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ORIGINAL PAPER



Mechanical, Fire Retardant, Water Absorption and Soil Biodegradation Properties of Poly(3-hydroxy-butyrate-co-3-valerate) Nanofilms

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Abstract

Biopolymers provide potential substitution to synthetic polymers derived from scarce petroleum materials which are not environmental friendly and biodegradable. However, there exists challenging or unanswered questions for biopolymers to be used in biomedical, film packaging, automobile, construction and commercial industries such as their mechanical performance, thermal and fire retardancy, and durability when exposed to water. In this study, we investigated one such potential biopolymer, poly(3-hydroxy-butyrate-co-3-valerate) (PHBV) for the aforementioned properties. At first, 0–15 wt% halloysite nanotubes (HNTs) was dispersed in PHBV polymer using ultrasonication process in presence of chloroform solvent. The solvent was then evaporated and PHBV/HNTs films were prepared by solution casting method. PHBV films without HNTs (neat) were also prepared for baseline comparison. Thermogravimetric analysis (TGA) and tensile tests were then performed to study the thermal and mechanical properties of these films. The horizontal burning test (HBT) was also carried out to investigate the fire retardancy behavior. Finally, the water absorption and soil biodegradability behavior of these composites were investigated by submerging the films in water and Alabama soil conditions. PHBV films with 3 wt% loading showed optimum enhancement in thermal stability and tensile properties. In contrast, films with 10–15 wt% HNTs loading showed superior fire-retardancy, better water resistance and faster soil degradation over neat counterpart.

Keywords Nanocomposites · HNTs · Fire retardancy · Water absorption · Soil biodegradation

Introduction

In recent years, wastage developed from the non-biodegradable petroleum products have raised alarming environmental concerns and health issues. Thus, attracted significant global awareness and attention of governments from many countries to remove or replace the petroleum based materials by greener, biodegradable and ecofriendly materials of high performance [1]. Biopolymers or organic plastics that are derived from different renewable sources such as vegetable oil, protein, starch etc. or from bacteria, fungi, and algae have provided suitable substitution with greener and sustainable energy technology not only by the conservation of the fossil fuel but also by reducing CO_2 emission. Therefore,

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biopolymers have potential for unlimited applications in automobile, food packaging, furniture, and construction industries [2]. Among such various potential biopolymers, PHBV, a member of polyhydroxyalkanoates (PHA) that is derived from 295 types of bacteria, has drawn significant attention due to its biodegradability, biocompatibility, and thermoplasticity [3]. Many research groups have recorded the structure, biodegradation, and mechanical properties of the PHBV [4, 5]. In spite of this, due to high cost, slow crystallization rate, high degree of crystallinity, and difficulty in processing limits, the wide application of the PHBV is still limited [6]. The other factors that contributes to this limitation is the relatively lower mechanical properties compared to synthetic polymers, lack of in-depth understanding of thermal, water absorption, soil degradability, and fireretardancy behavior for the aforementioned applications.

In recent years, researchers have used various blending options and filler materials to enhance the mechanical and thermal properties of PHBV composites. It has been reported that addition of small mass fraction of nanoparticles such as carbon nanotubes (CNTs), silicon dioxide (SiO₂), titanium

