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Study and Development of Linier Low Density Polyethylene (LLDPE) and Poly Lactid Acid (PLA) Biodegradable Compouns Using Compatibizer LLDPE-g-MA

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ABSTRACT

This study discusses composite polymer of LLDPE and PLA at a ratio of 100: 0, 80:20, 60:40, 40:60, 20:80, 0: 100 with 4 phr LLDPE-g-MA compatibilizer. The process of making composite was performed using rheomix, which was then molded into thin sheets using hydraulic hot press to test its mechanical properties, i.e. SEM, TGA and biodegradable. The test results of mechanical properties (tensile strength and elongation at break) showed that the less the composition of PLA in the composite, the higher the mechanical properties. SEM composite test results have indicated that the LLDPE/PLA composite has a smooth surface, indicating good compatibility between LLDPE and PLA. The TGA testing produced thermal degradation in the composite sample as the PLA compositions decreased. The biodegradable test results showed that the more the PLA composition increased, the higher the missing mass of the composite samples. Based on the test results, composite LLDPE/PLA can be used as a polybag plastic because it has strong mechanical properties and environmentally friendly due to the fact that it can be degraded by microorganisms.

Keywords:*composite polymer, LLDPE/PLA, mechanical properties, SEM, TGA, biodegradable*

1. INTRODUCTION

The making of LLDPE/PLA composite is deemed necessary to make environmentally friendly plastic while reducing dependence on the use of non-degradable plastics. Polymer composite comprising conventional polymers and biodegradable polymers is an effective way to address the issue (Yoo et al., 2010). The differences in the characteristics and properties between LLDPE and PLA cause the mixture to be incompatible and therefore a compatibilizer is required upon the mixing process in order that both can be perfectly mixed.

Previous research has been conducted on polyethylene and PLA composite, among others by Djellali et al (2013). The study has used a compatibilizerpoly (ethylene copolymer glycidyl methacrylate) resulting in a composite with a tensile strength and elongation at break of 8.9 MPa and 50.05%. Another research on the composite polyethylene and PLA is that of Madhu et al (2014) which has produced a polymer composite with better mechanical properties (tensile strength and elongation at break). The mechanical properties (tensile strength and elongation at break) obtained were 19.9 MPa and 147%. The research on polyethylene polymer and PLA composite by Madhu et al (2014) has used compatibilizer PE-g-MA or Maleic anhydride grafted polyethylene. From these studies it could be estimated that the most appropriate compatibilizer for polyethylene/PLA composite was PE-g-MA.

Based on the potentials mentioned above, polymer composites between polyethylene and PLA would be performed as the focus of this study. This study would make a composite of LLDPE/PLA in a rheomix with the help of compatibilizer in the form of LLDPE-g-MA or

Maleic anhydride grafted linear low-density polyethylene. Mechanical, SEM, TGA and biodegradable tests would be performed on the LLDPE/PLA composite results. The objective of the study was to obtain a polymer material which is economical, has good mechanical properties and is environmentally friendly for the manufacture of polybags.

2. THEORETICAL REVIEW

2.1. Composite

Composite is a material system which consists of a mixture or combination of two or more micro or macro constituents that differ in forms and chemical compositions and do not dissolve each other in order to obtain more specific characteristics and properties.

Constituents making up the composite consist of matrix and reinforcement. A matrix serves as a binder and transfers load to the reinforcement, while the reinforcement serves as the load-bearer. The matrix can be made of materials such as polymers, metals, carbon, or ceramic. Therefore, the composite can be classified based on the type of matrix, such as composites with metal matrix, composites with ceramic matrix, and composites with polymer matrix. Other matters affecting composites are interfaces of composites, on which the formation of a new surface for the load transfer between matrix and reinforcement occurs; composite interphase where a stronger bond between matrix and reinforcement occurs as well as adhesion or the bonding force of attraction between molecules.

