Degradation behaviour of plasticized PLA/CNTs nanocomposites prepared by the different technique of blending

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Abstract. The present research goals to investigate how the preparation technique became the factor to develop materials with a good combination of properties and optimum degradation ability. PLA/CNTs nanocomposites were prepared via melt blending and solution blending that were involved of unmodified carbon nanotubes (CNTs) and modified CNTs (mCNTs) at 1.5 wt.% loading. The surface morphology of nanocomposites was viewed by Field Emission Scanning Electron Microscopy (FESEM). The effect of 5 wt.% poly (ethylene glycol) (PEG) as plasticizer on nanocomposites were determined. The weight loss in soil degradation study was run for 6 months. The morphology study by FESEM confirmed the finding through the existence of a smooth fracture surface especially when PEG was loaded. In soil degradation analysis, neat PLA exhibited a low weight loss rate after 6 months. The maximum weight loss for both techniques was shown by PLA/PEG/CNTs from melt blending technique and PLA/PEG/mCNTs from solution blending, believed from the pore occurred bring to poor properties.

1. Introduction
Non-biodegradability plastics synthesized from petroleum-based products grip main consideration due to an environmental problem which is causes the waste disposal problem. Besides, these petroleum-based polymers are also limited sources and fluctuations in price [1]. Consequently, the awareness in the development of an alternate and biodegradable polymer from renewable resources can be seen lately. Concerning the processing properties, it is worth noticing that the tallying of plasticizer into highly filled (lactic acid) (PLA) can achieve lubrication in improving filler dispersion and assisting in viscosity control. An article reported the preparation of plasticized PLA by using poly (ethylene glycol) (PEG) by melt blending [2]. The dielectric properties and shielding effectiveness were improved by loading of 4.0 wt.% MWCNTs. Da Silva and coworkers used PEG and dibutyl sebacate (DBS) as plasticizer at 20 wt.% during melt blending of PLA/Gr [3].

Another study that is quite similar to the current study was reported by Chiang in 2014 [4]. They used graphene nanoplatelets at 0.3 wt.% and lower molecular weight of PEG, which was 200 g/mol. More particularly, plasticizer aids in the processing and extruding of the polymer at lower temperatures. Thus, it can increase flexibility and reduce cracking tendencies of finished products. In
In this context, the ideal plasticizer for PLA can be any biodegradable product necessarily non-volatile that has a relatively low molecular weight to produce a substantial lessening of glass transition (T_g) and increase in ductility. Besides, the PEG also gives benefit to enhancing the biodegradation rate since the neat PLA has a low tendency to degrade.

In the packaging of foods, microbial degradation of PLA should be considered especially microorganisms including fungi and lactic acid bacteria for their feasible capabilities of PLA degradation [5]. Numerous studies have been stated on soil degradation of PLA composites such as blending with natural filler and carbon-based materials. The polymer degradation rates could be controlled by blending with plasticizers, additives and often inorganic fillers. Indeed, several research works have reported on the biodegradation or hydrolytic degradation of different aliphatic polyesters, due to the hydrophilicity of the nanoparticles [6]. However, other work stated the nanofillers can be able to impede the degradation of the polyesters chain, assigning this effect to the enhanced barrier properties of nanocomposites [7].

In current study, poly (lactic acid) (PLA) as a matrix has been selected to be blended with carbon-based materials. The blending of these nanofillers with various loading was made by melt blending and solution blending to determine the effect of processing methods on properties and degradation behaviour of nanocomposites. The addition of PEG during blending was also performed. The nanocomposites were then analyzed for degradation, which covered soil degradation behaviour and hydrolysis study by solution immersion. The advantage of PEG was highlighted since the plasticizer showed good assistance in nanofiller dispersion in PLA and could increase the biodegradation rate of nanocomposites compared with neat PLA.

2. Materials and Methods

2.1 Chemicals and raw materials
Multi-wall carbon nanotubes (CNTs) were supplied by Global Science Resources with >9wt% purity and ash <1.5wt%. It has outer diameter close to 20–40 nm and length between 10–30 μm. PLA was supplied from Nature Works. Poly (ethylene glycol) PEG with average molecular mass 950–1050 g mol⁻¹, HNO₃ 65% and H₂SO₄ 95-97% were provided by Merck KGaA.

