Evaluation the Degree of Grafting on OPMF , SiO_2 Biocomposite

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Abstract **- Linear low density polyethylene (LLDPE) is a type of polymer was blended with filler SiO_2 at a ratio 95:5 , 90:10 and 85:15 by extrusion to study the degree of grafting of the product and compared it with other journal. The maleic anhydride (MA) was grafted into LLDPE-SiO_2 to determine the possible reaction. The LLDPE-g-MA composite filled with SiO_2 were extruded and melt-pressed in order to prepared samples for evaluating the degree of grafting (DOG) and Fourier-Transform Infrared Spectroscopy (FTIR) testing. The FTIR showed the interaction between LLDPE-g-MA and SiO_2 and it also will affect the mechanical strength. The FTIR testing for sample before and after purification were done. The result show that there are stretching vibrations Si-O-Si show for all sample. The DOG % is increasing when SiO_2 ratio is increasing.**

Keywords**:** Linear low density polyethylene, silicon dioxide, maleic anhydride, extrusion, degree of grafting, FTIR testing

I. INTRODUCTION

Natural fibre is a kind of hair like raw material that can be directly obtained from an animals, vegetables, or mineral sources. The fibre is converted into nonwoven fabrics such as felt or paper or, after spinning into yarns and into woven cloth. Although nature abounds in fibrous materials, especially cellulosic types such as cotton, wood, grains, and straw only small number can be used for textile products or other industrial purposes. In economic considerations, fibre is useful for commercial purposes is determined by such properties as length, strength, pliability, elasticity, abrasion resistance, absorbency, and various surface properties. Other than that, they are in elastic condition which can stretch when tension is apply. Then, they will partially or completely return to their original shape or length when the tension is released. They also are getting attention from researchers to utilize in polymer composites due to their eco-friendly nature and sustainability. The interest or an idea for the natural fibres as reinforcing material in composites primary have get an attention the past decades ago due to environmental concerns and also awareness of limiting petroleum resources to produce petroleum-based synthetic polymers. Additionally, it is related to adding value to agricultural products and solve environmental problems rise from agricultural products residue. Linear low desity polyethylene (LLDPE) is one of the thermoplastic polymer that easily manufactured and frequently used for thin sheets as it has greater elasticity than other types of polyethylene [11]. This polymer has same issue like other polymer thermoplastics which is difficulty in natural degradation. Filling the polymer with natural fibres is considered one of the solutions to improve its biodegradability. The modification of polymers is very importance as it can alter its properties. Among the methods of modification of polymers, grafting is one of the promising methods. Due to high demand and wide applications of polymers in many areas, modification of the polymers is gaining growing attention. The modification was also done to make the polymers more environmental approachable. Grafting is a method wherein monomers are covalently bonded (modified) onto the polymer chain.[16]

Oil palm mesocarp fibre (OPMF) is one of the potential natural fibres that can be used in bio-composites production. These fibres are lignocellulosic excess left over in the palm oil mill. There are 5.74 million hectares of palm oil were plant in Malaysia. It makes Malaysia become one of the country that has largest palm oil producing countries in the world [6]. There is 14 % of fibre content in palm fruit while 78% to 82% of the fruits is mainly biomass and moisture. From the data get by researching, the amount of oil palm biomass is expected to grow with increasing world demand for palm oil. The mesocarp fibre is only used purposely for as boiler fuel and potassium fertilizers preparation[8]. These usage produce a waste materials that create environmental problems when left on the plantation floor (S, Sreekala. G.Kumaran. & Thomas.1997). Since the demand of edible oil is expected to increase, there is expected that the amount of mesocarp fibre to grow beyond sufficient for boiler capacity. Therefore, utilization of these fibres as natural fibre reinforcement in composites is beneficial in creating biodegradable composites as well as high potential to reduce environmental problem of oil palm biomass.