In this experiment, a compatibilizer, maleic anhydride grafted linear low density polyethylene (LLDPE-g-MA) was used. It is a polymer compound derivative of polyethylene whose chains are grafted by maleic anhydride molecules. In the formation of LLDPE-g-MA, solvent polyethylene polymer and initiator were needed as a forming agent for free radicals in order to react with H atoms in the polymer

3. MATERIALS AND METHOD

3.1. Materials and Tools

The tools used in this study were Rheomix 3000 HAAKE, hydraulic hot press, Universal Testing Machine for testing the tensile strength and percentage of elongation, Scanning Electron Microscope (VE-8800 Low Voltage -Keyence, Co., Osaka, Japan) and Thermal Gravimetric Analysis tool. The materials used in this study were Linear Low Density Polyethylene (LLDPE) UF181051 with a specification of density from 0.919 to 0.923 g/cm3 and Melt Flow Index 0.8 to 1.2 obtained from PT Chandra Asri Petrochemical Tbk. Poly Lactic Acid (PLA) Ingeo 7001D and compatibilizer (LLDPE-g-MA).

3.2. Composite LLDPE/PLA

3.2.1. The Making of Compatibilizer LLDPE-g-MA

The making process of LLDPE-g-MA as a compatibilizer in the LLDPE/PLA mixture is as follows. The reaction of the making of LLDPE-g-MA was conducted in a reactor at a temperature of 120^{o}C. The materials included were LLDPE which were then dissolved in xylene and added with maleic anhydride (MA) as well as an initiator benzoyl peroxide (BP). Grafting reaction lasted for 5 hours. As the reaction completed, the mixture was washed using a solvent of methanol and acetone on a filter paper to remove unreacted MA. After the washing, the LLDPE-g-MA was filtered on the filter paper and then dried using a vacuum oven at the temperature of 60°C. The dried LLDPE-g-MA then underwent purification through extraction using acetone to purify the LLDPE-g-MA still containing unreacted MA as impurities in the LLDPE-g-MA expected to form. Following purification, the LLDPE-g-MA was dried again in a vacuum oven at 60°C. The final step to perform was an analysis to determine the percentage of the grafting or the amount of MA content grafted in the LLDPE and FTIR analysis.

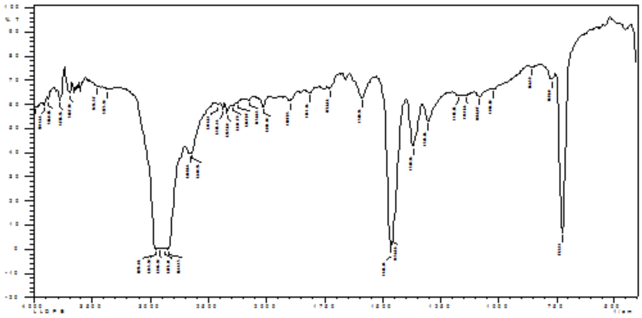
3.2.2. The Making of Composite LLDPE/PLA

The process of composite LLDPE/PLA making was carried out by means of rheomix 3000 HAAKE. The process that occurred in the rheomix is melt blending of PLA and LLDPE with an operating condition of a temperature of 200^{o}C, rotational speed of 50 rpm and a period of 7 minutes. In the process of making the composite, LLDPE/PLA, a compatibilizer LLDPE-g-MA as much as 4 phr of the mass of LLDPE/PLA was also added. The results of composite LLDPE/PLA/LLDPE-g-MA in the rheomix was then molded into thin sheets using a hydraulic hot press with the operating conditions of a pressure of 60 MPa, a temperature of 150°C and the press processing time of 15 minutes. The resulted composite already in the form of pressed sheets was then cut according to the size required for testing the mechanical properties, SEM, TGA and biodegradable tests.

