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Thermal-chemical and biodegradation behaviour of alginic acid treated flax fibres/ poly(hydroxybutyrate-*co*-valerate) PHBV green composites in compost medium

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ABSTRACT

In this study, thermal-chemical and biodegradation behaviour of green composites based on flax fibres untreated and treated with alginic acid treated, and poly hydroxybutyrate-*co*-valerate (PHBV) were studied under composting conditions. The biodegradability of PHBV composites and neat PHBV were assayed by monitoring CO_2 production from polymeric carbon under controlled aerobic composting conditions as per ASTM D5338 standard. During the biodegradation process, PHBV composites thermal-chemical and morphology properties were characterized by thermogravimetric analysis (TGA), fourier transform infra-red (FT-IR) and scanning electron microscopy (SEM) techniques. The ultimate biodegradation (mineralization) study results showed alginic acid treated flax/PHBV composites has higher rate of degradation than untreated flax/PHBV composite and neat PHBV. TGA analysis indicated that an increased t-onset temperature for alginic acid treated flax fibres/PHBV composites which was mainly due to the influence of 2% sodium alginate treated with flax fibres. FTIR results showed the increased degradation of PHBV composites was due to the hydrolytic chain scission mechanisms influenced by presence of alginic acid and flax fibres as compared to neat PHBV matrix. Morphological SEM analysis showed PHBV composites biodegradation were readily attacked by fungus but rather PHBV degradation by bacteria. This study found that the incorporation of flax fibres into PHBV matrix provides a benefit to the green composites with enhanced biodegradability.

1. Introduction

The growing concern about environmental pollution due to post consumer plastics waste disposal is posing a challenge to industry and academia for the development of eco-friendly and sustainable green materials. Globally, there is much research interest in the area of sustainable biopolymers and biobased materials from bioresources for green manufacturing. Polymer composites based on natural fibres is currently receiving much attention as eco-friendly materials as replacement for synthetic fibres in various industrial sectors applications, such as automotive, construction and packaging applications. This is mainly attributed favourable properties of the natural fibres such as low density, low cost and specific mechanical strength as well as environmental friendliness, renewability and economic sustainability (Luo and Netravali, 1999; John and Thomas, 2008; Faruk et al., 2012; Mohanty et al., 2002; Mohanty et al., 2018).

Microbial biopolymer mainly produced by microbial fermentation of renewable feedstock or directly extracted biopolymers from biomass are the new generation of materials and their renewability offers an intrinsic neutral carbon and save primary resources (Mooney, 2009; Muniyasamy et al., 2013; Sabapathy et al., 2019). Poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is a thermoplastic biopolyester produced by

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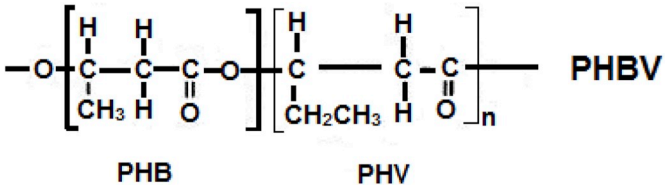
bacteria from microbial biosynthesis (Chen, 2009; Keshavarz and Roy, 2010). PHBV belongs to a class of poly (hydroxylalkonates) PHA. The PHA monomer with tailor made composition shows properties similar to conventional plastic materials, such as polyethylene (PE) and polypropylene (PP). Currently, the PHBV is increasing interest as most attractive materials in using various from various rigid packaging to biomedical applications such as suture, bone prostheses, and medicine capsules (Luo and Netravali, 1999; Richards et al., 2008; Jost and Langowski, 2015). Despite, the use of PHBV is very limited due to its drawbacks such as high cost, narrow processing window and thermally unstable during processing which lead a drastic reduction in molecular weight and brittle behaviours, low impact resistance (Arcos-Hernandez et al., 2012; Boyandin et al., 2012; Stloukal et al., 2015). To address these shortcomings, various efforts have been adopted to copolymerize the PHB repeating units with other monomers modifying and improve the inherent properties of biopolymers. Among that blending approach is considered to obtain PHB with other suitable less expensive thermoplastic polymer to modify the properties since it is more convenient and economical way. Interestingly, some studies showed that there was fully or partial miscibility which could lead to the improved properties and reduced cost with specific functionalities as like other conventional plastics (Chen, 2009; Keshavarz and Roy, 2010).

