

Sarah Amalina Adli¹, Fathilah Ali^{1,*}, Azlin Suhaida Azmi¹

¹ Department of Biotechnology Engineering, Kulliyyah of Engineering, International Islamic University Malaysia (IIUM), Jalan Gombak, 53100 Kuala Lumpur, Malaysia

ARTICLE INFO	ABSTRACT
Article history: Received 5 June 2018 Received in revised form 24 October 2018 Accepted 2 November 2018 Available online 6 November 2018	Nowadays, the usage of plastic packaging raises environmental concern as they accumulated on landfill. Hence, biodegradable polymer is introduced to substitute conventional plastic in the packaging industry. Currently, biopolymers are studied extensively and some of them shows potential to substitute non-degradable plastic, but one biopolymer (polylactic acid (PLA)) in particular stands out as it possesses the same properties as conventional plastic like polystyrene and polyester. Though, PLA's slow degradation rate and brittleness limit its application. Therefore, this study aims to overcome the limitations of PLA and widen its application by modifying them. In this study, algae is used as a filler to lower the cost and increase degradation rate while epoxidized palm oil (EPO) is used as plasticizer to increase the flexibility of PLA. Plasticized PLA (PLAEPO) is mixed using 5 wt% of algae filler content. The composite is prepared by two methods; solvent casting and melt mixing. For solvent casting, PLA and algae are dissolved in chloroform and casted by evaporation whereas for melt mixing, all materials are melt blended using an internal mixer. Characterization for the flexibility, thermal, mechanical and morphological properties of PLAEPO/algae composite is conducted by using flexibility test, differential scanning calorimetry (DSC), tensile testing and scanning electron microscopy respectively. After further discussion and consideration, it is decided that PLAEPO/ALG-5 is best prepared by solvent casting method.
Polylactic acid (PLA), biopolymers, epoxidized palm oil (EPO), algae	Copyright $ ilde{ extbf{c}}$ 2018 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

Plastics have been the main source of packaging materials in the industry nowadays [1]. Some of common examples include polyethylene (PET), polyvinyl chloride (PVC) and polystyrene (PS). However, all of the conventional plastics used in the packaging industry are derived from petroleum which is a diminishing natural resource [2]. The reason why these conventional plastics are favourable is because of their durability, which is the main functionality of creating a packaging [3]. Although these plastics have a high durability, they are all non-biodegradable. These results in

* Corresponding author.

E-mail address: Fathilah Ali (fathilah@iium.edu.my)



accumulation of waste on landfill as they took hundreds or thousands of years to decompose [4]. The best solution to counteract this problem is to come up with a biodegradable polymer, which means that they will decompose into the soil without affecting the environment.

Biodegradable polymer is defined as a polymeric material that converts to carbon dioxide, nitrogen and biomass when degrades [5]. Polylactic acid is a polymer synthesize from naturally occurring monomer and was first discovered by Wallace Carothers in 1932. They were mainly produced from basic materials like sugarcane, corn, whey or cellulose biomass. The basic materials are first processed into lactic acid via bacterial fermentation. Lactic acid is the basic monomer for polylactic acid. According to Hassan and Balakrishnan [6], Preparation of PLA can be done in three ways. The first is by ring-opening polymerization (ROP) of the dehydrated ring-formed dimer or dilactide, second by polycondensation and manipulation of the equilibrium between lactic acid and polylactide by removal of reaction water using drying agents, or third by polycondensation and linking of lactic acid monomers.

PLA is preferred due to its processability and biocompatibility, however PLA also possess certain weakness per say brittleness, poor melt strength, low thermal stability, slow degradation rate and high cost [7]. Therefore, some steps are required in order to modify PLA to meet its function. There are steps available in improvising PLA such as polymer-polymer blending, polymer-fillers and polymer plasticizer blending [7]. Polymer are usually blended with other polymer to improve mechanical properties, like what have been done by Yen *et al.*, [8] in blending PLA with poly methyl methacrylate (PMMA) in order to improve the toughness of the brittle PLA. While addition of fillers contributes in the reduction of cost and increase flexibility of the composites. Bulota and Budtova [9] had prepared a composite of PLA with algae filler and proven that the addition of the filler improves flexibility and mechanical strength of the composite. Furthermore, Rahman and Miller [10] stated that usage of PLA with algae shows potential applications in the near future. Addition of plasticizer such as polyethylene glycol (PEG) is another method as it helps in increasing elongation at break and decreasing the glass transition temperature [1]. As there are past research that showed promising result in blending PLA with PO as plasticizer and algae as a filler.