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dioxide (TiO₂), montmorillonite (MMT) and halloysite nanotubes (HNTs) in polymers significantly enhanced the mechanical, thermal and fire-retardant properties [7–10]. Among these nanofillers, MMT nanoclay and HNTs have particularly gain interest because of their organic nature and have been reported to improve PHBV's thermal, mechanical, durability and fire-retardant properties. However, organic modification of MMT is necessary to facilitate the intercalation and crosslinking with polymer chain. The surface modification of MMT, however, increases the thermal sensitivity of PHBV during processing leading to premature degradation resulting in poor nanocomposite performance [3, 11]. In contrast, HNTs, a member of kaolin group, extracted from mineral deposit do not require additional modifier to disperse into the polymer matrix. HNTs have tube like structure similar to CNTs with diameter typically smaller than 100 nm and length in between 500 nm to 1.2 microns [12]. The external surface of HNTs is mainly composed of the siloxane (Si-O-Si) groups, whereas, the internal surface consists of a gibbsite like array of aluminol (Al-OH) groups [13]. 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 on HNTs establishes hydrogen bonding with the polymer matrix during mixing, and thus favors uniform dispersion [14]. Furthermore, high aspect ratio as well as large surface area of HNTs ensure better interaction between nanofiller and polymer matrix [15, 16]. Also, due to the high aspect ratio, HNTs forms more effective, crack-free and protective layer on the surface during burning. As the polymer burns away, this layer consists of thermally stable nanoparticle residue acts as an insulator and protects the underlying material and re-radiates energy away from the surface [17]. In addition, HNTs possess the lower mass loss rate ability due to tubular structure during burning [18]. Several studies have reported that three types of nanoparticle such as sphere (silica), tube (multiwalled CNTs), and plate (clay) plays a vital role in reducing heat release rate (HRR) of the nanocomposites by forming nanoparticle layers [19, 20]. 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 properties [13, 18]. 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 [21, 22]. However, to the best of our knowledge, no comprehensive characterization of PHBV biopolymers, particularly focusing on the fire stability, water absorption and soil biodegradability behavior have been reported to date. Also, efforts have not been made to optimize the concentration of HNTs, and investigate its

impact on the overall morphological, mechanical, and thermal performance of these composites, including the durability, biodegradability, and fire-retardant properties.

In this study, we have processed neat and nanofilms by adding 3–15 wt% HNTs, and investigated the thermal, mechanical and fire retardancy properties using thermogravimetric analysis (TGA), tensile and horizontal burning tests. The water absorption and soil biodegradability behavior of these composites were also studied by conditioning the films in water for 315 h, and in Alabama soil for 12 weeks, respectively. The surface analysis of tensile fractured samples was also investigated through scanning electron microscope (SEM).

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 biological fermentation of renewable carbohydrate feedstocks. An unmodified tubular shaped HNTs was obtained by Natural Nano, Pittsford NY, USA, and Chloroform (\geq 99.5%) was purchased from Sigma Aldrich, Saint Louis, USA.

Processing of PHBV Films

Neat PHBV Films

At first, a solution was prepared by dissolving 10 g of PHBV in 120 ml chloroform using a continuous magnetic stirrer for 24 h. The solution was then vacuum mixed using 100 kPa pressure for 15 min at a speed rate of 1500 rpm to remove the entrapped air bubbles. Finally, the films were prepared by spreading the mixture on a glass plate and cured at room temperature for 24 h.

HNTs Added PHBV Films (Referred as Nanofilms from Here Onwards)

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. 10 g of PHBV polymer was then dissolved into the HNTs/chloroform solution, and the films were prepared following the exact procedure used for neat films. All the samples were cleaned and dried in an oven at 50 °C prior to running experiments to remove impurities and moisture that may have been observed due to environmental exposure.

Experimental Procedure

Thermogravimetric Analysis (TGA)

TGA was performed on TA Q500 analyzer to determine the decomposition temperature of PHBV films at a heating rate of 10 °C from 30 to 550 °C. Samples weighing 10–15 mg was used and tests were run in nitrogen environment. The decomposition temperature and residual weight percentages of these films with respect to temperature.

Tensile Test

Tensile test was performed on a Zwick Roell universal test machine equipped with a 2.5 kN load cell using a ASTM standard D882-02. A crosshead speed of 1.2 mm/min and grip to grip separation of 40 mm was used. A minimum of 10 samples of size $100 \times 10 \times 0.25$ (mm × mm × mm) was used for each type.

Horizontal Burning Test (HBT)

HBT was performed on the films to study the fire retardancy behavior with a modification to ASTM D635-10. The tests were performed on films of size $125 \times 13 \times 1.5$ (mm × mm × mm) in an environment having relative humidity of 65–70%. Standard propane flame was used to burn the films at an angle of 45°. A wire gauge of 10 mesh per 25 mm was used to collect the residue after burning. The linear burning rate was calculated by using Eq. 1.

Linear burning rate,
$$V = 60 L/t (mm/min)$$
, (1)

where L represents the burnt length in mm and t represents the time in min taken by the flame front to reach up to 100 mm distance.

