Bionanocomposites From Poly(3-Hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and Cellulose Nanofibres: Mechanical and Thermal Properties

Daphney Hlotse [a,*], Washington Mhike [a], Vincent Ojijo [b], Mxolisi Brendon Shongwe [a], Maya Jacob John [b,c]

[a] *Tshwane University of Technology, Pretoria, South Africa*

[b] *Council for Scientific and Industrial Research, Pretoria, South Africa*

[c] *Nelson Mandela University, Port Elizabeth, South Africa*

Editor's note: PHBH is a biodegradable polyester known for its non-toxicity and biocompatibility. Hlotse et al. explored the effect of cellulose nanofibres (CNFs) on PHBH bionanocomposites. Adding 1% CNF improved tensile strength and Young's Modulus due to hydrogen bonding, but higher concentrations led to agglomeration and reduced properties. PHBH/CNF bionanocomposites show potential as alternatives to traditional plastics.

doi: 10.22034/jams.2026.260206

How to cite: D. Hlotse et al., *Journal of Applied Material Science*, **2026**, *2*, 260206.

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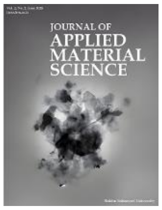
Journal of Applied Material Science **2026**, *2*, 260206
How to cite: D. Hlotse et al., *Journal of Applied Material Science*, **2026**, *2*, 260206.
Journal homepage: **jams.hsu.ac.ir**



Original Research

Bionanocomposites From Poly(3-Hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and Cellulose Nanofibres: Mechanical and Thermal Properties

Daphney Hlotse [a,*], Washington Mhike [a], Vincent Ojijo [b], Mxolisi Brendon Shongwe [a], Maya Jacob John [b,c]

[a] *Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa*

[b] *Centre for Nanostructures and Advanced Materials, Council for Scientific and Industrial Research, Pretoria, South Africa*

[c] *Department of Chemistry, Nelson Mandela University, Port Elizabeth, South Africa*

Abstract

Poly(3-hydroxybutyrate-co-3-hydroxybutyrate) (PHBH) is a biodegradable polyester that has attracted significant attention in research thanks to its remarkable qualities, including non-toxicity, biodegradability across various environments, and biocompatibility. Cellulose nanocrystals have emerged as the most-researched bio-based reinforcement, mainly due to their high mechanical properties, biodegradability, and the fact that they can be extracted from various waste biomass resources such as sawdust and bagasse. This study aimed to examine how cellulose nanofibres (CNFs) influence the mechanical and thermal properties of PHBH bionanocomposites. The PHBH bionanocomposites, incorporating CNFs of different concentrations, were produced through casting and melt-processing. The results obtained showed that the addition of CNFs as a reinforcement to the PHBH matrix enhanced the mechanical properties. At a 1% CNF loading, an enhancement in both tensile strength and Young's Modulus was observed. This improvement is attributed to the establishment of a hydrogen bonding network between PHBH macromolecular chains and the hydroxyl groups on CNFs. However, increasing the content of CNFs led to agglomeration during processing, which affected these mechanical properties. The resulting mechanical and thermal characteristics suggest that PHBH/CNF bionanocomposites could be effectively used as alternatives to conventional plastics in various applications.

Keywords: Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH); Cellulose nanofibers; Mechanical properties; Thermal properties.

* Corresponding author.
Email address: hlotsed@gmail.com (D. Hlotse)

Received 5 January 2026
Revised 1 May 2026
Accepted 15 May 2026
Available online 19 May 2026

https://doi.org/10.22034/jams.2026.260206

1. Introduction

Plastics originating from petrochemicals are being used more frequently, which negatively affects the environment due to their low biodegradability. As a result, these materials can persist in the ecosystem for many years. Additionally, burning this waste releases significant pollutants into the environment and leads to severe health issues. It can cause cardiac diseases, worsen lung conditions like asthma and emphysema, trigger rashes, fatigue, headaches, and even damage the nervous system [1]. Biodegradable plastics have gained prominence as potential solutions to this issue. Although biodegradable plastics can break down in the environment, they often suffer from low durability and stability. As plastic pollution increasingly threatens environmental stability, there is growing global interest in biodegradable polymers. As a result, it is important to manage these issues because the intended issue requires a specific degradation rate [2, 3].

PHBH is a type of copolymer within the group known as polyhydroxyalkanoates (PHAs). These are biodegradable polyesters generated by bacteria when there is an abundance of carbon source. PHBH offers numerous advantages as a biodegradable polymer, particularly due to its reduced rigidity compared to the poly(3-hydroxybutyrate) (PHB) homopolymer. This flexibility expands its potential for various industrial applications, especially in packaging [3, 4]. It is formed by incorporating randomly arranged units of 3-hydroxybutyrate (3HB) and 3-hydroxyhexanoate (3HH). Over the years, numerous reports have indicated that as the presence of 3HH units in a copolymer increases, both Young’s modulus and tensile strength tend to decrease. Simultaneously, this results in an increase in elongation at break due to the reduced crystallinity of the copolymer [5]. PHBH offers numerous benefits as a biodegradable polymer, featuring lower rigidity than the poly(3-hydroxybutyrate) (PHB) homopolymer. This characteristic expands its potential for industrial uses, particularly in the packaging sector. Due to its significant contributions to the polymer industry, PHBH has been extensively studied as a matrix in polymer blends. Its primary contribution is enhancing flexibility and reducing the rigidity of other components within these blends [3, 6].

