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Processability and Biodegradability Evaluation of Composites from Poly(butylene succinate) (PBS) Bioplastic and Biofuel Co-products from Ontario

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Abstract This study investigates the processability and biodegradability of composite bioplastic materials. Biocomposites were processed using twin-screw compounding of the bioplastic poly(butylene succinate) (PBS) with bio-based fillers derived from co-products of biofuel production. An extensive biodegradability evaluation was conducted on each biocomposite material, as well as the base materials, using respirometric testing to analyze the conversion of organic carbon into carbon dioxide. This evaluation revealed that the presence of meal-based fillers in the biocomposites increased the rate of biodegradation of the matrix polymer, degrading at a faster pace than both the pure PBS polymer and the switchgrass (SG) composite. This degradation was further confirmed using FT-IR and thermal analysis of the material structure before and after biodegradation. The increased biodegradation rate is attributed to the high concentration of proteins in the meal-based composites, which enhanced the hydrolytic biodegradation of the material and facilitated micro-organism growth. The SG-based composite degraded slower than the pure polymer due to its lignin content, which degrades via a different mechanism than the polymer, and slowed the biodegradation process.

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Introduction

In recent years, environmentally friendly biodegradable polymers and plastics have gained much attention around the world because of environmental pollution due to the plastic waste accumulation. These environmentally friendly polymers can undergo biological degradation in soil, compost, sewage, and marine environments, which circumvents waste accumulation. Biodegradation is an essential part of the process of environmental breakdown of polymer substrates into organic waste. The composting of biodegradable materials is becoming an alternative option to conventional disposal methods such as landfills or incineration. Through this process, biodegradable wastes and organic materials can be converted into humic substances, which can be utilized as an excellent fertilizer in agricultural applications [1]. Municipal solid waste (MSW) management through composting is an environmentally friendly process because it decreases the output of waste to landfills, while saving energy and yielding valuable organic compounds and nutrients that can be used in agriculture [1].

The annual disposal of petroleum–based synthetic polymers amounts to approximately 150 million tons. This waste is generated through disposable plastic materials, including the polyolefins used in packaging, bottle and moulding products [2]. After a decline from 2008 to 2009 due to the global economic crisis, the production and consumption of these polymers has continued to expand at a rapid rate [3]. From 2009 to 2011, world plastic production rose from 250 million tonnes to 280 million tonnes,

an increase of around 6 % per year [3]. In spite of this threat, the majority of the biodegradable polymers are not widely used due to their high production cost and limited range of applications for end-life products. Poly(butylene succinate) (PBS) is an aliphatic polyester that is synthesized by condensation polymerization. It possesses good mechanical properties, processability, biodegradability, compostability and low production cost compared to other biodegradable polymers.

Research has been conducted on the use of biological materials as fillers in polymer materials. A promising option is the use of biofuel co-products, materials created in the process of biofuel production. With the rapid growth of the biofuel industry in recent years, these co-products are quite abundant and can be obtained at a relatively low cost. Due to their high protein content, co-products such as soy meal (SM) are often used as a constituent of livestock feed, as they provide significant nutritional value. Biofuels, specifically biodiesel, are prepared by the transesterification of oils by the addition of an alcohol. Natural vegetable oils, such as soybean oil, are used to produce biodiesel, and must be extracted from the plant material. After the extraction, only solid plant matter is left behind. This plant matter is grinded into a fine consistency, creating a powder referred to as the meal.

Currently, there exists very little research on the use of these co-products in polymer composites. The fillers used in this study, canola meal (CM) and SM, are both produced by this process as the co-products of canola oil and soy bean oil, which may then be used to create biodiesel or other products. The filler corn gluten meal (CGM) is a high protein powder material that is a co-product of corn ethanol processing. It consists of the dried gluten slurry that is separated from the process during the extraction of the corn oil and germ [4]. It is hypothesized that the high protein content in these meals will contribute to an accelerated rate of biodegradation of the composite materials. Switchgrass (SG) is an abundant species of perennial grass that grows across North America. It grows easily and in many environments, and is mainly used as an energy crop. Unlike the meals, SG has relatively low protein content, and is mainly lignocellulosic in structure.

In recent years, many research studies have been conducted on the use of biofillers as reinforcement in biodegradable polymer composite systems. These materials, which are known as biocomposites, are composed of agriculture residues blended with biodegradable polymers and have become attractive [5–7]. In particular, plant based materials have been blended with synthetic as well as renewable polymers to produce biodegradable plastic for packaging, foams, and molded objects [8–10]. The use of plant materials in biocomposites offers potential for replacing petrochemical-based disposable plastics. The potential degradable nature of such biocomposites is also expected to provide solutions to the environmental issues associated with the disposal of conventional plastics. The use of biofuel co-products, such as SM, CGM and CM, and agriculture residues, such as wheat straw, have been successfully used in these studies in developing biodegradable composite materials. Furthermore, the development of biodegradable plastic from corn co-products [11] and films from corn carbohydrates have also been reported, with materials displaying 60–70 % biodegradation within 5 weeks [12]. Being inherently biodegradable in nature, these plant-based materials can be ideal raw materials for single-use biodegradable consumer products. However, their successful use in product development and subsequent disposal would require knowledge and understanding of their biodegradability, degradation end products and toxicity in different environmental conditions. Biodegradation studies are generally carried out in a soil or compost environment. Due to the high microbial diversity of compost, the biodegradation of these materials may be enhanced in this environment. This enhanced degradation potential for polymer materials may result in the production of CO_2, H_2O and cell biomass. Due to this observation, these materials are often declared to be environmentally friendly. These claims must be proven valid using established scientific methods. The biodegradability of these plastics provides these materials with novel and additional properties which may also be beneficial during their use. In order to extend their utilization, these materials must be biodegradable in natural environments, so that they can provide carbon and energy source for microorganisms. As defined by established research standards [13, 14], biodegradation is "degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of the exposed material and resulting in the production of carbon dioxide, methane, water, mineral salts and new microbial cellular constituents (biomass)".

