The Effect of Red Palm Oil concentration towards characteristics and biodegradability of PLA-Zinc film

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***Abstract*—Polylactic acid (PLA) film with antimicrobial agents which is zinc oxide (ZnO) is a common films that been used in the film packaging. Recently, the used of the plastic food packaging cause the environmental problem. This study were conducted to determine the characteristics and biodegradability of the PLA-Zinc film. The film is prepared by using solvent casting method with addition of RPO as a plasticizer. RPO amount gives impact towards the thickness of the films where higher thickness is formed when the RPO amount are higher. For the moisture content, as the amount of RPO is increase the moisture content in each films is decreased. FT-IR obtained obviously changes at peak 1748 cm^{-1} which representing ester group which are C=O stretching bonds. Combination 0.25RPO with PLA gave highest tensile value and lowest percentage of elongation at break. The solubility PLA with ZnO increase drastically but when added RPO, it become more decreases. These results suggest that the PLA/ZnO/RPO films could be used to replace non-biodegradable plastic.**

Keywords*— *Poly-lactic Acid (PLA), Zinc Oxide (ZnO), Red Palm Oil (RPO)

I. INTRODUCTION

The performance and potential of PLA for use in the antimicrobial packaging application has been investigated and been proved by a lot of researchers [1,2]. In worldwide, there are a lots of PLA-based materials containing antimicrobial agents such as metal, organic acids, plant extract or essential oils that have been incorporated into PLA to provide antimicrobial activity. PLA have been believed to perform as a suitable carrier of antimicrobial agents without showing an indivertible impact on the composting and potential biodegradation process [3]. This PLA-based antimicrobial has become the consumer preference for the natural food products with no or few preservatives and has been classified into active film food packaging, edible film packaging and coating film packaging. The antimicrobial packaging with biodegradability performance is expected to grow in the future for enhancing the food safety and quality by using the synthetic polymer that not harm the environment [3].

Like others biopolymers, PLA also need some additional modification or processing such as addition of plasticizer in order to develop useful antimicrobial materials. This is due to the properties of unmodified PLA which are high in brittleness, poor water vapor barrier, slow biodegradation rate, hydrophobicity and lack of reactive side chain group [4–7]. According to [8,9] , some changes may occur in the physical and mechanical properties of the packaging materials after been mixed with antimicrobial agents. They also stated that with excess amount of incompatible antimicrobial agents can reduce the psysico-mechanical properties of the composite materials. [10] studied the PLA/5% (w/w) of Nisaplin and EDTA with addition of glycerol acetate (GTA) as a plasticizer films and found some reduction in the elongation at break from 108.5% to 62.5% and impact strength from 5.4 to 3.4 J/cm^3 when compared to the raw PLA without plasticizer. The modification properties of PLA or other biopolymers with the addition of the plasticizer must be performed in order to increase the flexibility [11,12]. PLA is one of the raw material to produce film packaging because PLA is renewable and expected to improve the biodegradability performance of film packaging. To produce film packaging, addition of plasticizer are required because it can overcome film brittleness caused by the extensive intermolecular forces and improving the extensibility and flexibility of the films [18].

In this study, film packaging based on natural PLA and Zinc Oxide were produced. Casting method was applied because this method are commonly used for laboratory scale preparation of antimicrobial films from biopolymers and can get the uniformity of the thickness for the films sample. Red Palm Oil (RPO) is added into the film packaging as a plasticizer. The impact towards physical, chemical, mechanical and biodegradability is being investigated.

II. MATERIAL AND METHODS

A. Materials

Polylactic Acid (PLA) was obtain from Chemical Laboratory of Chemical Engineering UiTM Shah Alam. Zinc Oxide (ZnO) was obtain from Sigma, Chloroform was obtain from R&M chemical and Red palm oil (RPO) were purchased from Iko from Malaysia.

B. Film Production

The film were prepared by using solvent casting method (Heydari-majd et al., 2019). PLA/Zinc Oxide/Red Palm Oil was mixed with mechanical stirring of 600 rpm at 80°C for 30 min with varies of RPO amount as shown in Table 1. RPO was added as a plasticizer. For the first 15 min, the mixture of 2g of PLA with chloroform and 5% (w/w) of ZnO (based on PLA dry matter) were mixed. For the second 15 min, RPO were added to complete the solution. The film solution were poured over (80mm x 15mm) petri dishes placed on levelled surfaces. The film solution were dried at room temperature until the film were produced. Finally, the films were separated from the petri dishes for the analysis and evaluations.

