Degradability studies of PLA nanocomposites under controlled water sorption and soil burial conditions

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Abstract. Polymer blended nanocomposites based on polylactic acid (PLA) were prepared via a simple melting process and investigated for its biodegradation behaviour. The treated CNTs were surface modified by using acid treatment and characterisations of composites were done by using Fourier Transform Infra-Red (FTIR) and UV-Vis. FTIR spectra and UV-Vis peak confirmed the surface modification of CNTs. The water uptake and weight loss behaviour based on CNTs and m-CNTs loading at different temperatures (25°C and 45°C) were studied. It was found that the water absorption and weight loss of nanocomposites increased by the incorporation of CNTs and m-CNTs. Moisture induced degradation of composite samples was significant at elevated temperature. The addition of treated CNTs successfully reduced the water uptake and weight loss of nanocomposites due to less hydrolytic effect of water on nanocomposites. In soil burial test, the weight loss increases with addition of nanofiller. The loading of m-CNT reduced the ability of nanocomposites degradation.

1. Introduction
Biodegradable polymer is originated from renewable sources; as a result, it has a negative effect on environment as compared to petroleum based materials. Polylactic acid (PLA) offers several smart features that make it highly competitive with conventional non-biodegradable materials, such as good mechanical properties and the processability by standard techniques [1]. In the presence of water, PLA experiences important physical modifications: water plasticises and swells the material, its glass transition temperature is lowered and mobile and thus crystallisation kinetics is augmented. On a longer timescale, hydrolysis reduces - molecular weight, thus the physical and mechanical properties are also affected [2]. The hydrolytic degradation, above all, has been variously studied and the main factors affecting this phenomenon are quite well defined [3–6]. Surprisingly, on checking the literature, it can be noticed that when temperatures close to the glass, transition of PLA were studied, the effects of water were mostly assessed at times when the hydrolysis induced significant changes in the material, after a few days or weeks [4,7]. Obviously, it was difficult to understand to which extent other phenomena taking place in the material, such as opacification, crystallinity evolution or vice versa can develop independently [7,8]. Microbial degradation of PLA should be studied for packaging of foods containing microorganisms including lactic acid bacteria, and fungi for its possible abilities of PLA degradation. Several studies have been reported on soil degradation of PLA composites such as blending with natural filler [9-12] and carbon-based materials [13-15]. This work aims to study the water sorption and weight loss within a given time and at different temperatures, in order to analyse the phenomenon with water
in PLA. Besides, the trend in weight loss after soil burial in 180 days was focused. Also, the effect of surface modification of CNTs is one of the viewpoints needed to cover in this study.

2. Materials and methods

2.1 Chemicals and materials
Industrial grade multi-wall carbon nanotubes (CNTs) with >90wt% purity and ash <1.5wt% were supplied by Global Science Resources, Malaysia. Their main characteristic is outer diameter close to 20–40 nm and length between 10–30 µm. PLA was provided from NatureWorks, USA with grade 3251D, while 95-97% of H2SO4 and 65% of HNO3 were supplied by Merck KGaA, Darmstadt, Germany.

2.2 CNTs modification
The CNTs samples were modified by acid treatment. First, CNT 10wt% was immersed in 20% nitric acid (HNO3) to remove impurities. This carboxylic group was used as reaction precursor in the functionalisation. The mixtures of CNT and HNO3 were stirred for a few minutes and sonicated for 2 h, then diluted in water, filtered till to neutral pH, washed several times with deionised water and then dried overnight in oven at 60°C. Next, the dried mixtures of CNT were mixed together with pure 50 mL HNO3 and 150mL sulfuric acid (H2SO4) to reflux for 100 minutes. Finally, the CNTs were again filtered to neutral pH, washed several times with deionised water and then dried overnight in vacuum oven at 60°C, before it was used to prepare melt-blending with polymer matrix.

2.3 Nanocomposites preparation
PLA nanocomposites were prepared by melt-blending method. The PLA/CNTs and PLA/m-CNTs with weight ratios of 99.5/0.5%, 99.0/1.0%, 98.5/1.5% and 98.0/2.0% were incorporated. A Benchtop Two-Roll Mill (LRM-M-100) was used to disperse conductive filler in the polymer matrix. Blending process was carried out at 4 rpm for 20 min and at 170°C, which was slightly above the melting point of PLA.