However, PHBH has also shown limitations and disadvantages, such as a slow crystallization rate and vulnerability to heat treatment. Due to these properties, the thermal and mechanical properties, as well as melt processability, are not as advanced as those of plastics derived from petroleum. As a result, PHBH's performance is currently inadequate to substitute for petroleum-based plastics, and its use remains restricted. Numerous studies have been carried out to enhance the performance of PHBH, including blending it with other biopolymers or incorporating bio-based or natural fillers [7].

Several studies showed the improvement of PHBH enhancement through the incorporation of additives. Lee et al. investigated the rheological and thermal properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) composites, incorporating chemically modified cellulose nanofibres (PHBH/CNF). This showed that the resulting composites have improved properties and reduced crystal size [7]. Shazleen et al. focused on the optimization of cellulose nanofiber (CNF) loading and melt processing conditions for the fabrication of PHBH nanocomposites in a twin-screw extruder using response surface methodology (RSM). The results showed improvement in mechanical properties and crystallinity [8].

Yamagata et al. studied nonwoven polyester fibers, tough and entirely derived from biological sources, that are reinforced with mechanically defibrated cellulose nanofibres and designed to degrade in seawater. Results indicated that PHBH reinforced with CNF showed excellent toughness and underwent complete degradation [9]. Schmidt et al. also showed that reinforcement of nanocellulose into PHAs improves their mechanical and barrier properties, as well as the crystallinity of the bionanocoposities [10].

The aim of this study was to fabricate biodegradable bionanocomposites using PHBH and cellulose nanofibres as biofillers to improve the mechanical and thermal properties of the PHBH bionanocomposites. A masterbatch containing PHBH/CNF was produced using solvent casting to ensure uniform dispersion of CNFs with PHBH for scalable fabrication and improve interfacial adhesion, and melt processing was used to produce the final bionanocomposites. For industrial production, pulverization of the PHBH pellets and melting processing should be sufficient for fabrication without including solvent casting. The improved properties of the fabricated bionanocomposites can encourage their application in the medical and packaging industries as an alternative to petroleum-based and non-biodegradable materials.

2. Experimental

2.1. Materials

Cellulose nanofibres (CNFs) were supplied by Sappi, South Africa. Dichloromethane (DCM) was sourced from Associated Chemical Enterprises Pty Ltd (ACE). The PHBH, branded as Green Planet™ X331N, was provided in pellet form by KANEKA of Japan, with a melt flow index of 12 g/10 min and a density of 1.2 g/cm^3.

2.2. Sample preparation

The bionanocomposites were produced through melt processing using twin screw extrusion. A PHBH/CNF masterbatch was prepared to be incorporated with PHBH through melt-processing. Solvent casting was used to overcome the lack of pre-dispersion, which was observed during direct melt bending, leading to masterbatch preparation and solvent-assisted dispersion. Initially, PHBH pellets were dissolved in DCM at a 1:10 ratio with the help of a magnetic stirrer at room temperature. This was done to improve interfacial adhesion between PHBH and CNF, and to reduce agglomeration of CNF during melt-processing. Once the PHBH was fully dissolved, CNFs in varying weight percentages (as detailed in Table 1) were incorporated into the solution and dispersed by sonication. The resulting mixtures were then cast onto non-reactive stainless-steel plates and left to dry overnight under ambient conditions within a fume hood, ensuring complete evaporation of DCM before undergoing melt processing.

The bionanocomposites were processed using a Ninjing Giant A SHJ-20 twin-screw extruder, which was set to operate at temperatures ranging from 140°C to 160°C from the feed zone to the die. The screw speed was consistently maintained at 14 rpm throughout this process. After passing through the die, the extrudate was cooled in a water bath and then granulated with a pelletizer. The resulting pellets were dried in an oven at 60°C for eight hours before being subjected to injection molding. A TMC 30 machine (manufactured by TMC Technology Corp., Taiwan) was utilized to injection mold tensile test specimens. The fabrication approach was selected for scalable PHBH/CNF fabrication.

2.3. Experimental design

Table 1 illustrates the experimental design used in the research study of PHBH bionanocomposites reinforced with CNFs.

Table 1. PHBH bionanocomposites fabrication experimental design

Sample ID	CNF (wt%)
NEAT PHBH	0
PHBH_CNF (1)	1
PHBH_CNF (2)	2
PHBH_CNF (3)	3

2.4. Measurements

Tensile tests were carried out using a Lloyds RX Universal Material Testing Machine, model EZ50, fitted with a 5 kN load cell. The testing utilized dumbbell-shaped specimens conforming to the ASTM D638 standard. The samples' thermal transitions were analyzed using a PerkinElmer DSC 6000. Thermograms for differential scanning calorimetry (DSC) were collected during the second heating and cooling cycles, covering a temperature range from –40°C to 200°C. The thermal stability of the samples was evaluated using a Perkin Elmer Thermogravimetric Analyzer (TGA 4000) under a nitrogen atmosphere. The heating rate applied was 10°C per minute. Samples ranging in weight from 10 to 15 mg were heated, starting at an initial temperature of 30°C and reaching up to 600°C. A PerkinElmer Spectrum Two™ FT-IR Spectrometer fitted with an attenuated total reflectance (ATR) accessory, capable of covering a spectral range from 4000 to 500 cm^{-1}, was utilized to identify the samples' functional groups.

