

# Thermal and morphological properties of polyhydroxyalkanoate/ nanosilver composite

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**ABSTRACT** – Conventional plastic can lead to endless pollution as it took millions of years to be disposed of, hence an alternative to using biodegradable plastic replacing regular everyday plastic has highly participated. Polyhydroxyalkanoates (PHA) have the characteristics of a biodegradable plastic however, it exhibits low heat distortion temperature. The objective of this research is to investigate the effect of nanosilver additions on the thermal properties of the PHA composite and its morphology behavior. The PHA was initially dissolved into dichloromethane at room temperature. After that, the nanosilver particle (0, 0.25 and 0.5 wt% of PHA) was added dichloromethane and it was ultrasonicated at 10 minutes. Ultrasonicated nanosilver in dichloromethane mixture was mixed with PHA in dichloromethane for 20 minutes using a magnetic stirrer. Then, thin polymeric films with a thickness of 10  $\mu\text{m}$  were obtained by the solution casting method. The obtained films were then carefully dried at room temperature for 24 hours. The thermal properties and morphology analysis of PHA/nanosilver composite was investigated using thermal gravimetric analysis(TGA) and field emission scanning electron microscopy (FESEM). Based on thermal properties, PHA/0.5wt% nanosilver has shown a lower onset temperature compared to the pure PHA. This indicates that PHA/0.5wt% nanosilver has a slower degradation rate and higher thermal stability. In conclusion, nanosilver has greatly improved PHA properties into promising biodegradable plastics.

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## INTRODUCTION

Nowadays, with the development of technology and the increase in the global population, the application of plastic has been found worldwide in almost every aspect of life and industry such as the manufacturing industry ranging from automobiles to the food industry. In the aspect of the food industry, one of the most basic materials used in food packaging is plastic. This is due to its numerous advantages as a synthetic polymer, where the structure can be chemically manipulated to have a wide range of strengths and shapes. Other than that, plastic also has good properties of high chemical resistance and elastic, hence its usage is popular in many durable disposal goods and as packaging materials (Reddy et al., 2003). It is relatively low cost, has great mechanical, and has good barrier properties (e.g., oxygen, carbon dioxide, anhydride, and aroma compounds). However, petroleum-based, or conventional plastic materials such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyamide (PA), are undesirable as they are non-biodegradable and non-renewable sources and cause difficulty in their disposal as well as becoming a threat to the future environment if its accumulation in the environment is unbearably increasing from time to time. The production and disposal of conventional plastics not only create huge damage to the environment but also, water resources, and the entire ecosystem [1].

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, has low heat distortion temperature, and poor thermomechanical properties which make it less convenient to be used as biodegradable plastics [3]. Therefore, research has been done to improve the properties of PHA on 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 [4,5]. Nanosilver 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 polymer reinforcement.

The driving force for inventing biodegradable plastic is due to ineffective ways to decompose non-degradable plastics such as incinerating and recycling. Incinerating is bad for the atmosphere where it excretes hydrogen chloride and hydrogen cyanide and causes air pollution while recycling presents a major disadvantage where the sorting process is exhausting [6]. This concern of worsening the environment led to intense research efforts 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 different amounts of nanosilver in PHA composite. In addition, thermal properties, and morphology behavior of PHA composite will also be investigated.

## MATERIALS AND METHOD

### Materials

Nanosilver powder was purchased by Sigma- Aldrich, which will act as filler. Other reagents used in the experiment such as dichloromethane (99.9% purity) and polyhydroxyalkanoate (PHA) (Biopolymer, 99 % purity) were purchased by Sigma- Aldrich.

### Synthesis of PHA /nanosilver via solution polymerization method

0.4 wt/v of polyhydroxyalkanoate (PHA) was dissolved in 30 mL dichloromethane at room temperature. Next, the PHA solution was prepared without the addition of the nanosilver. The result obtained was a thin film of pure PHA. For PHA/nanosilver composite preparation, 0.075g (for 0.25wt%) of the nanosilver powder was added in 5 mL dichloromethane and it was ultrasonicated for 10 minutes. Next, this nanosilver suspension in dichloromethane was added to the PHA solution. The mixture was stirred using a magnetic stirrer at 25°C for 20 minutes at 1000 rpm before it is poured out on a petri dish. The PHA/0.25 nanosilver was left dried overnight to obtain a thin film. The step was repeated with the addition of 0.5wt% nanosilver suspension in dichloromethane to the PHA solution.

