

# Effect on Thermal Properties of Nanocellulose Fibre (NCF) Reinforced Biodegradable Polyhydroxylalkanoates (PHA) Composite

N. S. Nazaruddin<sup>1</sup> and S. S. Jamari<sup>2,\*</sup>

<sup>1</sup>Faculty of Engineering, Universiti Malaysia Pahang, 26300 Pahang, Malaysia.

<sup>2</sup>Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, 26300 Pahang, Malaysia.

**ABSTRACT** – Currently, biodegradable materials like polyhydroxyalkanoates (PHA) and polylactic acid (PLA) are receiving huge attention from the both scientific and industrial sectors. However, since PHA has poor thermal properties, there is a shortfall in the exploration of PHA ability with filler. Therefore, this research aim is to investigate the thermal effect of nanocellulose fiber (NCF) fillers with PHA polymer. The first solution of PHA composite is prepared by dissolving 1g of PHA in 40mL of dichloromethane at 30°C for 10 minutes. The PHA-NCF composite solution is prepared by adding 1wt%, 2wt%, 3wt%, and 4wt% of NCF dissolved in 40 mL of dichloromethane into the PHA solution. The mixture solution is agitated at 45°C with a magnetic stirrer for 10 minutes. The mixture is poured into a petri dish. The prepared films were characterized by Differential Scanning Calorimeter (DSC), Fourier Transforms Infrared Spectroscopy, (FTIR), and Thermogravimetric Analysis (TGA). The FTIR analysis shows that all PHA/NCF composite samples contain similar functional groups when compared with the pure PHA. No significant changes on the thermal properties of the PHA composite was observed with the addition of NCF fillers. However, comparison within the PHA/NCF samples shows that the PHA with 2% of NCF has a higher melting temperature and requires the highest enthalpy of melting. Hence, the addition of 2% of NCF is selected to be the optimum amount of NCF filler addition to the PHA composite.

## ARTICLE HISTORY

Received: 23 Feb. 2021

Revised: 13 April 2021

Accepted: 16 April 2021

## KEYWORDS

*Thermal analysis*

*Nanocellulose fiber*

*Polyhydroxylalkanoates*

## INTRODUCTION

Biodegradable plastics or bioplastics are polymer materials that produced from the renewable raw materials such as biomass, sugar, and vegetables fats. The advantage of bioplastics is the ability of this material to decompose naturally in soil to forms other products such as carbon dioxide, methane, water, and inorganic compounds [1]. The degradation properties increase the potential application of the bioplastic as well as becoming an alternative of the traditional plastics usage. The common synthesized bioplastics available are poly-lactic acid (PLA), poly-butyl styrene (PBS), and polyhydroxyalkanoates (PHA) [2]. Among the synthesized bioplastics, PHA is a newly manufactured and has potential for further investigation.

Polyhydroxyalkanoates (PHA) is a large biodegradable family of polymers which are produced from renewable carbon sources by microorganisms. The microbes produce PHA as a carbon storage, where they are stored in granule until the microbes have enough nutrients for growing and reproduction process. PHA monomers are 3-hydroxyalkanoic acids (3-HA), 3-hydroxybutyrate, 3-hydroxyvalerate, 3-hydroxyhexanoate and 3-hydroxyheptanoate that polymerize to produce polyesters-based polymer [3]. PHA is regarded as a renewable resource-based alternative to petrochemical polymers which has the potential to substitute polypropylene, polyethylene, and polystyrene, which are the three main polymers of the global polymer market [4]. Despite having such potential to substitute petrochemical polymers, PHA is poor in thermal properties. Therefore, filler addition in the PHA matrix in theory will be able to improve the thermal properties of PHA.

In this work, the investigation on the effect of filler addition, nanocellulose fibril (NCF), in the PHA polymer matrix will be investigated. Nanocellulose fibril (NCF) was chosen as the filler due to the high thermal stability properties as well as natural and renewable fibre material. The thermal properties of the PHA/NCF composites will further characterize using Differential Scanning Calorimeter (DSC), Thermogravimetric Analysis (TGA), and also Fourier Transforms Infrared Spectroscopy (FTIR) for the chemical properties.

