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BIODEGRADABILITY EFFECTS ON THE PHA/NFC NANOCOMPOSITE

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Abstract— Plastic has been harmful to the environment and lead to endless pollution due to years of disposal. However, its usage is undeniable hence an alternative to using biodegradable plastic replacing regular plastic is highly recommended. Polyhydroxyalkanoates (PHA) have all characteristics needed as a biodegradable plastic. However, it exhibits brittleness, poor thermo-mechanical properties, and low heat distortion temperature. Therefore, the objective of this paper is to investigate the effect of nanofibril cellulose (NFC) addition on the biodegradability properties of PHA composite. The biodegradation properties were investigated using a soil burial test. The samples were incubated for 7, 14, 21, and 28 days under control conditions, and weight loss for both characterizations was recorded to identify the effectiveness of NFC in the PHA composite. The results shows that the weight of samples was decreased with an increase in incubation time, while its percentage of weight loss was increased as the hydrophilicity of NFC caused the sample to degrade at a higher rate. Although PHA/NFC samples were having a lag time at the earliest stage, it is then degraded better than pure PHA after 21 days. In conclusion, the addition of NFC has greatly improved PHA properties where PHA/NFC 8% is the most sufficient nanocomposite to turn PHA into promising biodegradable plastics and safe for daily usage.

I. Introduction

Plastic application has been found widely in many life aspects where people use plastics to invent many things ranging from the automobile, medicine, and agriculture. Plastics structure can be chemically manipulated to have a wide range of strengths and shapes. The molecular weight is high, and it can easily be molded into any desired shape including fibers and thin films. Also reported is that plastic has high chemical resistance and elasticity hence usage is popular for many durable disposal goods and packaging materials [1]. However, it is unhealthy for the environment and plastic usage is escalating. Therefore, biodegradable plastics are invented as an alternative to petrochemical-derived non-degradable plastic.

Polyhydroxyalkanoates (PHA) is one of the promising biodegradable plastics that is made naturally by various microorganisms. It is biodegradable and has good physicochemical properties that will increase the commercial exploitation of biopolymers in different niche applications [2]. Unfortunately, despite the promising commercial potential, PHA with high monomeric composition tends to exhibit brittleness, low heat distortion temperature, and poor thermo-mechanical properties which makes it less convenient to be used as biodegradable plastics [3]. Therefore, research has been done to improve the properties of PHA as reported by Srithep, [4], and Gumel & Annuar [2], reinforcing fibers can be implemented into PHA to act as nanofillers and fill the gap in PHA composite thus making it a favorable biodegradable plastic. Nanofibrillated cellulose (NFC) has been found the most suitable nanofiller to fulfill the modifications needed by PHA due to its features of having a network-like structure which is good for reinforcement [4].

The driving force for inventing biodegradable plastic is ineffective ways to decompose non-degradable plastics such as incinerating and recycling. Incinerating gives bad effect to the atmosphere where it excretes hydrogen chloride and hydrogen cyanide and causes air pollution. Whereas recycling presents a major disadvantage where the sorting process is exhausting and time consuming [5]. This concern about worsening the environment led to the intense research effort to improve and enhance biodegradable plastic quality and performance. Therefore, by enhancing the improvement of PHA properties, it will promote the commercialization of PHAs and expand their range of applications. The objective of this study is to investigate the effect of nanocellulose fiber additions on the biodegradation properties of PHA composite which ranging from 0 -20 wt%.

II. Methodology

A. Chemicals

Nanocellulose fibril (NCF) acts as filler. NCF was isolated from the empty fruit bunches and purchased from the INTROP, UPM. Other reagents used in the experiment are dichloromethane (99.9 % purity, Sigma-Aldrich Brand) and polyhydroxyalkanoate (PHA) (Biopolymer, 99 % purity) were purchased from Sigma-Aldrich.

B. Production of PHA / NFC Nanocomposite

One gram of a mixture of PHA and NCF is dissolved in dichloromethane [6] at 45°C heated in the water bath. Firstly, the PHA solution is prepared at 0wt% of modified NCF by dissolving it into 40mL of dichloromethane. By this step, the thin layer of PHA is accomplished as result. Secondly, 0.01 g of cellulose nanofiber solid is then added with 40 mL dichloromethane and it is agitated at a speed of 1500 rpm. Next, 4wt% of modified NCF will be suspended in dichloromethane and then will be added into the PHA solution. The mixture was stirred by using a magnetic stirrer at 45°C for 10 minutes before it is poured out on a petri dish. The step was repeated with the addition of 8%, 12%, 16%, and 20% of NCF being suspended in dichloromethane to the PHA solution respectively.

C. Burial Test Method

Biodegradation studies under organic soil conditions were carried out inside a cup with a perforated cover. The soil biodegradation test lasts for a minimum of 7 days and a maximum of 28 days. NFC nanocomposite samples for every ratio (NFC 0%, NFC 4%, NFC 8%, NFC 12%, NFC 16%, NFC 20%) were divided into 4 parts (for each 7, 14, 21, and 28 days) with the same dimension as shown in Figure 1 before its being buried in approximately 2 cm height above the organic soil and 4 cm deep into the organic soil. After the allocated time was done, the samples were removed from the soil and thoroughly rinsed in water, dried, and weighed on the analytical balance to identify the weight loss [7].