Also, some important studies on the use of flax natural fibres as reinforcing agent in PHBV have shown comparable properties to synthetic PP/flax composites (Naoyuki and Doi, 1996; Oksman et al., 2003; Nerín and Asensio, 2007; Bax and Müssig, 2008; Graupner et al., 2009; Srubar III, Wright et al., 2012; Reddy et al., 2013). (Barkoula et al., 2010) studied PHBV/flax composites the effect of flax fibre content (20%, 30% and 40% wt) in PHBV matrix by mechanical properties evaluation, where the results of impact resistance and young modulus were increased while tensile strength was almost constant. Also, it was observed that the loss of mechanical properties upon incorporation of natural fibres which was attributed to the lack of adhesion between polar fibres and hydrophobic plastic matrix (Yan et al., 2014). It is well known that natural fibres are hydrophilic because of the strong polarized hydroxyl groups. To increase the compatibility and adhesion between fibres and matrix, it requires chemical modification of natural fibres (John and Anandjiwala, 2008; Pickering et al., 2016) and it was shown that the addition of chemical modifier in the natural fibres have improvement in the thermal-mechanical properties and stability of the composites system (Jiang et al., 2008; Lemes et al., 2010). In most cited literatures, the compatibilizers used in the natural fibre composites are synthetic and toxic. The most common plasticizers such as phalates, alhydrides and isocynates were listed as a reproductive toxin (Yan et al., 2014). Nowadays, the use of environmentally friendly plasticizers is becoming necessary criteria for design and preparing (bio)composites with meeting ecological compatibility during its service life and end-of-life disposal (Jiang et al., 2008; Lemes et al., 2010).

Recent years, significant research studies have been made in developing biocomposites made from biopolymers and natural fibres on the improvement of fibre/matrix interfacial adhesion and impact resistance (Mohanty et al., 2018). However, the effect and influence of alginic acid on the thermal-chemical properties and potential ultimate biodegradation behaviour of PHBV/flax composites have not been studied. Therefore, the present study the effect of 2% alginic acid treated with flax fibres on the thermal-chemical properties, degradation behaviours of PHBV/flax composites in comparison to untreated flax fibres PHBV composites and neat PHBV were studied under composting conditions. The ultimate biodegradability (mineralization) by measuring the end products CO_2 emission from PHBV/flax composites and neat PHBV were evaluated for 100 days. During the biodegradation incubation, the PHBV composites and neat PHBV samples before and after degradation were also analysed to relate the degradation behaviours by using TGA, FT-IR and SEM techniques.



Scheme 1. PHBV chemical structure.

Table 1
Physical-chemical properties of the compost material.

S.No.	Analysis	Compost
1.	Moisture (%)[a]	50-55
2.	Total Dry solids (%) [b]	55
3.	Volatile Solids (%) [c]	53
4.	pH of compost solution	7.1
5.	Total organic carbon amount (%)[d]	10.6
6.	Total nitrogen amount (%)[d]	0.9

[a] Moisture (%) content is measured during drying 102–105 °C by a moisture analyser.
[b] The amount of solids obtained by taking a known volume of compost and drying at about 105 °C for 10h.
[c] The amount of solids obtained by subtracting the residue of a known volume of compost after incineration at about 550 °C for 30 min.
[d] Results obtained from C and N elemental analysis from Innoventon laboratory services at–Nelson Mandela Metropolitan University.

2. Materials and methods

2.1. Materials

Commercially available biopolymer PHBV (PHB88/PHV12) plasticized with 10% citric ester, density 1.25 ($g.cm^{-3}$) and molecular weight of 600 ka was obtained from Good fellow Cambridge Limited (U.K). Scheme 1 shows the chemical structure of PHBV used in this study. Flax fibres was obtained from local farmers in the Eastern Cape Province of South Africa. The flax fibres contonized on Temafa Cottonization line by processing flax fibres through 1 pass Lomy (at speed 680 rpm) and 1 pass Cottonizer (at 1470 rpm) was produced needled-punched nonwowens with an area weight of 200 g/m^2. Sodium alginate was obtained from Sigma Aldrich.

2.2. Fabrication of flax fibre reinforced PHBV

In this study, 2% sodium alginate solution dissolved with distilled water (v/v) was used to treat the flax nonwovens. The flax nonwowens were immersed in 2% sodium alginate solution for 2 h. After that the solution was then drained out and the flax nonwovens was dried in air ventilated oven at 110 °C for 8 h. These nonwovens were used to prepare the PHBV composites.