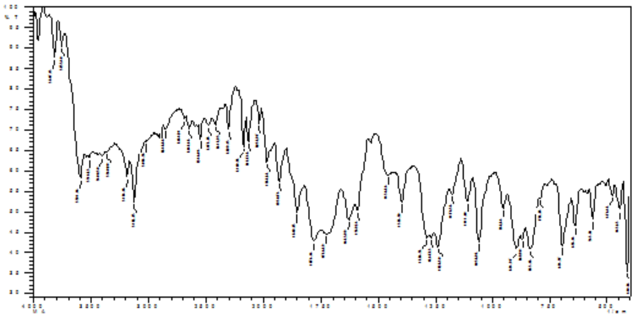
4. DISCUSSIONS

4.1. Compatibilizer LLDPE-g-MA

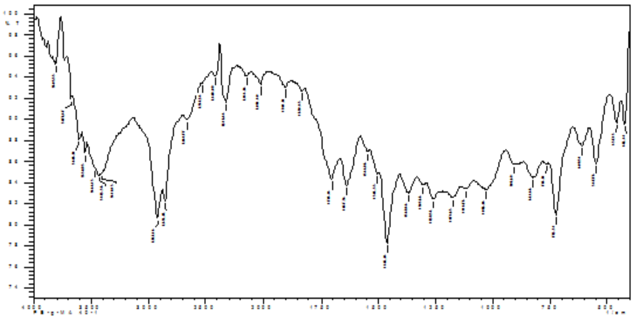
To find out the transplant or grafting of maleic anhydride (MA) into LLDPE, a test was conducted against the absorption of infrared waves by using FTIR. FTIR can identify functional groups formed on the sample. The application of infrared spectroscopy in the polymer research included qualitative aspects as the form of the determination of the structure of the sample was by observing the frequencies that are typical of functional groups FTIR spectra obtained by comparing the spectra of pure LLDPE and pure maleic anhydride with LLDPE-g-MA. This can be seen in Fig.1.



FTIR of LLDPE



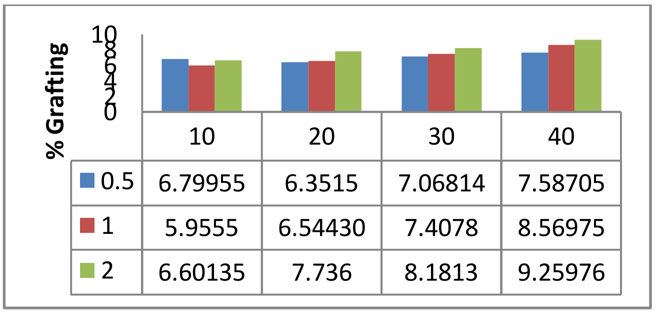
FTIR of PLA



FTIR of LLDPE-g-MA

Fig. 1. FTIR Graphic of LLDPE, MA and LLDPE-g-MA

In the image we can see new absorption bands which are a combination of the bonds between MA with LLDPE. This is evidenced by the appearance of the absorption peak wave number 2852.72 - 2922.16 cm-1, typical of CH2 and CH3 of LLDPE and the absorption peak at wave number 1830.45 cm-1, the absorption of the carbonyl group (C = O) of maleic anhydrous. Data% grafting of the process of making of LLDPE-g-MA with variable compositions of the MA and the amount of BP as can be seen in the Fig.2.



	10	20	30	40
🟦 0.5	6.79955	6.3515	7.06814	7.58705
🟥 1	5.9555	6.54430	7.4078	8.56975
🟩 2	6.60135	7.736	8.1813	9.25976

Fig. 2. Data% grafting of the process of making of LLDPE-g-MA

The research result indicated that the optimum compatibilizer for the process of making polymer composites is the composition of MA and BP respectively 40 and 2 phr with a percentage of grafting of 9.25976%

4.2. Composite LLDPE/PLA

4.2.1. Mechanical Property Test

The mechanical properties of composite LLDPE/PLA reviewed in this study are tensile strength and elongation at break. Fig.3 and 4 show the values of tensile strength and percentage of elongation of the LLDPE/PLA composite when compared to PLA and LLDPE. The results show that the higher the composition of LLDPE, the more the mechanical properties of the composite; on the contrary, PLA is very fragile or brittle as it consists of hydroxyl groups which tend to be amorphous with weak bonding interactions. It can clearly be seen in the respective values of tensile strength and elongation percentage of LLDPE and PLA, which are 21.42 and 1.56 MPa as well as 1251.19% and 2.94%. Kim (2004) and Djellali (2013) mention that the mechanical properties of polymer composites depend on the dispersion of the interphase adhesion bonding of each matrix and reinforcement. The adhesion bonds in question are chemical bond, physical bond or hydrogen bond that make up each matrix and reinforcement. As the adhesion bond of each matrix and reinforcement undergo dispersion there will be a transfer of tension (stress) of the matrix to the reinforcement or from reinforcement to the matrix, depending on the composition of the matrix and the reinforcement.