Figure 1: Dimension of the sample divided into 4 parts

D. Weight Loss Analysis

The weight measurement of the PHA/NFC samples were performed using an analytical balance before and after the biodegradation testing using the soil burial test method at each time duration test. The weight loss of the sample was calculated using Equation (1).

$$WL\,(\%) = \frac{W_O - W_t}{W_0} \times 100 \qquad (1)$$

where:
WL = Weight loss
Wo = Initial dry mass before degradation which is a 0-day sample
Wt = Residual dry mass of the sample after degradation at an exposure time

E. Scanning Electron Microscopy

Evolution with degradation time of the surface and cross-section morphologies was monitored with JSM-7800F scanning electron microscopy (SEM) with 100000x magnification.

III. Results and Discussion

A. Biodegradation Properties

After completion of incubating samples at 7, 14, 21, and 28 days, the sample was weighed using an analytical weighing balance and the result was illustrated in Figure 2. All PHA/NFC nanocomposites decreased with an increasing incubation period.

This is because the longer the sample is buried, the more microbial activity took place to degrade the sample hence making its weight decrease with time. The moisture from the soil has increased the growth of microorganisms that helps in degrading the PHA/NFC sample. The increasing amount of moisture condition in soil amended with PHA/NFC sample by increasing incubation period may attribute to an increase in the decomposition rate of degradable plastic [8].

Based on Figure 2 also, the weight of PHA/NFC 0% has slightly decrease in weight while PHA/NFC 8% has a major drop in weight from day 7 to day 28, which means PHA/NFC 8% experience higher degradation rate than PHA/NFC 0%. This is because NFC promotes a higher and faster rate of degradation to the sample as its hydrophilicity attracts moisture to enhance the rate of degradation, hence microbial growth will increase, and degradation of the sample will speed up. Therefore, the PHA/NFC that contains a higher concentration of NFC can degrade at a higher rate as the hydrophilicity of NFC is introduced to provide more growth of soil-inhabiting microbial communities [9].

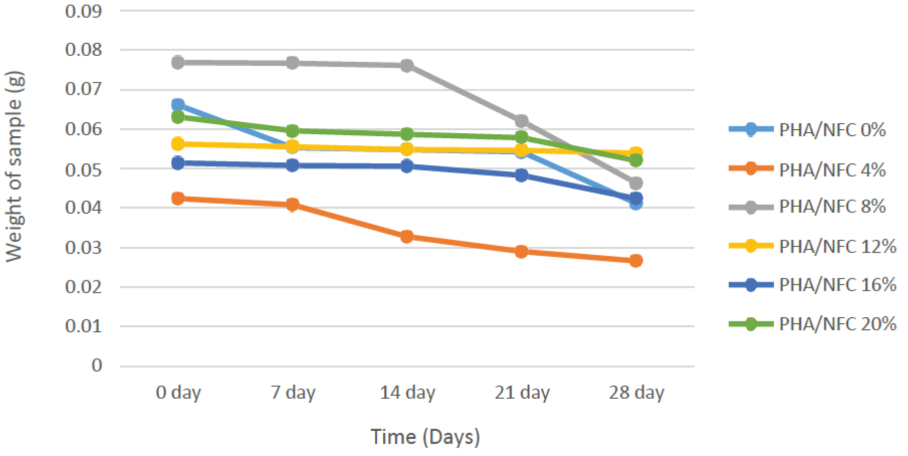


Figure 2: Weight of samples after being buried for 0, 7, 14, 21, and 28 days

Table 1: Weight loss of PHA/NFC samples

Time (Day)	PHA/NFC (wt% WL)					
	0%	4%	8%	12%	16%	20%
0	0	0	0	0	0	0
7	16.21	3.77	0.26	1.25	1.17	5.56
14	16.97	22.64	1.04	2.49	1.56	6.98
21	17.88	31.60	19.27	2.85	6.03	8.25
28	37.58	37.26	39.71	4.09	12.22	17.46

Table 1 shows that PHA/NFC nanocomposites that have a high concentration of NFC degrade slower during the first 7 days of incubation and start to increase after that. Slow degradation occurs due to the lag time between the start of composting and to start of the sample degradation as decomposition occurs by its ease of degradation [8]. This lag period is the time needed for microbial adhesion to reach the material's surface, then it will express and release the extracellular depolymerase [10].

PHA/NFC 0% degrades faster because it has no NFC content and most easily degradable plastic only took around 8 days to degrade to as much as 81.4% [11]. Therefore, the NFC content gives significant effect on the PHA to degrade higher after 7 days of incubation. From this observation, it can be manifest that the addition of NFC to PHA leads to a higher rate of degradation although it took a long time to degrade, the degradation rate recorded after 28 days of incubation is still higher than pure PHA with no additive.