The purpose of this research was to investigate the biodegradability of biocomposites made from PBS polymer and various proteinous meals of biofuel co-products, as well as natural fiber from SG, in controlled composting conditions. The use of biofuel co-product fillers serves several purposes. Because of their low cost, incorporating these fillers into composite materials can offset the higher cost of the biopolymer, while also providing a value-added application for the fillers. Due to their high protein content, these fillers may also serve to enhance the biodegradability of the composite material. PBS was chosen as the matrix polymer due to its established biodegradability and suitable properties for melt extrusion with biomass without causing thermal degradation. The biodegradability in the presence of compost of each biocomposite was correlated with that of its individual constituents, using aerobic biometer flask respirometric test methods which were designed for

biodegradable plastics, according to the procedure of Chiellini et al. [15]. To our knowledge, research on the biodegradability of these novel biocomposites is currently quite limited. The biodegradability study used in this project was based on a determination of the percentage of mineralization (estimated by measuring the emitted carbon dioxide) of the materials' carbon content versus time. Thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) were also utilized to analyze the degradation process of these materials.

Experimental

Materials

The poly(butylene succinate) used in this research was PBS 1020 (commercially named Bionolle 1020), obtained from Toyo Plastics Co., Ltd. (Japan), and manufactured by Showa High Polymer Co., Ltd. (Japan). The SM was obtained from Sharpe Farm Supplies (Guelph, Ontario, Canada). The CM was obtained from a local canola oil processing industry (Guelph, Ontario, Canada). The CGM was obtained from Casco, Inc. (London, Ontario, Canada). The switchgrass (SG) was obtained from Nott Farms (Clinton, Ontario, Canada).

Compounding and sample preparation

The PBS composite materials were prepared using a Micro 15-cc Twin Screw Compounder (DSM, the Netherlands), paired with a Micro 12-cc Injection Moulding Unit (DSM, the Netherlands). All composite samples were processed at 160 °C, with a screw rotation speed of 100 rpm. The materials were weighed and added to the micro-compounder in the weight ratio of 75 wt% polymer to 25 wt% filler for each composite, and 100 % polymer for the neat PBS. Each batch was processed in the micro-compounder for 3 min prior to injection moulding. After 3 min, the samples were transferred to the injection molding unit using a cylinder, also heated to 160 °C. Using the injection moulder, tensile, flexural, and impact samples were produced for each composite material, as well as neat PBS. All processing materials were dried for 24 h at 80 °C in a ventilated oven prior to processing in order to eliminate any moisture content from the material. Following the processing period, all test samples were stored in a desiccator at room temperature. A 48 h period was allowed before the materials were characterized.

Mechanical Characterization

Tensile and flexural testing of the PBS and PBS composite materials were conducted using an Instron 3382 Universal

Table 1 Chemical properties of the compost material

Analysis	Compost
Total dry solids (%)[a]	48
Volatile solids (%)[b]	53
pH of compost solution	7.5
Total organic carbon amount (%)	30.6
Total nitrogen amount (%)	3.6
C/N ratio	8.5

[a] The amount of solids obtained by taking a known volume of compost and drying at about 105 °C for 10 h

[b] The amount of solids obtained by subtracting the residue of a known volume of compost after incineration at about 550 °C

Testing Machine (Instron, USA). For tensile properties, each material was tested following ASTM D638. For flexural properties, each material was tested following ASTM D790. Impact testing of the materials was conducted following ASTM D256 using a TMI Monitor Impact Tester (Testing Machines, Inc., USA). The samples were aligned and notched using a TMI Notching Cutter (Testing Machines, Inc., USA). The impact strength of the notched sample was determined using a 5 lb. pendulum. In each test, five samples of the material were used to determine an average value and deviation.

Biodegradability test

A biodegradability test was conducted using 3 month-old compost, derived from properly aerated organic mature compost and kindly provided by Sunshine Environmental, Orangeville (Canada), as the composting medium. The compost material was sieved to a diameter of less than 0.8 cm, and its physical and chemical properties were analyzed according to the ASTM D6400 standard, as shown in Table 1. The biodegradability of the test materials was analyzed in biometer respirometric flasks following the procedure suggested by BioLab, University of Pisa [15]. The compost was mixed with finely ground perlite particles in a 1:1 dry weight ratio, which acted to maintain proper humidity and aerobic conditions, as well as provide noise elimination in the test. The polymer test materials were ground in a coffee grinder into fine particles with an average size of ≥ 100 µm. The particles were added to the compost mixture in a ratio of 1:6 (w/w sample to dry solids of compost).

