Blending of Low-Density Polyethylene and Poly-Lactic Acid with Maleic Anhydride as A Compatibilizer for Better Environmentally Food-Packaging Material

A H Setiawan¹,² and F Aulia¹,²

¹Research Center for Chemistry, Indonesian Institute of Science Kawasan PUSPIPTEK, Serpong 15314, Tangerang Selatan, Banten, Indonesia
²Technology Faculty-Pamulang University, Tangerang Selatan, Banten, Indonesia

Email: achmad.hanafi@gmail.com

Abstract. The common conventional food packaging materials are using a thin layer plastic or film, which is made of a synthetic polymer, such as Low-Density Poly Ethylene (LDPE). However, the use of these polymers has an adverse impact on the environment, because the synthetic polymers are difficult to degrade naturally. Poly-Lactic Acid (PLA) is a biodegradable polymer that can be substituted to synthetic polymers. Since LDPE and PLA have a difference in polarity, therefore the first step of research is to graft them with maleic anhydride (MAH) for increasing the properties of its miscibility. The interaction between them is confirmed by FTIR; whereas the environment issues characterized by the water adsorption and biodegradability. The FTIR spectra indicated that there had been an interaction between LDPE and MAH and LDPE/LDPE-g-MAH/PLA blend. Increasing PLA content in the blend affected to the increasing in their water absorption and biodegradable. Poly-blend with 20% PLA content was the optimum composition for environmentally food packaging.

Keywords: LDPE, PLA, maleic anhydride, compatibilizer, environment; food packaging.

1. Introduction
The common packaging plastic material is made from synthetic polymer. However, the use of this kind of polymer has a negative impact on the environment, due to its difficulty to degrade naturally, whether by biotic components such as micro-organisms decomposers or by abiotic components such as the sunshine. Therefore, it is necessary to develop technology increasing its degradability degree or even to look for new degradable materials. Utilization of natural polymers is an alternative packaging material, and it needs to be developed. In the packaging of foodstuffs, there are two different types of packaging functions, namely the primary packaging or containers are directly attached to the foodstuffs and the secondary packaging that are not directly attached to the food [1]. Edible coating such as bio-cellulose, carrageenan, chitosan, and beeswax are the natural polymer, but they can only be used for the food primer packaging. PLA is another natural polymer which is predicted suitable for a secondary foodpackaging. However, the price is higher than the synthetic polymer. Therefore, blending this natural polymer with the synthetic polymer is an alternative to making a packaging product more degradable. Since all type of food packaging should be non-toxic
and inert so that no chemical reaction occurs that can cause changes in color, flavor and other changes; besides also must meet special requirements such as protecting food from contamination, protecting the water content and fat, preventing the entry of odors and gases, protect food from sunlight, and resistant to pressure or impact [1]. This product can fulfill the requirements as a good packaging material.

PE is one of the elastomer synthetic material which has white and transparent properties and its melting point between 110-137 °C. In general, a property of PE is resistance to chemical materials. At room temperature, PE does not dissolve in an organic and inorganic solvent. There are some derivatives of PE (Figure 1), include *High-Density Polyethylene (HDPE)*; *Low-density Polyethylene (LDPE)*, *Linear Low-Density Polyethylene (LLDPE)*, etc. Some PE such as LDPE has a high structure with a short and long branched. However, HDPE has a straight branched. LLDPE has a straight branched with short branched [2]. HDPE polymer is harder but workable so widely used as a kitchen utensil bucket, for example, pan, also for wire and cable coatings. LDPE is always used for thin layer food packaging, plastics bag, and raincoat.

PLA is a natural polymer has a structure as the Figure 2, derived from renewable sources with an esterification process lactic acid obtained by fermentation by bacteria using substrates starches or simple sugars [3]. PLA has no reactive group at all on the side chains [4-5]. PLA can find in many plants such as rice, cassava, maize, and sago. Therefore, they can be renewable, and able to give nature biodegradable (compostable). Another advantage of the use of PLA including; able to improve the physical and mechanical properties, during the production process using a carbon dioxide gas, providing significant energy supply, and help improve the stability of the economic and the agricultural sector [6]. PLA has a heat-resistant property, strong, and an elastic polymer and capable of providing biodegradable nature of the PE.