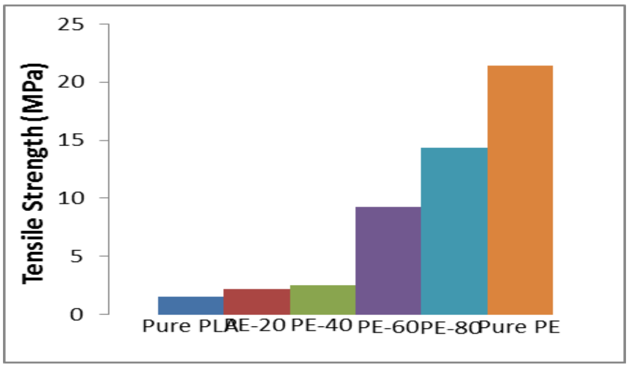


Fig. 3. Effects of LLDPE/PLA composition on tensile strength

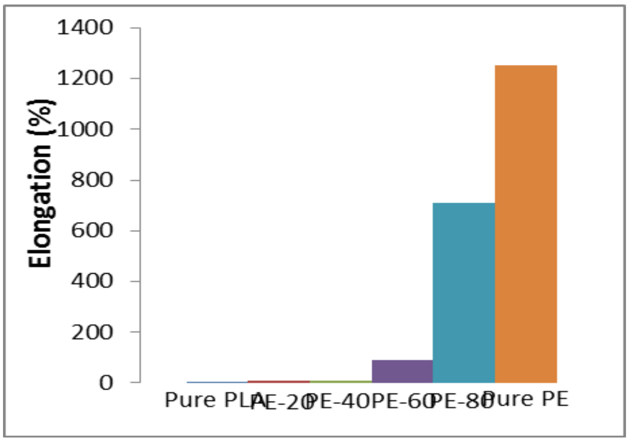
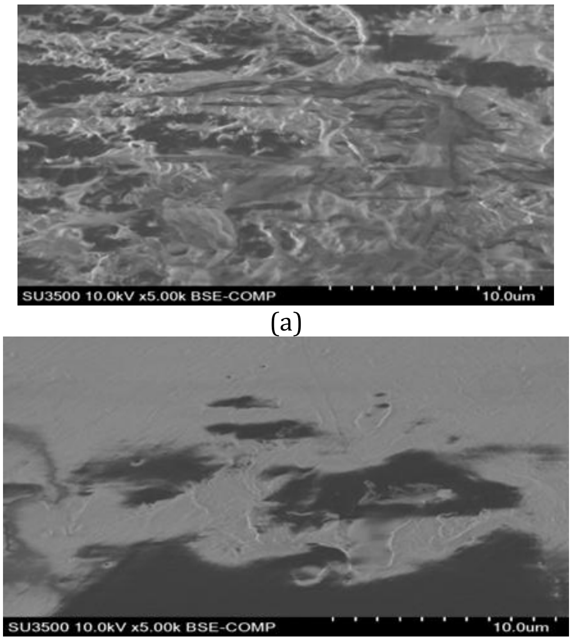


Fig. 4. Effects of LLDPE/PLA composition on percentage of elongation

4.2.2. *ScanningElectrone Microscope* (SEM) Test



(a)

(b)