2.3. Fabrication of flax fibre reinforced PHBV

The PHBV/flax fibre composite samples were prepared by solution casting followed by compression moulding. A calculated amount of PHBV was dissolved in chloroform and poured on a surface of flax fibre nonwoven mat of untreated and treated with 2% alginic acid. The fibre mat was dried at room temperature for 24 h and thereafter compression moulded at 160–180 °C into composite sheet of 1 mm thickness. To avoid the influence of residual moisture, all the PHBV/flax composite sheets were dried at 50 °C for 24 h and stored in a sealed bag at ambient temperature before any characterization and biodegradation studies were undertaken.

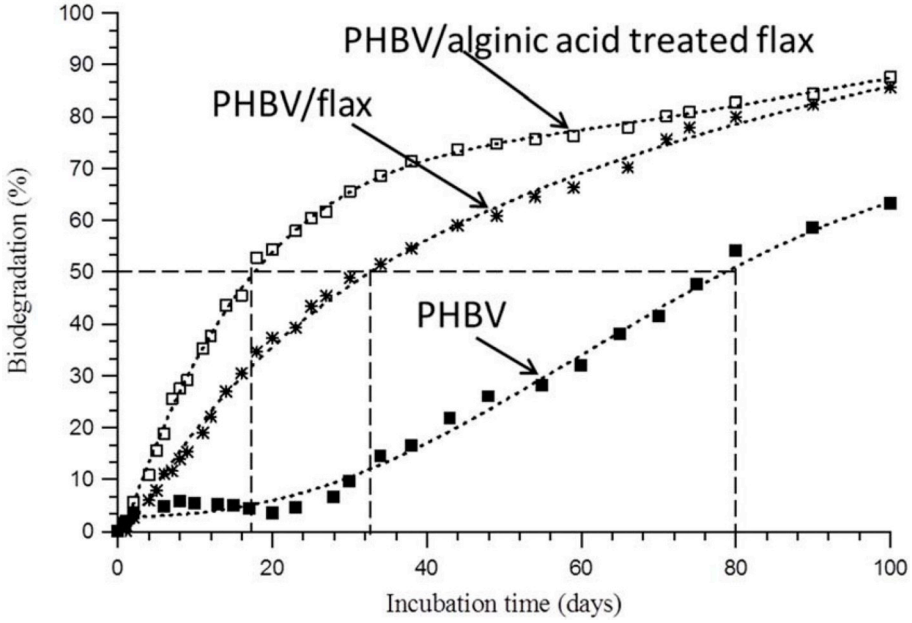


Fig. 1. Biodegradation results of PHBV and its composites under controlled compost conditions.

2.4. Biodegradation studies of PHBV composites

A respirometric CO_2 evolution method was used to measure the ultimate biodegradation of PHBV composites and neat PHBV under composting conditions as adopted protocol by Chiellini et al. (2004). In this study, 3 months old well areated mature compost derived from mushroom farm consisting of straw, hay, mulch and chicken manure was obtained from Grassmaster Inc, Port Elizabeth, South Africa. The compost was further sieved to a size of <8 mm, and its physical and chemical characteristics were determined as per ASTM D6400 standard for testing compostable plastics. Table 1 provides the physical-chemical properties of compost used in this study.

The test specimen of 10 mm × 10 mm was cut out of the sheet and was buried in the compost with a ratio of 1:6 (w/w) samples to dry solid of compost. The test mixture of compost and specimen was placed in a glass respirometricair tight apparatus of 1000 ml capacity. A beaker containing 50 ml of potassium hydroxide solution (0.5 N KOH) was placed on top of the test mixture to trap emitted carbon dioxide from the test samples during biodegradation. All test samples and blank were tested in three replicates. The setup was carried out in thermo static oven and was maintained at an optimum composting temperature of 58 ± 2 °C. At frequent time intervals between 3-5 days, the CO_2 traps were changed with new KOH solution and a 10 ml aliquot from the KOH with trapped CO_2 was titrated against HCl (1N) solution using phenolphthalein as an indicator. The total theoretical amount of CO_2 (t) in the test specimens were calculated from equation (1) below:

$$CO_2(t) = M_t \times C_t \times \frac{44}{12} \quad (1)$$

where M_t is the total dry weight of test specimen (g) added to the compost, C_t is the relative weight of the total organic carbon (g) in the test specimen.