B. Morphological Properties

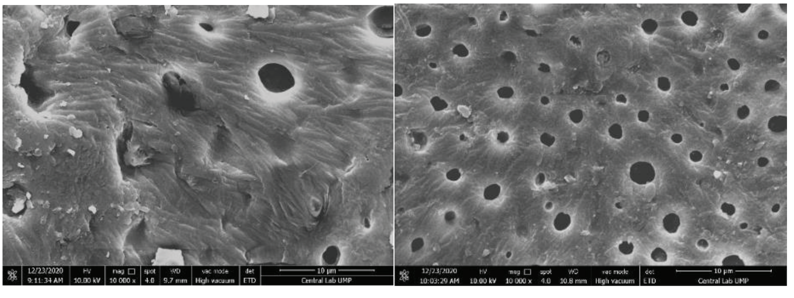
To confirm the biodegradability properties of PHA/NFC nanocomposite, the PHA/NFC 0% and PHA/NFC 20% were tested with Scanning Electron Microscopy (SEM) to visualize its morphological properties during degradation in organic soil as shown in Figure 3. It can be seen that the degradation of both PHA/NFC blends was getting denser as its incubation time increased as there was the presence of moisture from the soil that affected the degradation of the samples.

PHA/NFC 0% has bigger holes after 7 days of incubation while PHA/NFC 20% has smaller holes with slightly bumpy textured on the surface. This shows that PHA/NFC 20% undergo slower degradation than PHA/NFC 0% due to lag time occurred.

In contrast, after 21 days of incubation, PHA/NFC 20% has intense changes in the surface where bigger deeper holes were developed with cracks on the top of it suggesting that microorganisms have penetrated the sample matrix during degradation. Whereas for PHA/NFC 0%, the surface was getting denser from day 14 of incubation until day 28.

In essence, similar outcomes were obtained from SEM microscopy where there was moisture in the soil that caused the sample to be denser as they were prolonged incubated in soil conditions thus increasing the microbial growth and activity and enhancing the degradability of the samples [6].

The efficiency of NFC as filler to increase the degradation rate of PHA was verified as the surface condition was getting worse with deeper holes and surface exfoliation appeared after 28 days incubated compared to PHA/NFC 0%. The higher concentration of NFC present in PHA composite, the better it degrades under the control of the soil environment [12].



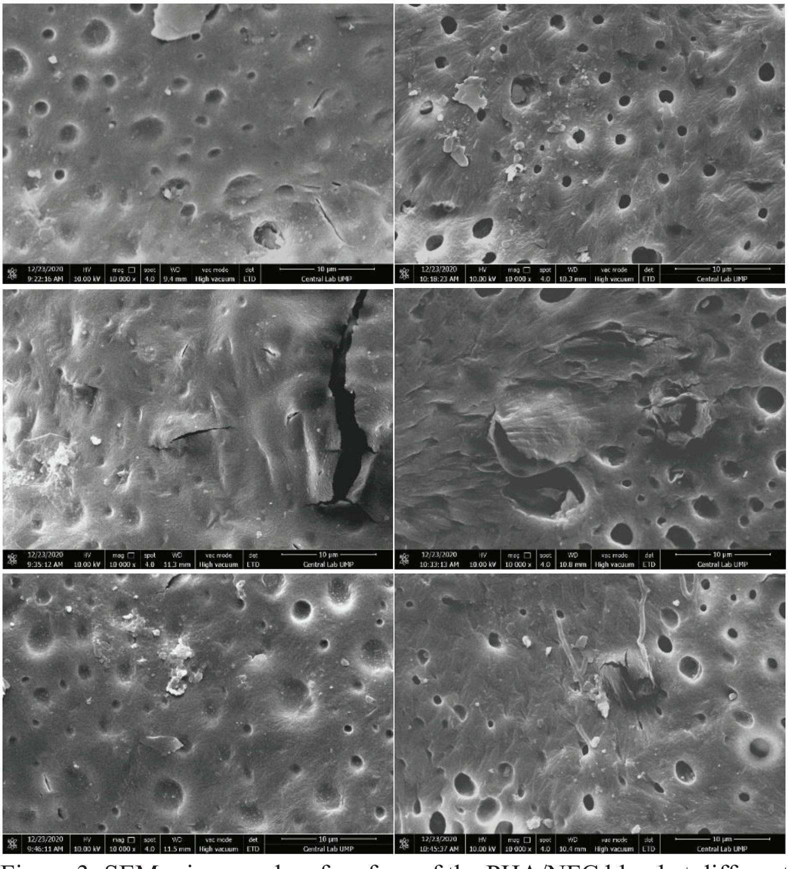


Figure 3: SEM micrographs of surface of the PHA/NFC blend at different degradation time buried in organic soil under 10000x magnification

IV. Conclusions

In summary, PHA can be a promising biodegradable plastic with help from NFC to modify its properties to have a higher rate of biodegradability. Therefore, from biodegradation characterization under the burial test method, it is recognized that the presence of NFC with a longer incubation period makes the sample degrade better. The NFC also gives the weight to be reduced as the moisture content enhances the growth and activity of microorganisms which lead to increasing in rate of degradation. This observation and investigation were supported by SEM microscopy test where more cracks developed by PHA/NFC at 20% although not at the earliest stage.

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