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PREPARATION AND CHARACTERIZATION OF PLASTICIZED POLYLACTIC ACID/STARCH BLEND

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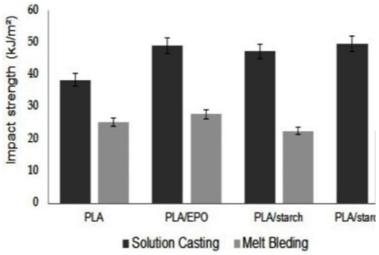
Graphical abstract



Abstract

Petroleum based packaging materials has raised environmental concerns due to its non-environmentally friendly degradation. Conventional plastic takes a long time to degrade and remains in the waste dump. Since then, attention to biodegradable plastics has been heightened for its greener degradation. Polylactic acid (PLA) is a renewable polymer with mechanical properties comparable to those of the conventional plastics. This study aims to improve the mechanical and thermal properties and reducing the cost of PLA production by blending PLA with starch as filler and epoxy palm oil (EPO) as plasticizer. The PLA/starch/EPO blends were prepared by solution casting and melt blending methods and properties of the blends were studied and characterized. The thermal properties of plasticized PLA/starch were investigated by Differential Screening Calorimetry (DSC) followed by Fourier Transform Infra-Red Spectroscopy (FT-IR) in order to observe the degree of interaction of plasticized PLA/starch blend. The mechanical properties were investigated using Universal Tensile Test.

Keywords: Polylactic acid, starch, Epoxy palm oil, biodegradable materials, melt blending, solution casting

1.0 INTRODUCTION

In recent years, concerns about petroleum based plastic waste are rising due to environmental and health concerns and the depletion of petroleum resources[1]. Considerable efforts in research have been devoted to develop biodegradable polymer from renewable resource. [1].PLA is a linear aliphatic polyester biopolymer via fermentation of starchy vegetables and seeds[2]. The distinctive features of PLA such as processability, biocompatibility and biodegradability favored its applications in textile, medical, and as a packaging material[3].However, elevated cost and low flexibility of PLA, has limited its applications in the packaging industry[2]. In order to reduce cost and improve PLA properties, PLA has been modified by blending with low cost fillers such as fiber[4], starch[5], wood flour[6], and talc[7].The addition of natural filler including starch increases the tensile strength and reduce PLA flexibility[2]. Recently, PLA and starch blend have been studied extensively[8],[5],[2]. Owing to the low cost, availability, renewability and biodegradability of starch, starch has been applied widely in food, textile, pharmaceutical, and packaging industries [3]. However, bioplastics composed of entirely of starch lack the strength and the toughness to withstand biotic and abiotic stress and have high water vapor permeability [3]. PLA behaves as a hydrophobic material yet starch is hydrophilic resulting in incompatibility between the two phases. The addition of compatibilizer[9], nucleating agent[8], and coupling agent[8] improved the adhesion between PLA and starch. The addition of these materials will increase the cost of PLA production[10].Plasticization of PLA/starch blend decreases the toughening effect of starch in PLA. Commercial plasticizer (e.g. phthalate and benzoates) works by filling the gaps between polymers chain altering its three-dimension structure, which leads to the polymer ductility. Synthetic non-degradable plasticizers cause unnecessary risks to health and the environment. For the later reason, vegetable oils (EVO) such as epoxy soybean (ESO),and epoxy palm oil (EPO) can be applied as a plasticizer and found to be non-toxic, abundantly found in nature, inexpensive, high viscosity and biodegradable[11]. Ali et al,[12] studied the mechanical properties of plasticized PLA/ESO blend and reported a decrease in glass transition temperature (T_g) and an increase of cold crystallization temperature and elongation at break of plasticized PLA. Emad et al. [13] *interestingly have* reported that the plasticization of PLA by EPO had improved the thermal and mechanical properties of PLA. The current study aims to develop biodegradable PLA bioplastic with improved mechanical properties. The effects of EPO on PLA/starch mechanical properties prepared by solution casting and melt blending techniques were investigated. The mechanical and thermal properties of the blend were investigated and discussed.

2.0 METHODOLOGY

2.1 Material

This study used PLA Ingeo 3251D (NatureWork LLC, Cargill, USA), cassava starch purchased as filler from Tan Ban Huat Sdn Bhd, and Epoxidized palm oil from Budi Oil Sdn Bhd as plasticizer for the blend; chloroform Aldrich Co. analytical grade used as solvent to cast PLA/starch film.