3. Results and discussion

3.1. Mechanical properties

The PHBH/CNF bionanocomposites underwent mechanical testing to evaluate their tensile strength, Young's modulus, and elongation at break (Figure 1). The incorporation of CNFs as reinforcement in the PHBH nanocomposites leverages the outstanding mechanical characteristics of cellulose nanofillers. Similar to other biopolymers, PHBH exhibits weaker mechanical properties when compared with more commonly used thermoplastic polymers.

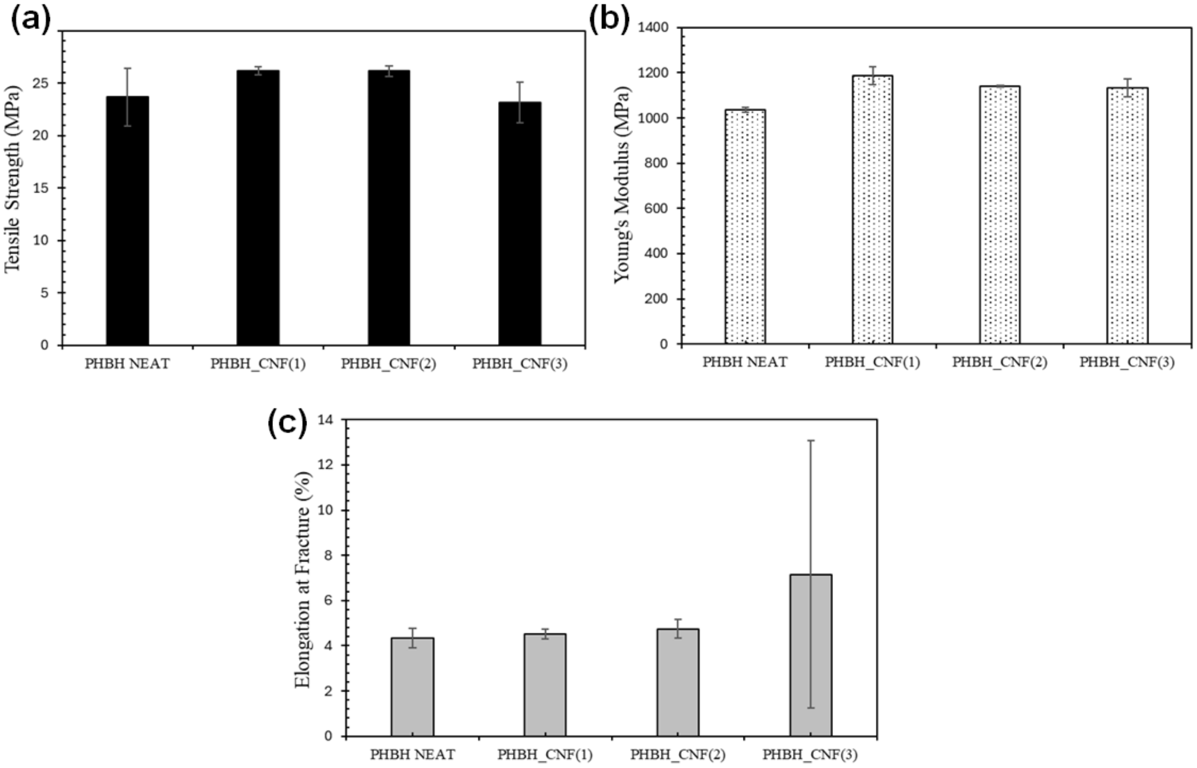


Figure 1. Mechanical properties of PHBH/CNF bionanocomposites showing: (a) Tensile Strength, (b) Young's Modulus, and (c) Elongation at Fracture.

Figure 1(a) demonstrates an increase in tensile strength from the original 23.67 MPa for neat PHBH to 26.18 MPa with a 1% addition of CNF and further to 26.16 MPa with a 2% inclusion of CNF, respectively. This is due to the ability of CNFs to disperse easily at low concentrations, allowing them to remain separate and form numerous effective load-bearing connections between fibrils and the matrix. Additionally, strong interfacial interactions enhance stress transfer from the flexible PHBH to the stiff CNFs, thus increasing tensile strength. The hydrogen bonds between the hydroxyl (OH) groups of CNFs and the carbonyl/ester groups in poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) play a key role. When CNF was added at 3%, there was a decrease in tensile strength because exceeding optimal loading causes fibrils to clump together, creating stress points that weaken the material. This explains why small additions are advantageous while larger amounts tend not to be beneficial [11-13].

Figure 1(b) shows an increase in Young's modulus from 1035.74 MPa for neat PHBH to 1187 MPa, 1140.95 MPa, and 1131.71 MPa with the addition of CNFs at concentrations of 1%, 2%, and 3%, respectively (Table 2). The increase is due to CNFs possessing exceptionally high elastic moduli. As a result, adding even a small quantity can significantly boost the composite's effective stiffness when they are evenly distributed. At low weight fractions, well-dispersed CNFs with high aspect ratios can either create a semi-continuous network or establish strong contacts between particles and matrix. This greatly improves storage modulus and stiffness even with small loadings. When dispersion and processing conditions are optimal, this effect is usually observed at 1–5 wt% for nanofibres [7, 8].