The percentage biodegradation was calculated the test sample polymeric carbon mineralized as CO_2 according to the expression below (Equation. (2)):

$$Biodegradation(\%) = \frac{(CO_2)s - (CO_2)c}{(CO_2)t} \times 100 \quad (2)$$

where (CO_2)s is the carbon dioxide from the test sample (compost + specimen), (CO_2)c is the carbon dioxide from the blank compost and (CO_2)t is the total theoretical amount of carbon dioxide in the test material.

A biodegradation curve was obtained by plotting percentage carbon dioxide released versus incubation time.

2.5. Characterization

2.5.1. Thermogravimetric analysis (TGA)

Thermogravimetric analyser model PerkinElmer Pyris (USA) was used to analyse the test samples by heating from 30 to 600 °C at a rate of 20 °C/min in a nitrogen atmosphere. Weight degradation temperature at 2% weight loss and sample degradation behaviours were analysed from derivative traces.

2.5.2. Fourier transform infrared spectroscopy (FT-IR)

FT-IR PerkinElmer Spectrum 100 (USA) was used to obtain the spectra of the test samples in the range of 4000–400 cm^{-1}at a resolution of 4 cm^{-1} and averaged over 32 scans.

2.5.3. Scanning electron microscopy (SEM)

FEI Quanta 200 (Eindhoven, The Netherlands) scanning electron microscope was used at an accelerating voltage of 15–20 kV in low

Table 2
Organic carbon content and theoretically calculated carbon dioxide $(CO_2)t$ of PHBV and its composites during compost biodegradation.

Run	Material code	Composition (wt.%)	Amount [mg]	C [%]	C [mg]	$(CO_2)t$ [mg]	Biodegradation (%) in days					
							15d	30d	45d	60d	80d	100d
1	PHBV	100	5021	58.3	2927	10733	4.9	9.5	22.6	32.0	54.1	63.2
2	PHBV/flax	70/30	5041	51.1	2574	9439	30.4	48.9	59.0	66.3	80.0	85.6
3	PHBV/flax/alginic acid	68/30/2	5053	45.3	2290	8398	45.1	65.5	73.7	76.3	82.8	88.0

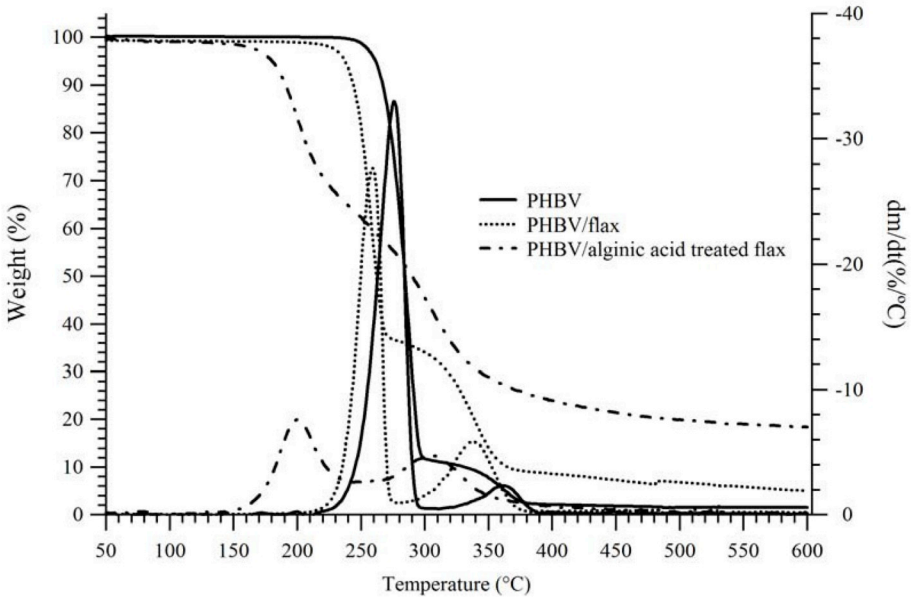


Fig. 2. TGA traces weight degradation (left axis) and derivative (right axis) of PHBV, PHBV/Flax and PHBV/alginic acid treated flax.

vacuum to observe the surface morphology of test specimens. A gold palladium coating of 20 nm thickness was coated on the surfaces of test specimens to avoid electron build up during the analysis.

3. Results and discussion

3.1. Biodegradation evaluation

Among different test methods for evaluating biodegradation of polymers, respirometric methods are guaranteed techniques for measuring the ultimate biodegradation (mineralization) of polymeric carbon mineralized as CO_2 in biotic conditions (Lucas et al., 2008; Muniyasamy et al., 2016). Other primary degradation tests such as weight loss, enzymatic assay and microbial counting and others are not validated methods for the scientific claims biodegradable and compostable polymeric materials (Muniyasamy et al., 2013; Nazareth et al., 2019). Fig. 1 and Table 2 show the aerobic biodegradation results of untreated and alginic acid treated flax PHBV composites, and neat PHBV under controlled compost conditions evaluated by respirometric method.

