

A study of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) biofilms' thermal and biodegradable properties reinforced with halloysite nanotubes

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Abstract

The aim of this study is to investigate and optimize the performance of a promising biopolymer, poly (3-hydroxybutyrate-co-3-hydroxyvalerate) which can potentially replace non-biodegradable synthetic polymers derived from toxic petroleum products. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) biofilms were prepared using solvent casting method, and its thermal properties were determined using thermogravimetric and differential scanning calorimetry techniques. Also, the durability and biodegradability of these films were studied by keeping the samples in water and Alabama soil conditions for various lengths of time. Our results showed that the thermal and moisture resistance of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) biopolymer can be enhanced significantly with the addition of low halloysite nanotubes concentrations. Also, the biodegradation process of the poly (3-hydroxybutyrate-co-3-hydroxyvalerate) films was faster with the addition of halloysite nanotubes attributed to the accelerated microbial microorganism reaction in the soil. This study led to cognize that the PHBV biopolymers added with halloysite nanotubes can be successfully used for various biomedical, industrial and structural applications, and then decompose at a desired faster rate afterward.

Keywords

Biopolymer, halloysite nanotubes, thermal properties, durability, biodegradation

Introduction

Environmental concern, waste disposal by incineration, depletion of nonrenewable resources, and scarcity of petroleum sources and energy requirements have raised alarming environmental concerns worldwide for the continuous applications of synthetic plastic-/polymer-based products. In contrast, the growing interest in biomaterials extracted from natural resources provided an excellent alternative to synthetic materials because of its environmentally friendly and 100% biodegradable nature.¹ One such biomaterial from a polyhydroxy alkonites (PHAs) family is poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) which is currently used or considered for film packaging, water filtration, and biomedical applications.^{2,3} The mechanical properties of PHBV polymer are almost similar to some polyolefins like polypropylene, which makes it an excellent alternative to many synthetic-based polymers. However, poor thermal stability, low crystallization rate, and lack of

durability and biodegradability information has limited their use in many potential possible applications in large volume.^{4,5}

In recent years, natural nanoparticles such as montmorillonite nanoclay and halloysite nanotubes (HNTs) have enhanced mechanical and thermal properties of biopolymers, while maintaining the composites bio-nature.^{4,6,7} Nanoparticles provide a large surface area for rapid phase interaction as well as more matrix interfacial adhesion. Conventional plastic engineering also elucidated the attractive properties of nanofiller-infused polymeric composites such as flame retardancy, surface

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advantage, material transparency, heat resistance, gas permeability reduction as well as barrier properties.^{8,9} Among these nanoparticles, HNTs, a member of Kaolin group has a high potential to be used as reinforcement materials. HNTs have tubelike structure similar to carbon nanotubes (CNTs) with a diameter typically smaller than 100 nm and length in between 500 nm to 1.2 microns.¹⁰ The external surface of HNTs is mainly composed of the siloxane (Si–O–Si) groups, whereas the internal surface consists of a gibbsite like an array of aluminol (Al–OH) groups.⁷ HNTs contain two types of hydroxyl groups, which are situated on the surface of the nanotubes and in between the layers which are called inner and outer hydroxyl groups, respectively. The presence of hydroxyl groups that form hydrogen bonding with the polymer matrix favors good dispersion.^{11,12} Furthermore, high aspect ratio and large surface area of HNTs ensure the good interaction between nanofiller and the polymer matrix, respectively.^{6,8} Several researchers have incorporated HNTs as a filler in various polymer matrices and reported significant enhancement in the tensile strength and stiffness, thermal stability, fire retardancy and moisture resistance.^{7,13,14} A few researchers have also investigated the durability and biodegradability of various polymer/clay nanocomposites such as poly (3-caprolactone)/clay, polylactide/clay, polyvinyl alcohol/clay, and poly (3-hydroxybutyrate)/clay composites.^{15,16} In addition to enhancement in durability, the researchers also found that nanoclay promulgates the biodegradation of polymeric composites.¹⁶ However, to the best of our knowledge, no study on the durability and biodegradation behavior of PHBV/HNTs films, specifically when exposed to water and soil conditioning, has been reported to date. Also, efforts have not been made to optimize the concentration of HNTs and investigate its impact on the overall morphological and thermal performance of these composites, including the durability and biodegradability properties.