Figure 1(c) illustrates the elongation at fracture of PHBH/CNF nanocomposites. It shows that as more CNFs are added, there is a gradual increase in the percentage of elongation. The elongation rises from 4.34% in pure PHBH to 4.52%, 4.74%, and 7.15% with the addition of 1%, 2%, and 3% CNF into the matrix, respectively. Well-dispersed CNFs act like tiny bridges across growing cracks. When the composite is subjected

Table 2. Mechanical properties of PHBH/CNF bionanocomposites

Sample ID	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation at Break (%)
NEAT PHBH	23.67 ± 2.77	1035.74 ± 10.61	4.34 ± 0.43
PHBH_CNF(1)	26.18 ± 0.41	1187 ± 38.85	4.52 ± 0.21
PHBH_CNF(2)	26.16 ± 0.50	1140.95 ± 3.30	4.74 ± 0.42
PHBH_CNF(3)	23.14 ± 1.92	1131.71 ± 39.40	7.15 ± 5.92

to strain, these fibers might pull out, slide, or fibrillate. This action absorbs mechanical energy and delays catastrophic fracture, resulting in increased elongation at break [14, 15].

Various authors have reported similar observations. Lee et al. conducted an investigation into the thermal, rheological, and mechanical properties of biopolymer nanocomposites composed of cellulose nanofiber (CNF) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH). Meanwhile, Shazleen et al. focused on optimizing both the content of cellulose nanofibres and processing parameters during melt extrusion in bionanocomposites made from poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). Zhang and colleagues investigated the impact of cellulose nanocrystals and nanofibres on the structural properties and characteristics of polyhydroxybutyrate-based nanocomposites [7, 8, 14].

Figure 2 demonstrates the stress-strain curves of the fabricated PHBH bionanocomposites. The results firstly show a linear region that indicates that the bionanocomposites were under elastic deformation. The PHBH/CNF bionanocomposites showed an increased slope in comparison to the neat, indicating the effective load transfer from the PHBH matrix to the well-dispersed CNF. The stiff CNFs restrict polymer chain mobility due to their high modulus.

The yield point indicates the onset of plastic deformation of the bionanocomposites. An increase in yield strength is observed as CNF serves as a focal point for stress concentration and areas of reinforcement. The plastic deformation region for PHBH/CNF bionanocomposites shows a reduced plastic flow, with the curve becoming less ductile. The PHBH/CNF 2% and 3% showed an increased strain region before fracture. The observed increase in elongation is caused by the well-dispersed fibres, functioning as miniature bridges spanning developing cracks and pulling out or undergoing fibrillation under strain. Providing evidence that the materials absorb mechanical energy and postpone catastrophic fracturing, ultimately enhancing the materials' elongation at break.

3.2. *Differential Scanning Calorimetry – DSC Analysis*

Figure 3 and Table 3 present the DSC results of the PHBH/CNF nanocomposites. The DSC curves display a

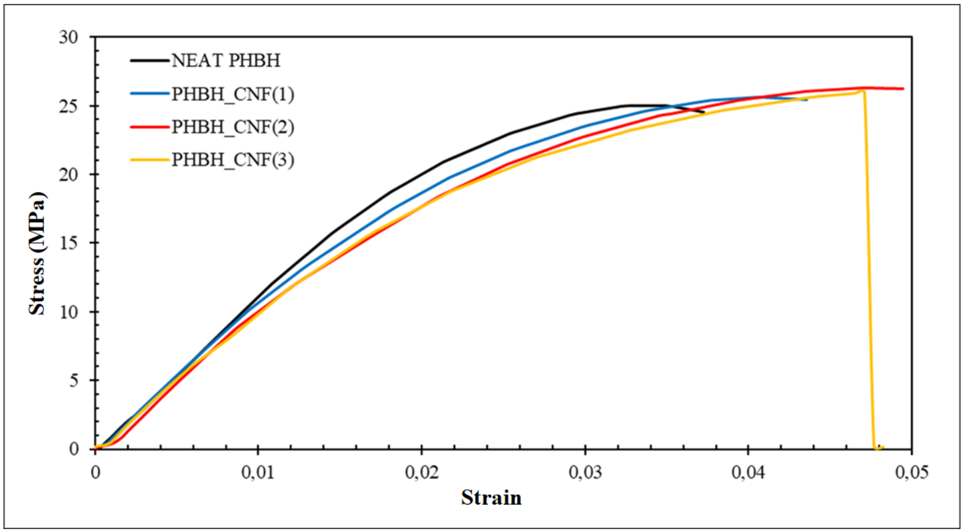


Figure 2. Stress-strain curves of PHBH/CNF bionanocomposites.