Water Absorption Behavior (WAB)

WAB or durability of films was investigated by submerging the 2×2 cm films in water for a time span of 2–315 h. The films were taken out of water at several intervals, dried with paper towel and the percentage of water absorption was calculated using Eq. 2.

Percentage water absorption =
$$\left[\frac{W_{f} - W_{i}}{W_{i}}\right] \times 100\%$$
, (2)

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

The coefficient of water diffusion was also calculated using Eq. 3.

$$D = \frac{\pi}{16} \left[\frac{\frac{M_{t}}{M_{\infty}}}{\frac{\sqrt{t}}{h}} \right]^{2},$$
(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 (SBT)

For SBT test, a basic nature soil (measured from the pH measurements) from Tuskegee, Alabama, United States of America was selected. The tests were performed using SBT method [23] at room temperature by burying the film of size 4×4 cm in a pit (100 cm deep and 10 cm wide) for 2, 3, 5, 8 and 12 weeks, respectively. A space of 30 cm was maintained between each film to make sure the aerobic degradation. After each interval, the films were removed, washed with distilled water, dried at 50°C for 8 h and weighed. The degree of soil degradation was calculated using Eq. 4.

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

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

Morphological Analysis

The morphology of neat and nanofilms with different HNTs concentration retrieved after the "Alabama soil" conditioning was characterized by optical microscopy using Olympus BX51 equipped with polarizer and analyzer (Olympus U-AN360P). All films were imaged in transmission mode at full extinction. The morphology of the tensile fractured films was analyzed using JEOL JSM-6400 field emission scanning electron microscope (FESEM) at an acceleration voltage of 15 kV. The film surface was coated with a thin gold film prior to FESEM using sputtering process to increase their conductance for observation.

Result and Discussion

Thermogravimetric Analysis (TGA)

Figures 1, 2 and Table 1 show the TGA result of neat and nanofilms. Results showed that the onset (Fig. 1) and maximum decomposition temperature (Fig. 2) of films increased with the addition of HNTs. TGA behavior of neat and nanofilms showed two step decomposition at 250 °C and



Fig. 1 TGA graph of neat and nanofilms with magnified decomposition region

350 °C, respectively. The first step or onset degradation can be attributed to the decomposition of crosslinked polymer chain. Consequently, the second step or final degradation is due to the decomposition of main block of PHBV polymer chain [24]. For 10 wt% HNTs films, the onset and maximum decomposition temperatures showed an enhancement of 6.45 °C and 5.94 °C in comparison to neat counterpart. At 500 °C, the residual weight percentage in nanofilms was also found higher in comparison to neat films (Table 1). The enhancement in thermal stability of nanofilms can be attributed to the crosslinking established between HNTs and PHBV polymer. 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 [25]. In addition, HNTs may have delayed the mass transfer of PHBV that was entrapped inside their lumen, and thus resulted in the enhancement of nanofilms thermal stability [26].

Tensile Testing

Tensile properties of neat and nanofilms is shown in Fig. 3 and Table 2. Nanofilms with 0.3 wt% HNTs loadings showed optimum enhancement with 35.66%, 65.07% and 8.84% increase in tensile strength, modulus, and elongation at break in comparison to neat films. However, a decreasing trend in these properties was observed at 5 wt% HNTs loading which could be attributed to increase in resin viscosity and sluggish nature of matrix/nanoparticle mixture. Also, the increase in void concentration resulting from HNTs agglomeration and volatile air bubbles entrapped due to high resin viscosity could have majorly caused this decrease at 5 wt% loading making the polymer brittle evident from sample breakage into pieces. In addition, at higher nanoclay loading, the filler–filler interaction leads to agglomeration as well as local stress concentration sites which ultimately reduce the mechanical properties of nanocomposites [27].

