Evaluation of Viscoelastic Properties of OPMF Biocomposites

Muhamad Afiq bin Abd Hamid, Dr Suhaiza Hanim Hanipah,

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*—This work investigate the mechanical and viscoelastic behaviour of oil plam mesocarp fiber (OPMF) reinforced linear low density polyethylene (LLDPE) biocomposites after chemical modification which is grafting copolymerization on the biocomposites. The OPMF was grafting copolymerization with different loading of oil palm mesocarp fiber (OPMF) by using maleic anhydride (MAH) as monomers (10%, 20%, 30%, 40%, 50% and 60% of OPMF). The OPMF-LLDPE bicomposites mixed and melt-blended in an extruder in order to prepared samples from characterization and mechanical properties test. For the tensile test showed that at loading 50% of OPMF the maximum amount of tensile stress can be can be loaded. Next for the stress relaxation test showed that the higher relaxation rate at the loading of OPMF is 40% content that means the stress relaxation is becomes the fastest. Besides, the cyclic test showed as increasing the loading of OPMF after grafting polymerization process shows that the biocomposites become more elastic behaviour. From this study, it was found that the grafting copolymerization on the OMPF-LLDPE biocomposites can increase the viscoelastic behaviour.**

Keywords*— Cyclic test, Grafting copolymerization, Linear low density polyethylene (LLDPE), Oil Palm Mesocarp Fiber (OPMF) and Stress relaxation test

I. Introduction

Oil palm mesocarp fibers (OPMF) are residue obtained from the production of oil palm, which are normally utilized for bio-composites (Shinoj et al., 2011) or bio-compost (Md Yunos et al., 2012) application. The effect of existence of a silica bodies and wax layer that are implanted on the surface of oil palm biomass are will be occur that the several of application of OPMF become hindered (Omar et al., 2014a,b). The contact between the fibers and matrix will be decreases if the present of silica bodies and wax layer on the fiber, so that, it will disturbing the fiber achievement in biocomposites applications (Shalwan & Yousif, 2013). Apart from that, lignocellulosic content of the fiber also critically affected to the bioconversion. For instance lignin decreases the hydrolysis rate by acting as a physical barrier, which hiders the cellulosic availability to the enzymes (Chaturvedi & Verma, 2013). Lignicellulosic materials also have lack of good interfacial adhesion and poor resistanve to moisture adsorption render the use of lignocellulosic filled-composites less attractive. These problems can be improved to some extent by treating the lignocellulosic fibres with right chemicals (Rozman et al., 2003).

The physical and chemical structure of the fibers can be change by using pre-treatment which are contain various method that can be apply to the fiber. These treatments are helpful for the fibers used in various applications as the filler agent or as the main structural component. These problems can be alleviated to some extent by treating the lignocellulosic fibres with suitable chemicals. Various chemicals modification has been employed to enhance the compatibility between the constituent materials. In this research, grafting copolymerization method is effective method for chemical modification. The free radicals of the cellulose molecule are introduced in the grafting copolymerization reaction. The cellulose is treated with an aqueous solution with selected ions and is exposed to a high energy radiation. Then the cellulose molecule cracks and radicals are formed. Next the radical sites of the cellulose are treated with a suitable solution which is compatible with the polymer matrix (Bledzki, 1999). Monomers that have been used for grafting onto polyolefin include maleic anhydride (MAH), citraconic anhydride, itaconic anhydride and itaconic acid. However, in this research, maleic anhydride has been chosen as a monomer. The function of the grafting copolymerization is to increase the efficient for improving the compatibility between polymeric matrices and natural fibers are by grafting of anhydride onto polymers. The result of reaction between maleic anhydride groups with hydroxyl groups on the surface of cellulosic fibers can be reduced hydrophilic behavior of the fibers.

The purposes of this research are to study the effect of grafting maleic anhydride onto linear low density polyethylene (LLDPE) with different loading of OPMF in the mechanical behaviour. Next, in this research also determine the behaviour of OPMF whether in viscoelastic or viscoplastic properties. The stiffer stress-strain curves under higher strain rates and a decay of stress under constant stain tensile/compression tests are refer to the viscoelastic.