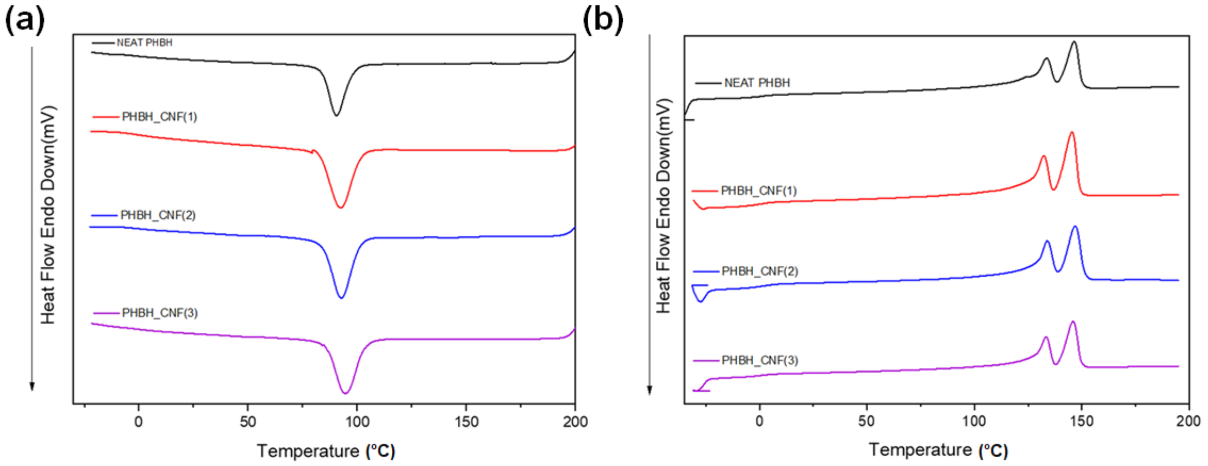


Figure 3. DSC results: (a) Second heating and (b) cooling curves of PHBH/CNF nanocomposites.

double melting peak, resulting from the sequential processes of melting, crystallization, and re-melting observed in PHBH. The first melting peak (Tm_1) shows that certain imperfect crystals, created during the initial heating and cooling process, melted and reorganized at Tm_1. These crystalline structures will stay intact until they melt again at a higher temperature, denoted as Tm_2. The second melting peak, Tm_2, represents the actual melting temperature of the nanocomposites [16, 17].

The results indicated a slight downward shift in Tm_1 and Tm_2 after adding 1% and 3% CNF. Specifically, Tm_2 decreased from 146.53 °C in pure PHBH to 145.41 °C with the addition of 1% CNF, and to 146.01 °C with the addition of 3%. When 2% CNF was added to pure PHBH, Tm1 and Tm_2 experienced a slight increase from 146.53 °C to 146.89 °C. This change can be attributed to modifications in the crystal structure caused by the addition of CNFs, leading to an increased number of thinner and more imperfect lamellae. Cellulose nanofibrils (CNFs) often act as heterogeneous nucleating agents, promoting the formation of crystal nuclei. However, they usually lead to growth into less-perfect or smaller and thinner lamellae structures. The presence of a higher proportion of these imperfect or thin crystals can cause a slight decrease in the apparent melting peaks and potentially alter the relative areas between Tm_1 and Tm_2 [8, 14, 18].

When 1% and 2% CNF were added to neat PHBH, Tc slightly decreased from 93.83 °C for the pure PHBH to 92.47 °C and 92.68 °C, respectively. However, adding 3% CNF led to an increase in Tc from the original temperature of neat PHBH at 93.83 °C up to 94.52 °C. This change is attributed to imperfect crystals forming during nanocomposite processing. The crystallinity percentage of the fabricated nanocomposites increases from 23.65% in neat PHBH to 26.00%, 64.04%, and 31.12% upon adding CNF at concentrations of 1%, 2%, and 3%, respectively. This enhancement is attributed to the extensive surface area provided by CNF, which acts as a nucleation site for PHBH crystallization. As a result, these sites decrease the energy threshold required for nucleation, facilitating easier formation of more crystals as cooling occurs. Furthermore, incorporating nanofillers speeds up crystallization by promoting heterogeneous nucleation [10, 19, 20].

Shazleen et al. made comparable observations, concentrating on the optimization of cellulose nanofiber

Table 3. Thermal properties of PHBH/CNF nanocomposites

Sample ID	T_{m1} (°C)	T_{m2} (°C)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)	T_c (°C)	T_{cc} (°C)	ΔH_c (J/g)	ΔH_{cc} (J/g)	X_c (%)
NEAT PHBH	133.73	146.53	11.1113	23.4108	93.83	-	- 51.8961	-	23.65
PHBH_CNF(1)	132.43	145.41	14.7759	21.6755	92.47	- 26.65	- 41.4046	- 1.1133	26.00
PHBH_CNF(2)	133.91	146.89	14.6491	20.5829	92.68	- 27.59	- 56.3964	- 4.6499	64.04
PHBH_CNF(3)	133.38	146.01	17.5205	26.0556	94.52	-	- 54.7905	-	31.12

content and processing parameters during the melt extrusion process of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) bionanocomposites [8]. Aigaje et al. reported similar findings in their review of the processing, properties, modifications, and environmental impacts of nanocellulose/biopolymer composites [20]. Schmidt et al. also observed comparable results during their investigation of polyhydroxybutyrate-based green bionanocomposites enhanced with cellulose nanocrystals, focusing on melt-processing and characterization analysis [10].