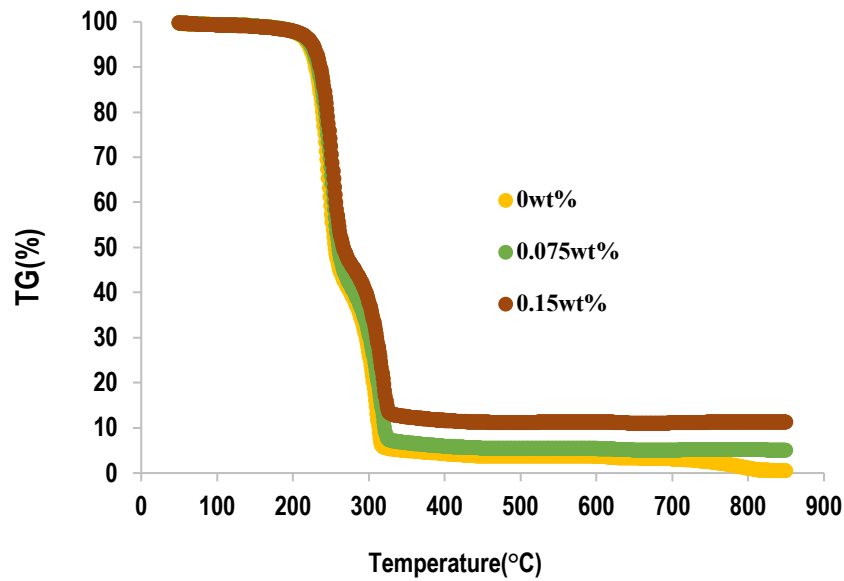
### Characterization

A thermal gravimetric (TGA) were carried out to determine the PHA/ nanosilver composites' thermal degradation and thermal stability. Approximately 15mg of each sample was heated from 30°C to 900°C at the heating rate of 10°C/min. The measurement was performed under nitrogen and air atmosphere by using an alumina pan. All kinetic parameters and decomposition temperature of samples were evaluated by using thermal data using Microsoft Excel [7]. A JSM-7800F FESEM was used to visualize the morphology of the nanosilver and polyhydroxyalkanoates (PHA). The samples were coated with platinum and were examined under the maximum magnification of 100 000x.

## RESULT AND DISCUSSION

### Thermal analysis

Thermogravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. The result obtained from TG analysis were illustrated in Figure 1 and its weight loss at onset temperature were tabulated in Table 1. Referring to Figure 1, the decomposition reaction for each sample occurs in a narrow temperature range and the curves of each sample had the same decomposition pattern but with a slight difference in slopes. This demonstrates that each type of polymer has different kinetic parameters and thermal stability temperatures [8]. TG curves of PHA/nanosilver composite were shifted toward higher temperature thus specifying thermal stability. The differences in thermal stability for each nanocomposite could be attributed to a different amount of nanosilver blend in the PHA composite. Previous work has proven that molecular weights play an important role in greatly influencing the thermal behavior of the composite [8]. From Table 1, PHA/0.5 wt% nanosilver shows a lower onset temperature compared to pure PHA. This indicates that PHA/0.5 wt% nanosilver has a slower degradation rate and, the composition with a slower degradation rate has higher thermal stability. This happens due to the presence of the nanosilver that lowers down the thermal degradation temperature of the PHA component thus making it degrade at a slower rate in the under-tested temperature region. Therefore, it is proven that the addition of nanofillers can greatly improve the thermal stability of nanocomposites by enhancing the filler-PHA matrix interaction through hydrogen bonding, hence making the composition a thermally stable material [9].