2.2 Blends Preparation

PLA and raw starch will be were dried overnight in an air circulating oven at 40 °C to remove moisture. Solution casting started with dissolved PLA and stirred using a magnetic stirrer in chloroform in a flask at room temperature for 24 hours, followed by the addition of starch and EPO (Table 1) before casting the film. The solvent was allowed to evaporate at room temperature for three days and then the dried film was crushed to be used for injection molding. Melt blending, of PLA starch and EPO was mixed using an internal mixer (Haake, polylab) at 180 °C, 50 rpm rotor speed for 15 min. The melted bioplastic was cooled at room temperature.

2.3 Injection Molding

Samples from casting and melt blending were molded into dumbbell shaped a Battenfeld HM 600 injection molding machine (Germany). Molding temperature profile was defined as following: 180/185/185/195 at 10 bar and a maximum of 20 bar. Specimens were prepared for tensile and dynamic mechanical analyses.

Table 1 Composition of plasticized PLA/starch film

Blend ID	PLA	Starch	EPO
PLA	100	0	0
PLA/starch(control)	95	0	5
PLA/starch/EPO	85	5	10

2.4 Characterization

2.4.1 Tensile Testing

The mechanical properties were evaluated from injection molded dumbbell-shaped specimens (gauge length of 11.5 mm and thickness of 5 ± 0.5 mm). Tensile properties were measured using a tensile machine (Shimadzu, Japan) equipped with a 1 kN force sensor at a crosshead speed of 10 mm min^{-1} at 23 °C.

2.4.2 Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g), melting temperature(T_m) and the cold crystallization temperature (T_{cc}) of the composites were measured using Metller Toledo (DSC D822, , USA). The sample (8.5 mg ± 0.5) was pre-sealed into a 40 µl aluminum pan. The thermal properties measured by heat-cool-heat cycle. Samples were heated from 25 – 200 °C at a constant heating rate of 10 °C min^{-1}. The thermogram from the second heating cycle was analyzed.

2.4.3 Fourier Transforms Infrared (FT-IR) Spectroscopy

Functional group interaction was identified by attenuated total reflectance (ATR) using Thermo scientific ISO 50 series, Fourier Transform Infrared spectrophotometer (FT-IR). The samples were scanned (16 scans) and spectra are collected between 4000 and 400 cm^{-1} wavenumber range at 4 cm resolution under atmospheric conditions.

2.4.4. Impact Test

For the Charpy impact strength rectangular, unnotched specimens of 12x5 mm were prepared then tested using Dynisco (SIMTIC OP7) all results were taken as the average reading of the measured samples.

3.0 RESULTS AND DISCUSSION

3.1 Thermal Analysis

3.1.1 Differential Scanning Calorimetry (DSC)

The effect of starch and EPO on the glass transition (T_g), and melting (T_m) temperatures is illustrated in Figure 1 (a and b). Table 1, shows that T_g and T_m were slightly influenced according to the preparation methods. The melt blended PLA/starch showed a decrease in the T_g compared to those of solvent casted PLA/starch and PLA/starch/EPO. The plasticization of PLA with 10 % EPO by solution casting and melt methods showed a lower T_g Compared of neat PLA from 56.6 °C and 58.5 °C to 52.2 °C (PLA/EPO) for both methods suggesting that the thermal behavior of PLA/EPO independent from its preparation processes. This result was reported as a typical behavior of adding a plasticizer which could be explained as partial miscibility between PLA and EPO that can be seen as downward shift of T_g which resulted in an increase of chain mobility of PLA [14],[12]. On the other hand melted and casted PLA/starch and PLA/starch /EPO showed no significant changes in T_g and T_m compared to neat PLA due to the poor solubility of starch in chloroform[15]. However, the sample prepared through melt blend showed increased T_g of PLA/starch by 4 °C.

This could be due to the interaction between the PLA and starch phases. The double T_m peaks were observed in DSC thermogram, that was attributed to the formation of irregular lamellar crystals that goes under melting (T_{m1}), recrystallization, and then melted again (T_{m2})[9].

