



RESEARCH ARTICLE

DEGRADATION PROPERTIES OF BIODEGRADABLE POLYMERS

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ARTICLE DETAILS

ABSTRACT

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Plastics have been a fundamental need in our daily life and most of the plastics are petroleum-based, it cannot be degraded in the environment. Polylactic acid (PLA) is known as a biodegradable polymer and it can be a potential substitute for the petroleum-based plastics. However, PLA is known to be brittle and it has a slow degradation rate. Therefore, the aim of this study is to modify PLA in order to overcome the limitations and broaden its application in the packaging industry. In the present study, PLA is incorporated with different fillers (starch and nanocellulose) and plasticized with epoxidized palm oil (EPO) to further improve its properties and increase the degradation rate. Solvent casting method is used for the preparation of the composites. The samples prepared were subjected to a soil test for six months. Mechanical properties of the composites were evaluated by tensile testing. The weight loss of composites were recorded monthly and the composites blends undergo characterization analysis using Scanning Electron Microscopy (SEM). The utilization of polymer blend composites is the most suitable alternative to improve the properties of PLA to be used in various applications. After further analysis it can be concluded that starch acts as a better filler compared to nanocellulose with the presence of EPO in the composites.

KEYWORDS

polylactic acid (PLA); biopolymers; epoxidized palm oil (EPO), starch, nanocellulose (NC).

1. INTRODUCTION

Plastics materials have been an essential necessity in several application in our daily lives. Some of the common examples are polystyrene (PS), polyethylene (PET) and polyvinyl chloride (PVC). The reason why these conventional plastics are favorable is because of their durability, which is the main functionality of creating a packaging [1]. Despite their high durability these plastics are petroleum-based and it cannot be degraded in the environment. Plastic waste residues have resulted in severe environmental pollution that has had a major impact on human and aquatic life on earth [2].

Biodegradable polymers are seen by many as a promising solution to defeat this issue because they are environmentally friendly [3]. These types of polymers are able to decompose in the soil without effecting the environment. Biodegradable polymer is divided into two groups: natural biopolymers which are derived from renewable sources consists of microbial, animal, plant and marine sources and synthetic biopolymers which are man-made polymers produced from renewable resources. Aliphatic polymers such as polyhydroxy butyrate (PHB), polycaprolactone (PCL) and polylactic acid (PLA) are of special interest because they can generate metabolites upon degradation [4,5]. Among all the synthetic biopolymers, PLA is currently the most prominent and potential material with the brightest development prospect.

PLA is a biodegradable polymer derived from renewable sources such as rice, corn and sugarcane it is one of the most outstanding biodegradable polymers because of its mechanical property, biological properties and thermoplastic processability. According to a study, PLA can be produced

from three different route [6]. The first is by polycondensation and manipulation of the equilibrium between lactic acid and polylactide by removal of reaction of reaction water using drying agents, second by ring-opening polymerization (ROP) of the dehydrated ring-formed dimer or dilactide and third by polycondensation and linking of lactic acid monomers. Hence, PLA is suitable for use in various application, especially in the packaging industry. Regardless of the positive features, PLA has disadvantages as well. PLA is brittle, has a slow degradation rate, high cost, and low thermal stability.

In order to reduce the cost and improve the flexibility of PLA, it has been modified by blending with low cost fillers such as Paddy straw powder, starch, bamboo fabric and cellulose [7-10]. Starch has been an attractive choice of filler for PLA because it enhances the biodegradability and plays an important role in lowering the expanse of PLA [11]. Besides starch, nanocellulose have gain many attentions from researches as application for filler because of its properties like biodegradability, being environmentally friendly, excellent mechanical strength and potential for chemical modification [12-14]. However, starch and nanocellulose has a poor compatibility with a hydrophobic polymer like PLA. To overcome this problem, it is necessary to introduce a plasticizer [8]. This plasticizer will be able to balance the toughness and ductility in PLA/starch composites and PLA/NC composites and increase the phase interactions. Nevertheless, it also helps in increasing the degradation rate of PLA because of its biodegradable properties.