**Figure 1.** TG analysis of AgNPs/PHA composite.

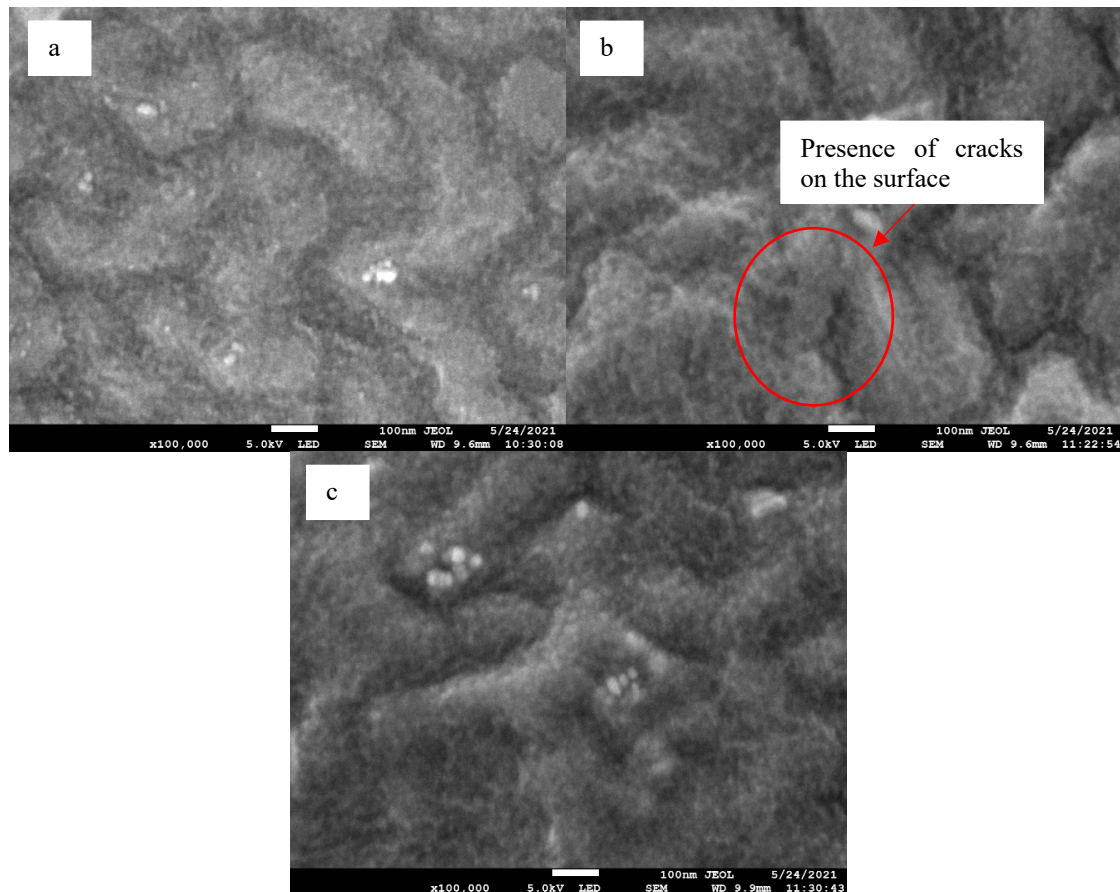
Table 1 shows that all composite with different ratios has three-step degradations. As the concentration of nanosilver is getting higher, the residual weight increase with increasing residual temperature. This represents more solid formation remains at the end of the thermal degradation process. The weight loss for all nanocomposite occurred in the temperature range of 160 °C – 325 °C due to structural degradation of the nanocomposite and the total weight loss was about 2% – 60%. Referring to Table 1, PHA/0.5wt% nanosilver shows higher weight loss and higher residual temperature compared to pure PHA which means that it has higher thermal stability. Its higher percentage of weight loss at degradation also indicates its properties of having a slower degradation rate. Hence, it is apparent that the incorporation of nanosilver had increased the thermal stability of PHA and substantially slow down the rate of degradation of the composite films within the temperature region [9].

**Table 1.** Degradation data for AgNPs/PHA composite.

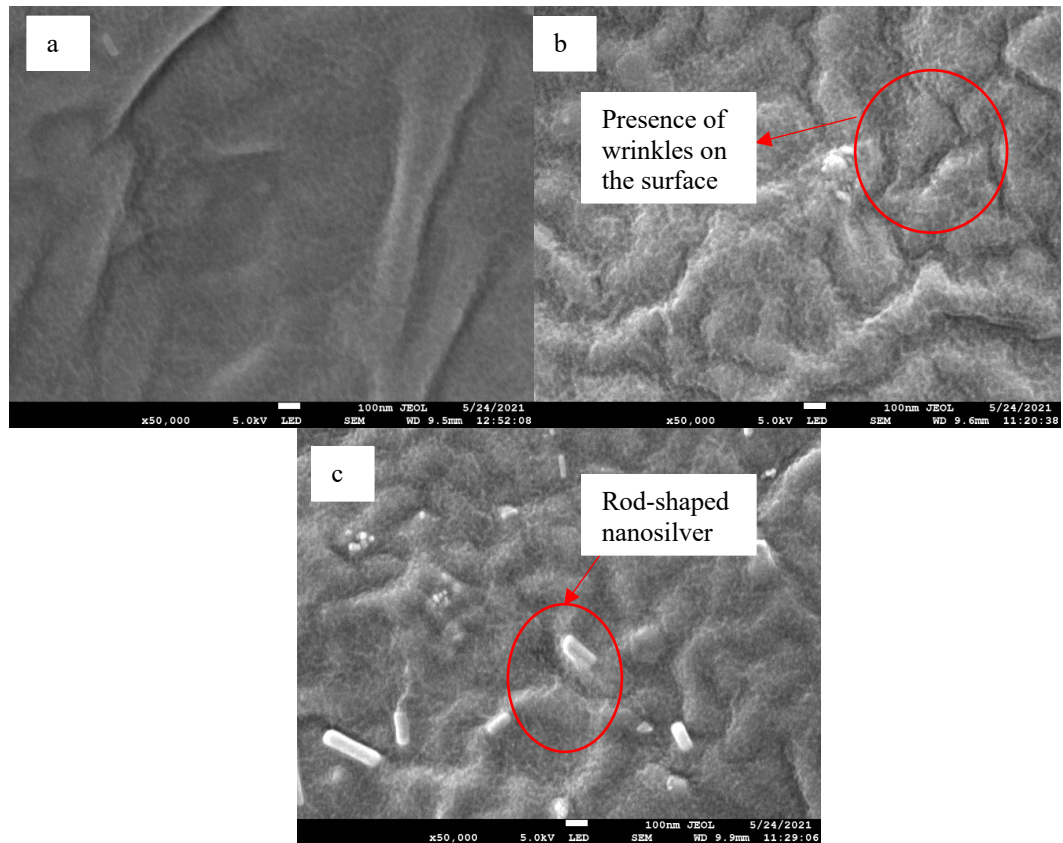
Sample	No. of degradation	Onset temperature (°C)	Weight loss at degradation (%)	Residual temperature (°C)	Residual weight (%)
Pure PHA	1	188.09	2.113	858.0	0.5009
	2	232.34	58.42		
	3	316.18	34.34		
PHA/0.25	1	187.72	1.252	858.5	5.114
	2	231.55	52.73		
	3	323.58	32.62		
PHA/0.5	1	161.43	2.020	858.9	11.29
	2	229.97	57.49		
	3	309.08	34.21		