3.2 Mecanical Analysis

3.2.1 Tensile Test

The effect of EPO on the mechanical properties of casted and melted for neat PLA,PLA/starch and PLA/starch/EPO blends were determined and data were shown in Figure 2 (a and b). The stress and strain curves showed that tensile strength of casted neat PLA has dropped (39.5 %) and melt blended (31.9%) by the addition of 10 % EPO. For PLA/starch the tensile strength dropped to 26.6 % and 53.9 %, for solution casted and melted samples, respectively. For plasticized PLA/starch sample, sample prepared by solution showed 36.2 % and for melt blended 45.9 %. The drop in tensile strength could be due to EPO intermolecular interaction resulting from phase separation of EPO from PLA matrix where some of EPO might has been incorporated into PLA matrix while the excess EPO accumulates at the interfacial area[14]. Silverajah et al.[16] and Chieng et al.[14] reported the increase in PLA rigidity and reduction of tensile strength occurred when the EPO load is above 1 wt%.

The elongation at break of casted samples increased with the addition of EPO in neat PLA (4.6 %) and PLA/starch blend (11.11 %). Interestingly, PLA/starch increased the elongation at break of neat PLA by 52.3 %. Starch has higher amylase content which resulted in an increase of elongation at break [17].

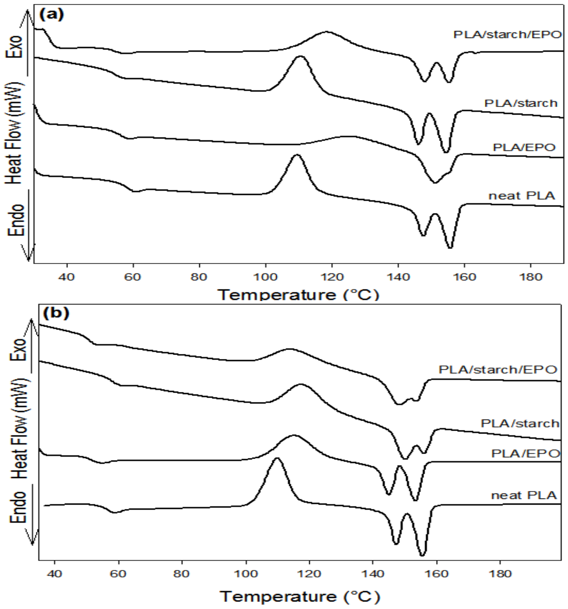


Figure 1 DSC thermogram for neat PLA, PLA/starch, PLA/EPO, and PLA/starch/EPO blends by (a) melt blending and (b) solution casting methods.

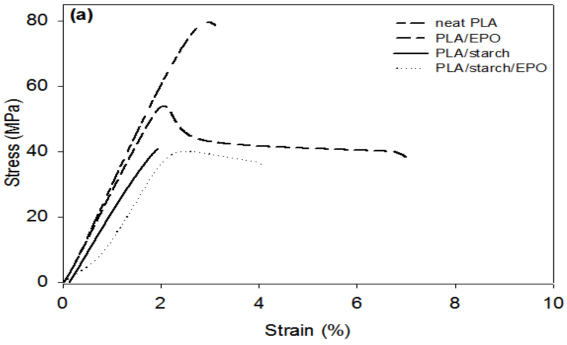
Table 2 DSC characteristics of PLA and its blend

Method	Solution Casting				Melt Blending					
Blend ID	T_g (°c)	T_{m1} (°c)	ΔH_{m1} (J/g)	T_{m2} (°c)	ΔH_{m2} (J/g)	T_g (°c)	T_{m1} (°c)	ΔH_{m1} (J/g)	T_{m2} (°c)	ΔH_{m2} (J/g)
PLA	57	148	10	156	16	58	148	9	154	15
PLA/EPO	52	145	11	154	13	52	145	26	154	15
PLA/starch	58	151	8	157	34	55	147	12	155	17
PLA/starch/EPO10	57	149	0.4	155	5	54	148	9	156	5

Moura [18], reported the presence of water as moisture acts as a plasticizer for starch in a PLA matrix. For solution casted PLA/starch, starch has relatively poor adhesion character due to the starch immiscibility in chloroform and also due to the presence of moisture resulting in PLA/starch blend ductility. Plasticization of PLA and PLA/starch via melt blending increased the elongation at break of neat PLA by 132.3 % and 35.2 %, respectively indicating that EPO reduces the intermolecular forces within the PLA chain, thus increasing the flexibility of PLA. As expected, starch increased the rigidity of PLA and it was shown by the drop in elongation at break of PLA from 3.1 % to 1.6 % due to the incompatibility.

