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Disposal Options of Bamboo Fabric-Reinforced Poly(Lactic) Acid Composites for Sustainable Packaging: Biodegradability and Recyclability

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Abstract: The present study was conducted to determine the recyclability and biodegradability of bamboo fabric-reinforced poly(lactic) acid (BF-PLA) composites for sustainable packaging. BF-PLA composite was recycled through the granulation, extrusion, pelletization and injection processes. Subsequently, mechanical properties (tensile, flexural and impact strength), thermal stability and the morphological appearance of recycled BF-PLA composites were determined and compared to BF-PLA composite (initial materials) and virgin PLA. It was observed that the BF-PLA composites had the adequate mechanical rigidity and thermal stability to be recycled and reused. Moreover, the biodegradability of BF-PLA composite was evaluated in controlled and real composting conditions, and the rate of biodegradability of BF-PLA composites was compared to the virgin PLA. Morphological and thermal characteristics of the biodegradable BF-PLA and virgin PLA were obtained by using environment scanning electron microscopy (ESEM) and differential scanning calorimetry (DSC), respectively. The first order decay rate was found to be 0.0278 and 0.0151 day^{-1} in a controlled composting condition and 0.0008 and 0.0009 day^{-1} in

real composting conditions for virgin PLA and BF-PLA composite, respectively. Results indicate that the reinforcement of bamboo fabric in PLA matrix minimizes the degradation rate of BF-PLA composite. Thus, BF-PLA composite has the potential to be used in product packaging for providing sustainable packaging.

1. Introduction

The use of non-biodegradable and non-renewable materials (*i.e.*, plastics, glass, metals) in packaging applications has raised environmental pollution concern and demand for safe managing of this waste. A large amount of packaging materials is produced every year, and they are discarded after the product has been used. The waste is generated from the packaging materials' disposal in landfill, also generating greenhouse gases [1]. Moreover, the emissions generated during incineration of the non-biodegradable materials pose human health hazards and environmental pollution concern [2]. Extensive research has been conducted in order to define alternative packaging materials with the emphasis on reducing environmental impact [2–4]. Recently, the application of bio-based materials in packaging has aroused considerable interest due to the growing needs of developing sustainable materials in order to minimize the environmental burden.

Among the eco-compatible polymers that have been used in packaging, poly(lactic) acid (PLA) is considered as one of the most promising thermoplastics owning to its good mechanical properties and mass capacity [4–6]. However, PLA requires chemical or mechanical modification with filler to enhance the impact strength and thermal stability, because of its low thermal stability and impact strength [7–11]. Moreover, scientists are looking for an alternative to conventional fillers to provide sustainable, economic and environmentally-friendly packaging. Numerous studies have been conducted on the production of eco-friendly polymeric composite (green composite) with the PLA to be used in packaging [4,6,12–15]. Studies reported that the application of natural fibrous biomass, such as bamboo, flax, hemp, jute, sisal, kenaf, *etc.*, is an effective alternative to conventional fiber, because of the abundant availability, low price, low density, excellent mechanical properties and Young's modulus [16–18].

Bamboo is recognized as a superior source of lignocellulosic fibers because of its rapid growth rate, high cellulose content and excellent mechanical properties [19,20]. Studies reported that the integration of bamboo fibers with biopolymers enhances the thermal stability and impact strength of composite [17,21]. Moreover, the unique properties of bamboo fibers, including biodegradability and the absence of noxious components, have attracted scientist's interest for being utilized as a filler or reinforcement in PLA composite [22,23]. In order to practice green and sustainable packaging, determination of the biodegradability and recyclability of the materials used in packaging is crucial. During biodegradation of composite materials in a landfill, aerobic microorganisms use oxygen to produce CO_2 and release energy from the carbon source for degrading the materials [6]. Equally, sustainable packaging would enhance the stakeholder interest to segregate and recycle the packaging materials, which minimize packing waste generation in the environment. Because of the ability to be

reshaped upon heating, natural fiber-reinforced PLA composites can be recycled directly by remelting and remolding into high value materials [24]. Moreover, recycled packaging materials can be reused for secondary applications at the end of their useful life.

While there has been a number of research works on the production of biocomposites for providing sustainable packaging by using bamboo fiber as a reinforcing agent in PLA composite (bamboo fabric-reinforced composites), there have rarely been studies conducted with the consideration of its disposal option, including sustainability and biodegradability. Therefore, the present study was conducted to determine the recyclability and biodegradability of bamboo fabric-reinforced poly(lactic) acid (BF-PLA) composites. The mechanical and thermal properties of recycled BF-PLA composite were determined and compared to BF-PLA composite and virgin PLA. The biodegradability of BF-PLA composite was evaluated in controlled and real composting conditions, and the rate of biodegradation of BF-PLA composites was compared to the virgin PLA. Morphological and thermal characteristics of the biodegradable BF-PLA and virgin PLA were obtained by using environment scanning electron microscopy (ESEM) and differential scanning calorimetry (DSC), respectively. Finally, the first order decay rate was determined to predict the half-life of BF-PLA composites and virgin PLA in controlled and real composting conditions.

2. Experimental Section
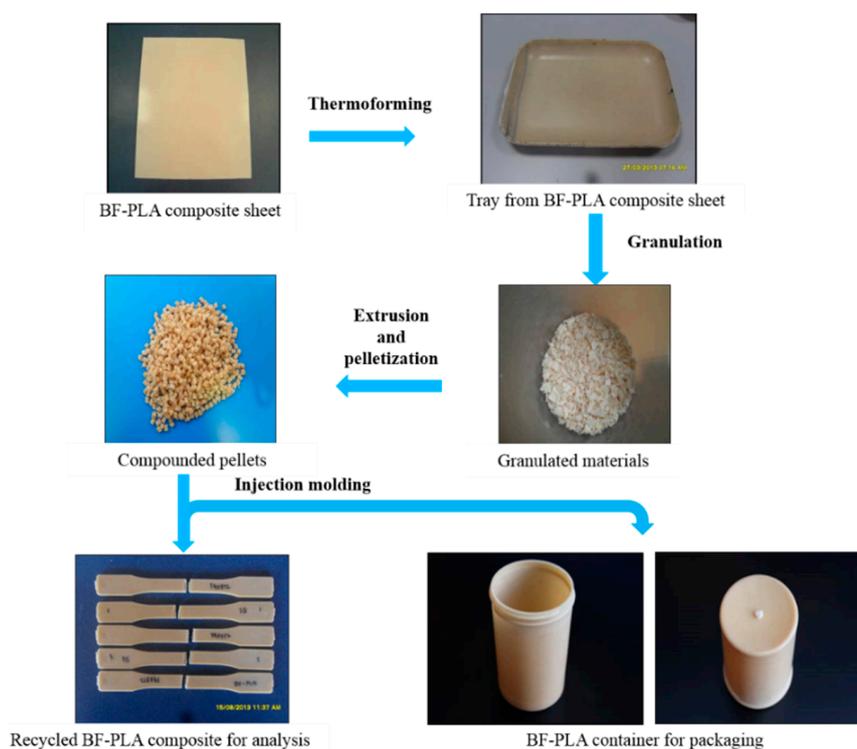
2.1. BF-PLA Composite Fabrication

Bamboo fabric was purchased from Industrial Textiles Limited, Auckland, New Zealand; PLA sheets (NatureWorks 2003D) were purchased from Alto Packaging Limited, Hastings, New Zealand. Bamboo fabric and PLA sheets (0.25 mm thickness) were cut into 390 mm × 390 mm. Subsequently, the bamboo fabric was dried at 80 °C for 24 h in a Moretto vacuum dryer (Moretto S.p.A, Massanzago, Italy) wherein the PLA sheets were dried overnight at 70 °C in an oven (Contherm Thermotec 2000, Contherm Scientific Limited, Lower Hutt, New Zealand) to reduce the moisture content. Five layers of bamboo fabric oriented in the warp-wise direction and six layers of PLA sheets were arranged alternately in a stack to gain a fiber weight fraction of 0.35. The BF-PLA composite sheets were then prepared using a compression molding process. The preparation of bamboo fabric-reinforced poly(lactic) acid composite was conducted following the method as discussed elsewhere [13]. After BF-PLA stacks were placed appropriately in the mold, the stacks were pre-heated at 160 °C for 2 min under no pressure to allow the permeation of PLA into the bamboo fabric. Finally, a pressure of 1.05 MPa was applied for 3 min at the same temperature, and then, the mold was cooled by circulating cold water. The composite was kept under the set pressure until it cooled to 25 °C.