## MATERIALS AND METHODS

### Chemicals

Nanocellulose fibril (NCF) acts as filler. NCF was isolated from the empty fruit bunches and purchased from the Institute of Tropical Forestry and Forest Product (INTROP), UPM. Other reagents that were used in the experiment are

dichloromethane (99.9 % purity, Sigma-Aldrich Brand) and polyhydroxyalkanoate (PHA) (Biopolymer, 99 % purity) were purchased from Sigma-Aldrich.

### Synthesis of NCF via Solution Polymerization Method at Different Ratio

The PHA solution was prepared without the addition of NCF by dissolving 1 gram of PHA into 40 mL of dichloromethane at 45 °C heated in the water bath. Next, the NCF (0 -4 wt% according to the PHA mass) was mixed in a 10 mL dichloromethane and stirred continuously at 1500 rpm until the NCF is fully dispersed. The NCF suspended in the dichloromethane was then added into the PHA solution. The mixture was stirred continuously at 45 °C for 10 minutes at 1500 rpm and then poured in the petri dish [5]. The mixture in left dried in the petri dish at room temperature for 5 hours to obtain a thin film (PHA/NCF composite) for further analysis.

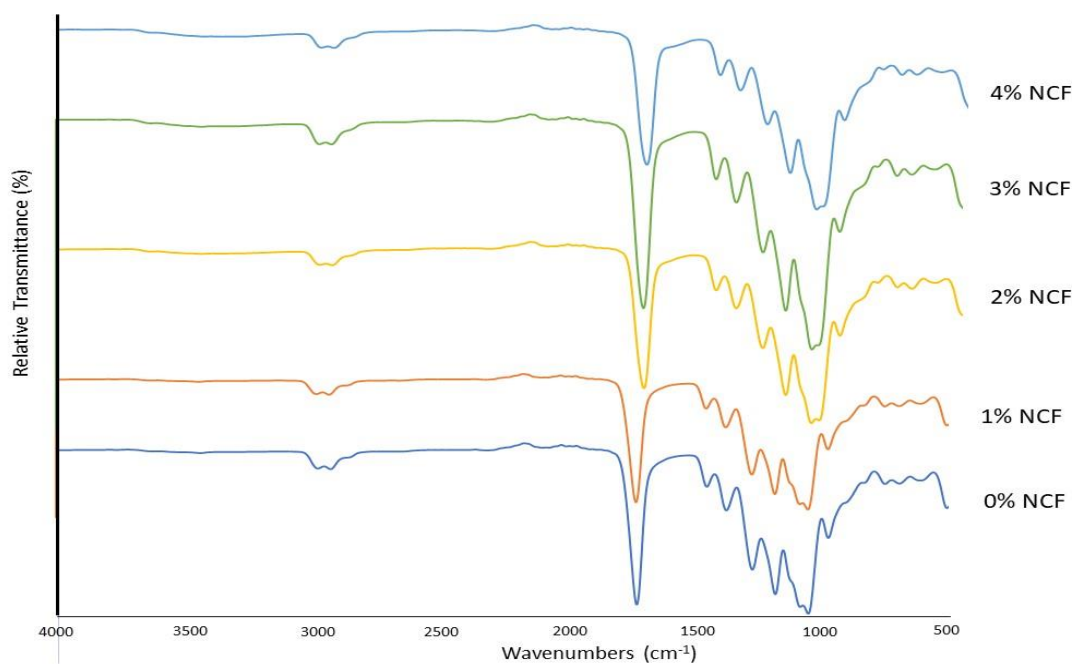
### Characterization of PHA/NCF Composite

The FTIR analysis of the PHA/NCF composite film was conducted with a PERKIN ELMER (Thermo Fisher Scientific Co., Ltd., USA) within 400  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ . The thermal properties of the PHA/NCF composite were done with a Perkin Elmer, DSC8000 instruments under a constant nitrogen flow of 50 mL/min were used. The samples were heated from 25 °C to 185 °C at 10 °C/min and kept isothermal for 60 seconds to determine the melting temperature,  $T_m$  and enthalpy of heat fusion,  $\Delta H_m$  (J/g). The TGA of PHA/NCF composite was carried out using Hitachi, STA7200 from 50 °C to 900 °C at a constant rate of 10 °C/min under a stable nitrogen atmosphere.