2.4 Nanocomposites characterisations
Fourier Transmission Infrared Spectroscopy (FTIR) analysis was carried out by using a Perkin-Elmer Model FTIR spectrometer and KBr method. The transmission of infrared spectra was obtained in the range between 400cm-1 to 4000cm-1 at room temperature. The spectra of the blends were used to determine the types of bonding in the blends.

In measuring the different molecule absorbs at difference specific wavelengths of electromagnetic spectrum region, a UV-VIS test was run by using UV-VIS machine, i.e. Shimadzu UV-1800. This method also shows absorption bands from functional group which exits in sample. Visible wavelengths cover a range from approximately 400 to 800 nm. The samples were put in the quartz cuvettes and the differences in the absorption band were observed.

2.5 Water uptake and weight loss tests
The samples were cut into 10 square-shaped. The samples were dried at 60°C for to reach a constant weight. Then, the samples were immersed into 50 ml beaker, each containing 30 ml of deionised water (DI) and placed in a laboratory in room temperature for up 28 days. The experiments took place in two temperature conditions, 25°C and 45°C. In every 7 days, the samples were taken from DI immersion and wiped with tissue paper to remove the water on surface. Water mass uptake of the samples was measured periodically. The percentage change of water uptake was calculated by Equation 1:

$$\Delta Wt = \frac{W_f - W_i}{W_i} \times 100$$

where, $\Delta Wt$ is moisture uptake, $W_f$ and $W_i$ are the mass of the specimen during and before aging, respectively.
After weighing, the same samples were dried in oven at 60°C to eliminate moisture. Then, the samples were weighed and the weight loss was recorded as in Equation 2. The samples were returned into water bath and the same procedure was repeated until 28 days immersion was completed.

\[
\Delta W_{\text{loss}} = \frac{W_i - W_f}{W_i} \times 100
\]

(2)

2.6 Soil burial test

The blended samples were buried under loamy sand-type of soil. The 10 square-shaped of samples were buried in the loamy sand at a depth of 15 cm, for 6 months. After 30, 60, 90, 120, 150 and 180 days of incubation, samples were cleaned by washing in distilled water, drained on tissue paper and then dried in oven until constant weight was reached. The progress of nanocomposite degradation was estimated by weight loss in the samples during the experiments performed. The calculation of weight loss is as shown in Equation 2.

3. Results and discussions

3.1 FTIR analysis

The method used to functionalise the pristine CNTs in this study was the acid treatment method which is described in the methodology section. Through this process, CNTs were oxidised and purified by eliminating impurities such as carbon and metal catalysts. The characteristic bands because of generated functional groups were observed in the spectrum of pure CNTs and surface treated CNTs is shown in Figure 1. The acid treated CNTs showed new peaks in comparison with FTIR spectrum of the untreated CNTs, which lacked hydroxyl and carbonyl groups. The peak at 3767 cm\(^{-1}\) was attributed to free hydroxyl groups. The peaks around 3467 cm\(^{-1}\), 2899 cm\(^{-1}\) and 1382 cm\(^{-1}\) were assigned to the O-H band of carboxylic acid group, and the peak at 1648 cm\(^{-1}\) was assigned to the C=O band for asymmetric carboxyl groups, demonstrating that there have been introduction of hydroxyl and carboxyl groups on the nanotube surface. This peak may also link to aromatic C=C stretches, which explained the appearance in both pure and modified CNTs. In addition, the peak appeared at around 1106 cm\(^{-1}\), apparently corresponded to the stretching mode C–O functional group of carboxylic acid. All new peaks appeared in m-CNTs confirmed the modification of CNTs.