II. METHODOLOGY

2.1 Materials

Linear low density polyethylene (LLDPE) was obtained in powder form from R&M Chemicals that was used directly as the raw material for this study. Silicon dioxide (SiO2) that was obtained from R&M Chemicals. It is chemically pure and has molecular weight of 60.08g/mole. Maleic anhydride that was obtained from Merck KGsA with molecular weight of 98.02g/mole and it will be grafted with LLDPE-SiO2.Dicumyl Peroxide with molecular weight of 270.37g/mole that was obtained from R&M Chemicals and it was used as an initiator.

2.2 *Synthesis of LLDPE composites:*

The total of weight of sample of mixture of LLDPE, peroxide, maleic anhydride and silicon dioxide is 100g. The function of peroxide is as initiator because of its effectiveness to introduce long chain branches in LLDPE. The mixture will be pre mixed in

the blender. Next, the mixture will be extruded on a Thermo HAAKEE twin-screw extruding machine at speed screw 20rpm and temperature 170°C. The mixture that have been extruded were melt-pressed onto 1mm thick sheets at 170°C for 10 minutes. The biocomposite of LLDPE-g-MA/SiO2 was prepared in three different weight percent (wt%) which are (93,2,4,1), (91,4,4,1) and (89,6,4,1) that represent weight percent of LLDPE, SiO2, peroxide and maleic anhydride respectively. This study is trying to mimic the contain of SiO2 in oil palm mesocarp fiber (OPMF). A study by S. Shinoj, OPMF has content about 1.8 wt% of SiO_2.

Table 2.1: Formulation of all sample of LLDPE-g-MA/SiO2

Sample	Weight percent (%)			
	LLDPE	SiO_2	Peroxide	MA
1	85	15	4	1
2	90	10	4	1
3	95	05	4	1

2.3 LLDPE composite characterization

Fourier transform infrared (FTIR) spectroscopy is a form of vibrational spectroscopy that is useful in the study of a variety of soil chemical processes. In the mid-infrared (mid-IR) range, vibrations arise from many environmentally important molecules such as organic acids, soil organic matter, mineral phases, and oxyanions. It is possible to utilize FTIR spectroscopy as a quantitative analytical method and also as a tool to determine bonding mechanisms in solids and on surfaces.

The FTIR spectroscopy will scan the sample of LLDPE-SiO2-g-MAH in a range of 400cm-1 to 4000cm-1. Parkin Elmer model was used in fort this study. The data will be collected and converted from interference pattern into a spectrum. Firstly, the plate of FTIR spectroscopy is wiped to remove the impurities and then the powder of LLDPE-SiO2-g-MAH will be placed on the plate. After that, characterization process was conducted.

2.4 Degree of grafting

2.4.1 Reaction product purification

Before titration process, it is prior to do purification process to remove any unreacted monomer from the sample taken. The procedures are as below:

1. 10 grams of raw samples were taken
2. The samples were boiled with xylene and precipitated with acetone subsequently.
3. The precipitated was filtrate using filter paper.
4. The precipitated was wash repeatedly using acetone.
5. Lastly, the sample was dried in under vacuum at 60 ^{0}C.

2/4.2 Chemical titration

Chemical titration of the polymer was done to measure the degree of grafting as well as the % monomer reacted [4]. The procedures are as below:

1. One gram of polymer was dissolved in boiling xylene. Then a few drops of water were added.
2. 10 ml of 0.05 M KOH methanol was added to the solution.
3. A drop 1% of phenolphthalein is added as indicator.
4. The solution was titrated with 0.03 M trichloroaceticacid solution in xylene.
5. The titration was stopped immediately when the colour remain constant for 30 seconds.

