



Selective degradation of biodegradable blends in simulated laboratory composting



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ABSTRACT

ATR-Fourier Transform infrared technique (ATR-FTIR) was used in combination with lab scale composting setup to investigate the selective composting of two-phase biodegradable blends based on Polylactic acid (PLA) or Polyhydroxybutyrate (PHB), toughened through melt blending with poly (butylene adipate-co-terephthalate) (PBAT), referred to as PLPT50 and PHPT50 respectively. All samples have been processed into films of 35 μm thickness by means of cast film process. The simulated lab scale composting setup with gas collection columns was used to measure cumulatively evolved CO_2 gas as an indication of extent of biodegradation. The results from gas collection revealed a decrease in the rate of CO_2 evolution as a consequence of blending. ATR-FTIR spectroscopy detected two distinctive $\text{C}=\text{O}$ ester bonds for PLPT50, PLA (1743 cm^{-1})/PBAT (1710 cm^{-1}), and also PHPT50, PHB (1720 cm^{-1})/PBAT (1710 cm^{-1}), indicating the phase separated morphology of blends. The absorption ratio of $\text{C}=\text{O}$ bond for PLA and PHB decreased gradually as a function of composting time leading to a decreased ratio of PLA/PBAT and PHB/PBAT ester bond absorption in the blends. SEM micrographs showed the formation of a porous three-dimensional (3D) network for both PLPT50 and PHPT50 through composting after 15 days. ATR-FTIR analysis shows that they are rich in PBAT content, thus indicating selective degradation of the PLA or PHB components in the blends. Investigation of the mechanical properties of the blends demonstrated a gradual loss of Young's modulus caused by the formation of defects through active microbial degradation and hydrolysis.

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1. Introduction

A shift toward elimination and reduction of the adverse effects of plastics in landfills and municipal wastes has provided many plastic manufacturers the opportunity to perceive the potential market of degradable polymers [1–6]. Recently, by further developments in technologies involved in production of bio-plastics, many research works have been dedicated to the development of processable blends from bio-based and biodegradable resins, with defined mechanical and morphological properties [1,7–12]. These blends can then be converted into plastic articles with the capability to degrade in composting environments and landfills [1,13–17].

Production of high quality high performance articles from bio-plastics is limited, due to their poor performances; particularly their mechanical, barrier and processing related properties [8]. In

packaging applications and film production industries, Poly(lactic acid) (PLA) has attracted much of the attention due to its good optical properties, high tensile strength and high modulus as well as its capability to be compostable [7,8,18,19]. Available commercial competitors to PLA are Poly(hydroxy alcanoates) (PHAs), which are not optically and mechanically advantageous [20–24]. However, their low production carbon footprint and their ability to be manipulated in production line by addition of co-monomers provide them with a potential to overcome many shortages [20,25].

Both PLA and PHB show brittle behavior and need to be modified before or through processing [8,25,26]. Blending has proven to be a promising technique to improve toughness of both resins [27–34]. Modifying resins of interest consist of elastomers or many polyester resins as well as polar modified resins, with low stiffness and high elongation at break [35–37]. Recently, an approach toward modification and toughening of PLA and PHB using biodegradable aliphatic polyesters or aliphatic and aromatic copolyesters has shown many advantages as these blends will still remain biodegradable to some extent [25,33,38,39].

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Some studies showed the effect of blending on the rate of disintegration of bio-plastic films in soil, simulated landfill and marine water as well as aquatic environments and industrial compost facilities [6,18,40–44]. These rates vary depending on the chemical structure of the resin, activity of soil and composts and the depth at which the samples are buried. To the best of our knowledge, no correlation between the behaviors of each phase in the blends and the rate and mechanism of biodegradation of blend's components have been studied. Published works on the degradation behavior of blends, have tried to relate the cumulative behavior of biodegradable films and articles, e.g. total CO₂ evolution and total weight loss, to their degradation and composting rate [6,9,18,40–44].

As mentioned above, measurement of evolved CO₂ is one of the techniques that can quantitatively determine the rate of degradation of the whole product, under aerobic active microbial conditions, as addressed by the ASTM D6400 [43,45,46]. Other techniques to determine the rate of degradation of a product include weight loss measurement, monitoring molecular weight change and the change in mechanical properties of the test products [18,40,41]. Nevertheless, none of these techniques can provide with a detailed structural change through blends degradation [18,40].

Due to close polarity of ester bonding and low interfacial tension between aliphatic polyesters, extraction and detection of phases using solvents is practically impossible. Seisler et al. showed the capability of FTIR spectroscopy in the analysis of phase separation and phase morphology of two-phase blends of biodegradable polyesters [34,47]. In a recent study by Dorgan et al., determination of monomer content in Poly (lactic acid) has been addressed by an FTIR assisted method [48]. They indicated the development of a double peak that corresponds to lactic acid absorption band in the spectrum range of 1400 cm⁻¹ to 1500 cm⁻¹. FTIR technique has been also used to follow the change in the chemical structure of polymers after degradation. Few works address the successful use of FTIR in following degradation of pure biodegradable plastics after composting [46,49].