The mixture was then placed in a glass hermetic flask with a capacity of 1000 mL. The mixture is contained between a bottom layer of 15 g of perlite, wetted with 15 g of water, along the bottom of the flask, and an upper layer of 15 g of perlite, wetted with 15 g of water, covering the compost mixture to preserve moisture content. Finally, a
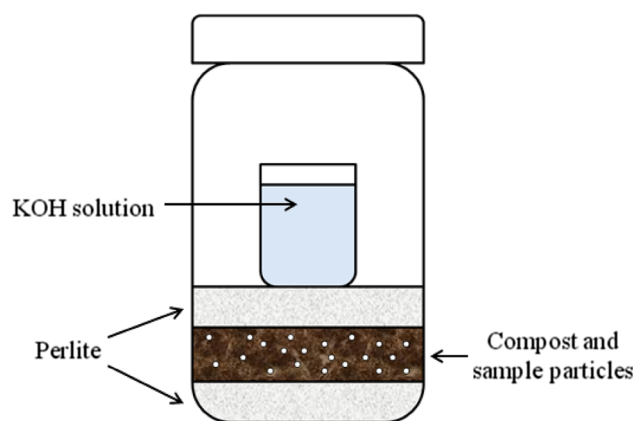
Fig. 1 Respirometric biodegradation flask system, redrawn based on figure from Chiellini et al. [15]

beaker containing 40 ml of potassium hydroxide solution (0.5 N KOH) was placed on the upper layer to trap emitted carbon dioxide [15]. All material samples were tested in triplicate. The activity of the compost was determined as is required by the standard method. Over the first 10 days of the test, the compost produced 65 mg of CO_2 per gram of volatile solids. The flask system is depicted in Fig. 1.

During the biodegradation process, the flasks were kept in an IsoTemp Oven (Fisher Scientific, USA), which maintained the samples at the optimum composting temperature of 58 ± 2 °C. The conditions within the oven and flasks were aerobic. The flasks were periodically removed from the oven to titrate the KOH solution. After titrations, each beaker was washed and refilled with fresh KOH solution of a known concentration. The test flask moisture was recorded with a moisture analyzer (IR 35 Electronic Moisture Analyzer). The moisture content of each flask (50–55 %) was maintained by measuring the weight loss due to evaporation, and adding deionized water to counteract such losses.

The biodegradation progress of the material was tracked by trapping all of the emitted CO_2 in the KOH solution. The carbon dioxide is emitted only by organic metabolization of the material by microorganisms, and so is representative of the total degradation due to biological factors. As gaseous CO_2 is emitted, it reacts with the KOH in the beaker. This reaction is shown below (Eq. 1):

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O \qquad (1)$$
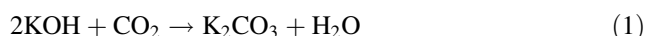
The beaker containing KOH is removed from the biodegradation flask and barium chloride (1 N $BaCl_2$) is added to the KOH–K_2CO_3 solution. This reaction is shown below (Eq. 2):

$$K_2CO_3 + BaCl_2 \rightarrow BaCO_3 + 2KCl \qquad (2)$$
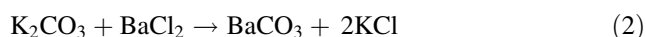
The barium carbonate formed in (Eq. 1) appears as a cloudy white precipitate. The remaining amount of KOH in

the solution can now be determined by titrating with 0.5 N HCl, using phenolphthalein as an endpoint indicator. This titration follows the reaction as follows (Eqn. 3):

$$KOH + HCl \rightarrow H_2O + KCl \qquad (3)$$

The theoretical quantity of carbon dioxide emitted in each flask (ThCO$_2$ in g per vessel) as a result of the total oxidation of biodegrading materials can be calculated using the expression (Eq. 4):

$$ThCO_2 = M_{total} * C_{total} * 44.01/12.0107 \qquad (4)$$

where M_{total} is the total dry mass of biocomposite, polymer or filler materials (g) added to the compost, C_{total} is the relative mass of total organic carbon (g) in the dry solids, 44.01 is the molar mass of carbon dioxide and 12.0107 is the atomic mass of carbon. Emitted CO_2 (%) was plotted versus composting time in order to obtain a biodegradation curve. The amount of biodegradation was determined as the percentage of the material carbon content converted into CO_2 according to the expression (Eq. 5):

$$Biodegradation(\%) = (CO_2)_s - (CO_2)_c / ThCO_2 * 100 \qquad (5)$$

where $(CO_2)_s$ is the amount of CO_2 produced in the sample and $(CO_2)_c$ is the amount of CO_2 produced in the control.

Analytical Characterization

Thermogravimetric Analysis (TGA)

The thermal stability of each composite and raw material was tested using TGA on a TGA Q500 machine (TA Instruments, USA). Samples were dried for 24 h in an 80 °C oven and sealed in plastic bags to eliminate moisture content. For each test, a 10–20 mg sample was heated from 30 to 600 °C with a temperature ramp of 20 °C/min.

FT-IR spectroscopy

The spectrum of each composite material was analyzed using a Nicolet 6700 ATR-FTIR(Thermo Scientific, USA). Each sample was mounted on the machine, and scanned 36 times to generate a spectrum of the material. The spectrum was output and subsequently analyzed as percent transmittance versus wavenumber (cm^{-1}).