Polymers can be degraded in the environment through a method known as biodegradation. biodegradation it is the breakdown of substances by the action of microorganisms. Based on the study on degradation of PLA

films on real composting soil for ninety days showed major fragmentations [15]. Based on this study it can be concluded that PLA are easily degraded with the presence of microorganisms in soil. Thus, the current study aims to cross over any barrier between properties of PLA and commodity plastic in the packaging industry by tailoring the PLA's properties. Two different type of fillers are compared in this study to conduct a thorough study on which filler would have a higher degradation rate based on altered ratios of the fillers and plasticizer in the composite. The effects of the altered ratios of the composites on mechanical, soil burial test, and morphological properties were investigated and discussed.

2. MATERIALS AND METHODS

2.1 Materials

PLA (Ingeo™ biopolymer 3251D) was purchased from Nature Works LLC, Minnetonka, MN, USA. Plasticizer, EPO (density of 0.979 g/cm³ with oxirane oxygen content of 2.84) was obtained from Budi Oil Enterprise Sd PLA (Ingeo™ biopolymer 3251D) was purchased from Nature Works LLC, Minnetonka, MN, USA. Plasticizer, EPO (density of 0.979 g/cm³ with oxirane oxygen content of 2.84) was obtained from Budi Oil Enterprise Sdn Bhd, Telok Gong, Port Klang, Selngor, Malaysia. Tapioca starch was purchased from Tan Ban Huat Sdn Bhd, Geotgetown, Pulau Pinang, Malaysia. Nanocellulose produced from microcrystalline cellulose. Chloroform was purchased from HmbG chemicals (analytical grades, Germany). Soil was used to test the degradation rate of the composites.

2.2 Preparation of PLA, PLA/EPO, PLA/EPO/Starch and PLA/EPO/NC composites

Ten gram (10g) of PLA was dissolved in chloroform for three hours at room temperature. EPO was then added followed by filler (starch or nanocellulose). The blend was left to mix for 24 hours in a fume hood. The blend was blended according to the compositions in Table 1 and Table 2 following the same steps mentioned above. The solution was poured into a petri dish and left to dry in the fume hood for 24 hours. The controlled blend composition ratio which is the PLA blend and the PLA/EPO blend is placed in Table 3.1. Various ratio of EPO, starch and nanocellulose were used to determine the blend that would influences the degradation rate. After the drying process, the samples were cut and molded into 2 cm x 2 cm with 0.3 cm thickness according to ASTM D5338 standard under a pressure of 1000 kPa at 190 °C for 10 min.

Table 1: Blend composition and ratio of PLA EPO using starch as filler

Sample Code	Composition Ratio		
	PLA (g)	EPO (wt %)	Starch (wt%)
PLA	100	0	0
PLA/EPO5	95	5	-
PLA/EPO5S5	90	5	5
PLA/EPO5S10	85	5	10
PLA/EPO5S15	80	5	15
PLA/EPO10S5	85	10	5
PLA/EPO15S5	80	15	5

Table 2: Blend composition and ratio of PLA EPO using nanocellulose as filler

Sample Code	Composition Ratio		
	PLA (g)	EPO (wt %)	Starch (wt%)
PLA/EPO5NC5	90	5	5
PLA/EPO5NC10	85	5	10
PLA/EPO5NC15	80	5	15
PLA/EPO10NC5	85	10	5
PLA/EPO15NC5	80	15	5

3. CHARACTERIZATION

3.1 Universal Tensile Test

Yield strength, Young's modulus and the elongation at break of composites was determined using Universal Testing Machine (Shimadzu, AGS-X, Japan). Samples were prepared according to 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.

3.2 Degradation Test

Composites size (2 cm x 2 cm x 0.3 cm) were buried in soil with a distance of 3 cm between samples in soil obtained from UK Perdana nursery. The weight loss of samples were weighted monthly by drying the samples in oven at 40 °C overnight. The weight loss is calculated using Equation below.

$$\% \text{ Weight loss} = \frac{m_0 - m_t}{m_0} \times 100 \quad (1)$$

Where m_0 is the initial mass of sample at initial day before biodegradation and m_t is the mass of sample after biodegradation.

