Effect of different red palm oil volume on characteristics and degradation of polylactic acid/zinc oxide film

S F A Karim1*, J Jai1, N A Saiful1, K H K Hamid1 and N Kamarudin1

1Department of Chemical Engineering, Universiti Teknologi MARA (UiTM) 40450 Shah Alam, Selangor, Malaysia

*Corresponding author : sitifatma9633@uitm.edu.my

Abstract. PLA/ZnO combination caused agglomeration, especially at a high concentration of ZnO. This condition improved by adding a plasticizer to smoothen the incorporation of ZnO into PLA. The work's objective was to study the changes in polylactic acid/zinc oxide (PLA/ZnO) film's properties incorporated with red palm oil (RPO) that acted as a plasticizer. The films were prepared using the solvent casting method. RPO's impact as a plasticizer was determined on the film's thickness, moisture content, functional group, mechanical properties, and solubility. More RPO increased the thickness because of the formation of more free volume in the polymer matrix. Otherwise, the moisture content has shown a different trend, which decreased with more RPO content. Fourier transform infrared spectroscopy proved that interaction occurred between each material in this film by sharpening the peak representing the ester group, C=O stretching bonds, 1365 cm⁻¹ (C-H bending), and 1216 cm⁻¹ (C-O stretching). The highest tensile strength obtained by PLA/ZnO/0.25RPO, showing the lowest performance in elongation at break. ZnO increased the solubility of PLA film, but the presence of RPO proportionally reduced the solubility. These results counsel that the PLA/ZnO/RPO films could be applied as an alternative to manufacture film packaging that needs high tensile strength and low elongation at break. Further study should be conducted for a range of one until 25 weight % of RPO over 100% PLA to determine the optimum formulation.

1. Introduction
Nowadays, polylactic acid (PLA) has become one of the recommended materials in film packaging. PLA is one of the raw materials to produce film packaging because PLA is renewable and expected to improve film packaging's biodegradability performance. Unique, most attractive biodegradable polymers, biocompatibility, and low price are the advantages of PLA [1]. However, pure PLA has limited properties such as low flexibility, brittle, rigid, poor thermal properties, poor crystallization behavior, and low water and gas barrier properties [2,3]. Another material is needed to enhance PLA film's weaknesses, such as the addition of filler, additives, or plasticizers. A slow biodegradation rate happened to PLA film because of the hydrophobicity and lack of reactive side-chain group in PLA film [4–7]. Combining PLA with other materials causes changes in the packaging materials' physical and mechanical properties after being mixed with additives. It could reduce the physomechanical properties of composite materials [8].

Zinc Oxide (ZnO) was added into PLA films as a filler that improved the film's thermal stability, and it is safe for human cells. Producing significant dispersion in PLA ternary systems enhanced polymer interaction and increased the flexibility and mechanical properties [2]. However, the high interfacial
tension between PLA and ZnO caused poor interfacial adhesion and led to ZnO's agglomeration on the PLA matrix [3]. The flexibility and extensibility of PLA film or other biopolymers could be improved by adding plasticizers [9,10]. Plasticizer overcomes the films' brittleness caused by extensive intermolecular forces [11]. Glycerol, sorbitol, and polyethylene glycol were the most commonly used plasticizer in the film [12]. Palm oil is an uncommon plasticizer that falls under a bio plasticizer used to modify the film's properties [13]. The triglycerides and unsaturated fatty acid in palm oil enhanced its ability to be used as plasticizers [14]. Based on the information obtained, no published paper has considered RPO's impact on PLA/ZnO films' properties. Therefore, the solvent casting method was used in this paper to enhance PLA/ZnO film with RPO's embedment. The changes in physical properties, chemical properties, and mechanical properties were determined. Besides, the solubility study was conducted to show the degradation ability of the film produced. The results provide an overview of replacing synthetic plasticizers with RPO.

2. Research Methodology

2.1. Materials
Polyactic Acid (PLA), (pallet from China), zinc oxide (ZnO), (Bendosen, Norway), chloroform (R&M chemical, Malaysia), and red palm oil (RPO), (Iko, Malaysia).