In this study, the threshold embrittlement and fragmentation of PHBV/flax and PHBV/alginic acid treated flax composite samples was observed visually after incubation for 12–15 days, while the neat PHBV after incubation for 58–60 days. The biodegradation results on cumulative carbon to CO_2 emission showed that the PHBV/alginic acid treated flax started an exponential phase after 3 days of incubation and approached 70% biodegradation within 35 days, whereas in the PHBV/flax, an exponential phase started after 7 days and approached 70% biodegradation in 65 days. In the case of neat PHBV, an exponential phase started only after 38 days approaching 63.2% biodegradation in 100 days. At the end of this test period, the percentage biodegradability of PHBV/alginic acid treated flax, PHBV/flax and PHBV were 88%, 86% and 63.2%, respectively. The obtained results indicate increased rate of biodegradation PHBV composites as compared to with the neat PHBV,

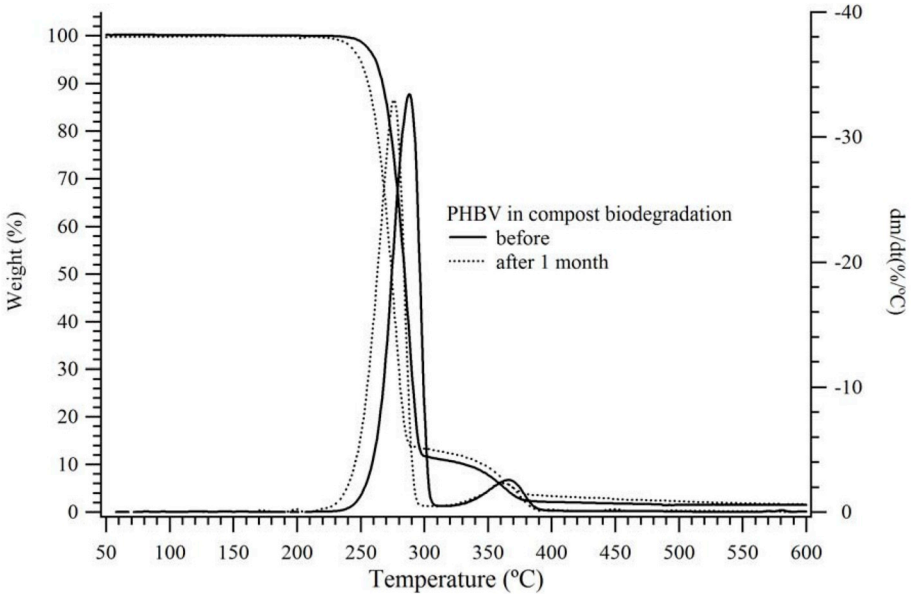


Fig. 3. TGA results (a) weight degradation (b) derivative traces obtained from TGA curve of PHBV before and after 1 month biodegradation in compost condition.