Results and Discussion

Mechanical Characterization

The mechanical properties of the biocomposite materials were investigated through tensile, flexural and impact testing. Table 2 compares the data obtained for each

Table 2 Mechanical properties of PBS biocomposites

Material	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Flex modulus (MPa)	Impact energy (J/m)
PBS	32.7 ± 1.7	215 ± 24.2	438 ± 9	565 ± 12	77 ± 15
PBS/CM (75/25)	21.7 ± 0.4	13.1 ± 2.9	793 ± 97	939 ± 69	43 ± 2
PBS/SM (75/25)	20.5 ± 0.2	11.1 ± 1.0	944 ± 15	1,026 ± 26	50 ± 4
PBS/SG (75/25)	26.0 ± 0.8	5.09 ± 0.3	1,310 ± 48	1,596 ± 18	34 ± 2
PBS/CGM (75/25)	20.3 ± 0.3	12.3 ± 2.1	781 ± 13	993 ± 65	39 ± 4
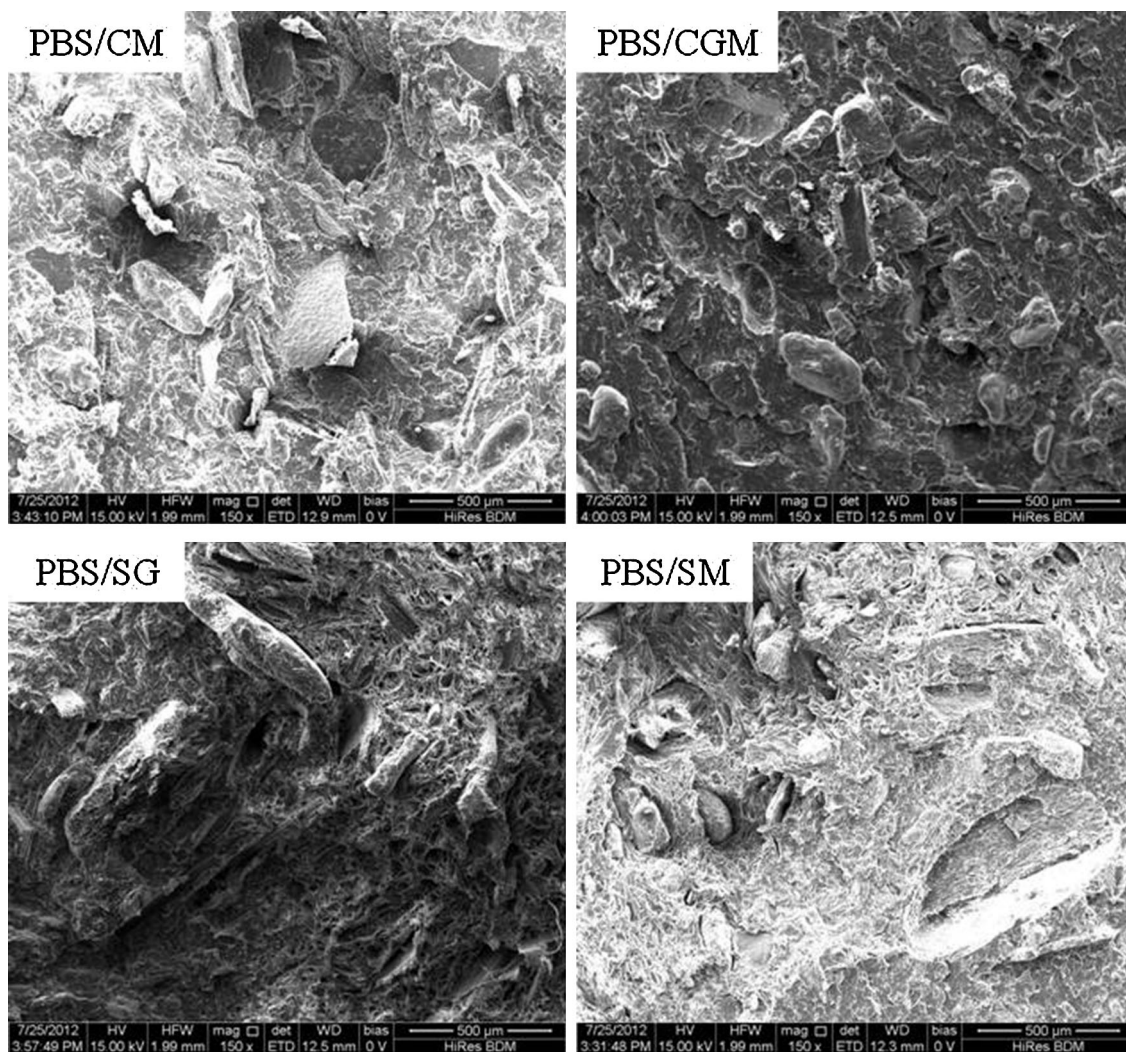
Fig. 2 SEM micrographs of PBS composite materials

biocomposite material to that of the neat polymer. The composite materials were also investigated using scanning electron microscopy in order to examine the interfacial adhesion between the filler particles and polymer matrix (Fig. 2).

