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

A H Setiawan[1,2] and F Aulia[1,2]

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

Email: achmad.hanafi@gmail.com

Abstract. The common conventional food packaging materialsare 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 hasan adverse impact on the environment, because the synthetic polymersare 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 issueis 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 hasa negative impact on the environment, due to its difficulty to degrade naturallywhether by biotic components such as micro-organisms decomposers orby abiotic components such as the sunshine. Therefore, it is necessary to develope technologyinincreasing 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 ishigherthan 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

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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 $^{\circ}$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 astructure 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.

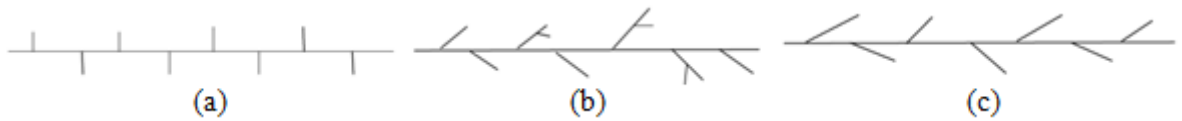


Figure 1. Polyethylene chain structure of (a) HDPE, (b) LDPE, and (c) LLDPE [2]

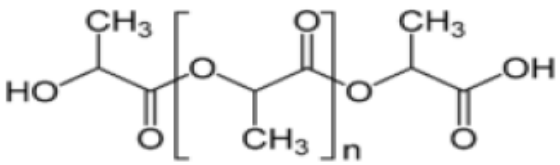


Figure 2. Polylactic acid structure [7]

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-DensityPolypropylene (LDPE) was made of Chandra Asri Petrochemical Ltd., Poly Lactic Acid (PLA) was donated by RC Biomaterials-LIPI Cibinong.

2.2. Instuments
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^{o}C.Then,0.15 mg LDPE-g-MAH and certain ratio of LDPE/PLA were addedso that thetotal w/w ratio were (100:0); (90:10); (80:20); (70:30); (60:40) and (50:50). Each compositionwasstirred 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).

$$\%WAI = \frac{(W_t - W_0)}{W_0} \, x \, 100\% \quad (1)$$

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 tosize 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

redried in the desiccator. Finally, the samples were weighed (W_t). The percentage of mass loss was then calculated by Equation (2).

$$\%W_{loss} = \frac{(W_0 - W_t)}{W_0} \, x \, 100\% \tag{2}$$

where % W_{loss}, W_0, and W_t 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 resultedafter cooling for 24 hours in a fume hood. Each of the starting material used for the synthesis of bio-composite was spectroscopicallycharacterized 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 wasa 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-Hoccurred in a wave number of 723.31 cm^{-1}. Those absorption bands wasa 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 MAHoccurred. Figure 5 shows the expectedreaction 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-; 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 amongLDPE, 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).