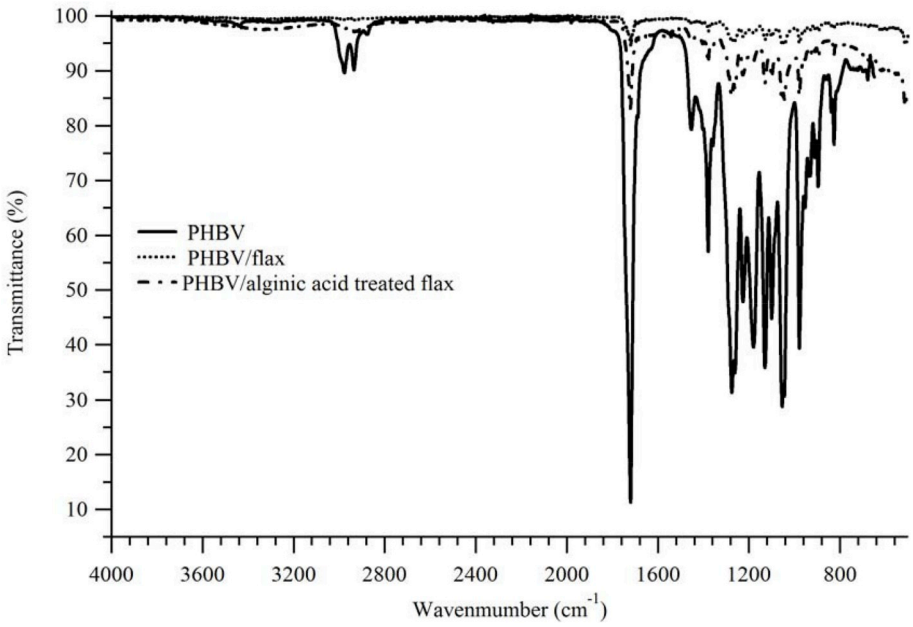


Fig. 4. FT-IR transmission spectra of PHBV, PHBV/flax and PHBV/alginic acid treated flax.

which is mainly agreement with the effect of flax fibres and alginic acid, since flax fibres are highly hydrophilic, its composite degradation are strongly depend on the environmental abiotic and biotic conditions. Authors (Davies and Bruce, 1998; Pickering et al., 2016; Mohanty et al., 2018) investigated the mechanical properties of flax fibres in environmental conditions both static and relative humidity (RH), where the dynamic moduli of flax fibres decreased remarkably with an increase of RH from 30 to 90%. The high moisture absorption and poor dimensional stability characteristics of flax fibres could be the main reason for favouring the accelerated biodegradation of PHBV composites. Particularly, the alginic acid treated flax fibres in PHBV composite lag phase reduction occurred within 3 days and 7 days for PHBV/flax fibres as compared to 38 days for neat PHBV (Fig. 1). This enhanced biodegradable was mainly due to the characteristics of alginic acid since it is water soluble and readily biodegradable. The present biodegradation results suggested that test conditions RH 50–52%, temperature 58–60 °C and present microorganisms in compost medium are favourable conditions for the accelerated biodegradation of PHBV/alginic acid treated flax fibres composites.

3.2. Thermogravimetric analysis (TGA)

Fig. 2 shows TGA analysis of PHBV, PHBV/flax and PHBV/alginic acid treated flax fibres green composites. TGA results showed the PHBV matrix has two step thermal degradation behaviour, a major degradation peak at 289 °C followed by minor degradation peak at 370 °C. The two step degradation behaviour of PHBV could be due to their composition of 10% citric acid plasticiser and additives formulated in the PHBV by the manufacture. These compositions were thermally degraded at two different degradation temperature as shown in (Fig. 2). In the case

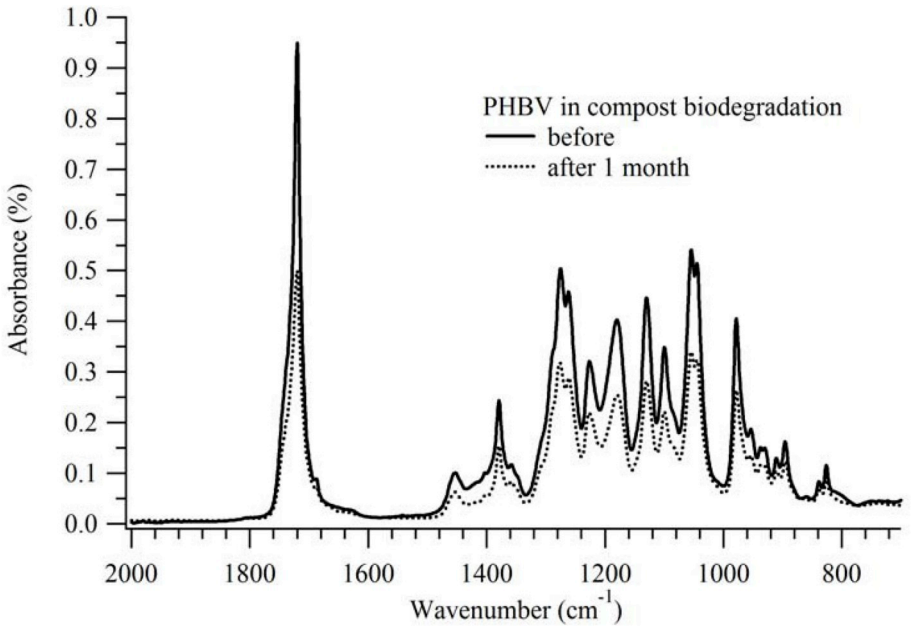


Fig. 5. FTIR absorption spectra of PHBV before and after 1 month biodegradation in compost condition.