Table 1: Amount of PLA, Zinc Oxide with varies of RPO volume

Sample	Composition		
	Polylactic Acid (PLA), g	Zinc Oxide (ZnO), (w/w)%	Red Palm Oil (RPO), mL
1	2.00	0%	0.00
2	2.00	5%	0.00
3	2.00	5%	0.25
4	2.00	5%	0.50
5	2.00	5%	0.75
6	2.00	5%	1.00

C. *Film Thickness*

The thickness of the film were measured by using a digital micrometer to the nearest 0.001 mm at five random positions around the film and average thickness was calculated.

D. *Moisture Content*

Moisture content of the films was determined using the method of drying oven. The films were dried at 60°C until constant weight was achieved using the universal oven. Before drying, the initial weight, g (M_i) of the film sample were recorded and the moisture content were calculated from the weight loss after the drying process, g (M) by using equation 1 [20].

$$Moisture\ content\ (\%) = \frac{M_i - M}{M_i} \times 100 \qquad \text{(E.q 1)}$$

E. *Fourier transform infrared spectroscopy*

Fourier transform infrared (FT-IR) spectra of the films were recorded at 4 cm^{-1} resolution and in the wavenumber of 4000-600 cm^{-1} by using Fourier Transform Infra-Red (FT-IR) machine. The film was directly placed on the ray exposing stage [21].

F. *Mechanical properties*

Mechanical properties of the films were evaluated by conducting tensile test. Tensile strength (TS) and elongation at break (EB) of the PLA/ZnO/RPO films were detected by Universal Testing Machine at 25°C. The initial span was set at 50mm and the crosshead speed at 50mm/min with load of 2.5kN [18].

G. *Biodegradability: Solubility in Water*

The solubility in water were measured based on literature [22]. A size of 40×20 mm sample for each type of films is prepared and the initial weight, g (M_0) of dry sample is determined after drying to a constant weight at 60°C in a universal oven. The weight samples is been immersed in the beaker with condition of room temperature for 24 hours that contain 50 mL distilled water and the beaker is sealed to prevent the evaporation of water and dust. After that, the sample is taken out and dry to a constant weight at 60 °C in a universal oven, and being weigh, g (M_2). The solubility of the sample is calculated using Equation 2.

$$Solubility\ (\%) = \frac{(M_0 - M_2)}{M_0} \times 100 \qquad \text{(E.q 2)}$$

III. RESULTS AND DISCUSSION

A. *Film thickness*

Figure 1 shows the average thickness for every each of the sample. The thickness of the film sample are ranged from 0.204 mm to 0.616 mm. PLA/ZnO/1RPO film shows the highest thickness which is 0.616mm but for PLA/ZnO/0.25RPO film shows the lowest thickness which is 0.286 but still thick compare to raw PLA and PLA/ZnO films. Addition of zinc oxide did not significantly affect the thickness of the films. It shows that with addition of RPO, the film become thicker compare to raw PLA and PLA/ZnO film and the higher the volume of the RPO, the thicker the thickness of the films.

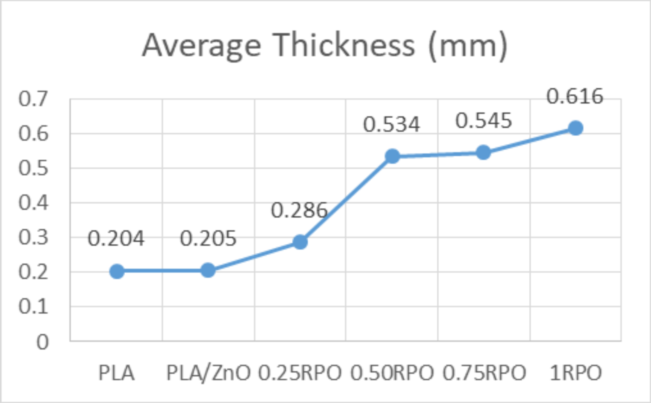

Figure 1: Average thickness for each sample

B. *Moisture content*

Figure 2 presents the moisture content each of the films. The lowest moisture content can prevent the oxidation at lipid and presence of water molecule inside the film packaging will give impact towards the food that we wrap [20]. For PLA film, the moisture content were highest, 0.84%, after PLA mixed with Zinc Oxide, the moisture content were decreased to 0.62%. Then, with the addition presence of RPO, the moisture content become smaller and decreased. At the highest content of RPO which were sample of PLA/ZnO/1RPO, the smallest moisture content were obtained because of the hydrophobic nature of the RPO which can affect the ability of the film to retain water. The smaller the volume of the RPO, the higher the moisture content in the film sample.