After titration are done for all the sample, the calculation for degree of grafting are as below:

- 5 x 10^(-4) gmol KOH was present initially as ,a
- Acid volume, b(L) x [acid ,c] (g mol/L)= g mol acid, d
- g mol acid, d = g mol KOH reacted, e
- Mol of Si02 onto PE= (a - e /2)(mol)
- Degree of grafting = (% Grafting =[(WG-Wi)/Wi] x 100

III. RESULTS AND DISCUSSION

3.1 Characterization of LLDPE sample

Figure 3.1 shows the results of functional group analysis for all three samples of LLDPE-g-MA/SiO2. The figure 3.1 shows the FTIR spectra for all sample before and after purification. Figure 3.1.1 showed the spectra for sample 1 before purification. There are peak at 3749 cm -1 show O-H stretching absorbance [1]. The 1738.81 cm-1 are peak in sample 1 represent a stretch and strong carbon group, (C=O) [1]. At 1366.14 cm-1 appeared due to Si-CH_3 vibrations.[13] At 1216 cm-1 is peak due to C-O-C stretching vibrations. Figure 3.1.2 shows a FTIR spectra for sample 1 after purification, 2915.74 cm-1, 2848.45 cm-1 is the presence of two new peaks indicates the presence of aliphatic chain from LLDPE [7].

Figure 3.1.3 and figure 3.1.4 show a FTIR spectra for sample 2 before and after purification respectively. Figure 3.1.3 show peak 2916.2 cm-1 and 2848.89 cm-. The peak at around 2900 cm^{-1} indicates the presence of C-H stretching that indicates strong alkane group [13]. 1735.07 cm-1 show the C=O stretching vibrations. 1466.53 cm-1 and 1376.12 cm-1 appeared due to C=C vibrations[8],1096.95 cm-1 is the wave number range 1000 cm-1 to 1100 cm-1 indicates SiO_2 connected with stretching vibrations of bridging oxygen atoms[13] , 804.6 cm-1 are attributed to symmetric stretching vibrations of Si-O-Si [15] and 718.67 cm-1 were due to stretching CH_2CH_2 and also provide evidence of grafting [13]. For peak after purification as show in figure 3.1.4, the peak 1541.25 cm-1 presence the stretch aromatic. The other peak was same as peak before purification.

Figure 3.1.5 and figure 3.1.6 showed a FTIR spectra for sample 3 before and after purification. Figure 3.1.5 shows a peak 2915.95 cm-1 and 2848.59 cm-1 indicates the presence of aliphatic chain from LLDPE,[7 1734.65 cm-1 show the C=O stretching vibrations, 1541.41 cm-1 presence the stretch aromatic, 1464.7 cm-1 presence of C=C, 1089.7 cm-1 is the wave number range 1000 cm-1 to 1100 cm-1 indicates SiO_2 connected with stretching vibrations of bridging oxygen atoms, 718.74 cm-1 presence the Si-CH_3 bond [15]. Sample 3 after purification has change the peak at 1541.41 cm-1 and appeared the peak at 1376.83 cm-1. The rest peak was remained same as before purification. The peak show the C=C bending vibrations [8]