2. Methodology

2.1 Material

NatureWorks (USA) supplied polylactic acid with grade Ingeo 3251D and average molecular weight of 148000 g/mol. Algae powder purchased from Algaefarmer (Selangor). Plasticizer epoxidized palm oil (EPO) obtained from Budi Oil Sdn. Bhd. (Malaysia) with density 0.979 g/cm³ and oxirane oxygen content of 2.84. Chloroform was purchased from HmbG chemicals (analytical grades, Germany) and used as it is.

2.2 Preparation of PLA and PLAEPO/ALG Composite 2.2.1 Solvent Casting

PLA beads and algae powder are oven dried for 24 hours at a temperature of 40°C before use. PLA is then dissolved in solvent for two hours. After that, algae powder is then added into PLA solution followed by EPO in a beaker and stirred for 24 hours. The solution is then poured onto a clean glass plates and left to dry until the solvent is vaporized for 24 hours. After that, the blend dried in an oven at 40°C for 12 hours. PLA, EPO and algae are mixed at ratio of 85:10:5.



2.2.2 Melt Blending

PLA, algae and EPO are blended using an internal mixer chamber (Haake, polylab, USA) with the same ratio of solution casting method. The operating conditions are temperature ate 180°C with rotor speed of 50 rpm for 15 minutes.

2.3 Flexibility Test

The flexibility of samples prepared by both methods are tested by a simple flexibility test in order to observe the rupture or broke part of sample upon applying a force.

2.4 Differential Scanning Calorimetry (DCS)

DSC (Mettler Toledo, DSC 822, USA) is used to determine the glass transition temperature (T_g) , melting temperature (T_m) and cold crystallization temperature (T_{cc}) behavior of the composites. Test condition is set from 25°C to 190°C at a heating-cooling-heating cycle at a rate of 10°/min. The thermal history is removed by scanning all samples at 180°C and hold for 2 minutes prior cooling to 25°C followed by second heating at 180°C. The thermal transition data obtained from the STARe software is analysed.

2.5 Universal Tensile Test

Yield strength, Young's modulus and the elongation at break of polymer blends are determined using Universal Testing Machine (Shimadzu, AGS-X, Japan). Samples are prepared according to America Society for Testing and Materials ASTM D-882 type-V with crosshead speed 5 mm/min, load cell of 5 kN and 30 mm gauge length. The results are taken as an average of 5 tests.

2.6. Scanning Electron Microscopy

Morphology of the composites are investigated using Scanning Electron Microscopy (JEOL, JSM-5600, UK). Samples are observed at magnification of x500, x1000, x5000 and x10000, and 15 Kv accelerating voltage. All samples are coated with palladium spatter.

3. Results

3.1 Flexibility Test

Flexibility test observes the rupture or broke part of test specimen, upon subjected to force where it bends until it finally reaches failure. Basically, brittle structure tends to break easily compared to flexible structure. For this part, the test had been done by trying to bend PLAEPO/ALG-5 composites prepared by the two methods, solvent casting and melt blending. Fig. 1 shows the flexibility test results carried on PLAEPO/algae composite prepared by both methods.

Based on Fig. 1, it can be observed that the flexibility of PLAEPO/ALG-5 composite prepared by solvent casting is more flexible than the composite prepared by melt mixing method. After bending, the composite prepared by solvent casting continue to bend and showed no sign of breaking upon force. While for the composite prepared by melt mixing, it easily breaks upon giving small pressure. Therefore, PLAEPO/ALG-5 composite prepared by solvent casting is more flexible than composite prepared by melt mixing.





Fig. 1. Flexibility test on PLAEPO/algae composites by (a) solvent casting (before bending), (b) solvent casting (after bending), (c) melt mixing (before bending), and (d) melt mixing (after bending)

3.2 Thermal Properties

Thermal properties of all PLAEPO blends is studied by using the differential scanning calorimetry (DSC). All the samples have undergone the heating-cooling-heating process, and the result obtain from the second heating is used for the analysis. The curves presented all three thermal transition temperatures which are glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting temperature (T_m).

The results for all the thermal transition temperatures for PLAEPO and PLAEPO/ALG-5 blends (solvent casting and melt blending) are tabulated on Table 1.