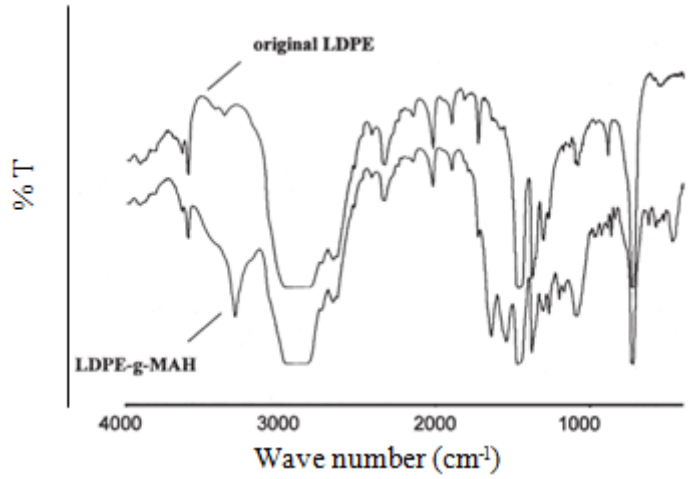


Figure 3. FTIR-spectra of original LDPE and LDPE-g-MAH

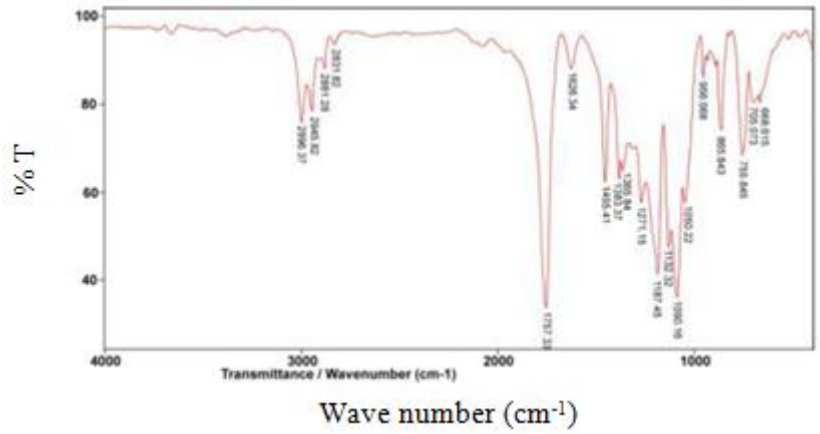


Figure 4. Pure Polylactic Acid Spectra

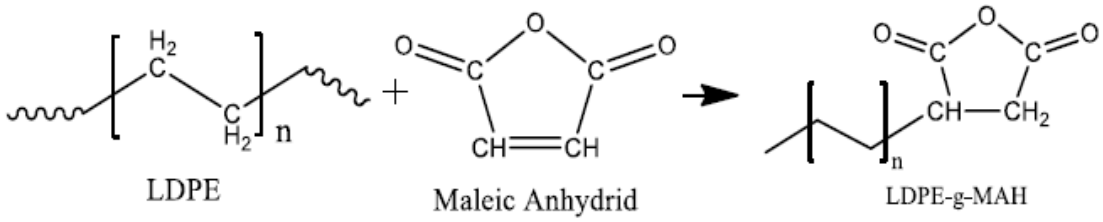


Figure 5. Reaction of LDPE and MAH

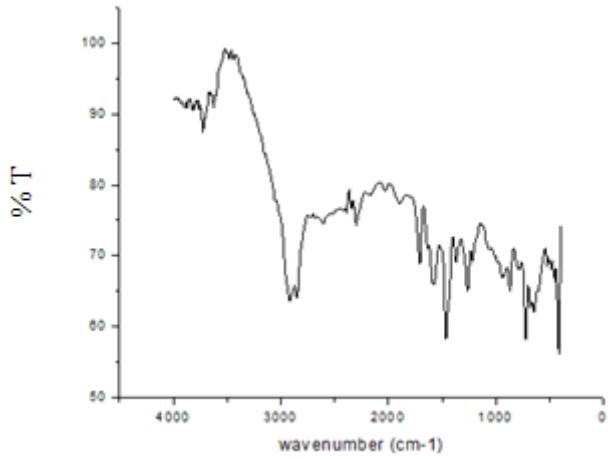


Figure 6. LDPE/LDPE-g-MAH/PLA FTIR spectra

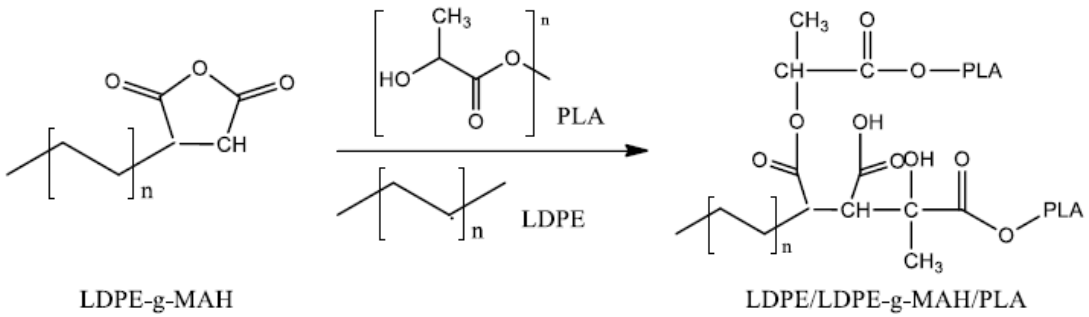


Figure 7. Reaction of LDPE, LDPE-g-MAH, and PLA

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 withthe formulawas described onthis ASTM. The water adsorption graftof 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 formulationof LDPE/LDPE-g-MAH/PLA will increase the percentage of water absorption. This can be explained since PLA has a goodbiodegradable 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 environmentwas 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 micro-organisms 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.