Fracture Surface Analysis

Figure 4a–d shows the scanning electron microscopy (SEM) images of fractured neat and nanofilms tested under tensile loading. A smooth surface found in neat films (Fig. 4a) could be attributed to the weak resistance offered by the material to crack propagation. In contrast, the nanofilms showed relatively rough surfaces with crack propagation at multiple locations (Fig. 4c, d), indicating the high resistance offered by the films to crack propagation. For instance, the average measured crack lengths (considering large crack) of neat, 3 wt%, 5 wt% and 10 wt% films are 261.5 μ m, 105 μ m, 213 μ m, and 268 μ m, respectively. The reduction in average crack length and formation of multiple cracks in 3 wt%



Fig. 2 DTG graph of neat and nanofilms with magnified maximum decomposition peak

| Table 1 TGA data of neat and nanofilms | 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 |

films (Fig. 4b) could be attributed to good interfacial bonding between the incorporated HNTs and PHBV resin [28]. In contrast, the tensile strength, modulus and elongation at break (Table 2) of 5-15 wt% samples were found lower than 3 wt% samples. Higher concentrations of nanoparticles loading results in increased filler-filler interaction leading to high density of agglomeration sites. Also, cavities were found in the fracture surface of PHBV/5 wt% HNTs and PHBV/10 wt% HNTs samples which are formed due the non-removal of entrapped air bubbles during vacuuming due to the rise in PHBV viscosity at higher HNTs concentration. The agglomerated HNTs sites and cavities results in high stress concentration sites that may have acted as precursor for crack initiation and premature failure [29].

Fire Retardancy Test (FRT)

FRT test was conducted at ambient conditions to determine the burning time as well as burning rate. Neat films were found to burn out and ignite faster than nanofilms (Table 3). The burning rate of neat films was found nearly twice the rate of 10-15 wt% nanofilms. Also, a contrasting burning characteristics was found between neat and nanofilms. The neat films started to drip immediately after the beginning of FRT (Fig. 5b) with faster burning rate and continued until





Table 2 Tensile properties of neat and nanofilms

| Nanocomposite type | Tensile modulus (MPa) | % Change | Tensile strength (MPa) | % Change | Elongation at break (%) |
|--------------------|-----------------------|----------|------------------------|----------|----------------------------|
| Neat PHBV | 308 ± 13.73 | 0.0 | 20.50 ± 1.57 | 0.0 | 2.23 |
| PHBV + 3% HNT | 508.42 ± 17.8 | 65.07 | 27.81 ± 2.44 | 35.66 | 8.84 |
| PHBV+5% HNT | 361.49 ± 14.7 | 17.37 | 24.68 ± 2.07 | 20.39 | 8.33 |
| PHBV + 10% HNT | 230.9 ± 6.67 | -25 | 22.79 ± 3.01 | 11.17 | 7.90 |
| PHBV + 15% HNT | 223.7 ± 15.8 | -27.37 | 20.57 ± 4.22 | 0.34 | 7.13 |

the material was completely burnt. On the other hand, the dripping rate was much lower at the beginning and the fire propagated gradually through the nanofilms maintaining constant flame with lower burning rate until the end of FRT (Fig. 5c, d). Moreover, all the nanofilms left char residue at the end. The barrier effect of HNTs may be the principal reason for reducing the flammability/increasing the FRP of the nanofilms [30]. This effect can be elucidated as: firstly, the HNTs act as insulator into the PHBV that protects the polymer from contact with fire [31]. Secondly, the formation of the char of HNTs plays a role as a heat resistant and fireretardant [32]. Also, the enhancement in fire retardancy of the nanofilms can be attributed to a reduction in mass loss rate that eventually causes lowers heat release and flame spread [33]. Figure 6 shows the residues of neat, 5 wt%, and 10 wt% nanofilms. A small amount of residue was left after the FRT for neat films (Fig. 6a), whereas, in 5-10 wt% nanofilms, a thick and dense amount of residues was found (Fig. 6b, c). This amount of residue formation is equivalent to the original HNTs loading after dehydration and dehydroxylation (shown in Scheme 1) [34]. Moreover, the naked visual inspection of samples showed significant variation in color after the tests. The residual materials of neat films was light brown, whereas the PHBV/HNTs samples were more blackish. The color of residual materials typically shows the formation of carbonaceous char on the surface of residue.