![Figure 1. FTIR analysis for pristine CNTs and modified CNTs](image)

3.2 UV-Vis Analysis
Figure below shows the different absorption peaks between pure CNT and modified CNT (m-CNT) when dissolved in deionised water. The spectrum absorption peak for pure CNT is at 325 nm and 385 nm, attributed to π-π* conjugation of aromatic C=C bonds and n-π* transition of carboxylic group C=O, respectively. The spectrum absorption peak for m-CNT appears at 692 nm, due to π-π* exciton-like transitions according to Beers Lambert Law. The change in absorbance at the given wavelength is due to the change in concentration. The fact that, the untreated CNTs do not show excitation state suggests that substantial surface oxidation did not occur.

![Graph](image)

**Figure 2.** The UV-VIS result for a) pristine CNTs, and b) modified CNTs

### 3.3 Water uptake of nanocomposites

Figures 3 and Figure 4 show the water absorption behaviour for nanocomposites with unmodified CNTs and modified CNTs at different temperatures. The neat PLA indicated hydrophilicity behaviour by absorbing minimum water for both at 25°C and 45°C. Obviously, by adding filler loading in all nanocomposites, arising rise in water sorption trend can be observed, parallel to the Fickian diffusion
behaviour. In Fick’s Law order, the concentration of gradient is the driving force for diffusion and amount of the component diffused in function of time [16]. In general, the water uptake of polymer is determined by two theories: (i) the free volume theory (controlled by the moisture diffusion through substrates) and (ii) the interaction theory (controlled by chemical bonding, e.g. H-bond at the polar site) [17,18]. The nanofiller absorbs water due to the presence of hydroxyl groups which absorb water through the formation of hydrogen bonding [19,20]. All composites showed sharp a sharp increment in water sorption in the beginning and then remained constant after 21 days. The water uptakes at 45°C are higher than at room temperature which reached to 1.951% for 2.0% CNTs loading as compared to 25°C, the water uptake was 1.208%. Higher temperature seems to accelerate the moisture uptake behaviour. This can be explained, at higher temperature, the diffusion process was successfully achieved when water molecules gaining higher energy. Other studies have also reported a similar trend for the ageing of polymer composites at elevated temperature [21,22].

Chemical surface modification can alter polarity and surface tension of the fibres. Hence, this would improve interfacial bonding and decrease the moisture absorption [23]. This was proven by values of water uptake as shown by m-CNTs nanocomposites in Figure 4(a) and Figure 4(b) as compared to untreated CNTs. For 2% m-CNTs loading, the weight loss in room temperature condition reduces to 1.194% while at 45°C, the value decreases to 1.525%. Right chemical treatment improves the filler quality, increases the filler yields and filler’s hydrophobicity and reduces swelling. This finding was similar to Chow et. al (2011) result which their study concluded the water sorption of PMMA/5HA treated zirconate coupling agent (ZCA) was lower than untreated PMMA/5HA composite [18]. This was due to the enhancement in the interfacial bonding between PMMA and ZCA treated HA which leads to better aqueous solution barrier and thus lowering the simulated body fluid (SBF) diffusion. Another finding was reported by Eng and co-workers (2014), where the silane treated OPMF observed lower water sorption rate because modified fibre is less hydrophilic as numbers of hydrophilic hydroxyl groups reduce by react with silane which leads to exclusion of water from substrate [16].

![Figure 3. Water sorption trend in 28 days observation for PLA/CNTs nanocomposites at a) 25°C and b) 45°C](image-url)
3.4 Weight loss behaviour after water sorption

PLA, one of the most well-known biodegradable polyesters, has been investigated in the pharmaceutical and biomedical applications, such as orthopaedic fixture materials, degradable sutures, absorbable fibres, and con-trolled-release devices, etc. Biodegradable polyesters are known to be degraded by the uptake of water followed by the hydrolysis of ester bonds [24]. The phenomenon may be caused by two reasons; (i) water molecules permeate into amorphous area in degradation, (ii) most of molecular chain of amorphous area is ruptured by random hydrolysis. Degradation studies were carried out in deionised water at 25°C and 45°C. Figure 5 describes the weight loss of PLA and PLA/CNTs nanocomposites as a function of time. At room temperature, PLA showed no degradation effect after 28 days compared with PLA/CNTs nanocomposites. The weight loss of PLA/CNTs with 0.5%, 1.0%, 1.5% and 2.0% CNTs were observed to be 0.191%, 0.247%, 0.721% and 1.013%. Along this degradation, the weight loss rate of PLA/CNTs at 45°C was higher than at 25°C. In that 4 weeks, the weight loss of PLA/CNTs increased twice for 1.5% and 2.0% CNTs. These changes can be related to the cleavage of PLA chains to shorter fragments which are caused by the hydrolysis of the ester linkage, followed by interchain transesterification and depolymerisation by back-biting (intra-molecular transesterification).