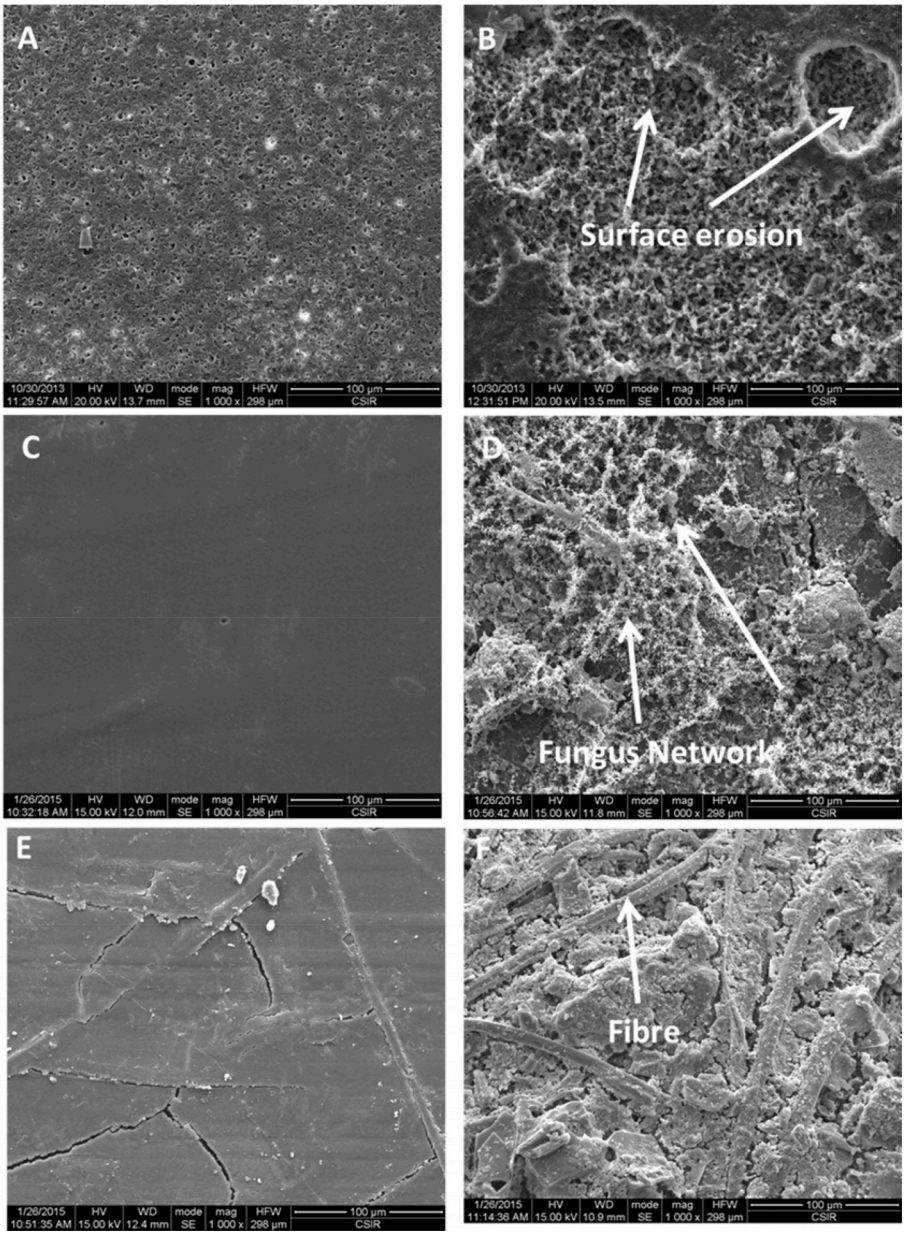


Fig. 6. SEM results of a) PHBV, b) HBV after 1 month in compost; c)PHBV/flax, d, PHBV/flax after 1 month in compost; e) PHBV/alginic acid treated flax and f) PHBV/alginic acid treated flax after 1 month in compost.

of PHBV/flax and PHBV/alginic acid treated flax composites, the major degradation temperature decreased to 260 °C and 200 °C, respectively as compared to PHBV. Similarly, the minor degradation temperature of PHBV composites decreased to 340 °C and 310 °C, respectively as compared to the neat PHBV. These results suggest that the presence of flax fibre influenced the thermal degradation behaviour of PHBV/flax composites confirming that there is some miscibility, where no further degradation step (Fig. 2). The decreased degradation behaviour of PHBV/flax composite as compared to neat PHBV could be due to the presence of cellulose (65%) and lignin (2.5%) in the flax fibres, where degradation occurs in between at 200–250 °C (Morey et al., 2009; Pickering et al., 2016). In the case of PHBV/alginic acid treated flax composite decreased thermal degradation as compared to PHBV/flax composite, which suggest that the alginic acid influenced increase the hydrophilic nature of the flax fibre, thereby lowering the degradation temperature (Fig. 2).

