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Thermophysical properties and biodegradation behavior of green composites made from polyhydroxybutyrate and potato peel waste fermentation residue

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ABSTRACT

Polyhydroxybutyrate (PHB) is one of most biodegradable bioplastic, but its high cost and brittleness limits its applications. In this study, low-value waste byproduct from a fermentation process of potato peel waste, called the potato peel waste fermentation residue (PPW-FR) fibers, were recovered and compounded with PHB to form biocomposites of tunable properties. The mechanical and thermal properties of pure PHB and biocomposites were investigated by thermogravimetric analysis (TGA), tensile and flexural tests, and dynamic mechanical analysis (DMA). Fiber content was shown to have a significant effect on the surface hydrophobicity and water absorption of the biocomposites. All absolute and specific mechanical properties and water absorption (by normalizing the measured parameters against the measured density (ρ)) were investigated. The biodegradability of PHB and biocomposites were evaluated in soil over 8 months. The surface morphology, chemistry and melting/crystallization behavior were monitored and characterized by microscopy, FTIR spectroscopy and differential scanning calorimetry (DSC), respectively. The biocomposites showed poor mechanical properties but extremely higher biodegradation rate as compared with pure PHB, especially when the fiber content was >15%. The degradation rate increased with increasing fiber content and positively correlated to the water absorption showing more cracks and deeper pits. FTIR spectroscopic analysis showed that the plant polysaccharides and PHB within the biocomposite were degraded with exposure time. At 50% fiber content the biocomposites were completely degraded by 8 months. These PPW-FR based biocomposites offer new opportunities for fast degrading biomaterials in agricultural and horticultural applications.

1. Introduction

Due to disposable problems at the end of life for synthetic and petroleum-based polymers, bio plastics derived from renewable resources have attracted extensive attention due to their low environmental impact. Some of the most common used bioplastics include thermoplastic starch, cellulose esters and ethers, polylactic acid (PLA), polyhydroxyalkanoates (PHAs), and bio- derived polyethylene (Chen and Patel, 2012; Mekonnen et al., 2013; Wei et al., 2014; Yu et al., 2006). PHAs are a family of biopolyesters that are biosynthesized by microorganisms (Chen and Patel, 2012; Mekonnen et al., 2013). Polyhydroxybutyrate (PHB) is the most common PHA and widely studied due to its good biodegradability and biocompatibility, which facilitate PHB to be used in various applications such as agricultural, marine and medical fields (Satyanarayana et al., 2009; Yu et al., 2006).

As compared with conventional plastics, PHB is still more expensive than conventional plastics, although various strategies have been developed to reduce the cost of PHB. Another problem with PHB is the high brittleness due to high degree of crystallinity which is also a crucial factor affecting its degradation performance in environments (e.g., heat, static seawater, UV lights, enzymes and soil composting) (dos Santos Rosa et al., 2001; Michel and Billington, 2012; Tsuji and Suzuyoshi, 2002). To improve its properties and biodegrability and in the meantime lower production cost, blending with other biodegradable polymers and fillers such as PLA, bast fiber and agricultural residues have become an attractive approach (Barkoula et al., 2010; Mousavioun et al., 2013; Terzopoulou et al., 2014). For example, the agricultural sector wants to use low energy

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and low value resources for such applications as short life-term agricultural mulch films and horticulture pots/containers. Hence, great efforts have been made to explore biobased solutions that replace petroleum-based plastics in this field.

Fermentation is one of the main methods to convert biomass waste (forest and agricultural residues, and animal waste) into value added products (alcohols and organic acids), which inevitably produce significant quantities of process byproducts know as fermentation residues (Coats et al., 2011; Liang et al., 2014b). These residues are carbon rich waste sources, which are majorly composed of lignin and unreacted carbohydrates for producing value added biofuels and bioproducts (Liang et al., 2014a). More recently, dried distillers grains with solubles (DDGS), a major co-product of the corn ethanol industry, have been used for the production of "green" composites using biodegradable poly(butylene adipate-co-terephthalate) (PBAT) and PHAs as polymer matrices (Madbouly et al., 2014; Muniyasamy et al., 2013). The addition of DDGS made the biocomposites easy to be bio-degraded in soil as compared with pure PHA, which makes these biocomposites commercially feasible for horticultural crop container (seedling tray). The fermentation bagasse residues were used in PVA biocomposites by Cheng et al. (2013). Another abundant agricultural waste is potato peel waste (PPW), which has been alternatively used for ethanol and organic acids production by fermentation despite being primarily used as local animal feed (Liang and McDonald, 2014; Liang et al., 2014b). Work by Kang and Min has used PPW for making flexible films for packaging applications (Kang and Min, 2010). Whereas the further utilization of the co-product from the PPW fermentation which was defined as potato peel waste fermentation residue (PPW-FR) in our previous work still requires more efforts in both academic and industrial fields (Liang et al., 2014b). A good potential application of PPW-FR is for biofuels as reported recently (Liang et al., 2014a; Liang and McDonald, 2014). Nevertheless, very limited information for other value added bio-products from the PPW-FR, for example biocomposites, is available.