## Morphological analysis

The characteristics and homogeneity of the nanosilver were studied using FESEM. The pure PHA, PHA/0.25wt% composite, PHA/0.5wt% composite were tested with field emission scanning electron microscopy (FESEM) to visualize its morphological properties. FESEM micrographs of the surface of the PHA/nanosilver were examined under 100000x magnification, (Figure 2), and 50000x magnification (Figure 3). The size and morphology of synthesized silver nanoparticles (AgNPs) were determined through the FESEM micrograph [10]. The FESEM images indicate that non-spherical nanoparticles with an average size ranging from 42 nm to 50 nm are produced. Figure 2 shows the morphology of pure PHA is smooth surface, while the nanosilver in the PHA/0.25wt% composite can not be seen compared to the PHA/0.5wt% composite. Based on Figure 2b, PHA/0.25wt% composite that was having obvious cracks and peeling on its surface while PHA/0.5wt% composite (Figure 2c) has slight cracks only. As Figure 3b, the PHA/0.25wt% composite had a rough and discontinuous surface with a few wrinkles as compared to the pure PHA. FESEM micrographs in Figure 3c on the surface of the PHA/0.5wt% composite under 50000x magnification show that the microstructure of the PHA/nanosilver composites and their corresponding cross-linked films. The film surfaces showed that nanosilver was found in the rod-shaped at the surface of the films of 0.5wt%. PHA with nanosilver composite film exhibits small distinct particles on the surface and they had a rough structure with irregular shapes. The results show that high temperatures were sufficient to disintegrate the PHA granules. Figure 3b shows that there is poor interfacial interaction between PHA and nanosilver. In addition, it was determined that the addition of cross-linking agent will improve the compatibility and interfacial interactions between PHA and nanosilver. These results may be affected by the functional groups that become compatible with PHA by reducing the difference in polarity between the polymers. The higher concentration of nanosilver present in the PHA composite, the better it degrades itself.



**Figure 2.** Morphology of a) pure PHA, b) PHA/0.25 composite, and c) PHA/0.5 composite at 100 000 magnification.



**Figure 3.** Morphology of a) pure PHA, b) PHA/0.25 composite, and c) PHA/0.5 composite at 50 000 magnification.

## CONCLUSION

In conclusion, PHA can be a promising biodegradable plastic with help from nanosilver to modify its properties to be thermally stable and has a higher rate of biodegradability. The nanosilver reinforced polyhydroxyalkanoates (PHA) composites were successfully fabricated by the solution polymerization method. From TG analysis, the PHA/0.5wt% composite was identified to have a higher percentage of weight loss, higher thermal stability, and a lower rate of degradation. FESEM images indicated the morphology and behavior of the PHA/nanosilver structure and composition. In conclusion, the addition of 0.5 wt% nanosilver in PHA exhibits optimum thermal properties since nanosilver 0.5wt% has shown lower onset temperature compared to pure PHA. This indicates that PHA/0.5wt% nanosilver has a slower degradation rate, and composition with a slower degradation rate has higher thermal stability. Above all observations obtained, PHA/0.5wt% nanosilver was found to be the most favorable PHA/nanosilver nanocomposite.

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