Review of the data provided in Table 2 reveals several trends in the material properties. In each of the biocomposite materials, the tensile strength and impact strength were significantly reduced from that of the pure PBS polymer. This decrease in strength can be attributed to crack initiation being facilitated by filler particles not properly adhering to the matrix [16]. The SEM micrographs of a fracture surface of each composite (Fig. 2) confirm this, displaying poor interfacial adhesion between the filler material and polymer matrix of the composites. The meal-based composites tended to have a better impact

Table 3 Chemical composition of biofuel co-product filler materials

Co-product	Moisture (%)[a]	Ash (%)[b]	Nitrogen (%)[c]	Protein (%)[d]	Carbon (%)[c]	Fat content[c]
SM	6.8	26.7	7.9	49.2	44.6	2.01
CM	9.0	29.0	6.2	38.6	46.0	3.34
CGM	10.2	18.8	8.9	55.5	51.6	0.88
SG	5.0	19.2	1.1	6.9	49.6	0.64

[a] Moisture (%) content is measured as the weight lost during drying $102 - 105\ °C$ by a moisture analyzer

[b] Ash (%) content is measured as weight at $600\ °C$ by TGA in N2 atmosphere

[c] Results obtained from C, N elemental analysis from Laboratory services at University of Guelph

[d] Results obtained using the Kjeldahl method

strength than the SG composite, but a lower tensile strength. As expected in biocomposites, the presence of the filler material severely reduces the ductility of the polymer; this is reflected in the elongation values, with the neat polymer reaching 215 %, while the composites tended to fracture at only 11–13 %. The elongation of the SG composite was less than half that of the meal composites, which can be attributed to the larger size of the SG fibers. The meals had a much finer particulate nature which allows for better dispersal throughout the polymer matrix, and subsequently a more consistent material with better ductility [16].

The addition of the biofillers also yielded an increase in the Young's modulus and flexural modulus of each biocomposite material relative to the pure PBS polymer. The presence of the filler material within the composite increases the rigidity of the material. The most significant increase in modulus was observed in the SG biocomposite, which can be expected due to the fibrous nature of the SG, which significantly affected the rigidity of this material, much more so than the meal based composites.

Biodegradation Analysis

Biodegradable biocomposites based on fossil-fuel feedstock and renewable resources are attractive in terms of production cost, processing, and performance, compared to conventional non-biodegradable polymers. Because environmentally degradable polymeric materials and plastics must be converted by microorganisms into final elemental products such as carbon dioxide, water and new microbial biomass (i.e. mineralization), it is important to understand what is necessary for the biodegradation of natural and synthetic plastics, as well as the involved physical–chemical and biological mechanisms. As such, obtaining information about the biodegradability of co-products from renewable resources is critical for the design and development of biodegradable polymeric materials.

The composition of the co-products from biofuel industries and SG from agricultural biomass is provided in Table 3. The percentage of carbon in the samples ranged from 44.6 to 51.6 %. CGM had the highest carbon content (51.6 %), followed by CM (46.0 %), SG (49.6 %) and SM (44.6 %) (Table 3). As expected, CGM and SM had high protein content (55.5 and 49.2 %, respectively). SG had a low protein content (6.9 %) due to its hemicellulose and lignin chemical composition (Table 3). A similar trend was observed in the nitrogen content in the samples.

The rate and extent of biodegradation of SM, CM, CGM and SG were evaluated in composting environments under controlled conditions. The adopted procedure conditions (temperature of 58–60 °C, pH 7–8 and moisture 50–55 %) are suitable for mesophilic and thermophilic microorganisms (bacteria and fungi) in organic mature compost environments (Table 1). This study was carried out using biometer flasks (air tight glass flasks) in which the oxygen concentration was controlled by mixing fine perlite particles with the compost. The layout and structure of these flasks is described in the experimental section (Fig. 1) [15].

In parallel, oxygen concentration was also monitored, and a positive reference material (micro-crystalline cellulose) was studied to ensure the sample was contained in an environment with a suitable oxygen content (Fig. 3). It has been shown that high water contents around soil bacteria and cellulolytic fungi, *Phanerocheate chrysosporium*, contribute to cell-wall hydrolysis, causing extracellular materials, including hydrolytic enzymes, to leak out of the cells [17]. In this study, areobic biodegradation of the materials was carried out for a 200 day incubation period under composting conditions. In this period, the meal-based biofuel coproducts achieved a biodegradability of of 90 % within 100 days, which was much higher compared to the SG composite, which required 170 days to achieve 90 % biodegradability (Fig. 3). The apparent difference in the rate and extent of biodegradability between the biofuel co-products (SM, CM, CGM) and SG may be due to their material composition (Table 3). The biodegradability of SM, CGM and CM is high due to their rich content of soluble sugars and partially digested carbohydrates and protein. These materials offer both an excellent carbon

Fig. 3 Biodegradation of filler materials and reference
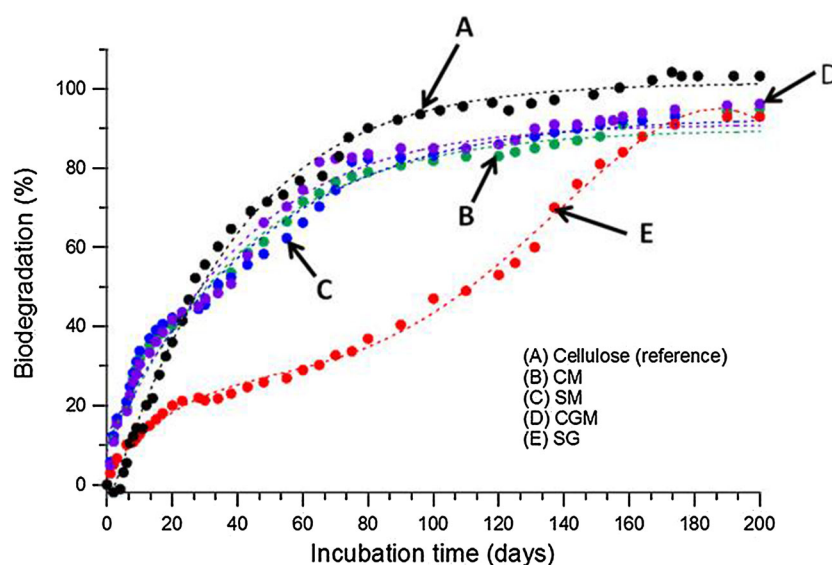
source for microbial growth, and a substrate for enzymatic hydrolysis. In contrast, SG contained large amounts of cellulose (31–38 %), hemicelluloses (26–32 %) and lignin (17–18 %) [18] and as a result degraded quite slowly (Fig. 3). Cellulose and hemicelluloses are hydrophilic and highly crystalline complex carbohydrate polymers, known for their slow enzymatic hydrolysis. Lignin is a highly hydrophobic organic polymer, which undergoes enzymatic oxidation.