In this study, we have processed neat and PHBV/HNTs composites by adding 0–15 wt.% HNTs and investigated the thermal performance using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In addition, the moisture absorption and biodegradable behavior of these composites were also studied by placing the composite films in water for 315 h, and in Alabama soil for 12 weeks, respectively.

Materials and processing

Materials

PHBV, a bacterial grade 100% biopolymer containing 12 mol% of valerite was purchased from Goodfellow Corporation, Coraopolis, USA. PHBV is an easily

melt processible thermoplastic polymer (pallet form) made from the biological fermentation of renewable carbohydrate feedstocks. An unmodified tubular-shaped HNTs were obtained by Natural Nano, Pittsford NY, USA, and chloroform ($\geq 99.5\%$) was purchased from Sigma Aldrich, Saint Louis, USA.

Processing of thin films

Neat films. At first, 10 gm of PHBV was dissolved in 120 ml chloroform using a continuous magnetic stirring for 24 h. The resulting solution was then vacuum mixed using 100 kPa pressure for 15 min at a speed rate of 1500 r/min to remove the entrapped air bubbles. Finally, the films were prepared by spreading the mixture on a glass plate and curing at room temperature for 24 h. The films were cured at room temperature for longer to ensure the complete evaporation of chloroform.

PHBV/HNTs films. At first, 3–15 wt.% HNTs was dispersed in chloroform using ultrasonication process for 1 h at an amplitude of 45% with 5/5 s on/off pulse rate. Ten grams of PHBV polymer was then dissolved into the HNT/chloroform solution and the films were prepared following the exact procedure used for the neat films.

Experimental procedure

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to analyze the melting temperature and crystallization behavior of the nanocomposites. Measurements were carried out on Q1000 analyzer in a nitrogen atmosphere. Ten to twelve milligrams of samples were encapsulated into the aluminum pan and heated from -20°C to 250°C at a ramp rate of $10^{\circ}\text{C}/\text{min}$. From DSC endotherms, the melting temperature (T_m) and enthalpy of fusion (ΔH_m) were determined. The degree of crystallinity was determined using equation (1)

$$X_c = \frac{\Delta H_m}{f_p \Delta H_m^0} \times 100\% \quad (1)$$

where ΔH_m (Jg^{-1}) indicates the melting enthalpy of polymer matrix, f_p represents the polymer weight fraction in the sample, and ΔH_m^0 (146 Jg^{-1})¹⁷ stands for the melting enthalpy of pure crystalline polymer matrix.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted by TA Q500 analyzer to determine the thermal decomposition of neat and PHBV/HNTs films. Ten to twelve milligrams of samples were used and the TGA, derivative

thermogravimetric (DTG) and residual weight percentages were recorded in a nitrogen atmosphere from 30 to 550°C.

Water absorption behavior

Water absorption behavior (WAB) of films was investigated by submerging the 2 × 2 cm samples in water for a time interval of 2–315 h. The films were taken out of the water after each interval, dried with a paper towel, and the percentage of water absorption was calculated using equation (2)

$$\text{Percentage water absorption} = \left[\frac{W_f - W_i}{W_i} \right] \times 100\% \quad (2)$$

where W_i and W_f are the initial and final weight of the films before and after conditioning.

The coefficient of water diffusion was also calculated using equation (3)

$$D = \frac{\pi}{16} \left[\frac{M_t}{\frac{M_\infty}{\sqrt{t}}} \right]^2 \quad (3)$$

where M_∞ is the maximum water uptake, M_t is the water uptake at time t , h is the sample thickness, and D is the diffusion coefficient.