Development of polymer blending technology has grown rapidly, both in science and in use commercially. The advantage of this technology is able to improve the properties or performance of the low-cost material. However, themostpolyblend is an immiscible blend, where the mix tends to very low entropy, resulting in the formation of polyblend with low mechanical properties both during the process and use. Mixed Polymer which has a mixed compatibility between the constituent components of polyblends can be made using reactive compatibility or different additives. Blending compatibility may affect the morphology and properties of polyblends. Mixing compatibility strategies focusing on applications such as plastic post-consumer recycling without sorting, production of multi-layer films, packaging products, as well as the development of new materials based on plastic/plastic elastomer/elastomer mixture [7,8]. A mixture of LDPE with PLA is an immiscible blend because there are differences in their polarity. Therefore, it is necessary to add a compatibilizer such as polyethylene-grafted Maleic anhydride (PE-g-MAH) in order to increase the properties of its miscibility blend [9,10]. This addition is conducted using grafting techniques. The techniques have been utilized in various fields of application, among others to change the properties of the parent polymer with a purpose, such as increasing the adhesive strength of the polymer [11], the biodegradation of polymers [12]. Based on the description above, this research will be conducted studies on the effects of adding PLA to LDPE against water absorption, functional group change, and biodegradability of polyblend.

*Figure 1.* Polyethylene chain structure of (a) HDPE, (b) LDPE, and (c) LLDPE [2]
2. Experimental Method

2.1. Materials
All starting compounds were purchased from E.Merck and used as such without any further purification, such as Maleic Anhydride (MAH) and Chlorobenzene; Low-Density Polypropylene (LDPE) was made of Chandra Asri Petrochemical Ltd., Poly Lactic Acid (PLA) was donated by RC Biomaterials-LIPI Cibinong.

2.2. Instruments
FTIR (Shimadzu FTIR-IRPrestige-21) with a potassium bromide (KBr) disks or films was conducted to determine the functional groups of compounds.

2.3. Preparation of LDPE-g-MAH
50 mL of Chlorobenzene was heated at three-neck round bottom flask until the temperature reaches 150°C. Then, 4.5 g of LDPE and 0.5 g MAH were added to the flask and stirred for 45 minutes. The mixture solution was poured into a petri dish and cooled for 24 hours in a fume hood.

2.4. Preparation of LDPE / LDPE-g-MAH / PLA
50 mL of Chlorobenzene was heated at three-neck round bottom flask and heated until the temperature reaches 150°C. Then, 0.15 mg LDPE-g-MAH and certain ratio of LDPE/PLA were added so that the total w/w ratio were (100:0); (90:10); (80:20); (70:30); (60:40) and (50:50). Each composition was stirred for 45 minutes. Further, the hot solution was poured and cooled for 24 hours in a fume hood. The samples were homogenized and pelleted with KBr. Then the pellet was examined by infrared light on the instrument of Prestige-21 Shimadzu IR at a region frequency between 3500 cm\(^{-1}\) to 400 cm\(^{-1}\). The obtained IR spectrum was analyzed to their appearance of their functional groups.

2.5. Test of Water Absorption Index (WAI) ASTM-570
The specimen was dried beforehand in an oven for 1 hour at 110°C and then weighed as the initial weight (W\(_0\)) and then soaked in distilled water for 24 hours. Picked up the sample and the water containing on the sample surface is removed with tissue paper, then weighted. Repeatedly the sample put back into distilled water for 10 seconds, and picked out, dried and weighted. The Immersion and weighing procedure were repeated until reached the constant weight (W\(_t\)). Water Absorption Index then was calculated by equation (1):

\[
\%WAI = \frac{(W_t - W_0)}{W_0} \times 100\%
\]

where % WAI, W\(_0\), and W\(_t\) respectively represent water absorption index (%), initial mass (g), and final mass (g).

2.6. Biodegradability Test
The sample was cut to size about 5cm x 1cm, then dried in a desiccator to obtain a stable weight (W\(_0\)). Samples were then buried in the ground for six days, and then cleaned by water soaking and then

![Figure 2. Polylactic acid structure [7]](image-url)
redried in the desiccator. Finally, the samples were weighed ($W_i$). The percentage of mass loss was then calculated by Equation (2).

$$\%W_{loss} = \frac{(W_o - W_f)}{W_o} \times 100\%$$

where $\% W_{loss}$, $W_o$, and $W_i$ respectively represent weight loss (%), initial mass (g), and final mass (g).