Fig. 5. Results of SEM Test a.)LLDPE b.) LLDPE/PLA

Fig. 5 shows the results of morphological observations on the surface of the composite samples relative to the LLDPE. The surface of the LLDPE is regular and overlapping, indicating that the LLDPE has strong bonds, i.e. the molecules are closely arranged, regular and close together hence the interactions of attraction between each molecular bond becomes strong. The morphological observation results of the LLDPE/PLA composite show smooth surface but the mixture of LLDPE and PLA show a slightly uneven one. Nikazar (2005) has stated that the smooth surface of the composite indicates that the compatibilizer has increased the compatibility between synthetic polymers and natural polymers as well as stabilized the morphology of the mixing process. The compatibility that occurs between LLDPE and PLA has caused the mechanical properties of the composite to affect each other, depending on their respective composition. Parts of the composite surface whose mixture is slightly uneven is the result of the addition of compatibilizerthat is not evenly mixed hence no bond between LLDPE and PLA occurs.

4.2.3. *Thermal Gravimetric Analysis* (TGA) Test

Fig. 6 shows the TGA test results of composite samples relative to LLDPE. In the LLDPE samples, mass reduction occurred in 32.37 minutes at the temperature of 300°C. The mass reduction occurred as an initial process of thermal degradation of LLDPE. The process of degradation of LLDPE occurred rapidly as evidenced by a sharp decrease in the mass at a temperature of 300-500°C. Tiwari and Baldev (2015) have stated that at such temperature range, LLDPE experiences degradation as a result of the release of monomer ethylene.

The composite samples experienced twice (2) occurrences of sharp declines of sample mass at the temperature range of 250-350°C and 350-500°C. Al-itry et al (2012) mentions that the PLA components experiencing degradation at the temperature range of 250-350°C are carbon and ether bonds, also called trans-esterification mechanisms, which forms cyclic oligomers; meanwhile, at the range of 350-500°C, a termination of the main chains of carbonyl bond or the elimination reaction and thermo-oxidation occurred.

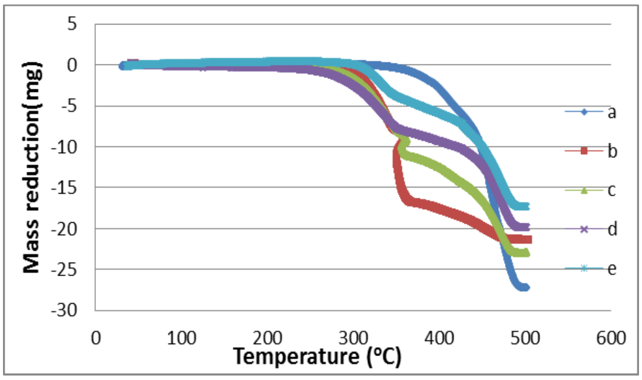


Fig. 6. Result of TGA Test a.) LLDPE b.) Composite 20/80 c.) Composite 40/60 d.) Composite 60/40 e.) Composite 80/20

TGA test results in this study showed the initial temperature of thermal degradation in the composite became lower as the PLA compositions decreased respectively by 301.6; 287.4; 267.4 and 301.2°C. Similar to the mechanical properties, the effect of the amount of LLDPE composition and PLA in the composites would determine the thermal properties of the composite samples. It is known that the melting point of PLA (200-220°C) is greater than the melting point of LLDPE (105-125°C) and thus the decrease of the number of PLA in the composites would make them degrade more quickly and hence it required no higher temperature to degrade. On a composite sample of PE-80 an increase in the temperature of thermal degradation occurred when compared with other compositions. This happened as the result of the uneven mixture in certain parts of PE-80 composite samples that has caused carbon and ether bonds in PLA, assumed to have degraded earlier, be trapped inside LLDPE without any occurrence of bonding.