The biodegradation testing of all the biocomposites in the study showed that sample composition plays a significant role in the compostability of the PBS matrix (Fig. 4). PBS is well known as a compostable polymer, and undergoes enzymatic hydrolysis and microbial bioassimilation to produce CO_2, water and microbial biomass. PBS/SM (75/25) reached 90 % biodegradability in 140 days, where as the other PBS based biocomposites, PBS/CM (75/25), PBS/CGM (75/25) and pure PBS (100 %), reached 90 % biodegradability in 160 days. The higher biodegradability of PBS/SM is mainly due to the composition of SM (soluble sugars and partially digested proteins, carbohydrates), environmental conditions (pH 7–8), and temperature (58–60 °C), all of which are important influencing factors for the enzymatic hydrolysis of materials by microorganisms. CGM has a higher content of protein and cellulose, which are highly crystalline complexes, well known for their slow enzymatic hydrolysis and consequent slow biodegradation. Although the PBS matrix polymer is susceptible to enzymatic hydrolysis, initial degradation is delayed due to its highly crystalline and brittle nature, causing it to undergo negative biodegradation in the first 30 days relative to the test control (blank compost without any sample material) (Fig. 4). These results suggested in the first 30 days neat PBS undergoes an acclimatization stage, in

which biodegradation is decreased due to its high crystallinity [19]. The initial lag phase started after 30 days, and the material then followed a trend similar to that of the PBS/CM and PBS/CGM composites. The lag phase was reached in 2–3 days by PBS/SM, and in 10–11 days by PBS/CM and PBS/CGM. In contrast, the PBS/SG composite showed much lower biodegradability (taking 90 days to reach 18 %) due to the high crystalline complex structure of cellulose and hemicelluloses in SG. It requires different hydrolytic metabolic enzymes for denaturing the cellulose, hemicelluloses and polyester groups. More importantly, SG contains 17 % lignin, which does not undergo hydrolytic enzymatic processes; instead, it requires oxidative enzymes, such as peroxidase, for biodegradation [20]. This is a possible reason for the decreased biodegradability of PBS/SG compared to neat PBS. After 90 days, the PBS/SG composite showed an acceleration phase. This could be due to the PBS crystalline region breaking into smaller chains and cellulose materials from SG, which are readily biodegradable in composting environments. It reached a maximum of 90 % biodegradation after 200 days of incubation. Results suggested that microbial enzymes, such as polysaccharide-degrading enzymes and glycosidase in rumen, perform catalysis of the plant materials. Conversely, cellulases and hemicellulases, including xylanases and laccase, were required for the effective biodegradation of the co-products in compost [19].

During the composting tests, small particles of the PBS/SM, PBS/CM, PBS/CGM, PBS/SG based biocomposites and neat PBS and were recovered from the test flasks. The particles were analyzed to determine the effect of mineralization on the molecular structure and thermal properties of the materials after 24 and 43 days of incubation. The recovered biocomposite and neat PBS material particles