Soil burial test

The biodegradation test of the films was done according to soil burial method.¹⁸ At first, the films of size

4 × 4 cm were placed in a pit dig in Tuskegee, Alabama soil under completely natural conditions for 2, 3, 5, 8, and 12 weeks, respectively. The samples were then taken out after each interval and washed with distilled water to remove the dirt. Finally, the samples were dried at 50°C for 8 h and weighed. The degree of soil degradation was calculated using equation (4)

$$\text{Percentage soil degradation} = \left[\frac{W_2 - W_1}{W_1} \right] \times 100\% \quad (4)$$

where W_1 and W_2 are the weights of the PHBV films before and after the soil degradation.

Result and discussion

Differential scanning calorimetry

Incorporation of HNTs in PHBV polymer positively affected the melting temperature of the resulting films as shown in Figure 1. The melting temperature of PHBV/HNTs films was found to increase linearly with a maximum of 163°C at 10 wt.% HNTs concentration, which is 10°C higher than neat films. The incorporation of HNTs with –OH group changes the intermolecular and intramolecular structure of PHBV polymer chains leading to a formation of arranged structure (crystalline) (Table 1) that may have affected the melting behavior of nanofilms.¹⁹ The formation of ordered structure and strong bonding between PHBV and HNTs can be attributed to the enhancement of melting temperatures in PHBV/HNT films. Also, the

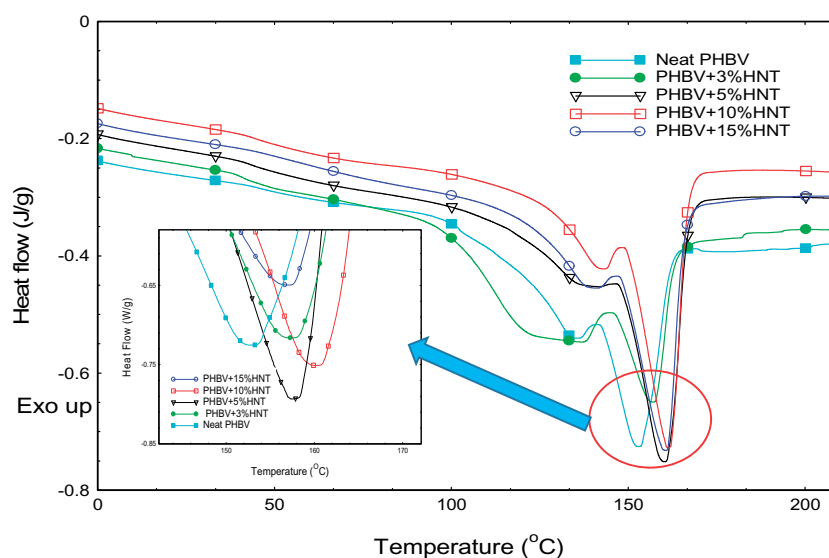


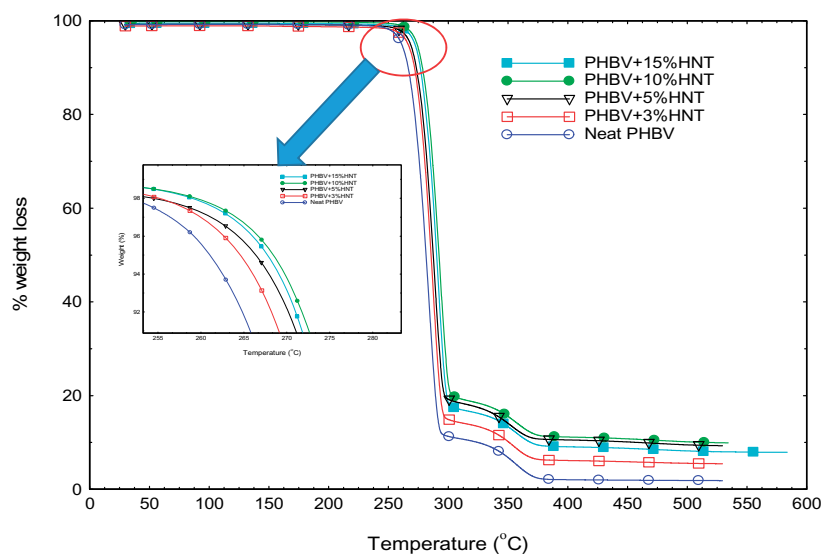
Figure 1. DSC graph of neat and PHBV/HNTs films.