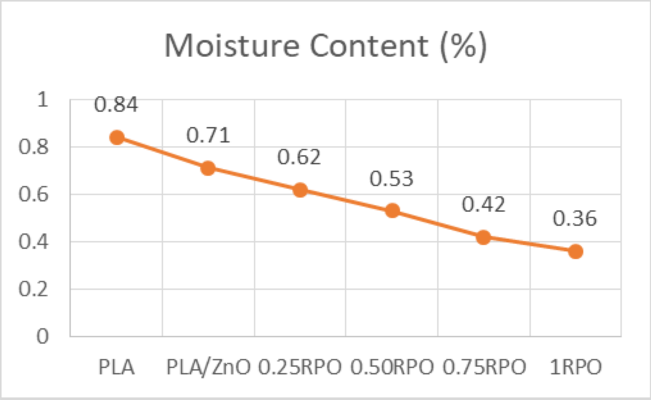

Figure 2: Moisture content each film sample

C. Fourier transform infrared spectroscopy

Figure 3 shows the FT-IR spectra of the film samples. FT-IR are obtained in the wavelength range of 4000 to 600 cm^{-1}. FT-IR spectra have been used to monitor the structural changes and functional groups of film samples at molecular level though a detailed analysis [23]. For PLA film sample, it shows the sharp peak at 1735 cm^{-1} which indicate ester group which are C=O stretching bonds, and at peak 1217 cm^{-1} shows the medium peak of C-O stretching bonds. When zinc oxide is added in the film, more sharpen peak are shows at C=O stretching bonds which is 1748 cm^{-1}. Meanwhile for the C-O stretching bond the peak are become wider and decreased to range of 1181 cm^{-1} to 1043 cm^{-1}. Different from the PLA films, in PLA/Zinc the small peak of C-H bending are presence at peak range of 871 cm^{-1} to 755 cm^{-1} due to the addition of zinc in the film sample. For PLA/Zinc with addition of RPO, it indicate the slightly decrease in C=O stretching bonds to 1747 cm^{-1}. For PLA/Zinc/0.25RPO it shows the sharpen C-O stretching bond peak at 1216 cm^{-1} to 1082 cm^{-1} due to the high concentrated but as the volume of the RPO increases, the C-O stretching bond become more sharpen and higher to the range from 1217 cm^{-1} to 1092 cm^{-1}. The bands at 1500 to 1000 cm^{-1} indicates the fingerprint region of oil. This range of spectrum was also reported in another publication [24].

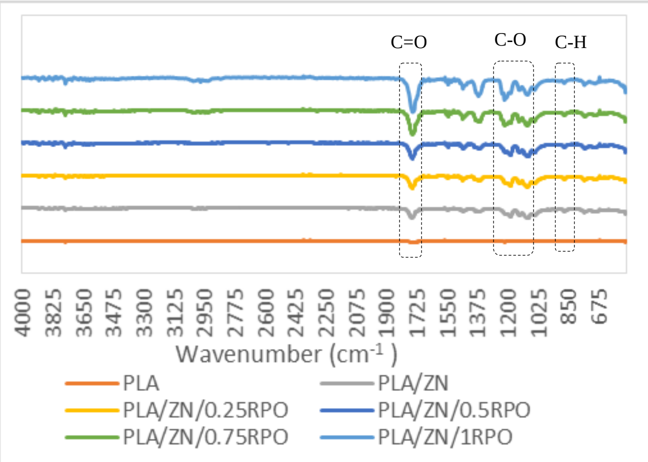

Figure 3: FT-IR spectra of the films sample

D. Mechanical properties

Tensile strength (TS) and elongation at break (EB) of the film are presented in Table 2. PLA/ZnO/1RPO showed the lowest tensile strength (0.0734Mpa) meanwhile for PLA/ZnO/0.25RPO shows the highest tensile strength (0.212Mpa). For PLA/ZnO film have greater tensile strength but lower in the elongation break. The elongation at break of PLA/Zn/RPO increased as the volume of RPO increased. Increased of elongation in the film is important because it is related to the increased adhesion strength and tenacity of the films. Tenacity measure the amount of energy a material can absorb before fracturing. Film that have more tenacious, it will exhibit a greater deformity capacity before rupture [25]. When the plasticizer is added which is RPO, the tensile strength is decreased and the elongation break became higher. It is because plasticizer have been used to overcome the brittleness of the films and to fills the space between the polymer chains, and will increase the separation between them and it will causing a decrease in the polar forces of attraction [20]. With the increasing amount of the RPO, the films increase the elongation at break and decrease the tensile strength.