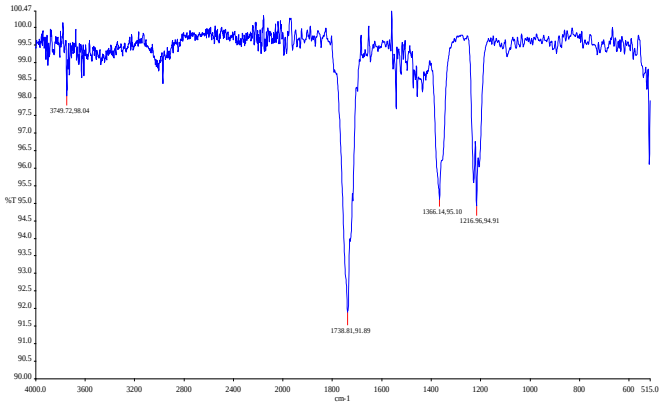

Figure 3.1.1 sample 1(95:5) LLDPE-g-MA/SiO_2

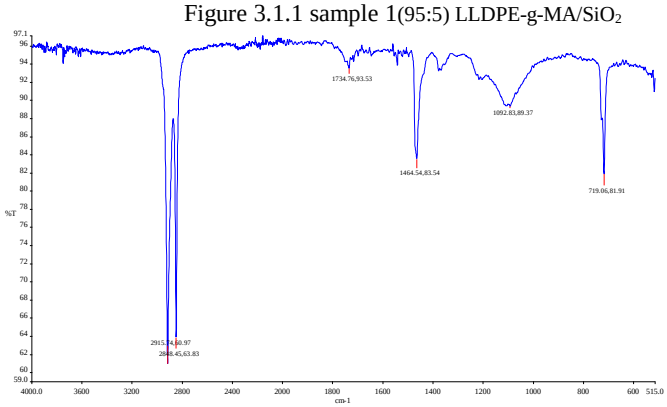

Figure 3.1.2 sample 1 after purification (95:5)LLDPE-g-MA/SiO_2

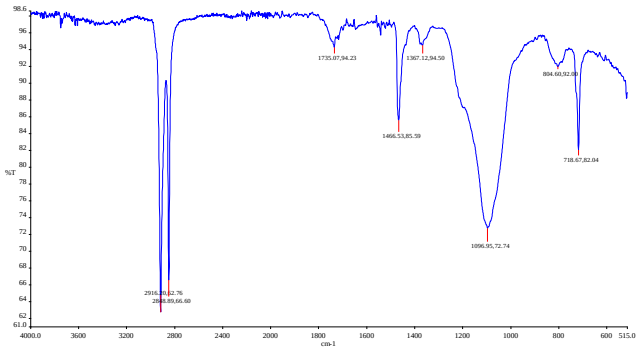

Figure 3.1.3: sample 2 (90:10) LLDPE-g-MA/SiO_2

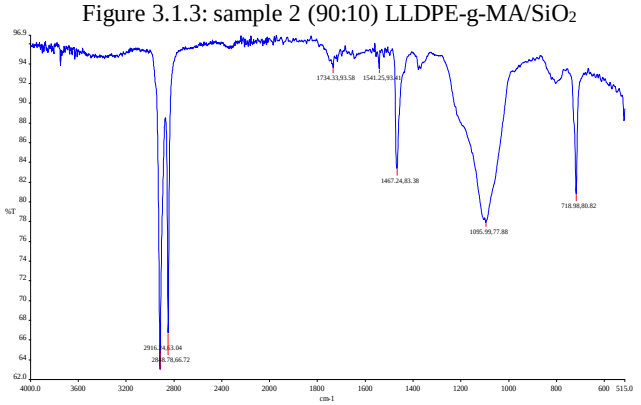

Figure 3.1.4:Sample 2 after purify cation (90:10)LLDPE-g-MA/SiO_2

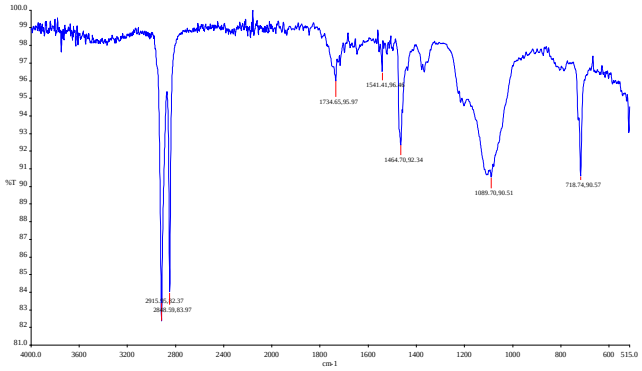

Figure 3.1.5: Sample 3 (85:15) LLDPE-g-MA/SiO_2

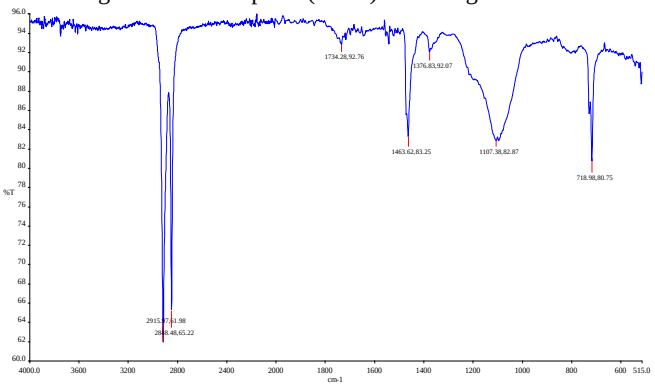

Figure 3.1.6: Sample 3 after purification (85:15) LLDPE-g-MA/SiO_2

3.2 Degree of grafting

From figure 3.3 showed the effect of amount of SiO_2 (%) used in each sample to the degree of grafting (%). Titration is done by using the 3 sample with a different ratio which is 95:05, 90:10, 85:15 for sample 1, sample 2 and sample 3 respectively. Before titrate, the sample is done a purification by using solvent xylene. The ratio 1:100 for sample to solvent is used. The purposed of purification is to remove any unreacted monomer in the sample In this experiment, the 3 grams of samples and 300 ml of xylene is used for every sample. The sample was poured into the beaker with solvent with temperature 150 ^oC. This is purposely to dissolved the polymer with the solvent. After dissolving done, acetone was added excessively directly after heating to form a solid precipitate. The precipitate was filter by using filter paper WHATMAN No1. The filtration is purposely to separate the precipitate and the solvent. The precipitate was put into the vacuum oven for 12 hours. This is purposely to remove the remaining solvent in the precipitate. The sample is ready to be used for titration experiment when the weight is constant. It is important to make sure that the weight of the samples from the purification process is constant to ensure there is no impurities exist. Chemical titration of the polymer was done to measure the degree of grafting as well as the % monomer reacted. One gram of the sample after purification was used for titration experiment.