2.2. Determination of the Recyclability of BF-PLA Composite

2.2.1. Recycling Process of BF-PLA Composite

Recycling of BF-PLA composite was conducted in four different phases, which were granulation, extrusion, pelletization and injection processes, as shown in Figure 1. The BF-PLA composites sheet was cut into small pieces using an SG granulator Model SG-2427H-CE (Shini Plastics Technologies,

New Taipei City, Taiwan) with a mesh spacing size of 5 mm in diameter. Compounding of the granulated material was achieved in a LABTECH (Type LHFS1-271822) (Labtech Machinery, Hertfordshire, UK) twin screw extruder at 13 rpm, and the temperature profile was kept between 180 and 200 °C. Then, the compounded materials were cut into pellets using the LABTECH strand pelletizer (Type LZ-120, Labtech Machinery, Hertfordshire, United Kingdom) and dried under vacuum at 60 °C for 48 h. Injection molding was then carried out on a BOY injection molder (capacity: 50 tons) (BOY machines Inc, Exton, PA, USA). The temperature in the molder was kept between 175 and 195 °C, wherein the injection pressure was 100 bar and the injection time was 0.6 s. Mohammad Rawi *et al.* [20] observed that the temperature range between 175 and 195 °C causes bamboo fabric degradation, but they are required for melting PLA. The mold was maintained at 30 °C.

Figure 1. Recycling process of bamboo fabric-reinforced poly(lactic) acid (BF-PLA) composite.

2.2.2. Characterization of Recycled BF-PLA Composite

In order to compare the properties of BF-PLA composite sheets and recycled BF-PLA composites, mechanical and thermal, the BF-PLA composite pellets were injected into a mold designed to produce specimens for tensile, flexural and impact tests analyses. The tensile, flexural and impact properties of the specimens were tested according to ASTM 638-10, ASTM 790-10 and ASTM D6110-10, respectively. For each test, seven replicate test specimens were taken, and the averages and corresponding standard deviation were calculated.

The glass transition temperature, melting temperature and crystallinity were determined using a differential scanning calorimeter (DSC) Q 100 (TA Instruments, New Castle, DE, USA). Analyses of the results were carried out with a TA Instruments Universal Analyser 2000 (TA Instruments, New Castle, DE, USA). The measurement was conducted on a 9 mg sample in an open aluminum pan under nitrogen

atmosphere at a 45 mL/min flow rate in a heating range of 20–220 °C a rate of 10 °C/min. The degree of crystallinity (X_c) can be determined from the heat of fusion normalized to that of PLA according to the following equation:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H^* \times W_m} \times 100 \tag{1}$$

where ΔH_m and ΔH_{cc} are, respectively, the melting enthalpy and the cold crystallization enthalpy of the sample, ΔH^* is the heat of fusion of virgin PLA (93 J/g) [25] and W_m is the weight fraction of PLA in composites.

Environmental scanning electron microscopy (ESEM), was used to examine the fracture surfaces of the recycled BF-PLA composites and the surfaces of virgin PLA. The samples were vacuum coated with gold before examination in ESEM (FEI Quanta 200F ESEM, FEI, Hillsboro, OR, USA). The sample chamber pressure was reduced to approximately 133.3 Pa, and the working distance ranged between 10 and 11.5 mm.

2.2.3. Yarn Length Measurement

The yarns were extracted from the bamboo fabric-PLA composites by Soxhlet extraction, which was similar to the method prescribed in the ASTM D 3171-11 standard. Specimens were cut from the composite panels, dried under vacuum at 35 °C for 12 h and kept in desiccators for 48 h to remove moisture. The specimens were then repeatedly immersed in boiling xylene with continuous recycling of the solvent in a Soxhlet apparatus, and the yarns were filtered from the solvent-matrix mixture by means of a small aperture wire mesh. The process was continued for 72 h. Extracted yarns were washed several times in hot xylene, dried and viewed microscopically to ascertain whether or not polymer matrix had successfully been removed from the yarn surfaces. The extracted yarns were separated on a glass slide and photographed through an optical microscope (Olympus BX60M, Olympus Scientific Solutions Americas Inc., Waltham, MA, USA). The average lengths were measured from a sample of 100 yarns using ImageJ software.

2.3. Determination of Biodegradability of BF-PLA Composite

2.3.1. Specimen Preparation

Virgin PLA and BF-PLA composite were cut from the compression-molded sheets of a 1.8 mm thickness. Specimen dimensions were approximately 20 mm × 20 mm. Five replicated test specimens were taken for each composting time from 10–70 days. A non-biodegradable organza bag (dimensions of 110 mm × 80 mm) with a mesh was used to retain and easily identify the samples for further analysis. The composting material in an intermediate state for both controlled and real composting conditions was provided by Living Earth Ltd., Auckland, New Zealand.

2.3.2. Biodegradability of Composites in Controlled Composting Conditions

The biodegradability test for virgin PLA and BF-PLA composites was performed in controlled composting conditions according to the ASTM D5338-11 standard. The water content of the compost was around 60% by weight at 58 ± 2 °C.

2.3.3. Biodegradability Composites in Real Composting Conditions

The compost environment was set up to be as similar as possible to household garden compost. A compost pile made of intermediate state compost was prepared at the Centre for Advanced Composite Materials (CACM), The University of Auckland, New Zealand, and used to assess the biodegradability of the virgin PLA and BF-PLA composites. This material was obtained in an incomplete decayed state and consisted mainly of plant and waste. Fresh green waste, such as grass clippings and twigs, was incorporated into the intermediate state compost to keep the decaying process going [26].