3.3 Scanning Electron Microscopy

The morphology of composites was investigated using scanning electron microscopy (SEM) (JEOL, JSM-5600, UK). For SEM observation, the degraded samples were sputter coated with gold and observed at 100 μm aperture and 10 KV accelerating voltage.

4. RESULTS AND DISCUSSION

4.1 Mechanical properties

Tensile test was carried out on the composites to investigate the effect of various ratios of EPO and filler on the mechanical properties of the composites. The test shows how a material react to force applied in strain. As observed from Figure 1, PLA composite exhibits the highest yield strength with 2.3 MPa. With the addition of 5 wt % of EPO to the composite the yield strength is decreased. The decreased in yield strength could be due to the intermolecular interaction between the EPO and the PLA matrix in which some of the EPO may have been incorporated into the PLA matrix while the excess EPO accumulates in the interfacial area. A researchers reported an increase of PLA stiffness and a decrease in yield strength occurred when the EPO load is above 1 wt% [13]. The tensile strength of composites continues to decrease with the increasing wt % of starch. This indicates a negative deviation from the rule of mixtures due to the incompatibility between hydrophilic starch and hydrophobic PLA [16]. The elongation at break of composites is highest when EPO content is 10 wt % and starts to decrease when EPO content is 15 wt %.

From Figure 2 it can be observed that there is similar pattern of the PLA/EPO/Nanocellulose composites to the PLA/EPO/Starch composites. With the increase of wt% of nanocellulose in the composites, the yield strength is decreased. Hence, with an increasing wt % of filler the Young's Modulus increases. With 15 wt % of starch, the Young's modulus is 0.52 MPa while with 15 wt % of nanocellulose, the young's modulus is 0.53 MPa. The increase in Young's modulus could confirm that starch and nanocellulose as fillers have a good adhesion to the PLA matrix [17]. The elongation at break for starch composite with 10 wt% EPO is the highest at 81 % and same goes with nanocellulose composite with 10 wt % EPO highest at 213 %. A high elongation at break indicates that the composite's ductility is increased. However, the elongation at break of composites starts to decrease with a higher wt % of EPO at 15 wt%. This could be due to the accumulation of excess EPO at the interfacial area of the composites [8].

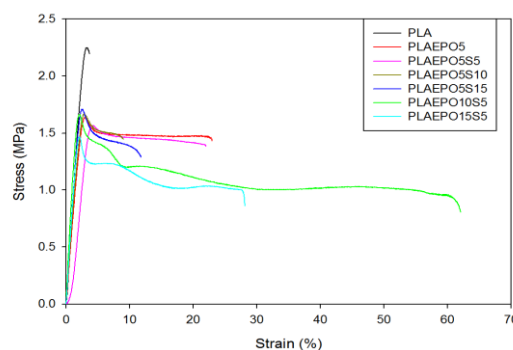


Figure 1: Effect of different ratios on PLA, PLA/EPO and PLA/EPO/Starch composites

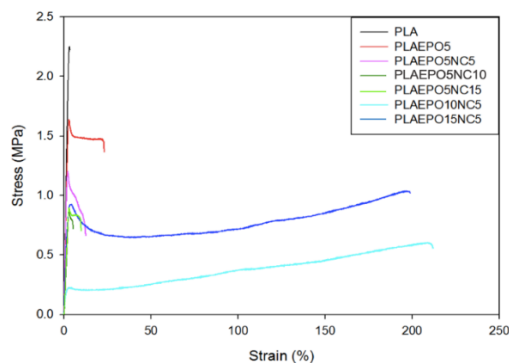


Figure 2: Effect of different ratios on PLA, PLA/EPO and PLA/EPO/Nanocellulose composites

4.2 Biodegradation

The influence of EPO content on biodegradability of composites in soil were assessed by the rate of degradation as shown in Figure 3 (a) and Figure 3 (b). Through the course of six months in soil, PLA composite exhibited the least weight loss of 1.79 % due to its slow degradation rate [18]. The rate of PLA degradation increased by 9.33 % by the incorporation of 5 wt % of EPO. With a higher wt % of starch in the composites the degradation rate increased by 11.07, 12.41, 13.34 %. Nevertheless, with the addition of a higher wt % of plasticizer the degradation rate was highest at 13.95 and 17.01 %.