2.2. Methodology

2.2.1. Film Preparation. The film was prepared using a solvent casting method [15]. PLA/ZnO/RPO was mixed with mechanical stirring of 600 rpm at 80 °C for 30 min with various RPO amounts, as shown in table 1. RPO was added as a plasticizer. For the first 15 min, 2g of PLA were mixed with chloroform and 5% (w/w) of ZnO. For the second 15 min, RPO was added to complete the solution. The film solution was poured over (80 mm x 15 mm) Petri dishes placed on leveled surfaces. The film solution was dried at room temperature until the film was produced. Finally, the films were separated from the Petri dishes for analysis and evaluation. The formulation of the films is tabulated in table 1.

| Sample name | PLA (g) | ZnO, (w/w)% | RPO, mL |
|-------------|---------|-------------|---------|
| PLA         | 2.00    | 0           | 0       |
| PLA/ZnO     | 2.00    | 5           | 0       |
| PLA/ZnO/0.25RPO | 2.00   | 5           | 0.25    |
| PLA/ZnO/0.50RPO | 2.00   | 5           | 0.50    |
| PLA/ZnO/0.75RPO | 2.00   | 5           | 0.75    |
| PLA/ZnO/1.00RPO | 2.00   | 5           | 1.00    |

2.2.2. Film characterization. The thickness was measured using a digital micrometer at five various points to the nearest 0.001 mm, and the average value was calculated. The film's moisture content was then measured by a simple drying method in an oven at 60 °C using a universal oven [16]. The initial weight (M_i) and final weight (M_f) were recorded. The final weight was taken after a constant weight was obtained. The moisture content (%) was measured based on the weight loss ratio over the initial weight. Fourier transform infrared spectroscopy (FTIR), brand Mettler Toledo was used to monitor the functional properties changes at 4 cm⁻¹ resolutions and 4000 - 600 cm⁻¹ wavenumber [17]. The performance of the film is shown by the mechanical properties and solubility in water. The setup condition for mechanical properties using the Universal Testing Machine was 50 mm initial span, 50 mm/min crosshead speed, 2.5 kN load, and at room temperature condition [18]. The degradation was measured in measuring the solubility of the film in water [19]. A 40 x 20 mm sample was dried in an oven at 60 °C until a constant weight was achieved, called initial weight (M_i). The sample was then immersed in 50 mL distilled water, 24 hours, at room temperature, in a sealed beaker to prevent water...
and dust evaporation. The sample was taken out and dried to a constant weight at 60 °C in a universal oven, and the final weight, g (M₂), was measured. The film's solubility was the ratio percentage of the difference between M₀ and M₂ divided by M₀.

3. Results and Discussion

3.1. Film thickness and moisture content

![Figure 1. The thickness and moisture content of the film](image)

The thickness of the film for packaging was critical since it affected the tensile strength and elongation at break [20]. Figure 1 shows the average thickness and moisture content for all films. It shows an increasing trend of thickness during a decreasing trend for moisture content. The highest thickness obtained was PLA/ZnO/1.00RPO, 0.616 mm, while the lowest, 0.204 mm, representing pure PLA film. Thickness increment only by 0.001 mm experienced by PLA film with ZnO's addition showing the insignificant function of ZnO in terms of film's thickness. Yasir likewise found that the expansion of ZnO did not altogether influence the thickness of the PLA film [21]. However, with the addition of RPO, the thickness increased proportionally. RPO's plasticizer character formed more hydrogen bonding and increased the film's solid content at once enhanced the thickness [22]. The secondary exist shows the percentage of moisture content. Low moisture content is needed to prevent the oxidation at lipid and water molecules' presence inside the film packaging [16]. PLA film has 0.84% moisture content in the film. ZnO's addition reduced the moisture content percentage to 0.71% because of the gap between PLA being replaced by ZnO. Therefore, the chances of moisture being trapped in the film become lower. The percentage of moisture content decreased with the addition of more RPO. RPO suggests the hydrophobic nature improved, which affects the ability of the film to retain water. Makhtar supported this condition that thermoplastic material has the highest moisture content without crude palm oil and palm olein oil [23].
3.2. Fourier transform infrared spectroscopy