3.3. Thermogravimetric Analysis – TGA

Figure 4 and Table 4 present the TGA and DTG thermographs, along with data illustrating the thermal behavior of the fabricated PHBH/CNF nanocomposites. Incorporating CNF into neat PHBH results in a reduction of both T_{onset} and T_{max} values. Specifically, T_{onset} drops from 295.47 °C for neat PHBH to 256.04 °C with a 1% addition of CNF, then to 272.38 °C at a concentration level of 2%, and finally settling at around 267.52°C when incorporated by an amount of 3%. The decrease in the onset degradation temperature of PHBH when 1–3% CNFs are added is usually attributed to the integration of these fibers into the polymer matrix, as they exhibit lower thermal stability. CNFs start decomposing at approximately 200–280 °C, which is notably lower than PHBH's typical degradation onset temperature, generally above 260–280 °C. Consequently, CNF can trigger thermal decomposition by catalyzing dehydration. This process leads to the formation of char residue and enhances the production of volatile compounds [19].

Furthermore, the interaction between PHBH and CNF may result in microstructural imperfections or localized stress concentrations that promote earlier thermal chain scission. While dispersion is typically sufficient at low CNF loadings (1–3%), interfacial bonding tends to be weak unless surface modification techniques are employed. The insufficient chemical compatibility between hydrophobic PHBH and hydrophilic CNF results in weaker interfacial adhesion, leading to heat accumulation at the polymer-fiber boundaries. This buildup can hasten thermal decomposition by reducing the energy required to break polymer chains near these interfaces. Similar mechanisms have been noted in PHBH/nanocellulose systems, where suboptimal interfaces lead to reduced thermal stability [21, 22].

The degradation temperatures (T_{max}) decreased from 307.79 °C for pure PHBH to 261.38 °C, 279.96 °C, and 283.53 °C with the addition of 1%, 2%, and 3% CNF to PHBH, respectively. This reduction is due to the large surface area rich in hydroxyl groups (–OH), which can promote the breakdown of ester bonds in polyhydroxyalkanoates at higher temperatures. These reactive surface groups can act as sites for chain breakage, subsequently reducing the thermal stability of the polymer matrix [23, 24]. In a study examining the incorporation of ultrafine cellulose, which is closely linked to CNF, into P(3HB-co-3HHx), it was found that T_{max} decreased from about 275 °C to roughly 260 °C. This decrease was attributed to the hydroxyl-rich nature of cellulose, offering additional sites for degradation initiation [25].

Research indicates that cellulose nanofibres or nanocrystals tend to start thermal degradation at lower

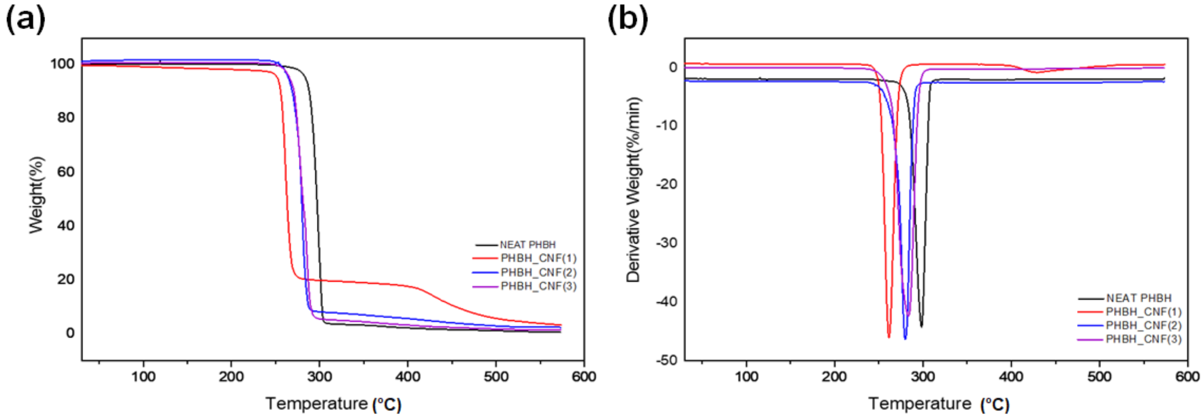


Figure 4. (a) TGA and (b) TGA curves of PHBH/CNF nanocomposites.

Table 4. Decomposition parameters of PHBH/CNF nanocomposites

Sample ID	T_0 (°C)	T_{max} (C°)	Residual (%)
NEAT PHBH	295.47	307.79	0
PHBH_CNF(1)	256.04	261.38	3.322
PHBH_CNF(2)	272.38	279.96	2.455
PHBH_CNF(3)	267.52	283.53	1.485

temperatures than pure, well-ordered cellulose. This is especially noticeable if they have been chemically treated or processed. When the decomposition of the nanocellulose begins, it can emit by-products like volatile acids and free radicals, which further hasten the degradation of the PHBH matrix [23]. At certain concentrations, CNFs may not be evenly distributed, resulting in localized defects where degradation is more likely to initiate. These "hot spots" can undermine the stability of the composite. Although well-dispersed CNFs can sometimes improve polymer stability, inadequate dispersion or aggregation of CNFs can cause instability instead. This happens because the local interface between the polymer and filler destabilizes when subjected to heat. This phenomenon is also seen in other nanoparticle-reinforced PHAs. For example, in PHB/nHA composites, a high concentration of nanoparticles leads to a reduction in T_{max} due to their catalytic effects [26].