The compost pile was built from wood with dimensions of 3 m in width, 1 m in length and 1 m in height. The compost had an initial temperature and water content of 40 °C and 40%–50%, respectively, and temperature was monitored throughout the biodegradation study with a Type-J thermocouple (Omega Engineering Inc., Stamford, CT, USA) attached to a Onset HOBO data logger (Onset Computer Corporation, Woburn, MA, USA). The moisture content of the compost was measured daily using a moisture analyzer (Sartorius Moisture Analyzer Model MA35, Sartorius AG, Goettingen, Germany). The pH value was regularly monitored and kept around the neutral pH value of 7, which is considered ideal for bacterial growth [26]. Initially, compost was added on the compost pile, and later, the specimens in the organza bag were placed on it and completely covered with compost. The specimens were placed approximately 20 cm from the top surface of the compost. Figure 2 shows how the specimens were located in the compost pile. After the specimens were covered with compost, the pile was closed and allowed to reach its normal composting temperature.
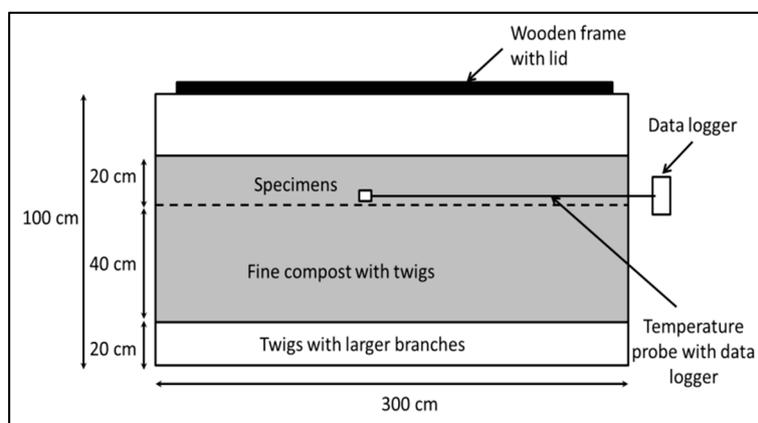
Figure 2. Schematic diagram of the compost pile used for the biodegradability test [19].

2.3.4. Weight Loss Determination

Virgin PLA and BF-PLA composite test specimens were removed from the compost every 10 days for 70 days and subsequently washed with water and dried in an air oven at 50 °C for 48 h. The weight loss of composted specimens was determinate by the following equation:

$$\text{Weight} \sim \text{loss} \sim (\%) = \frac{W_0 - W_1}{W_0} \times 100 \tag{2}$$

where W_0 and W_1 are sample weights before and after the composting test, respectively. The percentage of weight loss was taken from the average of five specimens.

2.3.5. Characterization of BF-PLA Composite

Thermal properties (*i.e.*, glass transition temperature, melting temperature and crystallinity) and morphological alteration of biodegraded BF-PLA composites and virgin PLA in controlled and real composting conditions were determined using DSC and ESEM, respectively, by following a similar method as described in Section 2.2.2.

3. Results and Discussion

3.1. Mechanical Properties of Recycled BF-PLA Composite

The mechanical properties (tensile, flexural and impact strength) of recycled BF-PLA composite are presented in Table 1. The tensile strength and tensile modulus of the recycled bamboo fabric-reinforced composite were found to be about 74.64 MPa and 4.9 GPa, respectively, wherein flexural strength, flexural modulus and impact strength were determined to be 155.9 MPa, 5.81 GPa and 71.81 J/m, respectively. Mohammad Rawi *et al.* [13] determined the mechanical properties of virgin PLA and BF-PLA composite, as tabulated in Table 1. A decrease of tensile properties and an increase of flexural properties were observed in recycled BF-PLA composite, when compared to the BF-PLA composite (initial material). The loss of tensile properties might be due to the alteration of composite matrices during the recycling process, including granulation, extrusion and injection [27]. Alternatively, the increased flexural properties (strength and modulus) might be because of shortened and dispersed bamboo fabric yarn in the composites during injection molding. Further, the shorter yarn could orient in the direction of the flow of the polymer, thereby aligning in the longitudinal direction of the specimens.

Table 1. Mechanical properties of virgin PLA, BF-PLA composites and recycled BF-PLA composites.

| Specimens	Tensile Properties		Flexural Properties		Elongation at Break (%)	Impact Strength (J/m)
	Strength, MPa	Modulus, GPa	Strength, MPa	Modulus, GPa		
* Virgin PLA	61.85 ± 2.22	3.38 ± 0.08	105 ± 5.35	3.72 ± 0.05	2.30 ± 0.72	37.51 ± 5.35
* BF-PLA	80.64 ± 1.80	5.92 ± 0.26	143 ± 1.59	4.50 ± 0.70	6.68 ± 0.10	103 ± 6.68
Recycled BF-PLA	74.64 ± 2.64	4.90 ± 0.58	156 ± 2.80	5.81 ± 2.56	4.28 ± 0.22	71.81 ± 1.05

*, Data collected from Mohammad Rawi *et al.* [20].

As can be seen in Table 1, the impact strength of the recycled BF-PLA composites dropped, when compared to the initial BF-PLA composites. The drop of the impact strength of the recycled BF-PLA composites was probably due to the composites turning brittle with the recycling process. This phenomenon can be related to the results of elongation at break shown in Table 1. It can be clearly seen that the elongation at break of recycled BF-PLA composites decreased compared to BF-PLA composite, consequently reducing the impact strength of the recycled BF-PLA composites. However, recycled material is always mixed with virgin material in an industrial situation [27]. Due to the reduction in the length and diameter of the yarn, fiber pull out can occur. The fracture mechanism initiated when the fibers broke at their weak cross-sections, which may lead to stress concentration formation. The

fracture may continue by the broken fibers being pulled out of the matrix due to the poor fiber–matrix interaction [28].

3.2. Thermal Properties of Recycled BF-PLA Composites

Figure 3 and Table 2 show the effects of the recycling process on the melting temperature (T_m) and glass transition temperature (T_g) of virgin PLA, BF-PLA composites and recycled BF-PLA composites. It was observed that the presence of bamboo fabric caused a negligible change in the T_g of BF-PLA and recycled BF-PLA composites. However, the melting temperature was found to increase slightly with the addition of bamboo fabric in the virgin PLA from 151.70–154.42 °C, wherein the melting temperature for the recycled BF-PLA was found to be 154.56 °C. Hence, the recycling process of BF-PLA composites had not influenced the melting temperature of the composites [29,30]. However, the recycled BF-PLA had a lower crystallinity (4.43%) compared to the initial BF-PLA composites (11.28%) and virgin PLA (13.14%). The crystallinity of recycled BF-PLA decreased possibly due to the limitation of crystallite growth in the presence of fibers scattered in the composites, which hampered the mobility of long polymer chains [31]. The decrease in crystallinity leads to the reduction of the tensile modulus in recycled BF-PLA composites as compared to initial BF-PLA composites. It is noteworthy that although the crystallinity of recycled BF-PLA is lower than virgin PLA, the tensile modulus of recycled BF-PLA is higher than that of virgin PLA. This phenomenon might be due to the presence of bamboo fibers in the recycled BF-PLA, which enhanced its tensile modulus as compared to the virgin PLA.
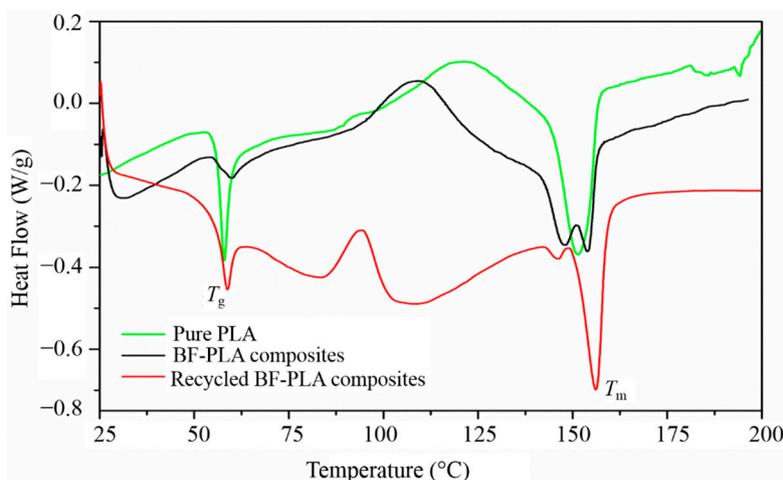

Figure 3. DSC thermograms of recycled BF-PLA composite, BF-PLA composite and virgin PLA.