FTIR spectra were used to monitor the structural changes and functional groups of film samples at a molecular level through a detailed analysis [24]. Figure 2 displays the % transmittance for all film obtained from FTIR wavelength range between 515 to 4000 cm\(^{-1}\). Four moderate peaks occurred at 1735 cm\(^{-1}\) for PLA film, indicating the ester group (C=O stretching bonds), 1456 and 1366 cm\(^{-1}\) for C-H bending, and 1217 - 1020 cm\(^{-1}\) regions represents ester group, the C-O stretching bonds. Almost similar peak region obtained by the previous researcher on PLA film, 1749 cm\(^{-1}\) designated to C=O of stretching of the ester group, 1450 and 1370 cm\(^{-1}\) for symmetric and asymmetric C-H bending deformation, and 1267-1045 cm\(^{-1}\) for C-O stretching [25]. The addition of ZnO had sharpened and shifted the 1735 cm\(^{-1}\) to 1748 cm\(^{-1}\). The C-H bending of the blending becomes more vital with the occurrence of sharper and wider peaks of 1456 cm\(^{-1}\) and 1358 cm\(^{-1}\). The peak is broader for the C-O stretching bond and decreased to a range of 1181 cm\(^{-1}\) to 1043 cm\(^{-1}\). Kim mentioned that those changes occurred because ZnO increased the nucleation density of PLA [25]. Meanwhile, new peaks observed in PLA/ZnO, the peak of C-H bending are present at a peak range of 871 cm\(^{-1}\) to 755 cm\(^{-1}\) representing ZnO. These changes suggesting that PLA and ZnO sharing the same functional group, and interaction occurred at this functional group. The addition of 0.20 and 0.50 RPO into PLA/ZnO reduced all peaks observed. However, the peaks 1747 cm\(^{-1}\) (C=O stretching) sharpen tremendously for 0.75 and 1.00 RPO, proving linkage between PLA/ZnO with triglyceride ester in RPO [14]. Peaks 1365 cm\(^{-1}\) (C-H bending) experienced the same peak improvement due to RPO consisting of an equal ratio of saturated and unsaturated fatty acids that increased C-H bending peak. The same goes to peak 1216 cm\(^{-1}\) (C-O stretching) also experienced a sharper peak with 0.75 and 1.00 RPO where the bands near 1200 cm\(^{-1}\) referring to the CC(=O)-O functional group [26]. Plus, a new peak appeared at 2970 cm\(^{-1}\) that expressed the weak motion of C=C in cis position. It occurred in considering the unsaturated esters in palm oil. Similar results were obtained where the C=C motion was shown by the band at 3010 cm\(^{-1}\) [26].

**Figure 2.** FTIR wavelength for the films
3.3. Mechanical properties

Figure 3. Mechanical properties performance of the films

Tensile strength and elongation at break are essential to film packaging because high tensile strength shows the ability of the film to sustain the tension given. In contrast, high elongation gave high ductility at once more likely to deform and not to break. Figure 3 shows the films' mechanical properties performance based on tensile strength (TS) and elongation at break (EAB). It shows the highest TS, 0.212 MPa obtained by PLA/ZnO/0.25RPO film, while the lowest TS, 0.0282 MPa represented by PLA film. Otherwise, the PLA/ZnO/0.25RPO film experienced the lowest EAB, 2.39%, and the PLA film has the highest EAB, 15%. ZnO increased the TS and decreased the EAB. Marra found ZnO's addition at 5% increased the TS and reduced the EAB at machine direction [27]. ZnO solidness caused positive collaboration among PLA and ZnO through hydrogen holding [3]. Contradict results obtained by Nasab [28] mentioning the addition of ZnO form 1 – 5 % reduced the TS by 16%, and ZnO stiffen the PLA film. A small increment of TS of PLA after the addition of ZnO being supported by FTIR results shows the interaction between PLA and ZnO occurred that fall on the same functional group with minor changes. RPO acted as a plasticizer to overcome the films' brittleness and fill the polymer chains' space. The presence of RPO shows higher TS and lower EAB if compared to PLA and PLA/ZnO film. However, more RPO decreased the TS and increased EAB. Jusoh [29] found similar results in which the decrement of TS occurred with more crude palm oil added into low-density polyethylene film by 9.34% with the addition of 5 w/w% crude palm oil. The presence of RPO increased the free volume network that causes an increment in separation between the polymer chain (EAB increased) and decrement in opposing forces of attraction cause the weakening of the interaction between the polymer chains (TS decreased) [16,29]. The results have been supported by FTIR finding that sharper peak formed at three points as explained in FTIR sections.
3.4. Degradation percentage