2.2 Preparation of samples
About 1.0 g of CNTs was added into 20 % of HNO₃ solutions and stirred in a few minutes. Then, the solution was sonicated for 2 hours. After that, the CNTs were washed with deionized water (DI) and isolated by filtering the product until no acidic. Then, the product was put in an oven at 40 °C for drying. The modification was pursued by heating the CNTs into 1:3 mixtures of concentrated HNO₃ and H₂SO₄ at 100 °C for 100 minutes. Then, isolated mCNTs was filtered and neutralized by washing with deionized water (DI) was dried in an oven. Since the current study was purposely to determine the effect of preparation techniques and plasticizer on the rate of degradation with a different type of nanofillers, the loading of nanofiller was set at 1.5 wt.%.

In the melt blending method, the material was blended via an internal mixer and the twin-screw rotator functioned at 180 °C for front and back screws. The speed was fixed between 3 rpm–5 rpm. PLA was fed into an internal mixer and molten followed by the addition of nanofillers till homogenous blending was gained. For 5 wt.% PEG loading, it was added after the PLA was in the molten state.

In the solution blending method, the amount of 1.0 g PLA was completely dissolved in 20 g of chloroform at 45 °C. The 1.5 wt.% of CNTs and mCNTs were dispersed in chloroform with the amount of 0.2 mg/mL. The PLA solution was consequently mixed with dispersed nanofiller in Teflon bottle and stirred for 4 h at 40 °C to obtain homogenous PLA nanocomposites solution. After sonication for another 10 min to continue the stability, the mixed solution was transferred into a petri dish and the solvent was evaporated in a fume hood to gain the film. For the nanocomposites with
PEG, the 5 wt.% PEG was added in a well-dispersed PLA solution. After that, the addition of dispersed nanofiller was done.

2.3 Characterization of samples

2.3.1 Field emission scanning electron microscopy (FESEM)
FESEM analysis topological and morphology analysis was performed at a magnification of 10–300,000×. The elemental analysis could be done at low voltage, low landing energy and large depth of focus with resolution of 0.8 nm at 15 kV and 1.2 nm at 1 kV. Before testing, the CNTs nanofiller was finely ground to powder form. As for the nanocomposite, the cross-sectional area of the fractured surface was used to evaluate the dispersion of nanofiller inside PLA nanocomposite.

2.3.2 Soil burial of biodegradable PLA nanocomposites
The biodegradability of the nanocomposite was studied by calculating weight loss of blends over time in a soil environment. A series of square-shaped samples, measuring around 10 mm x 10 mm were weighed and then buried in loamy sand-type soil. The samples were buried at a depth of 15 cm. After every 30 day of incubation till reached 180 days, samples were cleaned by washing with distilled water and dried to a constant weight in the oven. The degradation of samples was measured by weight loss of samples during the experiments. The calculation as in equation (1) where $\Delta W_{\text{loss}}$ is weight loss, $W_f$ is final weight and $W_i$ is the initial weight.

$$\Delta W_{\text{loss}} = \frac{(W_i - W_f)}{W_i} \times 100$$  \hspace{1cm} (1)

3. Results and Discussions

3.1 Morphology study by FESEM
The morphological images of PLA/CNTs shown in Figure 1 are for (a) unfilled PEG and (b) filled PEG nanocomposites. From Figure 1(a), it was observed that the undispersed CNTs nanofiller disappeared in Figure 3.2(b). This can be explained by the aid of the plasticizing effect of PEG in the nanofiller dispersion of the PLA matrix. The rough surface morphology in PLA/mCNTs as shown in Figure 1(c) was compared with the smooth surface fracture when PEG was loaded as viewed in Figure 1(d). The good dispersion of CNTs nanofillers in the PLA matrix was believed to be responsible for the enhancement of properties. In common, surface modification of CNTs enhances adhesion between CNTs and the PLA matrix due to functional groups. Due to high specific surface area, large aspect ratio and strong interfacial interaction of $-\text{COOH}$ and $-\text{OH}$ on mCNTs with PLA matrix, the PLA molecules can be easily bounded on the surface of CNTs, which can form an adequate number of nucleation centre and play the roles of crystal nucleus. A similar finding was reported by Yousefzade et al. [8].
Even without nanofiller modification, the dispersion of pristine carbon nanotube bundles could enhance the deagglomeration by covalent bonding created between the ester group in PLA and CNTs as shown in Figure 2. The loading of 1.5 wt.% mCNTs in PLA provided the smooth surface of thin-film where even a few pores can be spotted on the cross-section. One interesting finding to be highlighted in the current study is even high loading of mCNTs was inserted (1.5 wt.%), the smooth surfaces of nanocomposites can be viewed. An opponent with a study by Luo et al. in 2018 [9], they obtained the rough surface morphology of PLA thin film with 0.4 wt.% mCNTs. They prepared the film by solution casting using dichloromethane (DCM) solvent.