Table 4 also demonstrated the presence of residual material when CNFs were incorporated into PHBH. This occurs because CNFs can establish a network or interconnected structure within the polymer matrix, which hinders the movement of polymer chains and slows down mass loss upon exposure to heat. As a result, the process of volatilization is slowed down, promoting pathways that result in char formation. CNF networks act as barriers to mass transport for decomposition products, preventing their release and encouraging recombination into char. Additionally, aspects such as the filler–matrix interface, hydrogen bonding, and interphase interactions can inhibit pyrolysis and support residue creation [7, 14, 27-29].

Several other authors reported similar findings regarding the relationship between PHAs and cellulose biocomposites as well as nanocomposites. Li et al. studied the mechanical, thermal, and barrier characteristics of PHBH/cellulose biocomposite films produced through solution casting and observed residuals after adding cellulose [29]. Santo et al. observed similar behavior while investigating the use of cellulose nanofillers in producing polymer nanocomposites, focusing on their properties, processing techniques, and applications [27].

3.4. Fourier Transform Infrared Spectroscopy – FT-IR

The FTIR spectra are depicted in Figures 5 and 6, demonstrating the impact of CNF on the PHBH matrix. Comparable effects can be seen across all PHBH/CNF nanocomposites. CNFs are abundant in hydroxyl groups and display significant hydrogen bonding,

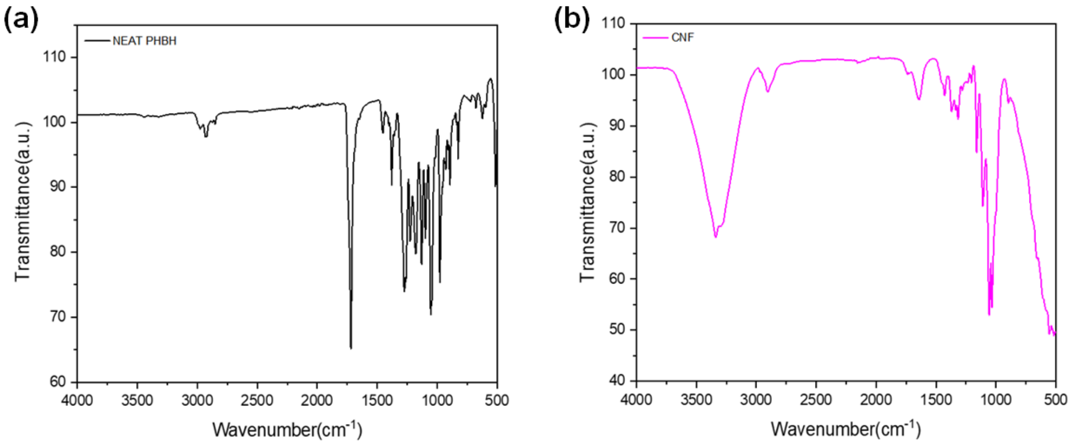


Figure 5. FT-IR Spectra of (a) neat PHBH and (b) neat CNF.

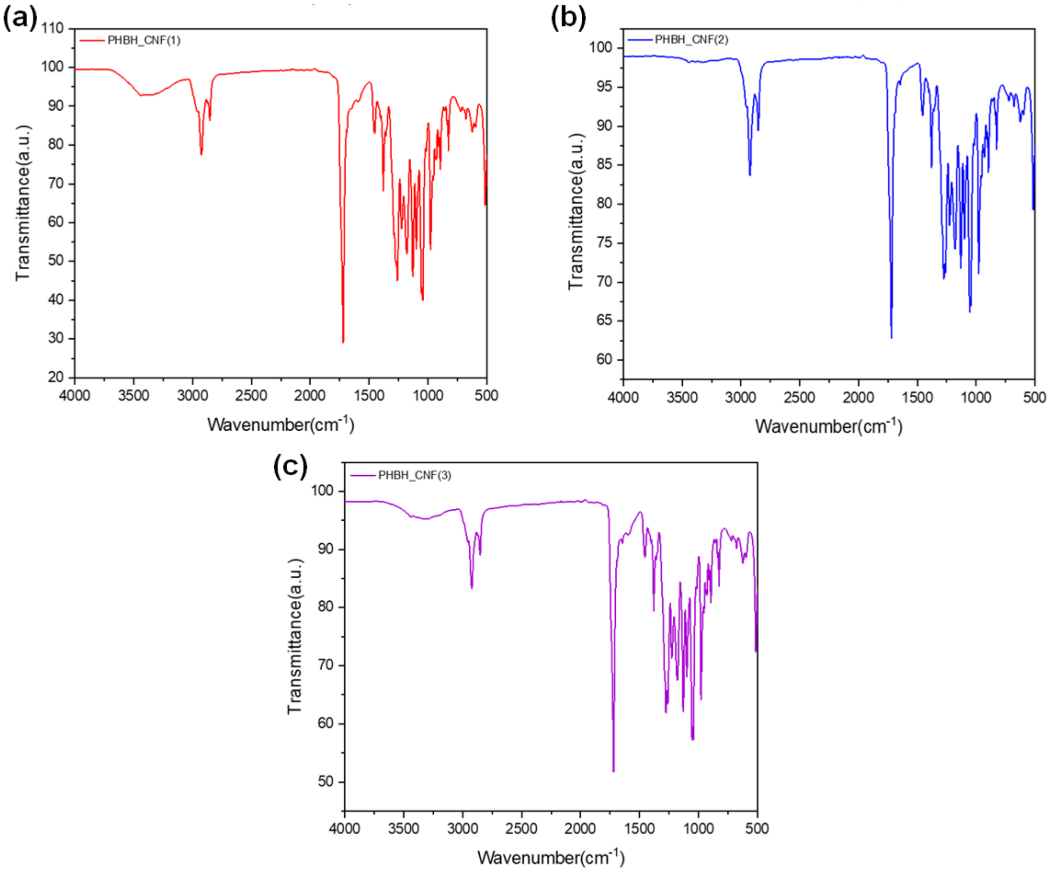


Figure 6. FT-IR Spectra PHBH/CNF nanocomposites containing (a) 1% CNF, (b) 2% CNF, and (c) 3% CNF.