**Fig. 4** Biodegradation of PBS and PBS biocomposites
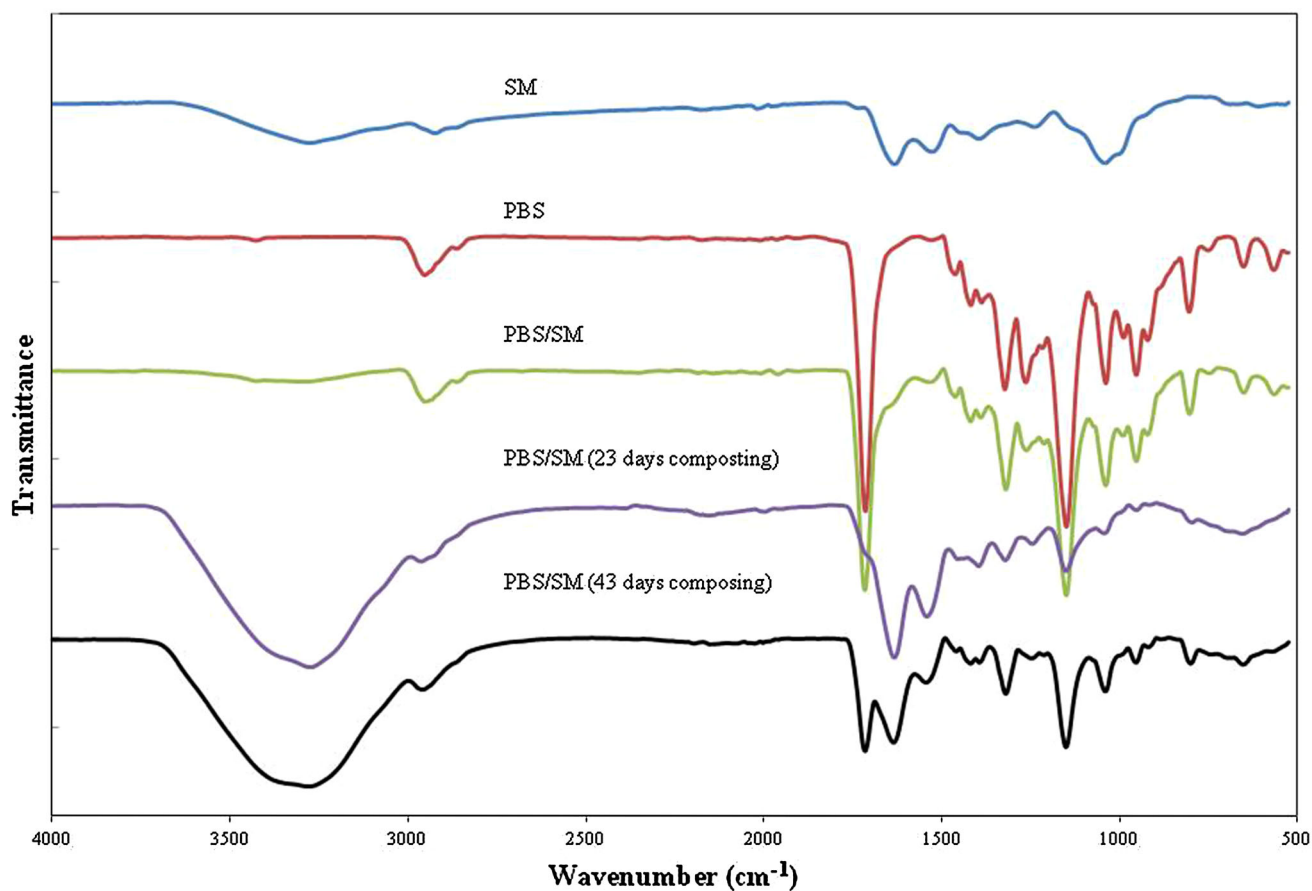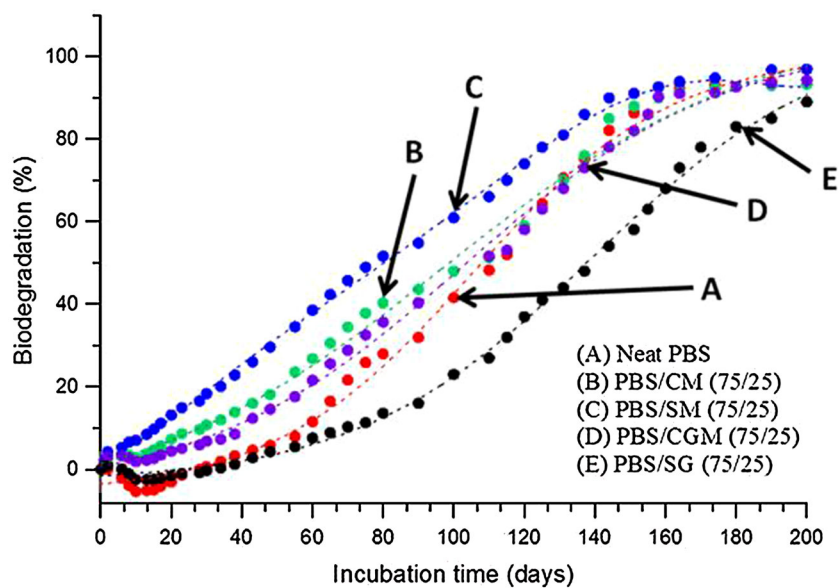
Fig. 5 FT-IR spectrum of PBS/SM after intervals of biodegradation

were washed with deionized water, then dried at 40 °C for 4 h. Oligomers can be produced through hydrolytic main chain scission along the polymer chain, and can permeate

out of the PBS polymer matrix into the microbial environment. This correlates with the observed reduction of the carbonyl absorbance (1,710 cm⁻¹) from enzymatic