II. METHODOLOGY

A. Preparation of fibers

Oil palm mesocarp fibers were obtained from Besout Palm Oil Mill (Sungkai, Perak, Malaysia). The palm species used was Elaeis guineensis Jacq. The samples were then kept in a controlled environmental condition of -20°C to avoid fungus growth. OPMF was prepared by washing with detergent and water to remove the remaining oil still present to improve good adhesion with the LLDPE (Olusunmade et al., 2016). After washing, the fibers were dried in a Universal Oven at 105°C for 24 hours (Hanipah et al., 2016). The dried fibers were then grinded by Cutting Mill SM100, sieved into 1000µm, and stored in a sealed plastic bag for biocomposites fabrication.

B. Grafting copolymerization

The process of grafting copolymerization was performed through extrusion as described by Krivoguz, Gulyev, and Pesetskii

(2010) with significant deviation as their study was focused on grafting LDPE and mLLDPE while this study is focusing grafting on the mixture of LLDPE and oil palm mesocarp fiber. The process was conducted in the twin-screw extruder with the reaction zone temperature in the extruder was at 170°C. Prior to running the extruder, the amount of fiber and LLDE, was weighed first according to the formulation follows by pre-mixing as shown in Table 1 below for a total weight of 80 g. For the amount of Anhydride are 5% from the weight of LLDPE while the amount of peroxide is 2% from the weight of Anhydride.

Table 1: The formulation of OPMF-LLDPE by using the Maleic Anhydride as a monomer with 5% WT from the weight of LLDPE

Sample	OPMF (WT %)	LLDPE (WT %)	Peroxide (WT %)	MAH (WT %)
1	10	90	2	5
2	20	80		
3	30	70		
4	40	60		
5	50	50		
6	60	40		

C. Biocomposite preparation

The materials were mixed and melt-blended in a twin-screw extruder model HAAKETM Rheomax CTW 100 OS at 170°C and a screw speed of 20 rpm. The extruded strand was pelletized. Extruded pellets were compressed into 3 mm thick film by Hydraulic Hot Forming Press Machine QC-602A (Cometech Testing Machine Co., Ltd.) at 170°C under pressure of 2000 psi with residence time at 20 minutes.

D. Mechanical tests

Mechanical tests were conducted by using a Texture Analyzer which is model TA-XT, Stable Micro Systems Ltd. This machine used at a controlled ambient temperature. The fibers' diameter measurements were performed using an optical microscope which is model Dino-Lite AM 4223 series. The diameter were measured at three different locations before the values were averaged (Omar et al., 2014a).

The stress relaxation test was conducted by stretching the fiber to a required strain, with the strain being held constant for a period of time while the stress decay was calculated (Xiang et al., 2015). Stress relaxation is accepted test methods for predicting the long-term mechanical performance of the composites. The true stress, from the experiment results are calculated by as: $\sigma = (F/A)(l/l_o)$, where F is the force, A is the surface area of the sample and l and l_o are the deformed and undeformed height of the sample (in mm), respectively. The true strain was obtained or calculated by using the equation $\varepsilon = \ln(l/l_o)$ (Mohammed et al., 2018).

True stress and true strain are used for accurate definition of plastic behavior of ductile materials by considering the actual (instantaneous) dimensions. True stress is the stress determined by the instantaneous load acting on the instantaneous cross-sectional area whiles the true stains are the rate of instantaneous increase in the instantaneous gauge length (*True Stress (σ T)*, n.d.).

True stress-true strain curves are often known as flow curves, which symbolize basic plastic flow characteristic of the material. The flow curve is often used to define two parameters characteristic of the material which are the strain hardening exponent and the coefficient of the strength of the material.