![Degradation percentage diagram](image)

**Figure 4.** Degradation percentage in terms of percentage of solubility for the films

In this paper, the degradation percentage was measured based on the solubility of the film. Solubility is one of the indicators for the water-resistance of composite materials [30]. Potential food packaging applications may require minor water solubility to enhance product quality and improve moisture barrier properties and water resistance. Numerous investigations have exhibited the signs of diminishing the solubility of the film in water [29]. Figure 4 shows the level of solubility of the films that speak to the film’s degradability. PLA/ZnO films have the highest degradation percentage, 3.08% shows the best film degraded in water. Degradation is high because the water molecules can quickly enter the void between PLA and ZnO [25]. A similar result obtained but using a different degradation method indicates ZnO as a reactant in the degradation reaction [31]. The films’ higher degradation rate is probably because of the faster disruption and diffusion of molecular interactions [32]. The PLA/ZnO/1.00RPO has the lowest, 0.25% degradation percentage by cause of the RPO. More RPO reduced the degradation percentage (solubility) because of the hydrophobic character of RPO. There got 70% of tocotrienols in vitamin E that presence in palm oil. The tocotrienols are having hydrophobic properties [33]. Long-chain non-polar hydrocarbon chains like ester, fatty alcohols, and fatty acid also contributed to the hydrophobic character [34]. Hydrophobic compounds will decrease the film solubility, while hydrophilic compounds will increase it [16].

4. Conclusion

Plasticizers in PLA/ZnO films are needed to enhance the film’s application. This paper successfully embedded RPO as a plasticizer into the PLA/ZnO film using a solvent casting method. RPO increased the thickness due to the formation of more free volumes in the polymer network. The hydrophobic character of RPO caused a reduction in moisture content present in PLA/ZnO film. PLA/ZnO/0.25RPO has the highest TS and lowest EAB, and at the same time, the TS increment was around 82% compared to PLA/ZnO film proving that RPO is an essential agent in PLA/ZnO film. Degradation by hydrolysis was performed, but RPO restricted the film’s solubility because of RPO’s hydrophobic character. Therefore, RPO can act as a plasticizer for PLA/ZnO film packaging. Based on the highest tensile strength, the recommended formulation was PLA/ZnO/0.25RPO. Further study should be conducted for additional RPO range between 1% to 25% over total amount of PLA to find the best film with the highest tensile strength and high elongation at break.

Acknowledgements

The authors acknowledge the Ministry of Higher Education Malaysia for supporting this work through two grants, FRGS/1/2018/TK02/UITM/02/9 and RAGS/1/2015/TK02/UITM/03/1.
REFERENCES

[1]  Wang Y Y, Yu H Y, Yang L, Abdalkarim S Y H and Chen W L 2019 Enhancing long-term biodegradability and UV-shielding performances of transparent polylactic acid nanocomposite films by adding cellulose nanocrystal-zinc oxide hybrids Int. J. Biol. Macromol. 141 893–905.

[2]  Tang Z, Fan F, Chu Z, Fan C and Qin Y 2020 Barrier properties and characterizations of poly(lactic Acid)/ZnO nanocomposites Molecules 25 1–12.