The weight loss of treated CNTs nanocomposites are lower than untreated CNTs as seen in Figure 6, which could be attributed to the superior combinations between the m-CNTs and PLA matrix. The enhanced interfacial interactions gave rise to improved dispersion and the wetting of CNTs in polymer matrix, enhancing the ‘bridging’ effect between matrix and nanofiller. Chemical modification on the filler surface is applied to promote adhesion between nanofiller and polymer matrix, hence to enhance the dispersion. This can provide compatibilisation with the polymer matrix by bridging, increasing specific interfacial areas and wrapping. This indicates that the m-CNTs is able to hinder the water diffusion into PLA/m-CNTs nanocomposites, avoid deterioration the bonding between PLA and m-CNTs which in turn, can prevent formation of microcavities [25]. The microcavities act as stress concentrators and initiate matrix cracking, leading to the reduction of molecular weight and mechanical properties.

![Figure 4. Water sorption trend in 28 days observation for PLA/m-CNTs nanocomposites at a) 25°C and b) 45°C](image)
3.5 Soil burial effect on weight loss
PLA is one of the hydro-biodegradation polymers that is well-known for being bioassimilable. The speed of biodegradations depends on temperature, humidity, number and type of microbes [26]. Figure 7 presents the biodegradability of the buried specimens in terms of weight loss. The neat PLA shows least degradation which was only 0.043% weight loss after 6 months as compared to PLA nanocomposites. However, a contrary phenomenon was observed by Wu et al. (2010), where they found
the degradation rate of neat PLA was higher than PLA nanocomposites [13]. This indicates that the presence of CNTs could retard the degradation of PLA. Obviously, for both untreated and treated CNTs nanocomposites, the weight loss increased with loading of nanofiller. The PLA/CNTs recorded by addition of 0.5%, 1.0%, 1.5% and 2.0% CNTs, the weight losses are 0.601%, 1.120%, 2.367% and 4.876%. This finding was similar with other researches [14,27]. The CNTs assemblies could be readily released from the nanocomposites surface due to the lack of adhesiveness of CNTs to PLA phase, which accelerated the degradation of PLA by the formation of porous structure.

In treated nanocomposites, the rate of degradation significantly reduced and was proven by mass in loss as 0.563%, 0.952%, 1.949% and 4.502% by nanofiller loading. This indicated that surface modification can influence the bio-disintegrability of CNTs. The compatibility in composites resulted by enhancement of interfacial bonding between PLA and nanofillers [28]. With addition of m-CNTs, it overcomes the problem of phase separation or aging in PLA/m-CNTs blends. The addition of m-CNTs will prevent the diffusion of short molecular chains, which will lead to loss of molecular weight.

![Figure 7](image-url)

**Figure 7.** Weight loss trend of nanocomposites with a) untreated CNTs and b) treated CNTs after 6 months’ soil burial

4. Conclusion
The water absorption of PLA nanocomposites increased with the incorporation of CNTs and m-CNTs. This attributed to the fragmentation and chain scission of polymer initiated by water diffusion under the water absorption environment (especially at immersion temperature, $T = 45^\circ C$) owing to the molecular weight reduction. The water uptake of PLA/m-CNTs nanocomposites was lower than that of PLA/CNTs due to surface modification of m-CNTs which could restrict the diffusivity of water. The decreasing rate in weight loss after soil burial analysis for PLA/m-CNTs shows the improvement of surface modification of nanofiller.

Acknowledgement
The authors gratefully acknowledge the Faculty of Chemical Engineering Technology, TATI University College (TATIUC) and University Malaysia of Pahang (UMP) for providing laboratory facilities and giving supports in this study.
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