced were analyzed using X-ray diffraction of Panalytical type Empyrean. The crystalline structure of the polymer is characterized by the appearance of high intensity on the diffractogram, while the amorphous structure tends to produce weak and wide intensity. The diffractogram of starch, OLLA and OLLA/starch film in this study is shown in Fig. 4. The degree of crystallinity was determined by compared the area of crystalline regions and the total area. Total area was sum of crystalline and amorphous area. The degree of crystallinity was calculated according to equation 1 as follows; [7,11].

$$\% \text{Crystallinity} = \frac{A_{cr}}{A_{cr} + A_{am}} \times 100\% \quad (1)$$

Where, A_{cr} is the crystalline area, and A_{am} is amorphous area.

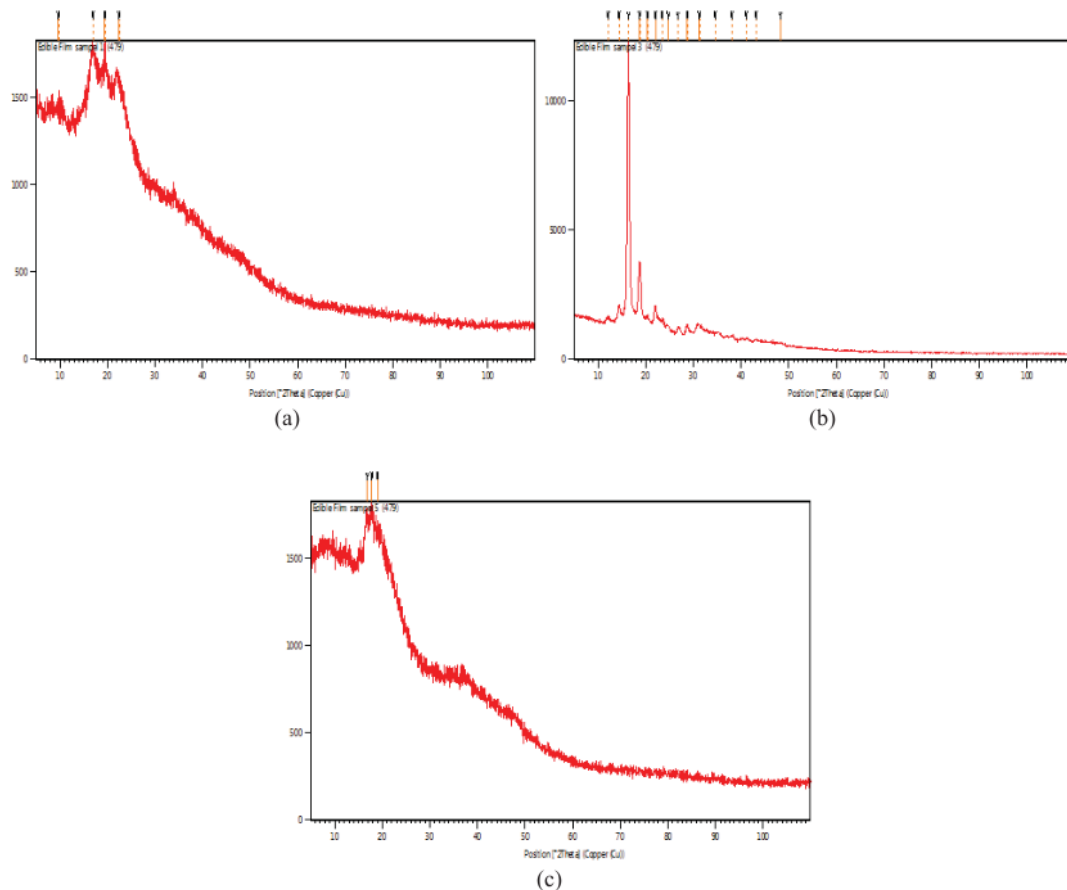


FIGURE 4. The XRD spectrum of (a) cassava starch film; (b) OLLA film and (c) OLLA/starch blend

Based on Fig. 4(a), the XRD characterization of cassava starch film shown that the peaks at $2\theta = 17,03^\circ$; $19,53^\circ$ and $22,48^\circ$. The crystalline area for cassava starch film was 1.7 cm^2 and the total area was 10.8 cm^2 . From equation (1) is obtained with a crystalline degree of 15.7%. The XRD characterization of OLLA film in Fig. 4(b) shown 2θ diffraction peaks at $16,41^\circ$ and $18,73^\circ$. In the OLLA film diffractogram obtained a crystalline area and a total area were 3.8 cm^2 and 12.6 cm^2 respectively, by using equation (1) the degree of crystallinity was obtained 30.1%. In Fig. 4(c), the OLLA/starch blend had the peaks 2θ at $17,82^\circ$ and $19,06^\circ$. The crystalline area, total area and degree of crystallinity of blend film were 2 cm^2 ; 10.4 cm^2 and 19.2% respectively. According to Maharana et al., (2009) [12] and Coulembier et al., (2006) [13], material with a degree of crystallinity of 30-40% is semicrystalline and below 30% is amorphous. Based on the degree of crystallinity, OLLA /starch film has an amorphous structure.

CONCLUSION

Blending OLLA /cassava starch produced films with a rough surface structure due to dispersion of starch into the OLLA matrix is not perfect. Effect of OLLA to Cassava Starch Ratio was greatly on the characteristics of blend film. The higher cassava starch content of the blend film, the tensile strength value decreases and elongation at break

increases. The OLLA/cassava starch ratio that produces the best film characteristics was 40/60. The degree of crystallinity of OLLA film, cassava starch film and OLLA/starch blend film were 30.1; 15.7 and 19.2% respectively.

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