PHBV: poly (3-hydroxybutyrate-co-3-hydroxyvalerate); HNT: halloysite nanotubes.

Table 1. Differential scanning calorimetry data of neat and PHBV/HNT films.

Sample	T_m (°C)	Change (%)	ΔH (J/g)	Change (%)	Degree of crystallinity X_c (%)	Change (%)
Neat PHBV	152.85	—	18.75 ± 0.21	—	12.84	—
PHBV + 3%HNT	159.77	+4.5	17.23 ± 1.95	−8.1	12.42	−3.27
PHBV + 5%HNT	161.11	+5.5	29.14 ± 1.18	+55.41	21.93	+70.8
PHBV + 10%HNT	162.64	+6.4	30.01 ± 0.59	+60.05	22.59	+76.0
PHBV + 15%HNT	160.84	+5.2	25.75 ± 1.86	+37.33	20.27	+58.0

PHBV: poly (3-hydroxybutyrate-co-3-hydroxyvalerate); HNT: halloysite nanotubes.

**Figure 2.** Thermogravimetric analysis graph of neat and PHBV/HNTs films with magnified decomposition region.

strong bonding between HNTs and polymer tends to absorb more heat to melt, resulting in higher melting temperatures. The degree of crystallinity of PHBV/HNT films was also found higher with a maximum of 76% increase at 10 wt.% over neat counterpart. However, the melting temperatures and degree of crystallinity of 15 wt.% HNTs films showed decreasing trend which could be due to the poor dispersion/agglomeration of HNTs. The strong interaction between polymer and nanotube forms crystal structure which resembles from the high degree of crystallinity (X_c) values found in PHBV/HNTs films (Table 1).¹⁷ Furthermore, neat and PHBV/HNTs films showed double melting point temperatures which can be attributed to the presence of two crystalline phases of different sizes, orders, and thickness in these samples.^{20,21}

Thermogravimetric analysis

Figures 2 and 3 and Table 2 show the TGA result of neat and PHBV/HNTs films. The onset and maximum decomposition temperature of PHBV films increased

with the addition of HNTs. The TGA graphs of neat and PHBV/HNTs films showed two-step decomposition at 250°C and 350°C, respectively. The first step/onset degradation can be attributed to the decomposition of the crosslinked polymer chain. Consequently, the second step/maximum degradation is due to the decomposition of main block of PHBV polymer chain.²² For 10 wt.% HNTs films, onset and maximum decomposition temperatures showed an enhancement of 6.45°C and 5.94°C in comparison to neat samples. Also, a slight weight loss observed between 60°C and 100°C in all films can be attributed to the release of moisture absorbed from the atmosphere. At 500°C, the residual weight percentage in PHBV/HNTs films was also found higher in comparison to neat films (Table 2). The enhancement in thermal stability of PHBV/HNTs films can be attributed to the good interfacial bonding between HNTs and PHBV polymer.²³ HNTs provides a thermal barrier to transfer the heat into the polymer as well as mass transfer barrier to form char during degradation process to create an obstacle for escaping volatile products.^{24,25} In addition,