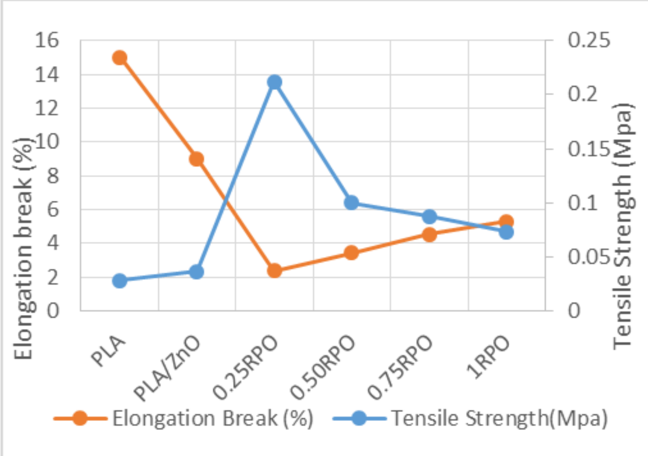

Figure 4: Graph of tensile strength and tensile strain

Table 2: Mechanical Properties

Sample	Tensile Strength (Mpa)	Elongation at break (%)
PLA	0.0282	15
PLA/5% ZnO	0.0369	9
PLA/5% ZnO/0.25 RPO	0.212	2.39
PLA/5% ZnO/0.50 RPO	0.0998	3.45
PLA/5% ZnO/0.75 RPO	0.0874	4.56
PLA/5% ZnO/1 RPO	0.0734	5.32

E. Biodegradability: Solubility in Water

Figure 5 shows the solubility of each films sample. Solubility are one of the indicator for water resistance of composite materials [26]. Potential applications of food packaging may require minor water solubility to enhance the product quality, improve moisture barrier properties and water resistance. A lot of studies have demonstrated the importance of decreasing the solubility of film in water [25].

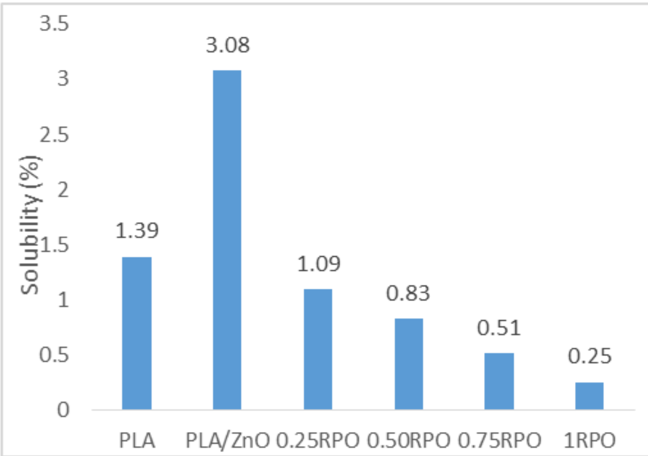

Figure 5: Solubility (%) each film sample

For PLA films, the solubility is 1.39% but when added the 5% of zinc oxide, the solubility of the films increase to 3.08%. This is due to the hydrophilic character of zinc oxide where it is strongly interact with water. For PLA/ZnO/0.25RPO the solubility is higher but for PLA/ZnO/1RPO the solubility become smaller. This is strongly because of the hydrophobic character of RPO. The higher solubility rate in the films is probably due to the faster disruption and diffusion of molecular interactions [27]. The more volume of RPO in the film sample, the lower the solubility of the film. Hydrophobic compounds will decrease the film solubility, while hydrophilic compounds will increase it [20].

IV. Conclusion

In this study, PLA/Zinc/RPO films was produced using solvent casting method in order to get the uniformity of the thickness of the films sample. It was found that the properties of PLA/ZnO films were influenced by the plasticizer content which is RPO. Increase amount of RPO will results on the thickness of the films which are became thicker and lower in moisture content. In particular, tensile strength was negatively influenced and elongation at break was positive influence. The solubility increase with presence of ZnO but after the presence of RPO, the solubility become decreases. These results suggest that the PLA/ZnO/RPO films could be used to replace non-biodegradable plastic.

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