To better understand the structure and surface morphology of residual char of these films, FESEM was employed. It can be seen that the neat films did not form any char but contains many holes and cracks that are distributed across the surface (Fig. 7a). In contrast, the number of holes and cracks were significantly less in 5–10 wt% nanofilms. Also, a carbonaceous char layer was formed in these films indicated by red arrows and a circle in Fig. 7b, c. Due to the hindering effect of HNTs, this char may have decreased the efficiency of heat and volatile transfer [35]. As a result, the burning rate in nanofilms was significantly lower than the neat counterpart.



Fig. 4 SEM images of tensile tested fractured film surfaces, a neat, b 3%, c 5%, and d 10% HNTs loading (at a low magnification × 100)

| Table 3Fire retardancyproperties (FRP) of neat andnanofilms | Specimens | Burning time (s) | % Change | Burning rate (mm/min) | % Change |
|---|---------------|--------------------|----------|-----------------------|----------|
| | Neat PHBV | 74.83 ± 19.24 | 0.0 | 62.48 ± 0.24 | 0.0 |
| | PHBV/3% HNTs | 91.79 ± 7.46 | +22.66 | 49.2 ± 0.06 | -21.15 |
| | PHBV/5% HNTs | 113.78 ± 6.15 | +52.00 | 39.0 ± 0.03 | -37.50 |
| | PHBV/10% HNTs | 124.94 ± 4.98 | +67.00 | 36.0 ± 0.03 | -42.30 |
| | PHBV/15% HNTs | 122.87 ± 10.09 | +64.19 | 36.61 ± 0.04 | -41.34 |

Water Absorption Test

Water absorption characteristics and corresponding data of neat and nanofilms are shown in Fig. 8 and Table 4, 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 a saturation level after 75 h with no significant change observed up to 315 h. The water absorption behavior of both neat and nanofilms demonstrated the Fickian diffusion behavior [36]. 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 barrier to water absorption by transforming the original water molecules diffusion path into a tortuous or maze like path [37]. Furthermore, the diffusion coefficient reduced linearly with the increasing HNTs concentration up to 10 wt% HNTs concentration.

Soil Burial Test

The morphology of neat and nanofilms with different HNTs concentration retrieved after the "Alabama soil" conditioning was characterized by optical microscopy shown in Fig. 9. The neat film surface was smooth prior to conditioning, whereas, the nanofilm surface was relatively

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Fig. 5 Horizontal burning test, a neat and nanofilms, b neat film during burning, c 5% HNTs, and d 10% HNTs nanofilms during burning



Fig. 6 Images of the residues after horizontal burning test, a neat sample, b 5%, and c 10% HNTs nanofilms



Scheme 1 Decomposition of halloysite

rougher due to the presence of HNTs. After 3 weeks of burial, there was no significant change in surface morphology in neat and PHBV nanofilms was found except some discoloration in both neat and nanofilms. It can be due to the absorption of water molecules and the presence of hydrolytic product which are responsible for the change in refractive index of these films [38]. Besides, the percentage weight loss in nanofilms was 3.86%, 6.6%, 6.1%, and 9% at 3, 5, 10, and 15 wt% HNTs concentrations. In contrast, the percentage weight loss in neat film was only 3.2%. The samples buried for 8 weeks showed a significant number of pits on the surface with the rest of the surface being slightly rougher than the non-buried samples. In addition, a network of cavities and surface erosion by bacterial consumption was observed on the nanofilms that are proportional to the HNTs concentration compared to the neat films. However, the cavity distribution and the surface erosion in nanofilms followed an inhomogeneous mechanism. It may be due to the enzymatic superficial degradation process of PHBV which is also reported by other researchers [39]. The enzymatic superficial degradation is associated with the inhomogeneous growth of microorganism on the sample surface as well as the contact of soil with the most eroded sample zone. After 8 weeks, no significant difference in degradation was found in nanofilms



Fig. 7 Field emission scanning electron microscopy (FESEM) of residual material after horizontal burning test, a neat, b 5%, and c 10% nanofilms (Color figure online)