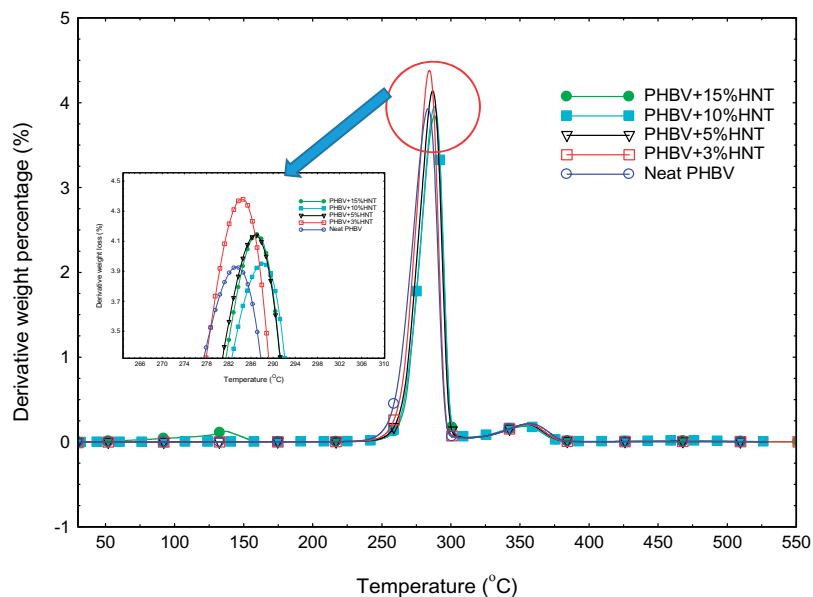


Figure 3. DTG graph of neat and PHBV/HNTs films with magnified maximum decomposition peak.

Table 2. Thermogravimetric analysis data of neat and PHBV/HNTs films.

Sample	T _{5%} (°C)	Change (%)	T _p (°C)	Change (%)	Residue content (%)
Neat PHBV	269.67 ± 0.5	—	282.71 ± 0.68	—	1.18
PHBV + 3%HNT	272.05 ± 0.79	+0.88	283.86 ± 0.97	+0.40	3.48
PHBV + 5%HNT	274.78 ± 0.10	+1.90	286.4 ± 0.65	+1.31	6.00
PHBV + 10%HNT	276.12 ± 0.09	+2.39	288.65 ± 0.57	+2.10	10.56
PHBV + 15%HNT	266.58 ± 1.20	−1.15	286.73 ± 1.85	+1.42	11.22

PHBV: poly (3-hydroxybutyrate-co-3-hydroxyvalerate); HNT: halloysite nanotubes.

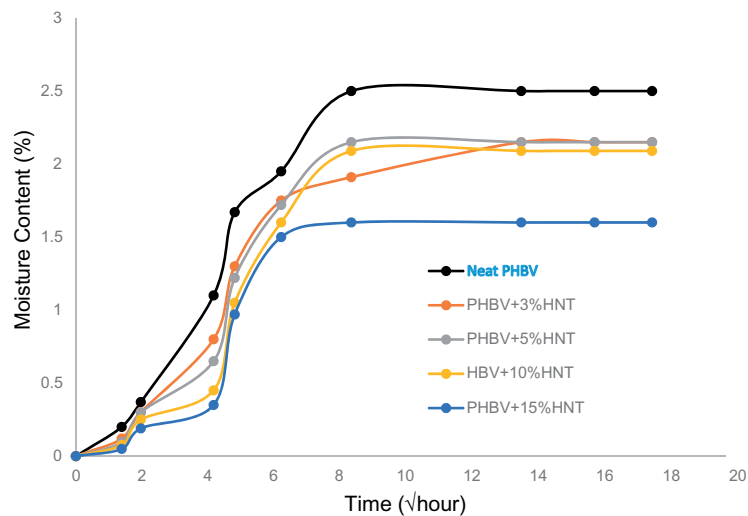


Figure 4. Moisture absorption behavior of neat and PHBV/HNTs films.

PHBV: poly (3-hydroxybutyrate-co-3-hydroxyvalerate); HNT: halloysite nanotubes.

HNTs may have delayed the mass transfer of polymer that was entrapped inside their lumen, and thus resulted in the enhancement of PHBV/HNTs films thermal stability.^{26,27}

Water absorption test

Water absorption characteristics and corresponding data of neat and PHBV/HNTs films are shown in Figure 4 and Table 3, respectively. Incorporation of HNTs in PHBV restricted the absorption of water demonstrated by the decreasing slope of the curve. Initially up to 50 h, the water uptake rate was higher, followed with gradual slowdown between 50 and 75 h, and finally reached to saturation level after 75 h with no significant change observed up to 315 h or more.

Table 3. Maximum water uptake (M_{∞}) and diffusion coefficient (D) of neat and PHBV/HNTs films.