In this study we address a reliable method to analyze the selectivity of composting of biodegradable blends. This understanding of phase-wise degradation will assist in future determination of biodegradation rate of blends of multiphase and multilayer structures made from biodegradable resins. These blends may have applications in food packaging and agricultural much applications as well as medical devices. These biodegradable plastics will also benefit municipal waste management and lower the environmental impact of landfilling if end up in an industrial composting facility which, in turn, can make the best use of it by adding nutrients to the soil rather than doing more damage to it.

2. Materials and methods

Amorphous grade polylactic acid (PLA) obtained from Natureworks, USA, is a copolymer of D&L lactic acid with about 10% D-monomer content and the molecular weight of about 150 kDa. The PLA density is about 1250 kg m⁻³. The Polyhydroxybutyrate (PHB) commercial grade P209 was obtained from Biomer, Germany with molecular weight ranging between 500 and 800 kDa. The reported density for PHB falls in the range of 1240–1260 kg m⁻³. Ecoflex F Blend C1200 was purchased from BASF Plastic Technologies USA with A/T ration of unity and the molecular weight of about 40 kDa as well as the density of about 1240 kg m⁻³. Film samples of pure materials as well as their 50wt%–50wt% blends were used for the composting study. These blends were made in the same condition as pure films as will follow. The said concentration for blends was chosen in order to help in comparing the result with available literature. All the samples have been processed using a twin-screw

extruder (Leistritz model ZSE 18 HP co-rotating) with 18 mm screw diameter and a length/diameter (L/D) of 40. We used elevating temperature profile of 160 °C/170 °C/180 °C/190 °C and the screw speed of 100 RPM and the melt were processed into films using a cast film die at 190 °C. The draw down ratio used allowed reducing the films thickness to 35 μm.

Spotlight 400, PerkinElmer FTIR spectrometer equipped with ATR accessory was used in the IR range of 600–4000 to investigate the film samples. For each spectrum, the data were collected with resolution of 4 cm⁻¹. A straight baseline was used from 1400 cm⁻¹ to 1500 cm⁻¹ for the deconvolution of asymmetric bending mode peak of CH₃. Another straight baseline from 1600 cm⁻¹ to 1750 cm⁻¹ was used to deconvolute the ester C=O peak. Prior to FTIR analysis to remove the residue of compost from the surfaces all of the samples were cleaned in a water bath and ultrasonic agitation was used to facilitate the cleaning process for 1 min.

A laboratory scale setup for composting was built based on ASTM D5338. This system was designed to yield the percentage of carbon dioxide released from the organic carbon content of the samples. Mature compost was obtained from Fafard Company, Canada. To remove non-reacting particles, the compost was filtered using Mesh 4 sieve. The water holding capacity of the compost was determined to be 219% and that of as received compost was 67%. The water content of the compost was adjusted to 70% of its holding capacity. In order to eliminate the shape effect on the film samples' composting rate and providing better coverage by compost 100gr of each film sample was cut into 5 × 5 cm² pieces and mixed into the 1:6 ratio of the compost. Cellulose filter obtained from Sigma–Aldrich (Milwaukee, WI) was used as positive control. The reported organic content of cellulose is 42.5%. Haake E52 immersion heat controller was used to keep the oil bath temperature constant at 73.5 °C. Using this oil bath the resulting composting vessel temperature was determined to be 55 ± 3 °C. The tests were performed in three replicates and the results were averaged. The evolved CO₂ was collected in a gradual cylinder filled with saturated Ba(OH)₂ solution (i.e. 0.1 M) and the unreacted solution was neutralized by 0.01 M HCL solution. The normalized CO₂ evolution was calculated according to ASTM D 5338 [50].

Parallel to composting, for disintegration test observations and mechanical investigations, strips of 15 × 2.5 cm² of pure samples and their blends were incubated at the same condition as composted samples.

Tensile tests were carried out in accordance to the ASTM D882 on an Instron (Norwood, MA) 3365 universal testing machine equipped with a 500 N load cell and using a crosshead speed of 5 mm/min.

The SEM micrographs were taken using a Jeol JSM 840 scanning electron microscope at 10–15 kV and samples have been coated with gold beforehand.

3. Results and discussions

3.1. Disintegration tests

Disintegration observation with time of pure and blend samples are depicted in Fig. 1. The results show that the PHB samples disintegrate in the early stages of the test at about 10 days, which is considerably faster than pure PLA as well as their blend with PBAT, which would last unbroken till about 30–45 days of incubation.

The results of PLA disintegration show longer stability compared to published works on thicker samples [42,43,51,52]. The latter would follow the suggested two-step degradation of PLA, which has been proposed by Grizzi et al. and Kale et al. [42,43] The hydrolysis, as Grizzi introduces as the first step, is an autocatalytic step and dependent on the thickness of the samples. Grizzi showed

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