III. RESULTS AND DISCUSSION

A. The effects of tensile test result by grafting copolymerization with different loading of OPMF

From the result at Figure 1, it show that result of tensile result. At 50% wt loading of OPMF, the true stress reach 3.5 MPa which is means this biocomposites have the maximum amount of tensile stress can be can be loaded almost until 3.5MPa before it failure. The loading of OPMF at 10% until 30% were increasing the value of true stress or tensile stress while the loading of OPMF at 40% were drop but the loading at 50% of OPMF were increasing as the highest value of tensile stress. The value of true stress at loading 60% of OPMF was drop.

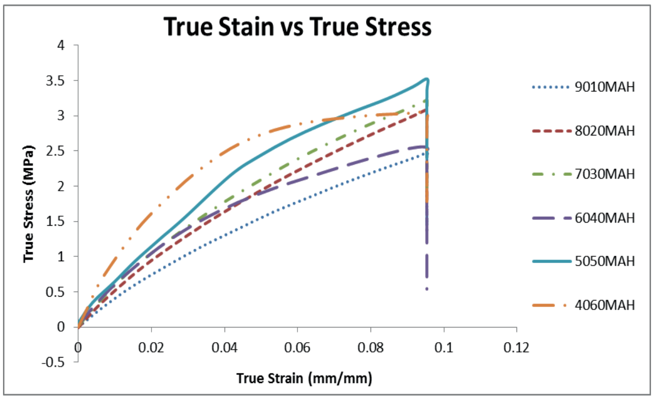

Figure 1: A typical stress-stain curve with various content of OPMF

So that, it shows that as increasing the loading of OPMF after the grafting copolymerization process, the tensile strength of OPMF-LLDPE biocomposites were increasing. The factor of the loading of OPMF at 40% and 60% are drop because stress may lead to failure process are slipping out of fibrils, disruption of the chemical structure and other else (Sreekala et al.,2001). Khalid et al 2018 done the study on tensile of OPM-PP. In their findings the tensile strength is reduce as the loading increase. The reducing of tensile strength is due to interruption caused by the fiber in transferring the stress along applied force due to lack of interfacial adhesion of the fiber and the matrix (Khalid et al.,2008).

Figure 2 depict the strain-strain curve the result of tensile test the 50% wt loading of OPMF biocomposites. This stress strain curve can be divided into 3 boundaries which are elastic, plastic and fracture regions where the approximate boundaries between the regions are highlighted. In the first region where strain was less than 0.044, in this region recommended that no or damage happens within the microstructure of the fiber when deformed under small deformation. However, for strain beyond 0.044 is the plastic region, it is likely that damages within the fiber caused deviation from the elastic line. Omar et al. (2014), through numerical work, suggested that region is related to the debonding of the silica-body and OPEFB fiber interface (Omar et al., 2014a). Finally, the sudden drop of stress at the fracture region observed complete failure of the fiber.

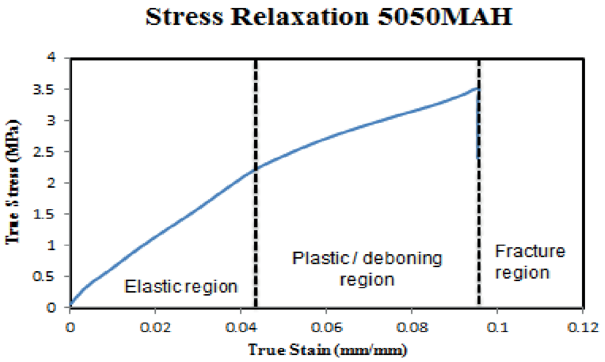

Figure 2: True Stress (MPa) vs True Strain (mm/mm) for the 5050MAH

B. *The effects of stress relaxation test result by grafting copolymerization with different loading of OPMF*

Figure 3 shows curve of relaxation behaviour of the composites having different loading of OPMF. The shapes of the entire curve are observed similar trend to the every each other with the presence of different loading of the fiber in between matrix layers. It shows that, the viscoelastic behaviour is evidenced from relaxation test result at all loading of OPMF as presented by the steady decrease of stress at the constant strain over time. Hanipah et 2017 have shown the similar observation from in their study of stress relaxation test of OPMF (Hanipah et al., 2017).