From the experiment, it is showed that the sample 1 has higher degree of grafting which is 2.102% compare to sample and sample 3 which is 1.532% and 0.676 % respectively. The higher the SiO_2 % grafting with LLDPE the higher the degree of grafting. A study by N.C Defader stated that the increasing concentration of monomer will increasing the tensile strength. The increase in tensile strength of grafted sample films may be due to cross-linking between the sample molecules and grafting monomer on to sample cause by the action of radiation [2]. Also stated by Richard Espiritu, increasing the concentration of monomer produced a marked increase in degree of grafting (DOG). It can be also observed that an increase in the total gamma radiation dose results in increase in the DOG of the membranes. This is due to the fact that more high energy radiation is supplied to cause the

formation of active sites for a monomer to tether to the polyethylene backbone.[3] It is can be related to this experiment where by increasing the percentage of SiO_2 to the LLDPE will affects to DOG value of the biocomposite. This experiment is also related to the emulsion polymerization rate and conversion rate a study by Cheng Wu Li. He stated that this study is to determine the polymerization rate too fast or too slow and the conversion rate to measure degree of polymerization rate. Based on his result, the effect of dosage of SiO_2 on polymerization rate is increasing with increasing dosage [1]. Thus, the degree of grafting will increase when the dosage of SiO_2 is increasing is acc

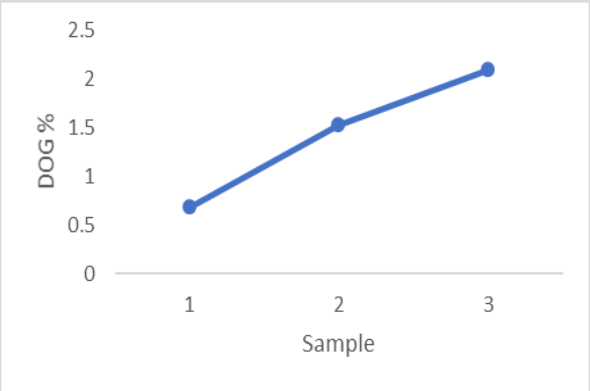

Fig 3.2: Degree of grafting of LLDPE-g-MA/SiO_2 composite with SiO_2 content.

IV. CONCLUSION

A very low grafting degree cannot be effective enough for modification of polymer materials, while a very high grafting degree can decrease some properties and increase the cost. The grafting degree is also the basis parameter for surface properties and structure analysis. Therefore, an accurately measured grafting degree may be the most important parameter for chemical modification of polymer materials in theory and practical. The increase % DOG when the amount of SiO_2 increase because more available reaction site with the monomer. In this experiment, the amount of Peroxide and Maleic Anhydrate is keep constant Thus, from this experiment, the result is accurate base from previous study. The degree of grafting is increasing as the percentage of silicon dioxide is increasing.