## EXPERIMENTAL RESULTS

### Effect of Chemical Properties on PHA/NCF Composite

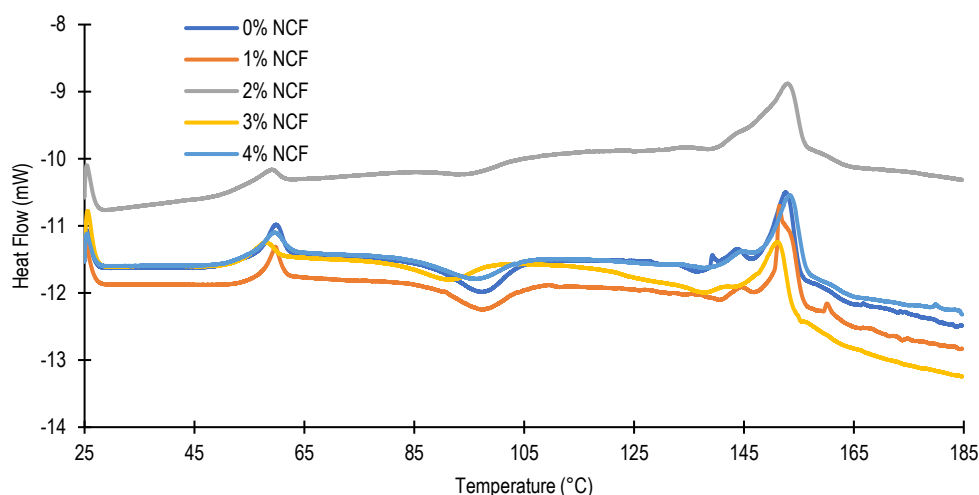
FTIR spectra reveal almost identical peaks of neat PHA (0 wt% NFC) and PHA/NCF composite as illustrated in Figure 1. The specific spectra of NFC include strong OH stretching in the range of 3600–3000  $\text{cm}^{-1}$ , CH and  $\text{CH}_2$  stretching vibrations between 3000 – 2800  $\text{cm}^{-1}$ , and CO and CC stretching bands in the range of 1200 – 900  $\text{cm}^{-1}$  [6]. The chemical structure of PHA monomers consists of – OH, - CO, -CH and C=O bonding [7] as proven with the FTIR spectra detected in Figure 1. As the similar chemical bonds presents in both matrix (PHA) and filler (NFC), therefore identical FTIR spectra were detected for the all the composites.



**Figure 1.** FTIR spectrum of PHA/NCF with various NCF content.

### Thermal Properties of PHA/NCF Composite

The thermal properties of the PHA/NCF composites, including its melting behavior, were investigated using DSC. Figure 2 shows that the DSC trends for all the composites is almost similar with two exothermic peaks and an endothermic peak detected. The result obtained is as shown in Figure 2 as the trend of the graph is similar, where after around 152 °C the sample start to degrade. From the figure also, it could be seen that the melting temperature of PHA polymer composite does not change drastically when NCF fillers were added. Thus, the addition of the nanocellulose fibrils into the polymer PHA does not offer major changes in the thermal properties.