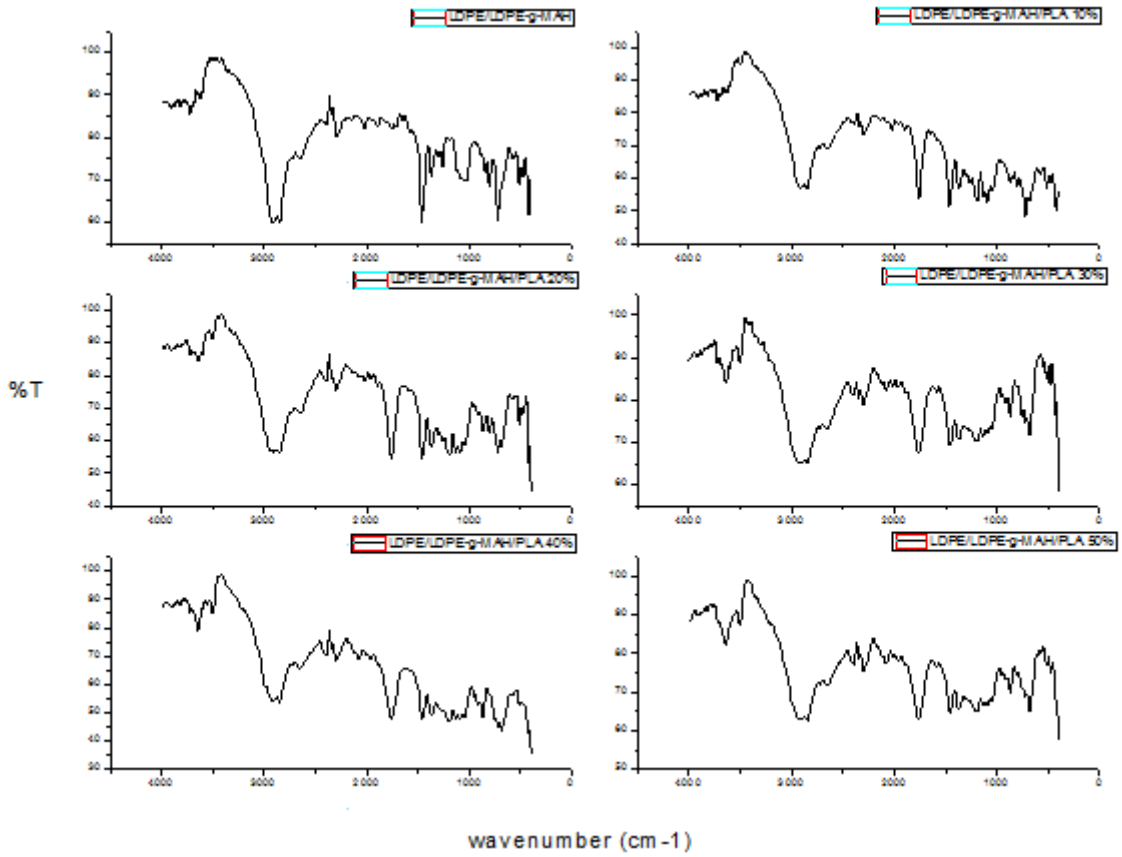


Figure 8. Spectra of LDPE/LDPE-g-MAH/PLA with the ratio LDPE: PLA (100:0); (90:10); (80:20); (70:30) ;(60:40) ;(50:50)

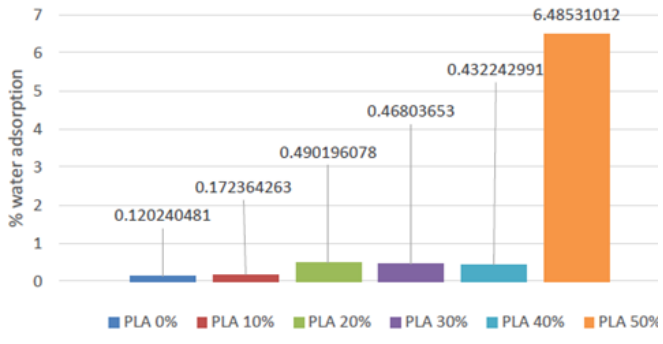


Figure 9. Water adsorption graft of polyblends

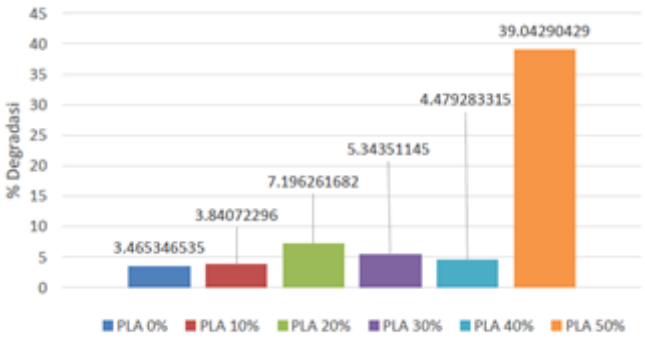


Figure10. Percentage of biodegradability of the polyblends

4. Conclusion

We concluded that the synthesis of green material polyblend LDPE/PLA grafting LDPE-g-MAH had interacted chemically. We further obtain thatthe 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.

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