The soil degradation rate in PLA/EPO/Nanocellulose composites shown in Figure 3 (b) exhibits similar characteristic as the PLA/EPO/Starch composites, where the degradation rate was increased with the increased wt % of filler at 11.29, 12.04, 12.30 % but increased further with a higher wt % of EPO at 13.06 and 15.37 %. Moreover, it is observed that the PLA/EPO/Starch composited has a higher degradation rate compared to the PLA/EPO/Nanocellulose composites.

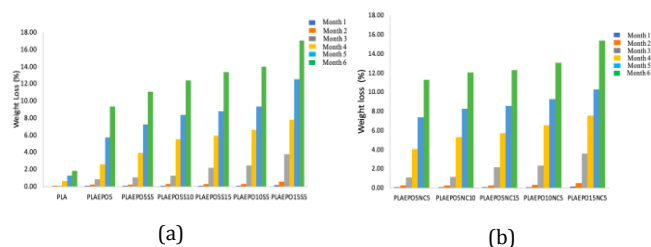


Figure 3: Weight loss % of composites in soil (a) PLA, PLA/EPO, PLA/EPO/Starch composites (b) PLA/EPO/Nanocellulose composites.

4.3 Morphological Properties

SEM is carried out to observe the surface morphology of PLA, PLA/EPO, PLA/EPO15S5 and PLA/EPO15NC5 composites. The results are obtained from samples buried in soil after 3 months degradation. The biodegradation of composites starts with plasticizer, followed by filler and then it goes to the matrix material which takes more time for degradation to occur [7]. According to the holes observed on the surface of the samples can be formed by the degradation of the interspherulitic amorphous phase region or between the crystalline region is due to microbial degradation [19]. It can be observed in Figure 4 (c) holes was visible on the PLA/EPO15S5 composite compared to the other composites. Thus, this could be an indication of the microbial attack as similar behavior was also observed [20].

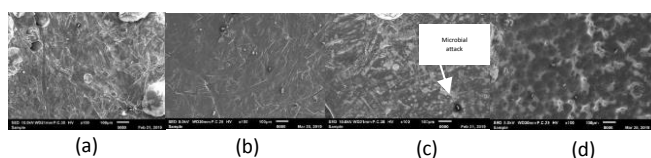


Figure 4: SEM images of (a) PLA, (b) PLA/EPO, (c) PLA/EPO15S5, (d) PLA/EPO15NC5

5. CONCLUSION

Various ratios of PLA, plasticizer and starch/nanocellulose were prepared to conduct a thorough study on the effect of different composition of the plasticizers and fillers towards the composites. The mechanical properties of composites improved the yield strength, Young's modulus and elongation at break due to uniform EPO dispersion in PLA matrix. Next, the degradation rate of composites was evaluated by obtaining the weight loss % of composites after six months of burial in soil. From the findings it can be concluded that the weight loss of PLA/EPO/starch composites were higher compared to the weight loss of PLA/EPO/nanocellulose composites. This is due to the structural differences of starch and nanocellulose when it is undergoing degradation. SEM images at 3 months of degradation confirmed that several holes and cracks are results of penetration of microorganisms on the surface of the composites. Thus, the utilization of natural filler, plasticizer and PLA can help in reducing waste accumulation in the environment because of its biodegradable properties.

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NOMENCLATURE

ASTM	American Society for Testing Material
ECO	Epoxidized Castor Oil
EPO	Epoxidized Palm Oil
ESO	Epoxidized Soy Bean Oil
NC	Nanocellulose
PET	Polyethylene
PEG	Polyethylene glycol
PLA	Poly(lactic) Acid
PCL	Polycaprolactone
PHB	Poly hydroxybutyrate
PP	Polypropylene
PS	polystyrene
PVC	polyvinyl chloride
ROP	Ring-Opening Polymerization
SEM	Scanning Electron Microscopy
°C	Celsius