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References

[1] Wu, C. (2005). Improving Polylactide / Starch Biocomposites by Grafting Polylactide with Acrylic Acid – Characterization and Biodegradability Assessment, 352–361. https://doi.org/10.1002/mabi.200400159

[2] Dafader, N. C. (2003). Effect of Monomer Concentration on the Degree of Grafting and Mechanical Properties of Grafted Rubber Film.

[3] Espiritu, R., Mamlouk, M., & Scott, K. (2015). ScienceDirect Study on the effect of the degree of grafting on the performance of polyethylene-based anion exchange membrane for fuel cell application. *International Journal of Hydrogen Energy*, *41*(2), 1120–1133. https://doi.org/10.1016/j.ijhydene.2015.10.108

[4] Hasanah, Z., Ninaya, A., Ain, Z., & Hamid, A. (2015). Grafting of poly (lactic acid) with maleic anhydride using supercritical carbon dioxide Grafting of poly (lactic acid) with maleic anhydride using supercritical carbon dioxide. https://doi.org/10.1088/1757-899X/87/1/012066

[5] Lei, J., Li, Q., & He, G. (2006). Polymer-Plastics Technology and Engineering Accuracy measurement of grafting degree of radiation-

[6] Then, Y. Y., Ibrahim, N. A., Zainuddin, N., Ariffin, H., Zin, W., & Yunus, W. (2013). Oil Palm Mesocarp Fiber as New Lignocellulosic Material for Fabrication of Polymer / Fiber Biocomposites, *2013*.

[7] Teh, C. C., & Ibrahim, N. A. (2013). com Response Surface Methodology for the Optimization and Characterization of Oil Palm Mesocarp Fiber-graft- Poly(butyl acrylate), *8*, 5244–5260.

[8] Birnin-yauri, A. U., Ibrahim, N. A., & Zainuddin, N. (n.d.). Effect of Maleic Anhydride-Modified Poly (lactic acid) on the Properties of Its Hybrid Fiber Biocomposites, 1–16. https://doi.org/10.3390/polym9050165

[9] Yang, Y. U., Ming, Y. U., Jingye, L. I., & Bo, D. (2011). Determining the degree of grafting for poly (vinylidene fluoride) graft-copolymers using fluorine elemental analysis, *22*, 25–29.

[10] Liu, W., Liu, T., Liu, T., Liu, T., Xin, J., Hiscox, W. C., … Zhang, J. (2017). Improving Grafting E ffi ciency of Dicarboxylic Anhydride Monomer on Polylactic Acid by Manipulating Monomer Structure and Using Comonomer and Reducing Agent. https://doi.org/10.1021/acs.iecr.6b05051

[11] *Compounding and Mechanical Properties of Biodegradable Hemp Fibre Composites*, 1307–1316. Retrieved from www.elsevier.com/locate/compscitech

[12] Ahn, Y., Jeon, J. H., Baek, C. S., Yu, Y. H., Thenepalli, T., Ahn, J. W., … Resources, M. (2016). Communication Synthesis and Non-Isothermal Crystallization Behaviors of Maleic Anhydride onto High Density Polyethylene, *53*(1), 24–33.

[13] Ahmad, A., & Al-malaika, S. (n.d.). Rubber in the Presence of Comonomer, *13*(4), 218–239.

[14] Barrios, V. A. E. (2014). FTIR – An Essential Characterization Technique for Polymeric Materials, (October). https://doi.org/10.5772/36044

[15] Gao, L., Iv, C. W. S., & Smith, M. (2013). Elastomeric microparticles for acoustic mediated bioseparations. https://doi.org/10.1186/1477-3155-11-22

[16] Hanipah. S.H (2008), a process for Melt Grafting Itaconic Anhydrate Onto Polyethylene, 1994