The rate-dependent behaviour at the loading of OPMF from 10% to 30% were found that become more stiffer stress-strain curves and stress relaxation become more slower so that mean the relaxation rate of composites become more decreasing. While the loading of OPMF at 40% was show the stress-strain curve become less stiff and stress relaxation is becomes the fastest, so that, the relaxation rate of composites become more increasing. Next, followed the loading of OPMF at 50% was show the stress-strain curve are the most stiff and stress relaxation is becomes the slowest, so that, the relaxation rate of composites become more decreasing. Finally, the loading of OPMF at 60% was found that the stress relaxation become faster than the loading of OPMF at 50% and it also same like the stress relaxation for loading of OPMF at 20%.

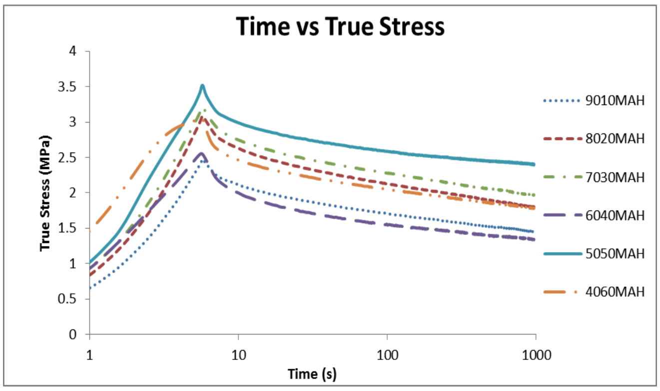

Figure 3: True Stress (MPa) vs Log Time (s) with various loading of OPMF

So that, from the result and observation of stress relaxation, it was found that the higher relaxation rate at the loading of OPMF is 40% content while the lowest relaxation rate at the loading of OPMF is 50% content. It shows that by grafting copolymerization process, the relaxation rate become high and stress relaxation are become fast when the loading of OPMF are increasing. Sreekala et al., studied about the effect of the treatment of fiber toward the stress relaxation, so that, the findings are alkali treatment decreased the relaxation rate of Oil Palm Fiber-Phenol Formaldehyde composites due to strong interfacial interlocking between fiber and matrix (Sreekala et al., 2001).

C. *The effects of cyclic test result by grafting copolymerization with different loading of OPMF*

The Figure 4 below shows the result of the cyclic test for each loading of OPMF after grafting copolymerization process. While The Figure 5, show the result of loading-unloading test with different loading of OPMF. From the result in Figure 5 show that, the loading of OPMF in 20%, 30% and 50% can loading the stress more than 7MPa while the rest of loading of OPMF like 10%, 40% and 60% can be loading the stress are less than 6MPa.

For the loading of OPMF at 50% in the Figure 5 (e) are show the value of elastic strain is 0.2602mm/mm while the value of plastic strain is 0.0122mm/mm and this loading of fiber can be load the stress around 7.4MPa, so that, it shows that in this loading of fiber are more in elastic behaviour than plastic behaviour.

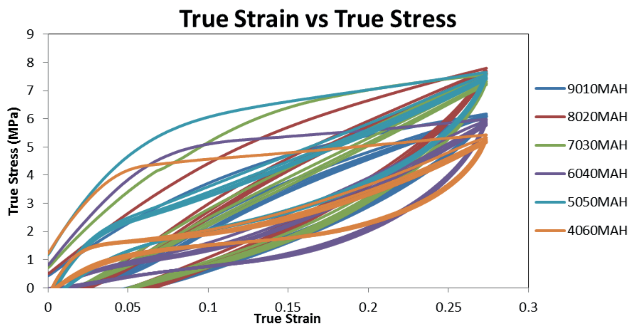

Figure 4: True Strain (MPa) vs True Stress (mm/mm) with various loading of OPMF.