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| Table 4 | Maximum | water | uptake | (M_{∞}) | and | diffusion | coefficient | (D) |
|-----------|--------------|-------|--------|----------------|-----|-----------|-------------|-----|
| of neat a | and nanofilm | ns | | | | | | |

| Slope | M _∞ (%) | D (mm ² /s) |
|-------|---|--|
| 0.16 | 2.5 | 7.96×10^{-8} |
| 0.14 | 2.15 | 5.19×10^{-8} |
| 0.14 | 2.15 | 4.57×10^{-8} |
| 0.14 | 2.09 | 3.58×10^{-8} |
| 0.11 | 1.6 | 4.51×10^{-8} |
| | Slope 0.16 0.14 0.14 0.14 0.14 0.11 | Slope M_{∞} (%) 0.16 2.5 0.14 2.15 0.14 2.15 0.14 2.09 0.11 1.6 |

over neat counterpart. However, after 12 weeks, the percentage weight loss in nanofilms was significantly higher with 16.53%, 42.27%, 30%, and 33% at 3,5,10 and 15 wt% HNTs loading. In contrast, the weight loss in neat film was only 10.07%. The highest percentage weight loss in nanofilms could be attributed to the presence of water molecule in HNTs structure that attracts more fungi or other microorganisms which may have produced more extracellular enzymes on nanofilms compared to neat film [40].

PHBV is a linear aliphatic polyester in which degradation proceeds through the scission of ester bonds by enzymatically catalyzed hydrolysis due to the presence of microorganisms in the soil as shown in Scheme 2) [41].

Figure 10a–d shows the IR spectrum of neat and nanofilms before and after 12 weeks of soil conditioning. The spectra of PHBV at 1700 cm⁻¹ band assigned to C=O stretching vibration of carbonyl groups became wider with the increase in burial time. The characteristic absorptions of CH₃ out of plane bending, C–O–H in plane bending, and C–O stretching vibration were found at 1455, 1377, and 1226 cm⁻¹, respectively [40]. The peaks of both neat and nanofilms were reduced in intensity after 12 weeks indicating the progressive degradation process. In addition, the N–H stretching at 3200 cm⁻¹, N–H bending at 1550 cm⁻¹, and P=O stretching at 1054 cm⁻¹

| Specimens | 0 weeks | 3 weeks | 5 weeks | 8 weeks | 12 weeks |
|--------------|---------|---------|---------|---------|----------|
| Neat PHBV | | | | - | |
| PHBV+3%HNTs | | R | | | |
| PHBV+5%HNTs | | | | | S) |
| PHBV+10%HNTs | | | | ł | |
| PHBV+15%HNTs | | | | | |

Fig. 9 Optical microscopy image of neat and nanofilms before and after soil biodegradation (×10 magnification)



Scheme 2 Catalytic hydrolysis of PHBV



Fig. 10 a-d FTIR spectrum of neat and nanofilms before and after 12 weeks of soil degradation

cell proteins related to the nucleic acids components. With time, the ratio of cell protein and nucleic acid components increases indicating the growth of microorganism [42]. These peaks confirm the absorption of microbial mass in all the films. Moreover, the band at 1640 cm⁻¹ associated with the -C=C- stretching vibration present in the degraded films was due to the breakage of ester link [40]. The chemical structure of the residual PHBV was not changed with the degradation

period. Therefore, the FTIR spectrum confirms that the degradation process proceeded by the micro-organisms originated from the surface and gradually expanded into the interior of the films [43]. FTIR results suggest the absence of degradation by-products on the surface of the films after washing with deionized water. It is believed that the oligomeric species that produced from the scission of the PHBV chain was leached out into the soil or by washing.

Conclusion

Neat and HNTs added PHBV films were processed and investigated for their thermal, mechanical, fire retardant, moisture absorption and biodegradation properties. The thermal stability of films such as decomposition temperature was found to increase with the increasing weight percentage of HNTs. Nanofilms at 0.3 wt% HNTs loading showed optimal enhancement in tensile properties due to better HNTs dispersion and good interfacial bonding between PHBV and HNTs. The burning rate of nanofilms was reduced significantly at higher HNTs loading due to the barrier effect of HNTs. In addition, the moisture absorption was also significantly reduced in nanofilms in comparison to neat films. The moisture absorption behavior of the neat and nanofilms followed the Fickian's distribution. Also, the biodegradation rate of films increased with the increase in HNTs loading. 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, automobile, construction and various other industrial applications.

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