Furthermore, the good distribution and dispersion affect the degree of crystallinity of nanocomposites. The homogenous structure with smooth fracture means excellent interaction between filler and matrix are recognized bringing to high crystallinity, thus enhanced the properties of nanocomposites. Hence, the barrier property result of nanofiller that acted as a nucleating agent may hinder the movement of plasticizer and contributed to the constancy of the mixture, preventing the plasticizer transmission to the surface. The stability of plasticizer is important to confirm it is well-functioned in nanocomposites.
3.2 Biodegradation analysis by soil burial study

Usually, the biological attack on polymer composite materials is influenced by fungal development or soil burial. Fungal growth is potential only in humid conditions and their mechanical properties are affected after long-term disclosure to microorganisms. The degradation of polymer composites due to biological factors is reliant on the chemistry of the composites, salinity and acidity of the soils [10]. From a physical viewpoint, two types of polymer degradation are heterogeneous and homogeneous, which is likewise known as surface and intramolecular degradation of the polymer.

Figure 3 shows the trend of the degradation of melt blending samples. It was found that PLA degradation occurred mainly through ester bonds' scission. The degradation of PLA under compost is a process containing four main phenomena. They are namely (1) water absorption; (2) ester cleavage and formation of oligomer fragments; (3) solubilization of oligomer fragments, and finally; (4) diffusion of soluble oligomers by bacteria, respectively. Hence, among the factor, which enlarged the hydrolysis tendency of neat PLA, eventually controls the degradation of PLA. The neat PLA results exhibited the slightest degradation which was only 0.04 % weight loss after 6 months as compared to PLA nanocomposites. It is worth highlighting that even though PLA degrades at a slow rate, it has the tendency to have complete biodegradability after a certain time and not polluting the environment after biodegradation [11]. Pantani and Sorrentino in 2013 examined the consequence of crystallinity on the biodegradation rate of injection-molded PLLA parts [12]. Their results confirmed that the degradation rate was affected by initial morphology. They resolved that the crystals shaped during degradation have less connectivity and are thus less effective at inhibiting whole swelling of the polymer. In difference way, they suggested that crystals formed before degradation present higher connectivity that promises a denser structure that is more resistant to enzymatic attack and oligomer diffusion.

One to be highlight in this research was the significant enhancement of biodegradability in certain PLA nanocomposites. PLA/PEG/CNTs had the highest weight loss which reached 12.00 % after six months. This can be relating to the performance of this nanocomposite in mechanical testing. The hardness of PLA/PEG/CNTs is low compared to other nanocomposites, which can be concluded the less compatibility of filler in the matrix. Hence, the weak interfacial bonding contributes to ease of the
breakage of ester bonds in the matrix. It can be observed the GO and mCNTs have a similarity in % weight loss with the presence of PEG which was revealed to range from 5.48–5.54 %.

Interestingly, after the addition of hydrophilic PEG, the degradation rate enhanced higher than nanocomposites without 5 wt.% PEG loading for all nanocomposites. The environmental degradation rate rose simultaneously with the loading of PEG fillings. The occurrence of carboxyl groups in modified nanofiller increased the hydrophobicity of PLA. It was leading to improving water resistivity which later led to slow biodegradation. This discovered that the modified nanofiller improve the stability of PLA by resisting the microbial attack during composting. Since the hydrophobic nature of PLA, it was difficult for water to penetrate the materials. But the excellent water solubility and hydrophilic characters of PEG in blends could aid absorb and keep the water. In the soil burial analysis, both PLA and nanofiller would carry out hydrolysis reaction therefore the linear chains would break down at the ester bond. This caused the loss of molecular weight and mass of nanocomposites.