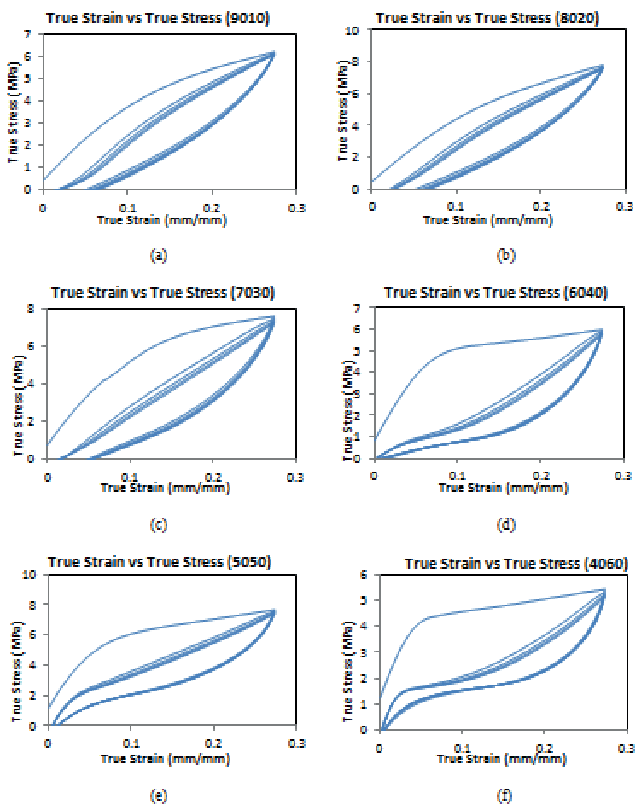

Figure 5: The result of cyclic test for each loading of OPMF; (a) 10% of the OPMF, (b) 20% of the OPMF, (c) 30% of the OPMF, (d) 40% of the OPMF, (e) 50% of the OPMF and (f) 60% of the OPMF.

From the overall result of loading-unloading test or cyclic test shows in the Table 2 below that as increasing the loading of OPMF after grafting polymerization process shows that the biocomposites become more elastic behaviour because the value of elastic strain was increasing as the loading of OPMF increasing.

Table 2: The value of elastic strain, plastic strain and stress loaded for each loading of OPMF

Loading of OPMF	Elastic Strain (mm/mm)	Plastic Strain (mm/mm)	Stress Loaded (MPa)
10%	0.2103	0.0617	6
20%	0.2031	0.0686	7.5
30%	0.2168	0.0561	7.3
40%	0.2594	0.0131	5.7
50%	0.2602	0.0122	7.4
60%	0.2626	0.0053	5.3

IV. CONCLUSION

From this study, the objectives were successfully achieved based on the result and all the samples were well prepared. An investigation of the effect chemical modification which is grafting copolymerization on fiber by using maleic anhydride (MAH) and study of viscoelastic behaviour of OPMF-LLDPE by mechanical test via tensile strength, stress relaxation and cyclic tests. The result for the tensile strength tests show, as increasing the loading of OPMF after the grafting copolymerization process, the tensile strength of OPMF-LLDPE biocomposites were increasing. This is because the better interaction between fiber and matrix. Stress relaxation and cyclic tested showed the viscoelastic behaviour. The loading of OPMF at 40% was show the stress-strain curve become less stiff and stress relaxation is becomes the fastest. While in the cyclic test shown the result, as increasing the loading of OPMF after grafting polymerization process shows that the biocomposites become more elastic behaviour.

ACKNOWLEDGMENT

Thank you to my supervisor, Dr Suhaiza Hanim Hanipah and Universiti Teknologi Mara.