In this study, our overall aims were to prepare green biocomposites from PHB and PPW-FR by melt mixing followed by injection molding, and to explore the potential applications of the PPW-FR waste in the fields of agriculture and horticulture as biocomposite materials. The specific objective of this work was to assess the effect of PPW-FR fiber loading on the properties and biodegradation behavior of resulting biocomposite. The interfacial bonding was estimated by calculation of an adhesion factor (A) from DMA measurements. The effect of PPW-FR loading on the thermal properties (i.e., thermal stability) and mechanical properties (absolute and specific tensile and flexural tests) and biodegradation performance in soil was studied. The wettability of the biocomposites surfaces by contact angle measurements was investigated. Short-term water absorption test was undertaken to predict the biodegradation performance. The surface morphology changes due to soil biodegradation of biocomposites and pure PHB as well were studied by microscopy. The influence of biodegradation on the melting behavior and crystallinity of PHB/biocomposites was studied using DSC.

2. Materials and methods

2.1. Materials

PHB powder was obtained from Tianan Biopolymer Inc. (Ningbo, China). PPW-FR was obtained from a sequencing batch fermentation reactor to produce lactic acid, the solids were separated by centrifugation, freeze dried, and Wiley milled to pass through a 0.5 mm screen process as described previously (Liang and McDonald, 2014; Liang et al., 2015). The chemical composition analysis showed the PPW-FR comprises of non-starch glucan (7.8%), galactan (5.1%), arabinan (4.4%), mannan (1.4%), xylan (1.5%) and starch (2.1%), lignin plus suberin (37.0%), protein (25.1%), lipids (7.7%) and ash (7.5%) (Liang and McDonald, 2014). The PPW- FR was dried in a vacuum oven to a moisture content (MC) <0.5% prior to use.

Sieve analysis was performed on milled PPW-FR (10 g) using standard test sieves (40, 60, 80, 100, 200 mesh and pan) on a Soil Test Inc., Model CL-300B shaker for 10 min, and the weight distribution was determined. The classified PPW-FR fractions were observed using an Olympus BX51 optical microscope in bright field mode and images captured using an Olympus DP70 digital camera. The PPW-FR fractions were vigorously dispersed in water and stained (bacteria stain either blue (Gram positive) or red (Gram negative)) to detect for the presence of bacteria.

2.2. Preparation of biocomposites

Dry PPW-FR powder (5, 15, 25 and 50%) was premixed with dry PHB powder (95, 85, 75 and 50%) in 2.0 g batches. The blended materials were placed in a Dynisco Lab Mixer Molder/Extruder (LMM), compounded (100 rpm for 10 min at 180 °C), and then injected into a preheated (160 °C) mold (discs, rectangular bars and dog-bone specimens). The mold was then air cooled to room temperature and the specimens were removed. The biocomposite samples containing respective loading (%) of PPW-FR powder were coded with P5, P15, P25 and P50. Control PHB sample was processed as the biocomposite samples to have the same thermal history.

2.3. Mechanical properties

All molded samples were conditioned at 65% relative humidity at 23 °C for at least 7 days. The tensile tests were performed on injection molded microtensile (dog- bone) specimens (10 replicates) according to ASTM Standard D1708 using an Instron 5500R-1132 universal test machine with a constant strain rate of 1 mm/min and strain measured using an extensometer (model 3542, Epsilon Technology Corp.). Three point flexural tests (modulus of rupture (MOR), modulus of elasticity (MOE)) were performed on injection molded bar specimens ($60 \times 9 \times 2\,mm^3$, 10 replicates) according to ASTM Standard D 790-07 at a crosshead speed of 1.31 mm/min and a span of 46 mm until specimen failure or 10% strain, whichever occurred first.

The biocomposite density (ρ, g/cm^3) was calculated based on the initial conditioned dry weight and dimensions (five replicates). All specific properties were calculated by normalizing the measured strength and moduli against the measured density (ρ) of each sample type.

2.4. Water contact angle measurement

The static advancing contact angle between a MilliQ grade water droplet (10 μL) and a piece of sample cut from molded disc ($12 \times 2\,mm^2$) was measured using the sessile drop method on a Thwing-Albert PG-2 Pocket Goniometer in triplicate. The contact angle was measured from the captured images at 0.5, 1, 2, 5, 10, 20 and 30 s and the data were processed using the Pocket Goniometer v3.3 software. Calibration was performed every 20 measurements.

2.5. Water absorption test

Water absorption test of conditioned (65% relative humidity at 23 °C) and preweighed biocomposite specimens (discs: $\Phi 24 \times 2\,mm^2$, five replicates) was conducted according to ASTM D570-98 procedure for 24 h. At the end specimens were removed and water wiped off on the sample surface with dry cloth, and