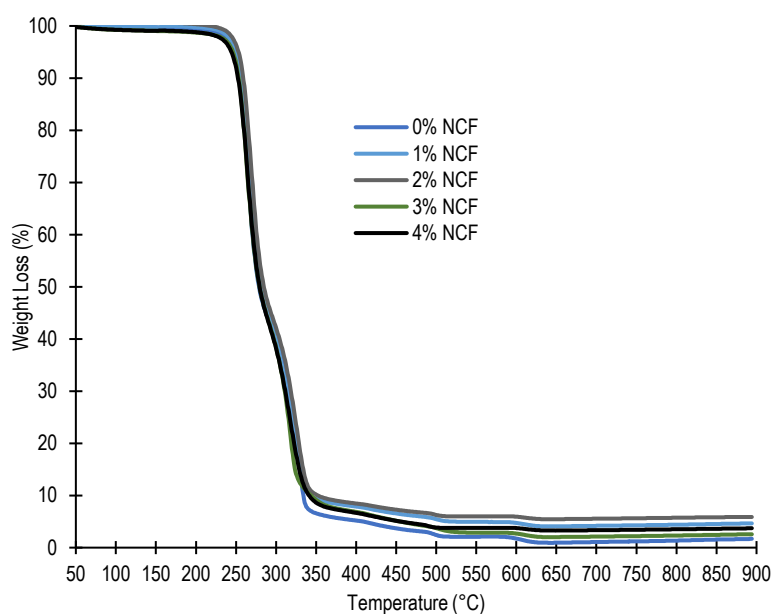


**Figure 2.** DSC curves of neat PHA (0 NCF) and PHA/NCF composites.

**Table 1.** Melting point and enthalpy of melting of PHA/NCF composites.

NCF content (%)	$T_m$ , °C	$\Delta H_m$ , J/g
0	152.67	6.46
1	151.44	8.83
2	152.98	13.80
3	151.12	9.83
4	153.39	10.94

Table 1 shows the melting point ( $T_m$ ) and the energy required ( $\Delta H_m$ ) for neat PHA and PHA/NCF composites. The melting temperature of the PHA/NCF composites is between 151 °C to 153 °C while, the recorded melting point of the neat PHA is at 152.67 °C. The higher the melting temperature, the stronger the intermolecular bond of the composite. From the table, we could see that sample with the addition of 4% of NCF had the highest melting temperature. However, a sample with 2% of NCF required the highest energy to melt which allowed this sample to be the best choice of all samples. According to Bugnicourt et al. [8], the typical range of PHA's melting temperature is around 160 °C to 175 °C. Thus, the characterization by the thermal analyses confirmed the purity of the product.



**Figure 3.** TGA thermograms of PHA/NCF composites at different NCF amounts.

Thermal sensitivity is known to be an important processing consideration for PHA biopolymers. The thermogravimetric from the TGA analysis are therefore presented in figure 3, with associated parameters being summarized in Table 2. Figure 3 showed the thermogravimetric data recorded for the neat PHA and PHA/NCF composites have similar

degradation trends, indicating the addition of the NCF into the polymer PHA also did not bring any significant changes in the thermal analysis. The thermogravimetric data for all samples relatively started to decrease drastically around 253 °C. It is mentioned by de Souza et al., [9] where the peak degradation of PHA was identified to be around 253.4 °C. Also, from Wang et al [10], it was stated that thermal degradation of NCF started at 223 °C, and the maximum degradation temperature is at 338 °C. The presence of the composite is confirmed by the result recorded from the analysis.

**Table 2.** Onset Temperature and percentage of weight loss for PHA/NCF composites.

NCF content (%)	2 <sup>nd</sup> Onset Temperature, °C	Weight Loss (wt%)	3 <sup>rd</sup> Onset Temperature, °C	Weight Loss (wt%)
0	315.0	38.25	478.9	2.98
1	308.8	35.80	492.8	2.80
2	311.3	37.10	493.6	0.90
3	307.3	36.06	476.2	4.00
4	308.0	35.90	482.4	3.00

From Table 2, we could see that the PHA composite sample with 2 wt% addition of NCF has lower temperature on 2nd onset temperature and higher temperature at 3rd onset temperature when compared to pure PHA. It could be seen here also that this sample had the highest weight loss compare to others at 2nd onset temperature which can indicate that it is more combustible. However, PHA with addition of 2 wt% of NCF is more stable thermally compared to pure PHA composite and other PHA/NCF samples [11].