Table 2. DSC numerical data of BF-PLA composites after the recycling process.

Samples	T_m (°C)	T_g (°C)	X_c (%)
Pure PLA	151.70	58	13.14
BF-PLA composites	154.42	58.23	11.28
Recycled BF-PLA composites	155.56	58.65	4.43

3.3. Morphological Appearance of Recycled BF-PLA Composites

The drop of impact strength in recycled BF-PLA composite might influence by the fiber damage during the recycling process. Moreover, the shortened fiber length might result in more strain concentrations and a higher risk of debonding [27]. This occurrence can be observed in the ESEM micrographs of composites. Figure 4 shows the fracture surfaces of BF-PLA composites (Figure 4a) and recycled BF-PLA composites (Figure 4b). It was observed that the yarns separated into single filaments and were cut into smaller sizes (Figure 4a). The ESEM image in Figure 4 b presents a number of fibers pulling out from the fracture surfaces of recycled BF-PLA composites. This was probably due to the weak interfacial bonding of the fibers and PLA matrix. It is noteworthy that, although the recycled BF-PLA composites slightly lose mechanical (tensile and flexural) strength and thermal stability, however, the mechanical (tensile and flexural) strength and thermal stability of the recycled BF-PLA composite were higher than the virgin PLA.


(**a**)   (**b**)
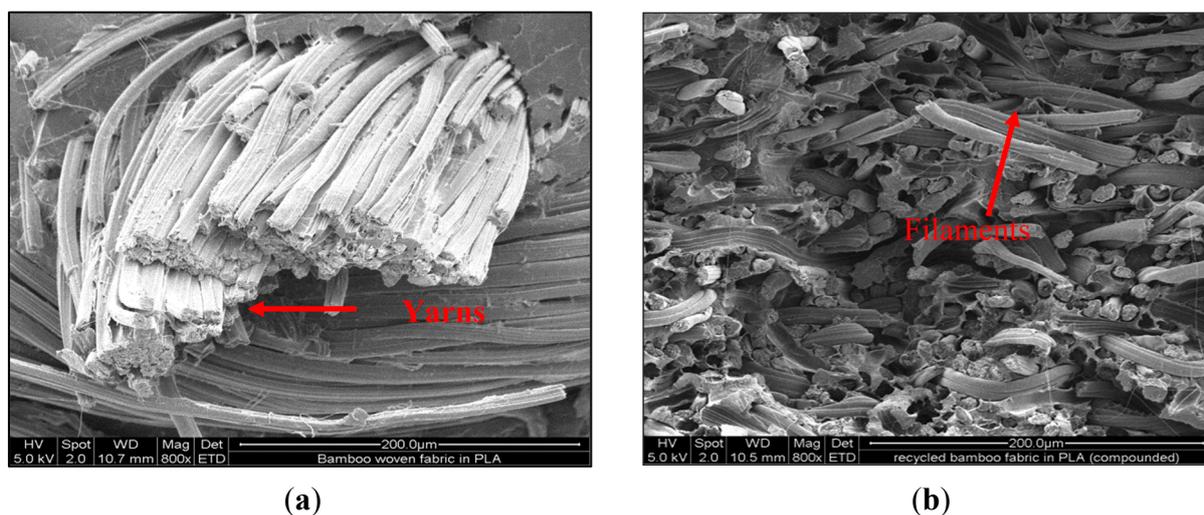
Figure 4. Environment scanning electron microscopy (ESEM) images of: (**a**) BF-PLA composite; and (**b**) recycled BF-PLA composite.

3.4. Yarn Length of Recycled BF-PLA Composite

The fabrics in the recycled BF-PLA composite were cut into smaller sizes. It was found that the yarn lengths for recycled BF-PLA composites dropped down under 5 mm, which was expected, as a mesh spacing of 5 mm in diameter was used during granulation. The percentage of yarns between 0.1 and 0.5 mm was about 82%; 14% of yarns were between 0.5 and 1.0 mm; and about 4% of yarns were between 1.0 and 5.0 mm. The presence of a large percentage of yarns in the range 0.1–0.5 mm is an indication that most of the yarns must be cut down during the process of extrusion, pelletizing and injection; since the high shear rates cause a reduction in the length of the yarns. This severe drop in yarn length was also attributed to the staple fibers usually being twisted into thick yarns. After the recycling process, the twisted bamboo yarns started to unravel. The fibers were separated from each other into single filaments (Figure 4b). This occurrence allowed them to be easily cut into small sizes along with a reduction of the larger diameter of the yarns into the smaller diameter of the filaments.

3.5. Weight Loss Determination of BF-PLA Composites

Figure 5 shows the percentage of weight loss of the biodegraded virgin PLA and BF-PLA composite in controlled and real composting conditions for 70 days. It was observed that virgin PLA degraded rapidly compared to BF-PLA composites in controlled composting conditions. About 45% weight loss was observed for virgin PLA at 30 days burial in controlled composting conditions. After 30 days, virgin PLA in controlled composting conditions became brittle, which made it difficult to measure the weight. Therefore, the weight loss measurement for virgin PLA composite in controlled composting conditions was discontinued after 30 days. In the case of BF-PLA composites, the percentage of weight loss increased with increased burial time. The weight loss of BF-PLA composite was found to be about 21% at 30 days, wherein the highest weight loss of about 62% was observed at 70 days. Thus, virgin PLA composite had a higher biodegradation rate than the BF-PLA composites in controlled composting conditions.
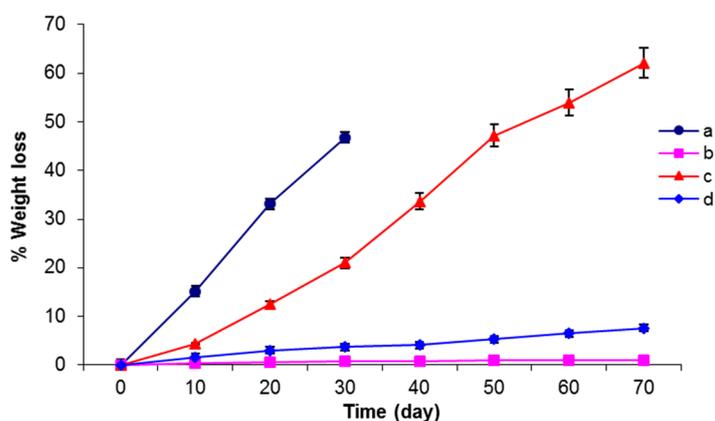

Figure 5. Percentage weight loss of virgin PLA and BF-PLA composites in control and real conditions. a, Virgin PLA in controlled composting condition; b, virgin PLA in real composting condition; c, BF-PLA composite in controlled composting condition; and d, BF-PLA composite in real composting condition.

Real composting studies give a clear representation of the time required for disintegration in this condition. This information can provide a foundation for deciding on compostable packaging materials and the planning of composting processes [1]. Biodegradation of the composites specimens in real composting conditions was found to be slower than controlled composting conditions. Virgin PLA did not show any degradation at the observation time of 10 days, while BF-PLA composites gradually degraded with time (Figure 5). At a maximum observation time of 70 days, the percentage of weight loss of BF-PLA composites was about 8%, wherein the weight loss was negligible for virgin PLA in real composting conditions. The temperature of the compost in real composting was 40 ± 1 °C (lower than the glass transition temperature), which probably led to the slower rate of biodegradation of the composites. Similarly, Bayerl *et al.* [26], Neppalli *et al.* [32] and Petinakis *et al.* [33] reported that virgin PLA has a very slow breakdown compared to natural fiber-reinforced composites. According to Bayerl *et al.* [26], the architecture of fiber structure in a PLA composite can influence the degradation behavior of the composite. A higher weight loss can be obtained in unidirectional samples compared to

short and long fiber specimens due to the fact that unidirectional fibers provide a much greater surface area of contact between the fibers and the PLA for hydrolysis and microbial action to take place [26].