leading to characteristic peaks primarily around the 3330–3400 cm-1 range. These wide peaks are attributed to hydrogen bonds. When 1% and 2% CNFs are added to PHBH, the prominent sharp ester carbonyl peak observed at 1721 cm-1 shifts downward. This suggests that hydrogen bonding or dipole interactions are taking place between the carbonyl groups of PHBH and the hydroxyls in cellulose. Such phenomena are commonly observed when polyesters are blended with fillers rich in –OH groups [9, 30].

A broad band within the 3300–3400 cm^{-1} range, typically much wider than moisture-related bands, indicates hydrogen-bonded –OH groups in cellulose. In the composite material, this band is present even at low concentrations of about 1%, although it may appear weak and superimposed on other –OH or moisture-associated bands. The presence of this –OH band in the composite—absent from pure PHBH—clearly signifies that CNF has been integrated into the material [9, 31].

For cellulose, typical peaks are observed around 2890–2900 cm^{-1} due to C–H stretching. Peaks between 1370 and 1440 cm^{-1} correspond to C–H bending or scissoring, while those within the fingerprint region at approximately 1000-1100 cm^{-1} result from C–O–C and C-O stretching. In PHBH/CNF nanocomposites, these signals either emerge or become more pronounced compared to pure PHBH, even with low loading levels; small yet detectable signals often appear. The well-dispersed CNFs interact with the PHBH matrix, causing slight shifts or broadening of peak positions, particularly for carbonyl (C=O), ether linkages (C−O−C), and hydroxyl groups (-OH). This suggests interfacial bonding or restricted mobility as commonly seen in other polymer/CNF systems [9, 29-31].

In conclusion, the FTIR spectra confirmed that the characteristics of both PHBH and cellulose are present in the nanocomposite, indicating successful integration within the PHBH/CNF nanocomposites [32].

4. Conclusions

The study focused on investigating the enhancement of PHBH properties by incorporating CNFs as biofillers. PHBH/CNF masterbatch of CNF reinforcements of 1wt%, 2wt%, and 3wt% contents through solvent casting to improve dispersion and interfacial adhesion on a scalable production. The masterbatches were melt-processed to fabricate PHBH/CNF bionanocomposites. Incorporating small amounts of CNFs into PHBH generally enhances its mechanical properties. This improvement is attributed to the efficient stress-transfer capabilities and microstructure alteration provided by the nanofibres. At low concentrations, specifically 1–2%, these well-dispersed cellulose nanofibres form strong interfacial bonds with PHBH, allowing for effective stress transfer from the polymer matrix to the rigid fibers and resulting in increased tensile strength. However, when CNF content rises to 3 wt%, agglomeration can occur, creating points where stress concentrates rather than being uniformly distributed; this compromises tensile strength. The thermal analysis shows that adding CNF alters the crystallization behavior of PHBH based on its concentration. This alteration results from the balance between nucleation effects and polymer chain movement. At a low CNF content, nanofibres primarily act as heterogeneous nucleating agents but slightly inhibit polymer chain mobility, which lowers both the crystallization temperature (T_c) and slightly affects melting temperatures (Tm_1 and Tm_2). Regardless of loading levels, overall crystallinity rises since CNF consistently aids in nucleation while also contributing its inherent crystalline structure to create a more crystalline PHBH matrix, despite fluctuations in melting or crystallization temperatures. Incorporating CNF into PHBH significantly influences its thermal degradation characteristics, as evidenced by TGA results. The decrease in onset ($_{\text{Tonset}}$) and maximum (T_{max}) degradation temperatures indicates that CNF facilitates the initial stages of thermal decomposition within the polymer matrix. This is likely due to a catalytic effect from hydroxyl groups on the surface of CNFs that promote ester bond cleavage in PHBH. Despite this accelerated breakdown, adding CNF enhances residual content after pyrolysis, underscoring cellulose's char-forming capability. The network created between CNFs and PHBH chains encourages stable carbonaceous residue formation during pyrolysis, thereby increasing the final residual mass. Thus, while CNF leads to lower T_{onset} and T_{max} values, it supports forming a thermally durable residue at later stages. Overall, the fabricated binanocomposites show that the PHBH matrix can be altered by the addition of nanofillers such as cellulose nanofiber. The fabricated bionanocomposites can be used in various applications such as the medical and packaging industries.

Acknowledgments

Department of Science and Innovation (DSI) Bioinnovation (DSI CON 2265/2021) and the Council for Scientific and Industrial Research (CSIR) for financial support, and Tshwane University of Technology (TUT) for academic support.

Conflict of Interest

The authors declare no conflict of interest.

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