[3]  Zhang R, Lan W, Ji T, Sameen D E, Ahmed S, Qin W and Liu Y 2021 Development of polylactic acid/ZnO composite membranes prepared by ultrasonication and electrospinning for food packaging Lwt 135 1–9.

[4]  Suryanegara L, Nakagaito A N and Yano H 2009 The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites Compos. Sci. Technol. 69 1187–92.

[5]  Taib R M, Ramarad S, Arifin Z, Ishak M and Todo M 2010 Properties of Kenaf Fiber / Polylactic Acid Biocomposites Plasticized with Polyethylene Glycol.

[6]  Faludi G, Dora G, Renner K, Móczó J and Pukánszky B 2013 Biocomposite from polylactic acid and lignocellulosic fibers: Structure-property correlations Carbohydr. Polym. 92 1767–75.

[7]  Tudorachi N and Lipsa R 2011 Poly (vinyl alcohol)-g-Lactic Acid Copolymers and Films with Silver Nanoparticles Journal of Applied Polymer Science 122(2) 1109 - 1120.

[8]  Cooksey K 2007 Contaminants Effectiveness of antimicrobial food packaging materials Food Addit. Contam. 22(10) 980-7.

[9]  Ozkoc G and Kemaloglu S 2009 Morphology, Biodegradability, Mechanical and Thermal Properties of Nanocomposite Films Based on PLA and Plasticized PLA J. Appl. Polym. Sci. 114(4) 2481-2487.

[10]  Ljungberg N and Wesslén B 2002 The effects of plasticizers on the dynamic mechanical and thermal properties of poly(lactic acid) J. Appl. Polym. Sci. 86 1227–34.

[11]  Wang X, Sun X, Liu H, Li M and Ma Z 2011 Barrier and mechanical properties of carrot puree films Food Bioprod. Process. 89 149–56.

[12]  Nguyen Vu H P and Lumdubwong N 2016 Starch behaviors and mechanical properties of starch blend films with different plasticizers Carbohydr. Polym. 154 112–20.

[13]  Kamarudin S H, Jusoh E R, Abdullah L C, Ismail M H S, Aung M M and Ratnam C T 2019 Thermal and Dynamics Mechanical Analysis of Polypropylene Blown Films with Crude Palm Oil as Plasticizer Indones. J. Chem. 19 545.

[14]  Fatma S, Karim A, Aliah N, Mohammad A, Adawiyah R, Aziz A and Ibrahim K 2020 The Effect of Red Palm Oil Concentration towards Characteristics and Biodegradability of PLA-Starch Film 20 1240–5.

[15]  Heydari-Majd M, Ghanbarzadeh B, Shahidi-Noghabi M, Najafi M A, Adun P and Ostadrahimid A 2019 Kinetic release study of zinc from polylactic acid based nanocomposite into food simulants Polym. Test. 76 254–60.

[16]  Bilal Ahmad Ashwar, Asima Shah, Adil Gani, Umar Shah, Asir Gani, Idrees Ahmed Wani, Sajad Mohd Wani F A M 2014 Rice starch active packaging films loaded with antioxidants—development and characterization Starch/Stärke 67 294–302.

[17]  Orsuwan A, Shankar S, Wang L F, Sothornvit R and Rhim J W 2016 Preparation of antimicrobial agar/banana powder blend films reinforced with silver nanoparticles Food Hydrocoll. 60 476–85.

[18]  Wang X, Sun X, Liu H, Li M and Ma Z 2010 Food and Bioproducts Processing Barrier and mechanical properties of carrot puree films Food Bioprod. Process. 89 149–56.

[19]  Romero-Bastida C A, Bello-Pérez L A, Garcia M A, Martino M N, Solorza-Feria J and Zaritzky N E 2005 Physicochemical and microstructural characterization of films prepared by thermal and cold gelatinization from non-conventional sources of starches Carbohydr. Polym. 60 235–44.

[20]  Datta D and Halder G 2018 Enhancing degradability of plastic waste by dispersing starch into
low density polyethylene matrix. *Process Saf. Environ. Prot.* **114** 143–52.