3.6. Thermal Properties of Virgin PLA and BF-PLA

Figure 6 and Table 3 show the thermal properties of virgin PLA and BF-PLA composites during the biodegradation process in controlled composting conditions. It was observed that the peak corresponding to T_g completely disappeared in DSC thermographs of virgin PLA and BF-PLA composites during the biodegradation process in controlled compositions at 58 °C. A similar observation was also reported by Saadi *et al.* [34]. This disappearance of T_g is associated with a reduction in the molecular weight of the virgin PLA and BF-PLA composites. Moreover, the disappearance of the T_g during the biodegradation process indicates that the amorphous phase of PLA was predominantly hydrolysed and removed. Rudeekit *et al.* [35] reported that temperature is a major factor in PLA degradation, since it causes rapid weight of PLA matrix. In fact, the rubbery state of PLA allows the best absorption of water in the polymer matrix. The soluble oligomers can be released by hydrolysis in the medium of degradation and assimilated by microorganisms, such as fungi [34].
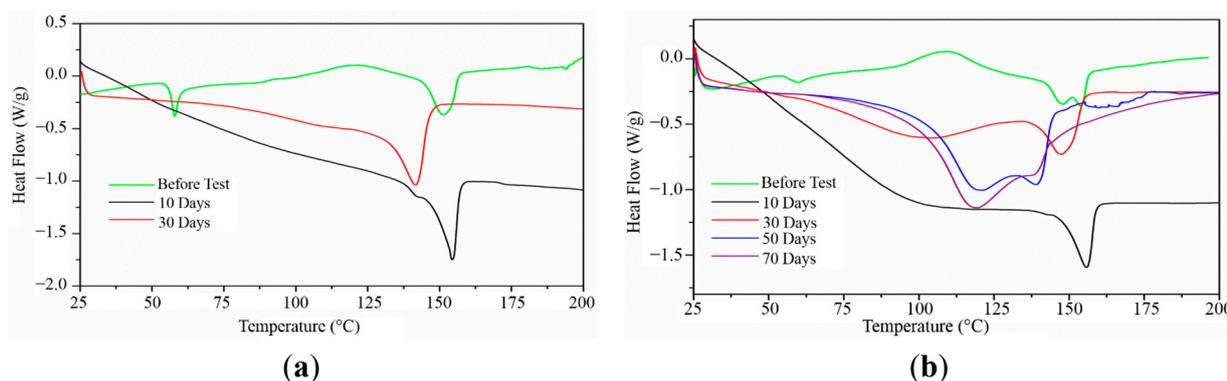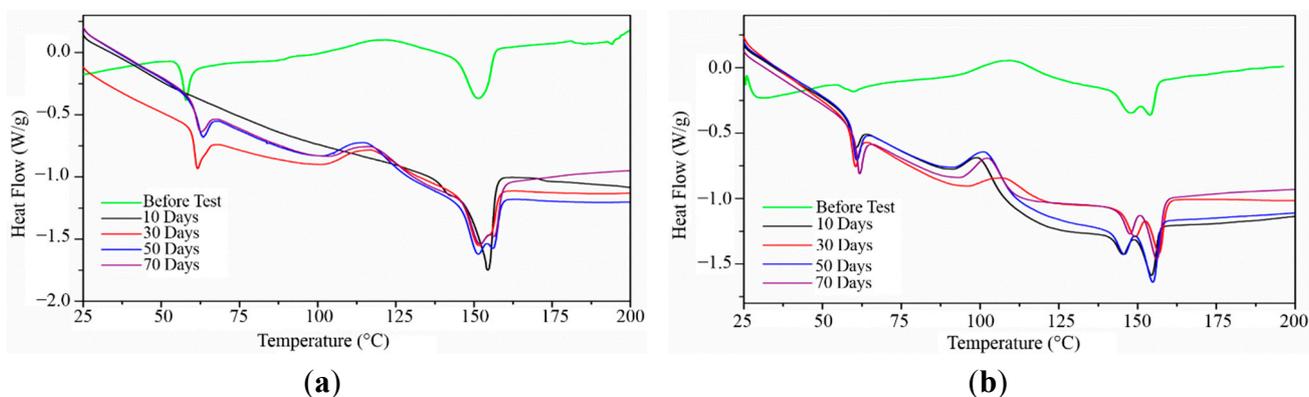

Figure 6. DSC thermograms of virgin PLA (**a**) and BF-PLA (**b**) composites in controlled composting condition.

Table 3. DSC numerical data of BF-PLA composites after biodegradation in controlled composting conditions.

Samples	T_m (°C)	T_g (°C)	ΔH_m (J/g)	ΔH_{cc} (J/g)	X_c (%)
Pure PLA					
Before test	151.70	58	30.49	18.27	13.14
After 10 days	154	–	–	–	35.55
After 30 days	142	–	–	–	43.75
BF-PLA Composites					
Before test	154.42	58.23	17.23	10.41	11.28
After 10 days	155.93	–	21.20	14.19	11.60
After 30 days	148.45	–	21.58	–	35.70
After 50 days	141.11	–	54.76	–	90.59
After 70 days	116.03	–	52.50	–	86.85

It appeared that the T_m values for the virgin PLA and BF-PLA composite were 151.70 and 154.42 °C, respectively, indicating that the inoculation of bamboo fabric in PLA enhanced the melting temperature. However, the T_m values of virgin PLA (151.70 °C) and BF-PLA (154.42 °C) composites were found to increase with the biodegradation times up to 10 days and decreased for the subsequent studied biodegradation times. The increase in T_m values was attributed to the damage in the amorphous phase of the PLA. The decreasing number of ester linkages in the chain during the biodegradation can result in the stiffening of the chain, which leads to an increase of the T_m in the earliest days of the biodegradation [36]. The fact that there are decreasing T_m values indicates that the degradation occurs not only in the amorphous phase of the PLA matrix, but also in the crystalline regions. The occurrence of damage in the amorphous phase and the formation of small fragments that are easily crystallizable led to an increase in the degree of crystallinity in the earliest days of biodegradation. From Table 3, it was observed that the crystallinity of virgin PLA and BF-PLA composites increased with the biodegradation times. The increase of crystallinity by the privileged biodegradation of amorphous areas of semicrystalline polymers has also been observed by Kale *et al.* [1]. However, the percentage of crystallinity of BF-PLA composites decreased from 90.59% down to 86.85% with the further increase of biodegradation time from 50–70 days. After 50 days of biodegradation, the degree of crystallinity starts to reduce, as further hydrolysis yields smaller fragments of the crystalline region that can be assimilated by the microorganisms [34].

Figure 7 and Table 4 show the DSC thermographs of virgin PLA and BF-PLA composite biodegradation in real composting conditions. The figures indicate the trivial changes in T_m and T_g values for both virgin PLA and BF-PLA composites during the biodegradation time of 10–70 days. Similarly, Bayerl *et al.* [26] observed the insignificant changes of T_g values during the biodegradation studies of flax-reinforced PLA composites in the real composting conditions. However, the percentage of crystallinity of virgin PLA and BF-PLA also revealed the marginal changes with the biodegradation times. This was happened probably due to the low temperature of the compost around 40 °C in real composting conditions, which is lower than the glass transition temperature. As the hydrolytic degradation rate of PLA depends on the temperature, a low compost temperature leads to the hydrolysis process becoming complex, which results in slow biodegradation of PLA matrix by the microorganisms' attack [34].