4.2.4. Biodegradable Test

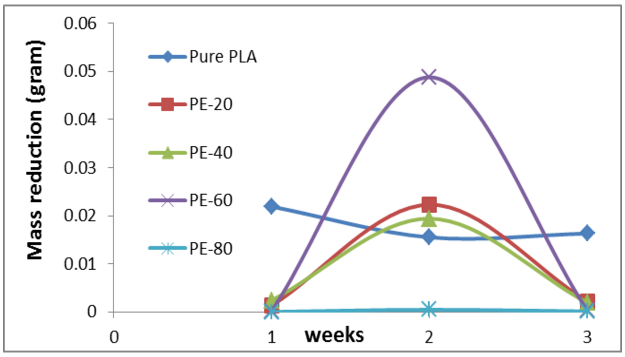
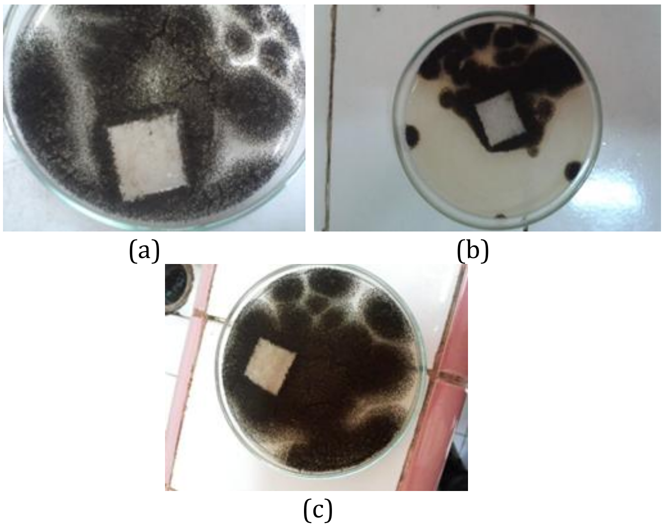


Fig. 7. Effects of the composition of LLDPE/PLA on the missing mass

To find out whether the LLDPE/PLA composite produced is an environmentally friendly plastic, biodegradable testing was conducted on the composite samples. Fig. 7 is the graph of the composite degraded every week relative to the PLA. In the figure above it can be seen that the greater the composition of LLDPE and the less the PLA, the smaller the mass of the composite loss, eaten by the fungi Aspergillus Niger. This is due to the molecular structure of the PLA in the form of short branching chains, making it easier for fungi to break these bonds for use as a substrate for their growth (Widyasari, 2010). The degradation process that occurred is as follows: the microorganism, in this case Aspergillus Niger, will produce enzymes capable of breaking down lactic acid into smaller segments with a lower molecular weight hence composite materials easily degraded in the environment (Nakamura et al, 2005). Results of lactic acid hydrolysis by enzymes would be used as a source of nutrients for microorganisms (Vinhas et al, 2007).

Fig. 7 above also shows that there is a fluctuation of reduction in the mass of the composite every week. It is assumed that the more time used for testing, the more the masses are reduced as a result of their being eaten by microorganisms; yet, irregularities occur in each sample. The biggest mass loss of each composite occurs during the second week. It happened because different initial treatments of PDA media and fungi inoculation were performed on the biodegradable tests on the first and third week as well as the second week. The different initial treatments produced different fungal growths in each sample. It is shown in Figure 8 where, in the second week, in the container, there was no increase of number of microorganisms when compared with the results of the first and third weeks.



(a) (b)

(c)

Fig. 8. Biodegradable Testing of composite sample 60/40 a.) Week 1 b.) Week 2 c.) Week 3

From the results of the tests it is proved that the biodegradable composite LLDPE/PLA can be used as an environmentally friendly plastic polybag because it can be degraded by microorganisms when compared to that of LLDPE

5. CONCLUSION

- The Optimum compatibilizer for polymer composites processing is the composition of MA and BP, by 40 and 2 phr respectively with the grafting percentage of 9.25976%.
- The best result of the mechanical property test is the composite of 80/20 with a value of tensile strength and elongation break of 14.3 MPa and 708.36%.

The composite LLDPE/PLA explains that the composite has better characteristics than the PLA mechanical properties and the biodegradable properties and thermal degradation of LLDPE. The 80/20 composite results indicate the best mechanical properties, thermal degradation and biodegradable properties plastics to be applied as polybag plastics due to its good resistance and environmentally friendly characteristics according to the standards for polybag plastic manufacture

6. ACKNOWLLEDGEMENT

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