3. Results and Discussion

3.1. Functional groups of LDPE and LDPE-g-MAH

MAH grafting process aims to increase the compatibility between matrixes to be reacted, particularly for a matrix which has a different polarity. In this study LDPE-g-MAH used to hold two compounds that have reactive groups with different polarity, i.e. LDPE which have reactive groups in the form of a double bond is nonpolar, and PLA has reactive groups such as hydroxyl group (OH-) which is polar. A sheet transparent and solid white has resulted after cooling for 24 hours in a fume hood. Each of the starting material used for the synthesis of bio-composite was spectroscopically characterized by FTIR. Figure 3 is a spectrum of original LDPE and LDPE-g-MAH and Figure 4 is a pure polylactic acid spectra.

As depicted in Figure 3, the wavenumber of 2848.86 cm$^{-1}$, there was a strong peak of CH$_2$ groups, while at the wave number of 1463.97 cm$^{-1}$ represent the absorption of C-H group. The functional groups H-C-H occurred in a wave number of 723.31 cm$^{-1}$. Those absorption bands was a typical absorption for polyethylene [2]. The wavelength of 2916.37 cm$^{-1}$ indicates the absorption of C-H stretching from MAH, and the absorption peak in the region of 1707 cm$^{-1}$ shows the absorption of a carbonyl group (C = O) of MAH. In addition, the wave number of 1217.08 - 1263.37 cm$^{-1}$ represents an absorption of a C-O group of MAH. These results indicated that an interaction between LDPE and MAH occurred. Figure 5 shows the expected reaction takes place in this work.

The characteristics of functional groups on pure PLA (Figure 4) is 3571 cm$^{-1}$ as the -OH stretch (free); 2997 cm$^{-1}$ (asym), 2946 cm$^{-1}$ (sym), 2881 cm$^{-1}$ stretch -CH$_2$; 1757 cm$^{-1}$ -C O carbonyl stretch; 1456 cm$^{-1}$ -CH$_3$ bend. The wavenumber of 1382 cm$^{-1}$, and 1365 cm$^{-1}$ indicate a -CH- deformation including symmetric and asymmetric bend; the wave number of 1225 cm$^{-1}$ -C O bend; the peak at 1194 cm$^{-1}$, 1130 cm$^{-1}$, 1093 cm$^{-1}$ represent the -C-O- stretch; 1047 cm$^{-1}$ -OH bend; 956 cm$^{-1}$, 921 cm$^{-1}$ -CH$_3$ rocking; 926 cm$^{-1}$, 868 cm$^{-1}$ stretch -C-C- [6].

Figure 6 is a typical FTIR spectra of polyblend LDPE/LDPE-g-MAH/PLA. It can be seen from the figure that the methine group of the LDPE was disappeared on the polyblend spectra. The carbonyl group in MAH spectra at 1710 cm$^{-1}$ was a shift to carbonyl ester group at MAH spectra showed at 1755-1761 cm$^{-1}$. The shift position of the carbonyl group is caused by the esterification between LDPE-g-MAH and the carboxylic group of PLA. Figure 7 is a reaction mechanism proposal for the reaction among LDPE, LDPE-g-MAH, and PLA. Figure 8, were a series of LDPE/LDPE-g-MAH/PLA spectra with the ratio of LDPE: PLA were (100:0); (90:10); (80:20); (70:30); (60:40) and (50:50).
Figure 3. FTIR-spectra of original LDPE and LDPE-g-MAH

Figure 4. Pure Polylactic Acid Spectra

Figure 5. Reaction of LDPE and MAH
3.2. Determination of water adsorption

Analysis of Water Adsorption Index (Absorption of Water) is necessary to know the properties of bioplastics on their water resistant. The first step of this test is an evaporation of moisture on the polyblend by using the electric furnace for 10 minutes at 100°C to remove the water that remains in the sample and then weighed. Test of Water Absorption Index (WAI) ASTM-570. Calculated Water Adsorption with the formula was described on this ASTM. The water adsorption graft of all ratios of polyblends can be seen in figure 9. According to this figure, it can be concluded that generally, the more PLA added to the formulation of LDPE/LDPE-g-MAH/PLA will increase the percentage of water absorption. This can be explained since PLA has a good biodegradable property which able to broken down by the water, thus affecting to their degradation properties.