Figure 7. DSC thermograms of virgin PLA (**a**) and BF-PLA (**b**) composites in real composting condition.

Table 4. DSC numerical data of BF-PLA composites after biodegradation in real composting conditions.

Samples	T_m (°C)	T_g (°C)	ΔH_m (J/g)	ΔH_{cc} (J/g)	X_c (%)
Pure PLA					
Before test	151.70	58	30.49	18.27	13.14
After 10 days	155.05	61.94	29.71	16.37	14.34
After 30 days	151.51	61.47	26.97	12.81	28.16
BF-PLA Composites					
Before test	154.42	58.23	17.23	10.41	11.28
After 10 days	154.46	60.24	14.18	6.66	12.44
After 30 days	156.86	60.28	18.44	9.45	14.87
After 50 days	154.92	60.61	17.70	11.27	10.64
After 70 days	156.9	61.71	18.51	12.46	10.01

3.7. Morphological Alteration of Virgin PLA and BF-PLA Composites

3.7.1. Morphological Alteration of Virgin PLA

For the first comparison, the degraded samples were analyzed by their morphological changes that were visible to the naked eyes. Figure 8 displays the surface of virgin PLA degradation in controlled and real composting conditions. In Figure 8a, the PLA sheet degraded under controlled composting conditions, which was initially transparent and became increasingly opaque and white in appearance at 10 days. The virgin PLA sheet also became brittle and started breaking apart after 10 days of testing. After 20 days, the virgin PLA sheet was broken into coarse pieces, and some of it disappeared. Only a few small pieces of the virgin PLA were detected at 30 days composting in controlled composting conditions. Meanwhile, there was no considerable change observed for virgin PLA in real composting conditions at a biodegradation time of 30 days (Figure 8b).
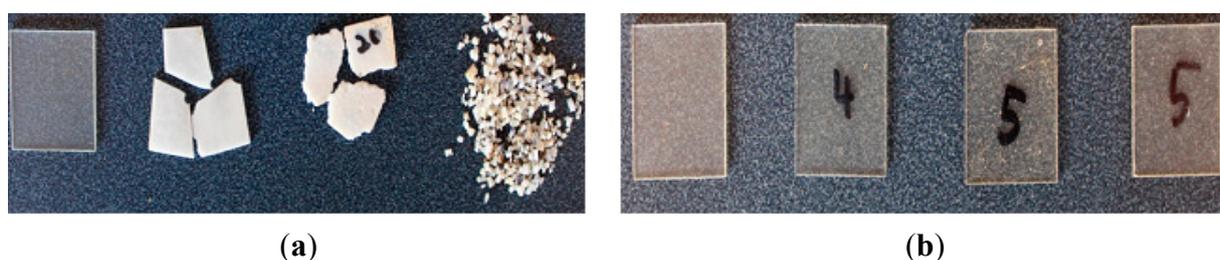

(a)   (b)

Figure 8. Photographs for the biodegradation of virgin PLA in controlled (**a**) and real composting conditions (**b**).

Figure 9 shows the ESEM images of virgin surfaces during biodegradation testing in controlled (a) and real (b) composting conditions. Before the test, the specimen surface was smooth and blemish free. For the specimen under controlled composting conditions, hydrolysis of the polymer chains was indicated by a roughening of the surface texture after 10 days of degradation. Figure 9a(2),(3) show distinct areas of microorganism attack, signs of perforations and physical disintegration. The Figure 9a(3) also shows a magnified view of the surface; of particular note is the clearly-observable porous texture. However,

there were no significant changes observed on the surface of the PLA composite specimens up to 30 days of biodegradation in real composting conditions (Figure 9b).
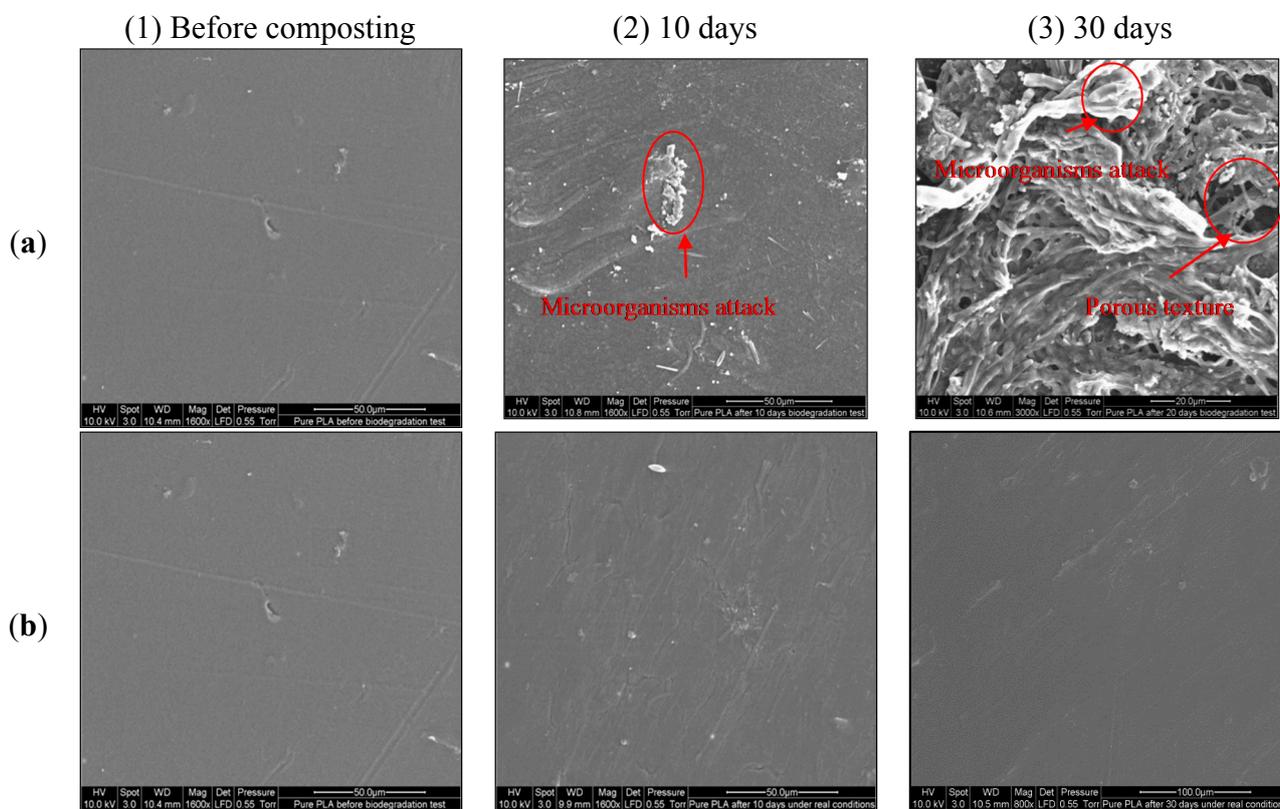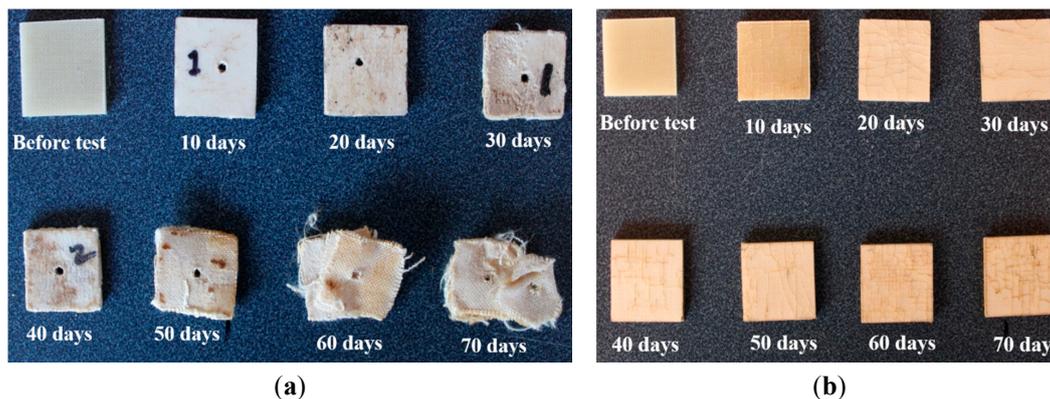