[21] Arfat Y A, Ahmed J, Al Hazza A, Jacob H and Joseph A 2017 Comparative effects of untreated and 3-methacryloxypropyltrimethoxysilane treated ZnO nanoparticle reinforcement on properties of polylactide-based nanocomposite films. *Int. J. Biol. Macromol.* **101** 1041–50.

[22] Karim S F A, Hamzah N A N, Aziz R A A and Ibrahim U K 2020 The effect of plasticizers towards the characteristics of methylcellulose film packaging. *IOP Conf. Ser. Mater. Sci. Eng.* **845**.

[23] Mohd Makhtar N S, Muhd Rodhi M N, Musa M, Ku Hamid K H, Shuhada N, Makhtar M, Najwa M, Rodhi M, Musa M, Halim K, Hamid K, Mohd Makhtar N S, Muhd Rodhi M N, Musa M and Ku Hamid K H 2013 Thermal behavior of tacca leontopetaloides starch-based biopolymer. *Int. J. Polym. Sci.* 2013.

[24] Norfarahin A H, Sanny M, Sulaiman R and Nur Hanani Z A 2018 Fish gelatin films incorporated with different oils: Effect of thickness on physical and mechanical properties. *Int. Food Res. J.* **25** 2503–10.

[25] Kim I, Viswanathan K, Kasi G, Sadeghi K, Thanakkasaranee S and Seo J 2019 Poly(lactic acid)/ZnO bionanocomposite films with positively charged ZnO as potential antimicrobial food packaging materials. *Polymers (Basel)*. **11**.

[26] Guerrero A, Anguebes F, Castelán M, Morales V, Química F De, Autónoma U, No C, Av E, Juárez C B and Carmen C 2014 Fourier Transform Infrared-Attenuated Total Reflectance (Ftir-Atr) Spectroscopy and Chemometric Techniques for the Determination of Adulteration in Petrodiesel/ Biodiesel Blends. *Quim. Nova* **37** 392–7.

[27] Marra A, Silvestre C, Duraccio D and Cimmino S 2016 Polylactic acid/zinc oxide biocomposite films for food packaging application. *Int. J. Biol. Macromol.* **88** 254–62.

[28] Nasab M S, Tabari M and Azizi M H 2018 Morphological and mechanical properties of Poly(lactic Acid) / zinc oxide nanocomposite films. *Nanomedicine Res. J.* **3** 96–101.

[29] Jusoh E R, Ismail M H S, Abdullah L C, Yunus R and Rahman W A W A 2013 Effect of crude palm oil as plasticiser on the mechanical and morphology properties of low density polyethylene blown film. *Int. J. Mater. Eng. Innov.* **4** 302–13.

[30] Wu Z, Huang X, Li Y C, Xiao H and Wang X 2018 Novel chitosan films with laponite immobilized Ag nanoparticles for active food packaging. *Carbohydr. Polym.* **199** 210–8.

[31] Anžlovar A, Kržan A and Žagar E 2018 Degradation of PLA/ZnO and PHBV/ZnO composites prepared by melt processing. *Arab. J. Chem.* **11** 343–52.

[32] Kaya M, Khadem S, Cukmak Y S, Mujtaba M, Ilk S, Akyuz L, Salaberria A M, Labidi J, Abdulqadir A H and Deligöz E 2018 Antioxidative and antimicrobial edible chitosan films blended with stem, leaf and seed extracts of Pistacia terebinthus for active food packaging. *RSC Adv.* **8** 3941-3950.

[33] Fatehi P, Baba A S, Eh suk V R and Misran M 2020 Preparation and characterization of palm oil in water microemulsion for application in the food industry. *Br. Food J.* **122** 3077–88.

[34] Farooq A, Shafaghat H, Jae J, Jung S C and Park Y K 2019 Enhanced stability of bio-oil and diesel fuel emulsion using Span 80 and Tween 60 emulsifiers. *J. Environ. Manage.* **231** 694–700.