As observed from Table 1, the T_g value for PLAEPO is the lowest which is at 50.62°C. The two other samples have a higher T_g value than that of PLAEPO, with the PLAEPO/ALG-5 prepared by melt blending method having the highest value at 56.91°C. Glass transition temperature, T_g is known to be the transition temperature where the composite will change from a glassy state to a rubbery state, and low T_g signifies that the transition from glassy state to rubbery state is easier [12].

For the value of T_{cc} , it can be seen that sample of PLAEPO/ALG-5 prepared by melt blending has the lowest T_{cc} value at 86.69 °C. The cold crystallization occur above T_g , when the polymer chain gain sufficient mobility to arrange themselves into ordered structure (crystalline structure) by chain folding [13].

For the melting behaviour, all samples exhibit two T_m peaks. These two peaks of T_m is a result of slow crystallization rate of PLA [3,14]. For both T_{m1} and T_{m2} , the value does not differ very much for PLAEPO sample and PLAEPO/ALG-5 sample prepared by solvent casting. However, the T_m value for PLAEPO/ALG-5 sample prepared by melt blending is slightly lower than the other two samples. The reason for increase in T_m values could be cause by the effect of the algae filler affecting the mobility of PLA chains, thus resulting in poor interfacial adhesion between polymers [15].



Table 1

Thermal transition temperatures of PLAEPO and PLAEPO/ALG-5 (solvent casting and melt blending)

Sample	Tg (°C)	Tcc	Entalphy	T _m (°C)			
		(°C)	(mJ)	T _{m1}	Entalphy (mJ)	T _{m2}	Entalphy (mJ)
PLAEPO	50.62	102.91	18.86	145.18	-114.25	154.99	-125.39
PLAEPO/ALG-5	52.90	121.66	23.41	150.19	-94.62	156.04	-100.82
(Solvent casting)							
PLAEPO/ALG-5	56.91	86.69	136.66	134.12	-142.11	147.96	-150.37
(Melt blending)							

3.3 Mechanical Properties

Tensile test is carried on the composites to investigate the effect of different preparation method on mechanical properties of PLAEPO composites. The test indicates how a material respond to force applied in strain. Unfortunately, as composite prepared by melt blending method is very brittle, the reading for tensile testing are impossible to be recorded. The result for mechanical properties will therefore be discuss only on PLAEPO and PLAEPO/ALG-5 composites. From Fig. 2, it can be observed that PLAEPO exhibits the highest tensile strength of 1.6 MPa, indicating a good filler-matrix interaction [16]. PLAEPO also have moderate value of elongation at break, 129%. Whereas, PLAEPO with algae loading of 5% shows a 78% value of elongation at break. The decrease in elongation at break may be explained by addition of fillers, as the composite becomes more rigid due to the addition of fillers and resulted in less deformation [14]. For the tensile strength of PLAEPO with 5% algae loading, a value of 1.23% MPa is recorded. The tensile strength of the composite slightly decrease from PLAEPO as the addition of filler causes a higher filler-filler interaction instead of fillermatrix interaction, which might also cause stiffening effect in the composite.



Fig. 2. Effect of processing method on PLAEPO composites; stress-strain

3.4 Morphological Properties

SEM is carried out to observe morphological properties on PLAEPO and PLAEPO/algae composites. The results are obtained from fracture surface of sample after failed tensile testing. As observed from Fig. 3, it can be seen that all samples have voids, indicating the presence of plasticizer EPO. SEM images obtained from a research done by Raina [17] on PLA blended with starch and EPO clearly shows that starch granules are trapped in the PLA matrix, indicating incompatibility as starch



acted as a crack initiator being formed. As algae fillers cannot be seen from Fig. 3, it is assumed that the filler is miscible in the PLA matrix.



Fig. 3. SEM micrographs of PLAEPO and PLAEPO/ALG-5 (solvent casting and melt blending) (a) PLAEPO (b) PLAEPO/ALG-5 (solvent casting) (c) PLAEPO/ALG-5 (melt blending)

4. Conclusions

PLAEPO/ALG composites are succesfully prepared in different ratios. This are done by varying the algae content from 1, 3, 5 to 10 wt% in order to observe which PLAEPO blends composition will have a better properties in terms of tensile strength, flexibility, and dispersion in PLA matrix. Characterization PLAEPO/algae composites are done by using DSC, tensile test and SEM. Basically characterization tests are carried out in order to observe which blends composition will have the best properties for packaging material. It is concluded from all the test that PLAEPO/ALG-3 with 3% algae loading exhibit the best properties among other PLAEPO/ALG composites.