Figure 9. ESEM images of virgin PLA in controlled and real composting conditions. (**a**) Controlled composting conditions; and (**b**) Real composting conditions.

The rate of hydrolytic degradation of PLA is dependent on the temperature and humidity level. In general, high temperature and humidity may cause PLA to degrade rapidly [28]. In the controlled composting conditions, temperature was maintained at 50–60 °C, and the moisture content of the compost was ~60%. Thus, the changes in the specimens degraded under controlled composting conditions could be attributed to the higher temperature of the compost corresponding to the glass transition temperature of the PLA sheet (T_g = 58 °C). Meanwhile, embrittlement of the PLA sheet may occur with a reduction in molecular weight. During the biodegradation, random chain scission of the ester groups might lead to a reduction in molecular weight. The moisture and heat in the compost attacks the PLA sheet chains and splits them apart, forming smaller polymer fragments and, finally, lactic acid. The microorganisms present in an active compost consume the smaller polymer fragments and lactic acid. PLA degradability is induced by the hydrolysis and cleavage of the ester linkages in the polymer backbone [28,35].

### 3.7.2. Morphological Alteration of BF-PLA Composites

The biodegradation pictures of BF-PLA composites under the controlled composting condition (a) and the real composting condition (b) are shown in Figure 10. The images of the specimens in controlled composting conditions over 60 days revealed the absence of PLA on the surface of the composites

(Figure 10a). The figure also displays that the layers of bamboo fabric were separated from each other at 60 days and 70 days of composting, indicating the degradation of PLA in between the fabric. On the other hand, microcracking was found on the surface of the BF-PLA composite, and the level of microcracking was raised with increasing the biodegradation time in real composting conditions (Figure 10b). The microcracking of BF-PLA occurred due to the absorption of moisture by the bamboo fabric. PLA matrix near the fiber-matrix interface of the BF-PLA composite may be somewhat degraded by the absorption of water by the bamboo fabric or penetration of microorganisms through the fiber–matrix interface.
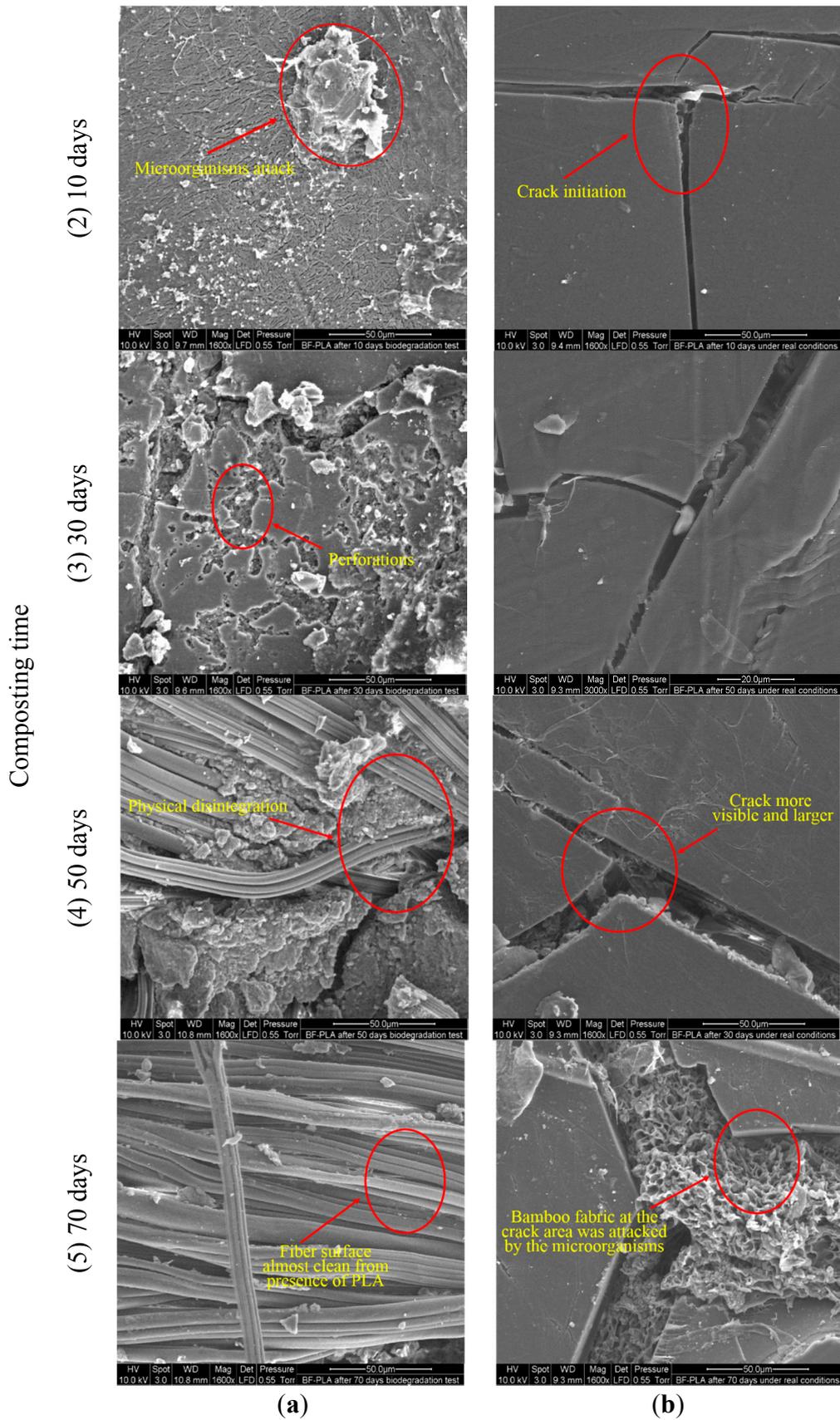

Figure 10. Biodegradation of bamboo fabric-reinforced PLA composites in controlled composting conditions (**a**) and real composting conditions (**b**).