3.3. Determination of biodegradability

The percentage degradation of polyblend by soil environment was carried out by weighing the mass of polyblend before and after an experiment. Figure 10 represents the percentage of biodegradability of the polyblends. From this figure, it can be estimated that there has been a reduction in the mass of polyblend after buried in the soil for 6 days. It may there is the biotic components such as microorganisms decomposers in the soil which able to degradable the polyblend. Based on the plot of the graph, it can be concluded that the existence of PLA on the polyblend of LDPE / LDPE-g-MAH / PLA affected to their better degradation. These results are consistent with studies conducted by [13] in which the PLA to be mineralized into CO$_2$, water, and other simple biomass perfectly after 4-6 weeks.
Figure 8. Spectra of LDPE/LDPE-g-MAH/PLA with the ratio LDPE: PLA (100:0); (90:10); (80:20); (70:30); (60:40); (50:50)

Figure 9. Water adsorption graft of polyblends

Figure 10. Percentage of biodegradability of the polyblends

4. Conclusion
We concluded that the synthesis of green material polyblend LDPE/PLA grafting LDPE-g-MAH had interacted chemically. We further obtain that the increase of PLA percentage on the polyblend will increase the water absorption properties and their biodegradability. Poly-blend with 20% PLA content is the optimum composition for environmentally food packaging.
5. References

[1] Julianti E and Nurminah M 2012 Properties of plastic and paper packaging and their influence to the foods Agriculture Technology Department North Sumatra University (Thesis)

[2] Peacook A J 2014 Hand Book of Polyethylene Structures, Properties, and Applications Marcel Dekker Inc.

[3] Shogren R L, Doane W M, Garlotta D, Lawton J W and Willett J L 2004 Biodegradation of starch/polylactic acid/poly (hydroxy ester ether) composites bars in soil Poly. Deg. and Stab. 79(3) 405-411

[4] Rasal R M and Hirt D E 2009 Improving the properties of the polylactic acid Plastics Research online Clemson, SC

[5] Wang J H and Schertz D M 2010 Synthesis of grafted polylactic acid and polyhydroxy-alkanoate by a green reactive extrusion process In ACS symposium series 1043 439-453

[6] Auras R, Harte B and Selke S 2006 An overview of polylactic acid as packaging materials Mac. Biosci. 4(9) 835-864

[7] Ploypetchara N, Suppakul P, Atong D and Pechyen C 2014 A blend of polypropylene/polylactic acid for medical packaging application: physicochemical, thermal, mechanical, and barrier properties Energy Procedia 56 201-210

[8] Marsyahyo E, Soekrisno, Rochardjo H S B and Jamasri 2005 Investigation of chemical surface treatment of ramie fiber (buehmerianuavea) on surface topography, tensile strength, and single fiber fracture modes Proceeding of International Seminar on Product Design and Development. Material Development, Gajah Mada University

[9] Parameswaranpillai, J, Joseph G, Jose S and Hameed N 2015 Phase morphology, thermo mechanical, and Crystallization behavior of compatibilized and PP-g-MAH compatibilized polypropylene/polystyrene blends. J. of App. Poly. Sci. 132(24)

[10] Xin L, June Z, Lin Z, Hongxia J and Ruofei J 2014 Study on mechanical properties and thermal stability behaviors of PP / PP-g-MAH / ABS-g-MAH blends. Plas. Sci. and Tech. 912

[11] Song Y W, Do H S, Joo H S, Lim D H, Kim S and Kim H J 2006 Effect of grafting of acrylic acid onto a PET film surfaces by UV Irradiation on the adhesion of PSAs J. Adhesion Sci. Technol. 20(12) 1357-1365

[12] Hendri J, Ginting I and Laila A 2008 Gamma radiation studies on the binding of acrylic acid grafted chitosan polyethylene Proceeding of 2nd National Science and technology Seminar, Lampung University

[13] Hakkarainen M 2002 Aliphatic polyesters: abiotic and biotic degradation and degradation products In Degradable aliphatic polyesters 113-138 Springer Berlin Heidelberg

Acknowledgements

The authors would like to express great gratitude to “Riset Unggulan 2016” of Research Center of Chemistry, Indonesian Institute of Sciences which is funding this work research.