Sample	Slope	M_{∞} (%)	D (mm^2/s)
Neat PHBV	0.16	2.5	7.96×10^{-8}
PHBV + 3%HNT	0.14	2.15	5.19×10^{-8}
PHBV + 5%HNT	0.14	2.15	4.57×10^{-8}
PHBV + 10%HNT	0.14	2.09	3.58×10^{-8}
PHBV + 15%HNT	0.11	1.6	4.51×10^{-8}

PHBV: poly (3-hydroxybutyrate-co-3-hydroxyvalerate); HNT: halloysite nanotubes.

The water absorption behavior of both neat and PHBV/HNTs films demonstrated the Fickian diffusion behavior.²⁸ Also, the water absorption percentage in nanofilms was significantly lower in comparison to neat films. HNTs due to high aspect ratio upon uniform dispersion/exfoliation provides a barrier to water absorption by transforming the original water molecules diffusion path into a tortuous or maze-like path.²⁹ Furthermore, the diffusion coefficient reduced linearly with the increasing HNTs concentration up to 10 wt.% HNTs concentration.

Biodegradation study

Figure 5 shows the biodegradation results of neat and PHBV/HNTs films. After one week, the weight loss in PHBV/HNTs was found significantly higher in comparison to neat samples. The percentage weight loss in PHBV/HNTs films was 3.65%, 6.4%, 6.05%, and 8.25% at 3, 5, 10, and 15 wt.% HNTs concentration. In contrast, the percentage weight loss in neat PHBV films was only 2.22%. The weight loss in these samples continued to follow similar trend up to 12 weeks. After 12 weeks, the percentage weight loss in 3, 5, 10, and 15 wt.% PHBV/HNTs films was 16.53%, 42.27%, 30%, and 33% in comparison to the neat PHBV films. PHBV acts as an energy source for many microorganisms which colonizes on the surface of the PHBV and secretes enzymes to degrade the PHBV into hydroxybutyrate (HB) and hydroxyvalerate (HV) components.³⁰ Two hundred and ninety-five types of

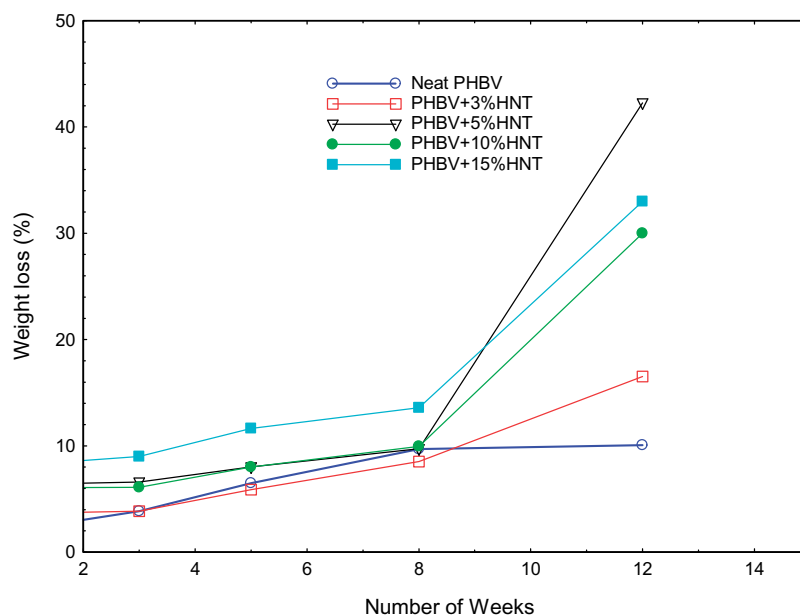


Figure 5. Weight loss percentage vs. number of weeks of neat and PHBV/HNTs films. PHBV: poly (3-hydroxybutyrate-co-3-hydroxyvalerate); HNT: halloysite nanotubes.