Fig. 3 shows TGA weight degradation and derivative traces PHBV before and after 1 month incubation in compost biodegradation. The results show that after 1 month of incubation the major degradation temperature of PHBV slightly decreased from 289 to 275 °C but there was no significant change in the minor degradation temperature which was around 360 °C (Fig. 3). These results suggest that the presence of microorganisms in the adopted compost conditions were able to degrade the material at 280 °C rather than the component whose degradation temperature corresponds to 360 °C. In the case of composites, flax and alginic acid treated flax have influenced to modify both major and minor degradation step behaviour of PHBV component material as shown (Fig. 2).

3.3. Structural changes

Fig. 4 show the FT-IR characterization of investigated test samples. The functional group of alcohol bearing O-H wave number 3200-3600 cm^{-1} was slightly increased for PHBV/alginic acid treated flax as compared to the PHBV/flax and no hydroxyl peak for neat PHBV. This FTIR results evidenced the alginic treated flax fibres in the PHBV

composite has higher hydrophilic characters than PHBV/flax and neat PHBV. The hydrophilic characters of alginic treated flax fibres PHBV composite has greatly influenced during the biodegradation in compost conditions (Fig. 1).

FTIR traces of PHBV samples analysed before and after 1 month biodegradation in compost are shown in (Fig. 5). The FTIR results suggest that the absorbance of PHBV functional groups bearing alcohol wave numbers at 1050-1150 cm^{-1}; carbonyl at 1670-1820 cm^{-1}; ether at 1070-1150 cm^{-1} have been decreased after 1 month incubation. These results could be due to the fact that the hydrolytic degradation of the PHBV underwent enzymatic hydrolysis followed by microbial assimilation of small molecules of hydrolysable PHB and PHV monomers. Therefore, the reduction in the absorbance peak corresponding to carbonyl (1710 cm^{-1}) occurred by the action of microbial enzymatic hydrolysis process (Arcos-Hernandez et al., 2012; Corti et al., 2010). It is generally accepted that hydrolysis is one of the initial degradation processes for the hetero polymers mediated by microbial hydrolytic enzymes.

3.4. Morphology investigation

SEM results (Fig. 6) show the biodegradation behaviour of PHBV and its composites at microscopic level during incubation. The PHBV composites show different microbial degradation behaviour compared to that of PHBV matrix (Fig. 5) where it was visually observed fungus mycelia growth PHBV/flax composites and followed by SEM analysis evidenced. However, in the case of neat PHBV, there were some surface erosion observed by SEM. Authors (Mokhothu and John, 2016; Muniyasamy et al., 2016) also observed similar surface erosion degradation behaviour of PHBV, in which they concluded that these surface erosion PHBV degradation behaviour is mainly due to bacterial attack rather than fungus. On the other hand, the PHBV/flax and PHBV/alginic acid treated flax composites were readily attacked by fungus. A network of fungus could be seen on the surface of the PHBV composites as shown in (Fig. 6d and f). These surface morphology results suggest that the presence of natural fibres and water soluble alginic acid were influenced the degradation caused by fungus in the case of composites rather than bacteria degradation in the case of PHBV. Another interesting aspect noticed in the results indicate that the degradation occurred randomly distributed in both composites and the matrix. This could be due to low molecular weight amorphous compounds in the PHBV, which were being easily enzyme hydrolysed and solubilised to permeate into microbial cell (Kumagai et al., 1992).

4. Conclusions

The alginic acid treated flax fibre significantly influenced in the biodegradation of PHBV composite as compared to the PHBV/flax and neat PHBV. Thermal, structural and morphological characterization results suggest that the degradation process occurred through hydrolysis followed by microbial assimilation. The microbial attack of PHBV composites by fungus and neat PHBV by bacteria was evidenced by surface morphology analysis. The green composites of PHBV/flax have short survival period in compost conditions and their valuable organic nutrients after biodegradation may be useful for enriching agriculture soil.

Declaration of competing interest

Authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bcab.2019.101394.

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