Figure 11 represents the ESEM images of BF-PLA composite in controlled and real composting conditions. By analyzing the ESEM images in Figure 11a, the surface of the PLA composite specimens degraded under controlled composting conditions, indicating signs of microorganism attack, perforations and physical disintegration. It can also be seen that PLA on the surface of the composites started to break and fall away from the fabric surface after 50 days. After 70 days, the ESEM images of specimens indicate that the fiber surface is almost clean from the presence of PLA. Figure 11b reveals that the bamboo fabric, which was exposed at the crack area, was attacked by the microorganisms. This demonstrates that the incorporation of bamboo fabric enhances the microorganisms' affinity to the composites in real composting conditions and increases the biodegradation of composites. However, the rapid degradation of virgin PLA in controlled composting conditions indicates that bamboo fabric and virgin PLA require different conditions for optimum degradability. This could be related to the different types of microorganisms present in different composting conditions.
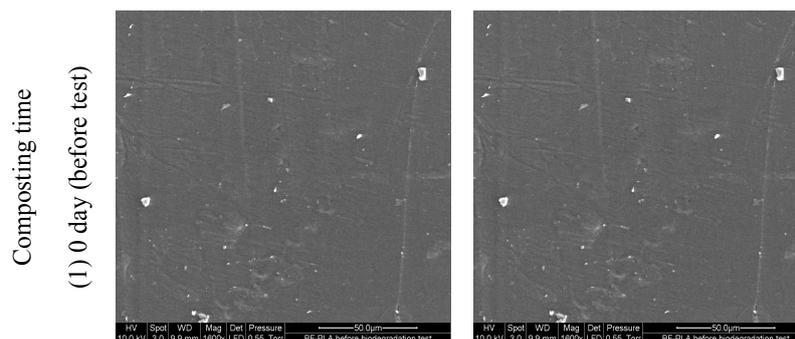
Figure 11. *Cont.*

Figure 11. ESEM images of bamboo fabric-reinforced PLA composites in controlled composting condition (**a**) and real composting conditions (**b**).

However, the microorganisms within a compost pile can be psychrophilic, mesophilic or thermophilic. According to Saadi *et al.* [34], the microorganisms causing the degradation of PLA matrix are various bacterial species (*i.e.*, *Actinomycetes* spp., *Amycolatopsis* spp., *Bacillus* spp. and *Brevis* spp.) and fungi (*i.e.*, *Fusarium moniliforme* and *Penicillium roqueforti*). From the observations of optical and ESEM images of biodegradable BF-PLA composite, it can be estimated that the monitored weight loss of the BF-PLA composites can be attributed to the composting conditions and the presence of the bamboo fabric in the PLA composites.

3.8. Determination of the Half-Life of Virgin PLA and BF-PLA Composites

Assuming first order decay, from an initial quantity C_0 to C in time gives:

$$C = C_0 e^{-kt} \tag{3}$$

where k is the decay constant, C_0 (g) and C (g) are the initial weight and weight after biodegradation studies at time t(min) of the composites, respectively. By arranging Equation (3), we get,

$$\frac{C}{C_0} = e^{-kt} \tag{4}$$

Taking the natural log of both sides:

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{5}$$

If t (day) is plotted against $\ln(C/C_0)$, the decay rate can be calculated from the slope and intercept of the plot, as shown in Figure 12. By rearranging Equation (5),

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{6}$$

$$t = \frac{\ln\left(\frac{C_0}{C}\right)}{k} \tag{7}$$

At half-life ($t_{1/2}$) of the composites, $C = 2C_0$,

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k} \tag{8}$$

This approach assumes that first order decay does not allow for an initiation period during which the microbial community becomes activated or acclimated. This regression was used to estimate the biodegradation half-life from the numerical output of the specimens. Table 5 shows the estimate of half-life time and k values for the virgin PLA and BF-PLA composites in different composting conditions. The biodegradation half-life times for controlled composting conditions confirm that the virgin PLA is a fast degrading material. The BF-PLA composites half-life (46 days) was longer than that of the virgin PLA (25 days). With regards to the samples in real composting conditions, the biodegradation half-life of virgin PLA (866 days) was longer than the BF-PLA composite (770 days). Kale *et al.* [1] demonstrated the decay rate of virgin PLA and BF-PLA composites in controlled and real composting conditions following the first order hydrolysis process.
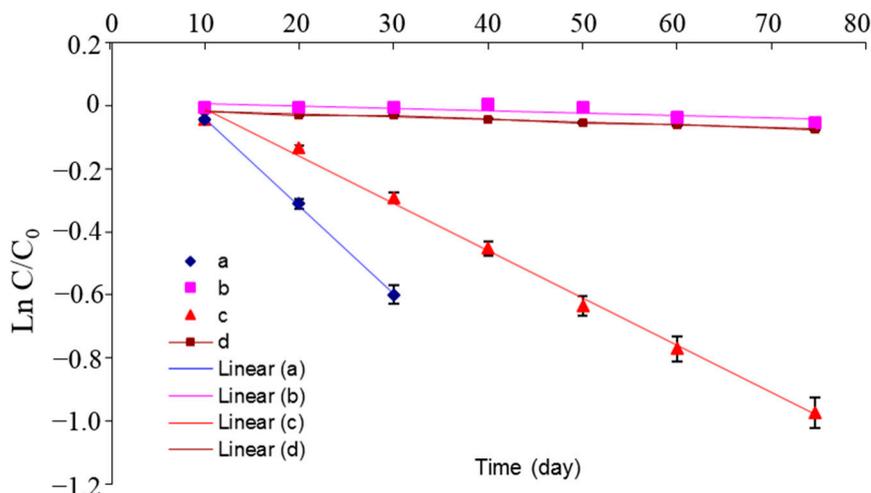
Figure 12. Degree of biodegradation against degradation time for virgin PLA composite and BF-PLA composite a, virgin PLA in controlled composting condition; b, virgin PLA in real composting condition; c, BF-PLA composite in controlled composting condition; and d, BF-PLA composite in real composting condition.

Table 5. Decay rate and half-life of virgin PLA and BF-PLA composites in controlled and real composting conditions.

Composting Conditions	Samples	Decay Rate, K (day^{-1})	Half-life, $t_{1/2}$ (day)	R^2
Controlled	Virgin PLA	0.0278	25	0.99
	BF-PLA composite	0.0151	46	0.98
Real	Virgin PLA	0.0008	866	0.96
	BF-PLA composite	0.0009	770	0.95

4. Conclusion

The goal of the present study was to identify the recyclability and biodegradability of BF-PLA composites. Determination of the mechanical properties of recycled BF-PLA composites revealed the increased flexural properties and decrease of the tensile properties and impact strength. The presence of bamboo fabric in BF-PLA and recycled BF-PLA composites slightly influenced the glass transaction temperature and the melting temperature of the composites. However, it is noteworthy that the mechanical (tensile and flexural) strength and thermal stability of recycled BF-PLA composite were higher to the virgin PLA. Determination of the biodegradability of BF-PLA composites revealed that the biodegradation PLA matrix potentially depended on the presence of bamboo fabric and the composting conditions. The incorporation of bamboo fabric enhanced the microorganism affinity to the composites in real composting conditions. However, the rapid degradation of virgin PLA in controlled composting conditions indicates that bamboo fabric and virgin PLA require different conditions for optimal biodegradability. The biodegradation half-life of BF-PLA composites (46 days) was found to be longer than that of the virgin PLA (25 days), indicating that the reinforcement of bamboo fabric in PLA matrix minimizes the rapid microbial decay of BF-PLA composite. Thus, BF-PLA composite has the potential to be use in product packaging for providing eco-friendly and sustainable packaging.

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Author Contributions

M.R. Nurul Fazita conducted the experimental work of this manuscript under the supervision of Krishnan Jayaraman and Debes Bhattacharyya; M.R. Nurul Fazita and M.K. Mohamad Hafiz wrote the first draft of the manuscript; Md. Sohrab Hossain conducted data analysis and critically reviewed the manuscript with the assist of Abdul Khalil H.P.S.. All authors read and approved the final draft of this manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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