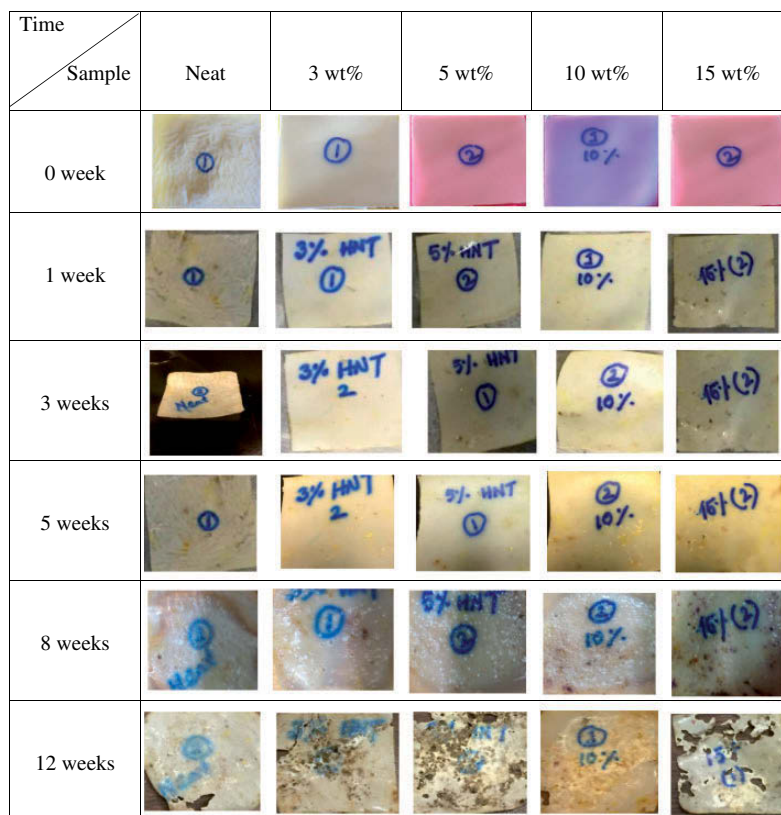


Figure 6. Neat and PHBV/HNTs films before and after soil burial conditioning.

bacteria and mold were isolated from different soil, which assists PHBV to degrade.³¹ Further, the addition of increasing concentration of HNTs accelerated the degradation rate with highest at 15 wt.%, which is in agreement with the biodegradability of polyhydroxybutyrate/layered silicate nanocomposites.³² Figure 6 shows the physical appearance of PHBV/HNTs nanocomposites before and after 12 weeks. All the samples were smooth before biodegradation. After three weeks, no significant change in films appearance was observed except some discolorations and stains. The discoloration in these films is due to the presence of organic components in PHBV polymer which acts as a catalyst for microorganism growth and thus alters the pH of the material.³³ After five weeks, blemished surfaces was observed which may be due to the action of depolymerase secreted by the degraders.² The biodegradation rate was more pronounced after eight weeks. The stains after three weeks led to form deep holes and complete disintegration of the films after 12 weeks. The biodegradation of PHBV occurs by the combination of hydrolysis as well as microbial metabolism. But, in this study, we have found that the water absorption decreases as the HNT percentage increases which ensure that the biodegradation of PHBV nanocomposites was not due to the hydrolysis completely. On the other hand, the presence of water molecule in HNTs

structure assisted in more microbial attachment with PHBV/HNTs films compared to the neat films.

Conclusion

Neat and PHBV/HNTs films were processed and investigated for their thermal, moisture absorption and biodegradation properties. The thermal stability of the PHBV biopolymeric films such as decomposition and melting temperatures were found to increase with increasing percentage of HNTs. In addition, the moisture absorption was also significantly reduced in HNTs-added PHBV films in comparison to neat PHBV counterpart. The moisture absorption behavior of the neat and PHBV/HNTs films followed the Fickian's distribution. Also, the biodegradation rate of the films increased with the increase in HNTs concentration. This study led to cognize that the HNTs can be successfully utilized to enhance the performance of biopolymers, particularly the PHBV polymer investigated in this study for biomedical, film packaging and various other applications.

Declaration of Conflicting Interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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