Fig. 6 **a** TGA of PBS, wt% versus temperature, **b** DTGA of PBS, derivative weight versus temperature
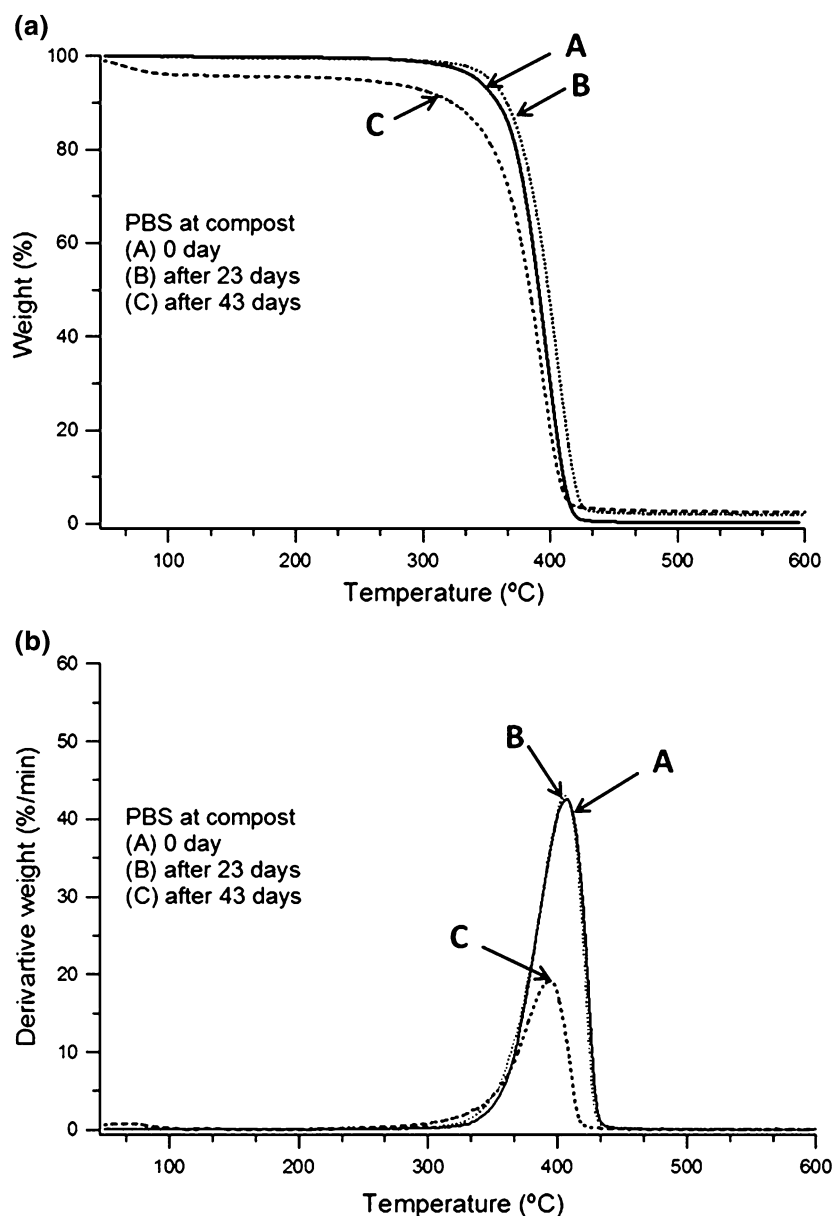
hydrolysis after 24 days, and increasing hydrolytic absorbance (3,200 and 1,510 cm^{-1}) (Fig. 5). The FT-IR results clearly indicated that after biodegradation, the absorbance of the carbonyl groups (ester and keto) were reduced, and hydrolytic groups (OH) were formed. This suggested it undergoes enzymatic hydrolytic processes, and indicates the presence of biodegradable fragments of hydrolysed groups, which are susceptible to microbial assimilation. After the utilization of the hydrolyzed groups, microbial enzymes further broke down the hetero-chain PBS matrix, which increases the carbonyl groups and decreases the OH groups (Fig. 5). These results are similar to those found by Corti et al., [21] suggesting that the decrease in carbonyl groups is due to the microbial assimilation of low molecular weight groups, especially on the amorphous region.

The increase in carbonyl groups is due to the breaking down of the hetero chain of the bulk material, especially on the crystalline regions, and the scission of long chains into smaller chains, which are which more easily hydrolysed.

An evaluation was conducted on the effect of biodegradation on the thermal behaviour of the material, with the intent of finding a correlation between the thermal properties and mineralization. Thermal analysis was conducted on small samples of material removed from the biodegradation system after 23 and 43 days of composting. A small particle of material was removed from the biodegradation flask at each of these intervals, washed with deionized water and then dried at 40 °C for 4 h prior to analysis. Figure 6a, b show the effect of biodegradation on the neat PBS polymer through TGA. From these graphs, it can be seen that while

the initial curve and curve after 23 days are quite similar, there is significant deviation in the material after 43 days of biodegradation, which correlates very well with the onset of biodegradation in PBS from the respirometric study. In the material that composted for 43 days, both the onset and peak degradation temperatures occurred at significantly lower temperatures than in the uncomposted material. These results indicate that composting system condition and microbial population present in compost is suitable for the biodegradation of PBS polymer matrix.

There is a need to further research and understand the effects of microorganism species, population and enzyme specificity depending on differing microbial environments on the biodegradation process of biocomposites based from biofuel co-products and SG (agricultural biomass). The biodegradation of PBS composite materials based on bio-fuel co-products was greatly increased compared to that of the neat PBS. The results of this study demonstrate that a composting microbial system provides a favourable environment for the biodegradation of PBS composite materials. Hydrolysis has a considerable influence on the extent and rate of biodegradation of biodegradable polyesters such as PBS due to microbial activity. This is because hydrolysis is one of the primary processes of degradation and is followed by the microbial assimilation of carbon sources (mineralization). It has been established that microorganisms demonstrate a different enzyme specificity for the metabolization of cellulose and biodegradable PBS in composting conditions.

Conclusions

The results demonstrated that introduction of biological filler materials had a significant effect on the rate of bio-degradation of the composite material. The study conducted on the raw filler materials revealed the difference in degradation rate and mechanism between the meals compared to the SG filler. The data showed that the rate of aerobic biodegradation of the proteinous meals was twice as high as that of SG. This rapid biodegradation behaviour in the meals is due to their higher protein content, while the degradation of the SG is delayed by its high lignin content, which requires oxidative degradation. This same trend was observed in the biocomposites, in which the proteinous meal-based biocomposites degraded at a faster rate than both the neat PBS matrix material and PBS/SG biocomposite. The presence of proteinous meals has enhanced the initial growth of microorganisms, and thus facilitated a more rapid hydrolysis of the matrix polymer.

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