The effect of incorporating EPO, starch and starch EPO combination into PLA matrix on the impact strength is shown in Figure 3. Overall, the impact strength of solution casting blend have better values then melt blended blends. Solution casted plasticize PLA/starch increased impact strength of neat PLA value from 38.4kJ/m^2 to 49.6 kJ/m^2 followed by PLA/EPO (49 kJ/m^2) and PLA/starch (47 kJ/m^2) possible due to interaction between PLA's hydroxyl group, epoxy group in EPO and starch which increased the interfacial adhesion and increased the impact strength[16]. Melt blended as observed from the figure showed that the plasticized PLA has the lowest impact strength (22.4kJ/m^2) close to that of PLA/starch (22.7 kJ/m^2). Chieng et al.[14] had reported that the presence of excess epoxy group increases the chance of plasticizer-plasticizer interaction resulting in poor adhesion in PLA matrix [14] This result was reflected in the T$_g$ values from DSC curve (Figure1), and elongation at break.

Yield strength and Young's modulus data of neat PLA and its blends were determined, and shown in Figure 4 (a and b). EPO had no significant effect on the yield strength of casted neat PLA. Starch incorporation through solution blend into PLA and PLA/EPO increased the yield strength by 11.2 % and 10 %, respectively. As for melt blended, the incorporation of starch into PLA matrix and PLA/EPO decreased the yield strength by 25 % and 24%, respectively.



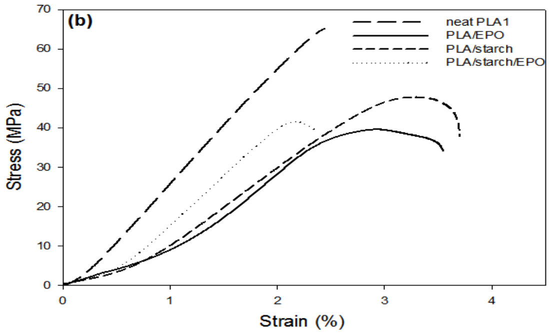


Figure 2 Tensile strength of neat PLA. PLA/EPO, PLA/starch, PLA/starch/EPO prepared by (a) melt blending and (b) solution casting techniques.

From Figure 4 (a), PLA loaded with starch or EPO and their blends showed an increase in Young's modulus of PLA by 12.5 %, 36 % and 35 %, respectively. The presence of starch acted like a rigid filler resulting in the reduction of PLA ductility[17]. Silverajah et al.[16], attributed the increase of Young's modulus to the loading of EPO above 1 wt%.

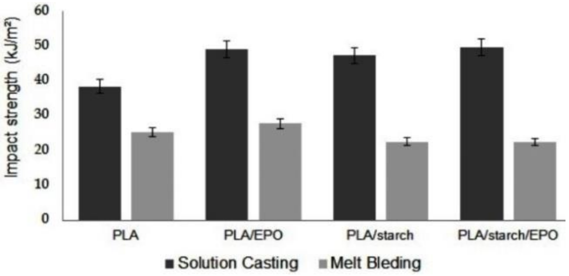


Figure 3 Impact strength of neat PLA, PLA/EPO, PLA/starch, PLA/starch/EPO prepared by melt blending and solution casting techniques.

Oppositely, the blend which was prepared by solution casting showed that plasticization of neat PLA and PLA/starch /EPO has a drop in the Young's modulus of PLA by 37 % and 65 %, respectively, indicating that EPO behaved as a plasticizer for PLA chains compared to that of the blend of PLA/starch which had the lowest Young's modulus (Figure 4 (b).