## CONCLUSION

In conclusion, the addition of the nanocellulose fibrils (NCF) able to maintain the thermal stability of the polyhydroxyalkanoates (PHA) polymer composite. The result from thermal analysis gave out almost similar conditions even with the addition of NCF fillers. Thus, from the five different samples ran for all analysis, PHA composite with an addition 2 wt.% of NCF exhibited high melting temperature indicating stronger intermolecular attraction between molecules. Other than that, PHA composite with a 2 wt% of NCF also showed a slightly better thermal stability since it has the highest temperature to start degrading in TGA result.

## ACKNOWLEDGMENT

This work was financially supported by the Internal Grant Scheme (RDU1803104) awarded by Universiti Malaysia Pahang.

## REFERENCES

- [1] K. Major-Gabryś, A. Grabarczyk and S. Dobosz, "The Compositions: Biodegradable Material – Synthetic Resins as Moulding Sands Binders," *Archives of Foundry Engineering*, vol. 16, no. 4, pp. 75-78, 2016, doi: 10.1515/afe-2016-0087.
- [2] M. Sharma, and H. Dhingra, "Poly-β-hydroxybutyrate: A Biodegradable Polyester, Biosynthesis and Biodegradation," *British Microbiology Research Journal*, vol. 14, no. 3, pp. 1-11, 2016, doi: 10.9734/bmrj/2016/25430.
- [3] M. Mariano, and A. Dufresne, "Nanocellulose: Common Strategies for Processing of Nanocomposites," *Nanocelluloses: Their Preparation, Properties, and Applications*, pp. 203-225, 2017, doi: 10.1021/bk-2017-1251.ch011
- [4] K. Changwichan, T. Silalertruksa, and S. Gheewala, "Eco-Efficiency Assessment of Bioplastics Production Systems and End-of-Life Options", *Sustainability*, vol. 10, no. 4, pp. 952,2018, doi: 10.3390/su10040952.
- [5] F. Valentini, A. Dorigato, D. Rigotti, and A. Pegoretti, "Polyhydroxyalkanoates/Fibrillated Nanocellulose Composites for Additive Manufacturing," *Journal of Polymers and the Environment*, vol. 27, no.6, pp. 1333-1341, 2019, doi: 10.1007/s10924-019-01429-8.
- [6] L. Wang, K. Okada, Y. Hikima, M. Ohshima, T. Sekiguchi, and H. Yano, H. "Effect of cellulose nanofiber (CNF) surface treatment on cellular structures and mechanical properties of polypropylene/CNF nanocomposite foams via core-back foam injection molding," *Polymers*, vol. 11, no. 2, pp. 1–18, 2019, <https://doi.org/10.3390/polym11020249>.
- [7] J. Coates, "Interpretation of Infrared Spectra, A Practical Approach. Encyclopedia Of Analytical Chemistry," 2006, doi: 10.1002/9780470027318.a5606.
- [8] E. Bugnicourt, P. Cinelli, A. Lazzeri, and V. Alvarez, " Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging," *Express Polymer Letters*, vol. 8, no. 11, pp. 791-808, 2014, doi: 10.3144/expresspolymlett.2014.82
- [9] R. G. de Souza, M. Michels, G. Fajardo, I. Lamot, and J. de Best, "Optimization of Green Extraction and Purification of PHA Produced by Mixed Microbial Cultures from Sludge," *Water*, vol. 12, no. 4, pp. 1185,2020, doi: 10.3390/w12041185.
- [10] L. Wang, K. Okada, Y. Hikima, M. Ohshima, T. Sekiguchi, and H. Yano, H. "Effect of cellulose nanofiber (CNF) surface treatment on cellular structures and mechanical properties of polypropylene/CNF nanocomposite foams via core-back foam injection molding," *Polymers*, vol. 11, no. 2, pp. 1–18, 2019, <https://doi.org/10.3390/polym11020249>.
- [11] M. Ioelovich, "Nanocellulose—fabrication, structure, properties, and application in the area of care and cure," *Fabrication And Self-Assembly Of Nanobiomaterials*, pp. 243-288, 2016, doi: 10.1016/b978-0-323-41533-0.00009-x