References

Bledzki, A. (1999). Composites reinforced with cellulose based fibres. *Progress in Polymer Science*, *24*(2), 221–274. https://doi.org/10.1016/S0079-6700(98)00018-5

Chaturvedi, V., & Verma, P. (2013). An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value added products, 415–431. https://doi.org/10.1007/s13205-013-0167-8

Hanipah, S. H., Mohammed, M. A. P., & Baharuddin, A. S. (2016). Non-linear mechanical behaviour and bio-composite modelling of oil palm mesocarp fibres. *Composite Interfaces*, *23*(1), 37–49. https://doi.org/10.1080/09276440.2016.1091681

Hanipah, S. H., Yu Xiang, L., Mohammed, M. A. P., & Samsu Baharuddin, A. (2017). Study of Non-linear Mechanical Behavior of Oil Palm Mesocarp Fibers. *Journal of Natural Fibers*, *14*(2), 153–165. https://doi.org/10.1080/15440478.2015.1093575

Khalid, M., Ratnam, C. T., Chuah, T. G., Ali, S., & Choong, T. S. Y. (2008). Comparative study of polypropylene composites reinforced with oil palm empty fruit bunch fiber and oil palm derived cellulose. *Materials and Design*, *29*(1), 173–178. https://doi.org/10.1016/j.matdes.2006.11.002

Md Yunos, N. S. H., Baharuddin, A. S., Md Yunos, K. F., Naim, N., & Nishida, H. (2012). Physicochemical property changes of oil palm mesocarp fibers treated with high-pressure steam. *BioResources*, *7*(4), 5983–5994. https://doi.org/10.15376/biores.7.4.5983-5994

Mohammed, M. A. P., Omura, T., Samsu Baharuddin, A., Omar, F. N., Hafid, H. S., Wakisaka, M., … Zabidin, Z. (2018). Micromechanical investigation of milled and unmilled rice grains through experimental study and finite element analysis. *Biosystems Engineering*, *176*, 48–58. https://doi.org/10.1016/j.biosystemseng.2018.10.006

Olusunmade, O. F., Adetan, D. A., & Ogunnigbo, C. O. (2016). A Study on the Mechanical Properties of Oil Palm Mesocarp Fibre-Reinforced Thermoplastic. *Journal of Composites*, *2016*, 1–7. https://doi.org/10.1155/2016/3137243

Omar, F. N., Mohammed, M. A. P., & Baharuddin, A. S. (2014a). Effect of silica bodies on the mechanical behaviour of oil palm empty fruit bunch fibres. *BioResources*, *9*(4), 7041–7058. https://doi.org/10.15376/biores.9.4.7041-7058

Omar, F. N., Mohammed, M. A. P., & Baharuddin, A. S. (2014b). Microstructure modelling of silica bodies from oil palm empty fruit bunch (OPEFB) fibres. *BioResources*, *9*(1), 938–951. https://doi.org/10.15376/biores.9.1.938-951

Rozman, H. D., Saad, M. J., & Ishak, Z. A. M. (2003). Flexural and impact properties of oil palm empty fruit bunch (EFB)– polypropylene composites — the effect of maleic anhydride chemical modification of EFB, *22*, 335–341. https://doi.org/10.1016/S

Shalwan, A., & Yousif, B. F. (2013). Investigation on Interfacial Adhesion of Date Palm/Epoxy using Fragmentation Technique. *JOURNAL OF MATERIALS&DESIGN*, (July). https://doi.org/10.1016/j.matdes.2013.07.083

Shinoj, S., Visvanathan, R., Panigrahi, S., & Kochubabu, M. (2011). Oil palm fiber (OPF) and its composites: A review. *Industrial Crops and Products*, *33*(1), 7–22. https://doi.org/10.1016/j.indcrop.2010.09.009

Sreekala, M. S., Kumaran, M. G., Joseph, R., & Thomas, S. (2001). Stress-relaxation behaviour in composites based on short oil-palm fibres and phenol formaldehyde resin. *Composites Science and Technology*, *61*(9), 1175–1188. https://doi.org/10.1016/S0266-3538(00)00214-1

True Stress (σ T). (n.d.). Retrieved from http://academic.uprm.edu/pcaceres/Courses/MatEng3045/EME8-2.pdf

Xiang, L. Y., Hanipah, S. H., Mohammed, M. A. P., Baharuddin, A. S., & Lazim, A. M. (2015). Microstructural, mechanical, and physicochemical behaviours of alkali pre-treated oil palm stalk fibres. *BioResources*, *10*(2), 2783–2796. https://doi.org/10.15376/biores.10.2.2783-2796