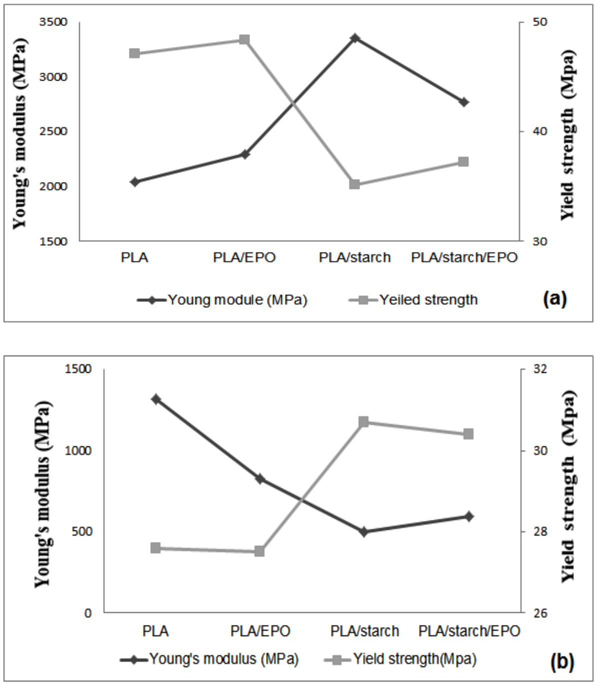


Figure 4 Young's modulus and yield strength of neat PLA, PLA/starch and PLA/starch/EPO prepared by (a) melt blending and (b) solution casting.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

ATR-IR was used to determine the interaction between the functional group of neat PLA, starch and PLA/starch/EPO and data were shown in Figure 5. The distinctive peaks of neat PLA can be seen in casted and melt blended samples spectra as clear stretch of carbonyl group at 1750 cm^{-1} along with -C-O- in formyl group at 1180 cm^{-1}, –C-O- in –C=O at 1127 cm^{-1}, ~1081 and 1042 cm^{-1} and C-H bending at 1500–1400 cm^{-1}. Samples prepared through solution casting of PLA/EPO showed no significant effect on the carbonyl group peak at ~1751 cm^{-1}. The carbonyl group of PLA typically shifted to a lower wavenumber for poor interfacial adhesion blend composites[19]. A shift in -C-O- of formyl group were observed in casted and melted PLA/EPO and PLA/starch spectra from 1180 cm^{-1} to about 1181cm^{-1}. In the current study, there was no significant spectra peaks shift for casted and melted. The plasticization of PLA/ starch blend essentially had no effect as the carbonyl peak remained at ~1751 cm^{-1}. A small shift of –C-O- in -C-H-O group in of PLA/EPO and PLA/starch/EPO blend was observed from 1180.6 cm^{-1} of neat PLA to 1181.5 cm^{-1} and 1180.3 cm^{-1} as result of EPO plasticizing effect (Figure 5(a).

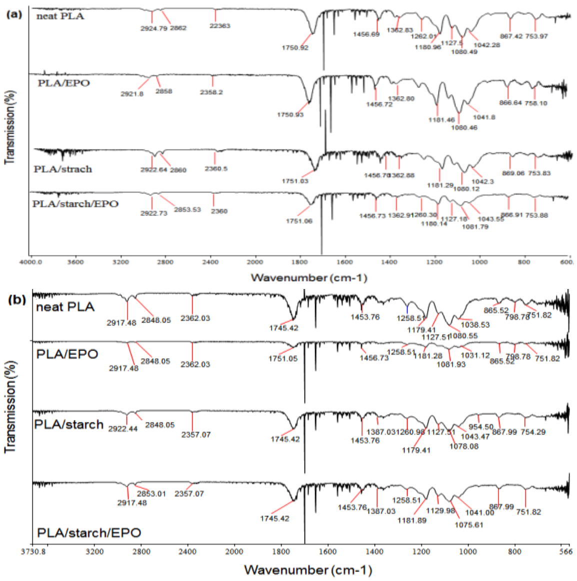


Figure 5 FT-IR spectra for neat PLA, PLA/starch and PLA/starch/EPO prepared by (a) melt blending and (b) solution casting.

4.0 CONCLUSION

PLA showed promising thermal and mechanical properties with incorporation of starch as filler and EPO as plasticizer. We observed that plasticization of PLA/starch blend improved the mechanical properties of neat PLA in casted and melted samples. Each method demonstrated improved properties in different characteristics. Solution casting method improved the elongation at break, yield strength and impact strength of neat PLA. While melt blending method decreased the T$_g$, and improved the young's modulus of neat PLA.

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