References

- [1] Piergiovanni, L., & Limbo, S. (2016). Plastic Packaging Materials. In Food Packaging Materials (pp. 33–49). inbook, Cham: Springer International Publishing.
- [2] Taylor, P., Tang, X. Z., Kumar, P., Alavi, S., & Sandeep, K. P. (2013). Recent Advances in Biopolymers and Biopolymer-Based Nanocomposites for Food Packaging Materials Recent Advances in Biopolymers and Biopolymer-Based Nanocomposites, 37–41.
- [3] Jamshidian, Majid, Elmira Arab Tehrany, Muhammad Imran, Muriel Jacquot, and Stéphane Desobry. "Poly-lactic acid: production, applications, nanocomposites, and release studies." *Comprehensive Reviews in Food Science and Food Safety* 9, no. 5 (2010): 552-571.



- [4] Zhang, Bing, and Muxi Kang. "Life-Cycle Assessment for Plastic Waste Recycling Process: Based of the Network Evaluation Framework." In *Re-engineering Manufacturing for Sustainability*, pp. 377-382. Springer, Singapore, 2013.
- [5] Balázs, Imre. Modification of Biopolymers: Chemistry, Interactions, Structure and Properties: Ph. D. Thesis. Budapest University of Technology and Economics, Department of Physical Chemistry and Materials Science Laboratory of Plastics and Rubber Technology, 2013.
- [6] Hassan, Azman, Harintharavimal Balakrishnan, and Abozar Akbari. "Polylactic acid based blends, composites and nanocomposites." In *Advances in natural polymers*, pp. 361-396. Springer, Berlin, Heidelberg, 2013.
- [7] Ren, Jie, ed. *Biodegradable poly (lactic acid): synthesis, modification, processing and applications*. Springer Science & Business Media, 2011.
- [8] Wu, Jyh-Hong, Ming-Shien Yen, Chien-Wen Chen, and M. C. Kuo. "Mechanical Properties and Isothermal Crystallization Behaviour of Poly (lactide)/Poly (methyl methacrylate)/α-Cellulose Composites." *Journal of Polymers and the Environment* 24, no. 4 (2016): 318-327.
- [9] Bulota, Mindaugas, and Tatiana Budtova. "PLA/algae composites: morphology and mechanical properties." *Composites Part A: Applied Science and Manufacturing* 73 (2015): 109-115.
- [10] Rahman, A., & Miller, C. D. (2017). Microalgae as a Source of Bioplastics. Algal Green Chemistry. Elsevier B.V.
- [11] Alam, Aplikasi Pembungkus Mesra. "Plasticizing poly (lactic acid) using epoxidized palm oil for environmental friendly packaging material." *Malaysian Journal of Analytical Sciences*20, no. 5 (2016): 1153-1158.
- [12] Chieng, Buong Woei, Nor Azowa Ibrahim, Yoon Yee Then, and Yuet Ying Loo. "Epoxidized vegetable oils plasticized poly (lactic acid) biocomposites: mechanical, thermal and morphology properties." *Molecules* 19, no. 10 (2014): 16024-16038.
- [13] Fortunati, E., M. Peltzer, I. Armentano, L. Torre, A. Jiménez, and J. M. Kenny. "Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites." *Carbohydrate polymers* 90, no. 2 (2012): 948-956.
- [14] Rajesh, Gunti, and Atluri V. Ratna Prasad. "Tensile properties of successive alkali treated short jute fiber reinforced PLA composites." *Procedia Materials Science* 5 (2014): 2188-2196.
- [15] Silva, Kodikara. "Environmentally friendly packaging materials from renewable resources as alternatives for oilbased polymers." PhD diss., 2011.
- [16] Haafiz, MK Mohamad, Azman Hassan, HPS Abdul Khalil, MR Nurul Fazita, Md Saiful Islam, I. M. Inuwa, M. M. Marliana, and M. Hazwan Hussin. "Exploring the effect of cellulose nanowhiskers isolated from oil palm biomass on polylactic acid properties." *International journal of biological macromolecules* 85 (2016): 370-378.
- [17] Awale, Raina Jama. *Thermal, Mechanical and Degration Behaviours of Plasticized Polylactic Acid/starch Blends*. Kulliyyah of Engineering, Internatinonal Islamic University Malaysia, 2016.