![Figure 3](image-url)  
**Figure 3.** Weight loss of neat PLA and PLA nanocomposites with 1.5 wt.% nanofillers prepared by melt blending technique.

Figure 4 exhibits the % of weight loss for thin film samples prepared by solution blending. The percentage of weight loss increased with rise in the period. The PLA exhibited a small rate of weight loss after the sixth month which was 0.06 % but slightly higher than PLA prepared from the melt blending method. The presence of nanofillers enhanced the degradation rate compared with neat PLA. The trend showed a positive result for Gr and mCNTs where they exhibited a high weight loss after the third month of analysis. Therefore, the merger of carbon-based materials into a decomposable polymer matrix represented a promising approach not only for enhancing the polymer performance but also for growing its biodegradation rate in composting conditions. Nevertheless it is well known that the biodegradation mechanism of PLA comprises chemical hydrolysis, the role of microorganisms and how they are affected by the existence of nanoparticles is still not well understood [12].

Also, instead of improving the dispersion capability in the PLA matrix and decreases the brittleness of PLA nanocomposites, the presence of PEG is useful to resolve the plastic-based disposal problem especially. This is verified through the trend performed by nanocomposites added with a plasticizer. Their results showed high weight loss compares with unfilled PEG. The maximum weight loss was obtained from PLA/PEG/mCNTs where it recorded an 8.94 % of weight loss. About the melt blending sample, this value increased up to 2.40 % confirmed the pores observed on a surface fracture from FESEM analysis affected the rate of biodegradation.
Figure 4. Weight loss of neat PLA and PLA nanocomposites with 1.5 wt.% nanofillers prepared by solution blending technique.

The degradation of PLA and nanocomposites can occur in three different ways: (1) scission of the main chains, (2) scission of the side chains and (3) scission of the intersectional chains. Besides, the degradation ability is induced by a series of factors such as photodegradation, oxidation, hydrolysis, thermolysis, enzymolysis and biodegradation [13]. As shown in Figure 5, biodegradation of polymers generally takes place in two main steps: primary degradation, in which fragmentation of the polymer chain ensues due to hydrolysis or another oxidative reaction, and ultimate biodegradation, where the microorganisms assimilate the low PLA M_w chains are formed.

PLA degradation upon disposal in the environment is more challenging because PLA is largely unaffected to attack by microorganisms in soil or sewage below ambient conditions. Based on a research [14], the polymer must first be hydrolyzed at elevated temperatures at about 60 °C to decrease the M_w before biodegradation can commence. Under surroundings of high temperature and high humidity, as inactive compost, for example, the PLA degrades rapidly and disintegrates within weeks to months. The primary mechanism of degradation occurs in a two-step process which also starts with hydrolysis and is followed by the bacterial attack on the fragmented residues. During the initial phases of degradation, the high M_w polyester chains hydrolyzed to lower M_w oligomers. Microorganisms presented in the soil then began to digest the lower M_w lactic acid oligomers, producing carbon dioxide and water. The rate of hydrolysis was accelerated by acids or bases and was reliant on temperature and moisture content.
4. Conclusion
The nanocomposites prepared by melt blending and solution blending was successfully done. FESEM analysis showed the PLA/PEG/mCNTs from melt blending had smooth morphology. Nanocomposites from solution blending exhibited pore on the surface. The morphology study is parallel with the degradation ability of samples. The sample with the smooth surface has low degradation which expected has better properties. In biodegradability analysis, neat PLA from both techniques showed from 0.04–0.06 % of weight loss. Even the degradation was at a low rate, this proves that this biopolymer has a future in reducing the environmental problem. PLA/PEG/CNTs from melt blending had the highest weight loss that reached 12.00 % after six months. The maximum weight loss from solution blending obtained from PLA/PEG/mCNTs where it recorded an 8.94 % of weight loss.

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