Accelerated weathering studies on the bioplastic, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)

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A B S T R A C T

The effect of accelerated weathering exposure time on the bioplastic, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) was studied. The chemical structure and thermophysical property changes of solvent cast PHBV films were examined by a combination of optical microscopy, size exclusion chromatography, FTIR and ^{1}H NMR spectroscopies, tensile testing, and differential scanning calorimetry (DSC). The exposed PHBV surfaces experienced surface crazing upon weathering. The molar mass of weathered PHBV was shown to decrease due to chain scission which was dominant over the crosslinking reaction mechanism, and compositional analysis showed the polymer degradation was non-random between the hydroxybutyrate-hydroxyvalerate units. The degree of crystallinity for PHBV was shown to increase significantly (by about 20%) upon weathering. Tensile tests showed that the weathered PHBV exhibited reduced ultimate strength and elongation to break, while the Young's modulus increased ascribing to an increase in crystallinity. Different degradation mechanisms (Norrish I/II, radical initiation, crosslinking, and hydrolysis) of PHBV are proposed and confirmed based on the experimental findings. This study provides degradation insight for PHBV exposed to both UV radiation and moisture.

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1. Introduction

Driven by the awareness of developing a sustainable society, biobased plastics (e.g., polyhydroxyalkanoate (PHA), polylactic acid (PLA), polycaprolactone (PCL), and lignocellulosic derived materials) have gained considerable attention over the past decades due to their renewability [1–11]. Of the microbial biosynthesied PHA bioplastic family, poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) are the two most common types produced as bacterial intracellular granules [6,12]. Furthermore, PHA can also be biodegraded readily by microbial hydrolytic enzymes and therefore will not accumulate in the environment [13–15]. The ester bonds (−COO−) of these above mentioned bioplastics are very susceptible to hydrolysis during exposure to various natural environments such as marine and waste environment [6,15,16].

Most of the degradation studies on PHA have focused on the biodegradation behavior of PHB and PHBV when exposed to water [17], soil [13,18,19], waste compost [20], and enzymes [14,21]. These reports show that water plays a key factor during the whole biodegradation process. However, only a few studies have been conducted on weathering exposure, notably UV-A [22,23] and UV-B [24] degradation of PHB and photodegradation of PHBV [25]. For PHB, there are many competing mechanisms (radical initiation, crosslinking, and Norrish types I/II) of photodegradation to UV radiation [22]; whereas the degradation mechanism of aliphatic polyesters PLA and PCL mainly follow Norrish Type II reaction [9,25]. Due to polymer chain cleavage during photodegradation, the molar mass, crystal structure, crystallinity, and thermal/mechanical properties are all influenced [9,26].

Weathering of traditional plastics such as high density polyethylene (HDPE) and polypropylene (PP) based materials have been well studied [27–30]. Exposure to the combination of UV radiation and moisture can result in more significant degradation of material as compared with samples that were exposed to UV radiation alone. Sample surfaces experience dry/wet cyclical erosion with intermittent water spray and crazing forms on the surface which enables UV penetration deeper into the polymer. Furthermore, water spray can wash away the degraded surface layer and expose a clean surface for further degradation.

Due to the limited studies that have been conducted on the

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weathering behavior of PHBV and therefore enhance our understanding how PHBV degrades. The aim of this work was to study the degradation mechanism of high hydroxyvalerate (HV) content PHBV during accelerated weathering. The surface morphology, chemical structure, plus thermal and mechanical properties of the PHBV film were monitored with exposure time.

2. Experimental

2.1. Materials and sample preparation

PHBV was biosynthesized in a 20 L laboratory bioreactor fed a mixture of volatile fatty acids from fermented diary manure by mixed microbial consortia inoculated with activated sludge [12,31]. The bioreactor was aerated and operated as a sequencing batch reactor using a hydraulic and solid retention time of 4 d. The crude PHBV was extracted with $CHCl_3$ from the acetone prewashed lyophilized bacterial biomass at a yield of 39%. The crude PHBV was purified by precipitation in cold petroleum ether (boiling point range 35−60 °C) and used for subsequent experiments. The number- and weight-average molar mass ($M_n = 7.5 \times 10^5$ g/mol and $M_w = 3.7 \times 10^5$ g/mol, respectively) of PHBV were determined by size exclusion chromatography (SEC). The HV mol% was 33% as determined by gas chromatography mass spectroscopy (GCMS) and ^{1}H NMR spectroscopy [12]. The isolated PHBV was dissolved in $CHCl_3$ (15 mg/mL), stirred for 30 min, poured into a Teflon mold to cast the PHBV films (thickness of 70 μm), air-dried, and finally vacuum dried prior to use.

2.2. Accelerated weathering test

Accelerated weathering tests of the PHBV films (10 replicates) were conducted in a xenon-arc weatherometer (Q-Sun Xe-1-S). The films were exposed to a repeated 2 h cycle of radiation followed by 2 h of radiation plus water spray. The average irradiance was 0.70 W/m^2 at 340 nm with a chamber temperature of approximately 70 °C (light step) [32]. The irradiance was measured and monitored regularly, and the bulb was changed periodically to maintain constant irradiance. Samples were collected periodically from 10 specimens randomly for analysis between 0 and 1000 h [27].

2.3. Characterization techniques

2.3.1. Morphological changes

Unweathered controls and weathered PHBV sample surfaces were observed using an Olympus BX51 optical microscope in bright field-reflection mode and images were captured using an Olympus DP70 digital camera.

2.3.2. Size exclusion chromatography (SEC)

The M_n, M_w and polydispersity (M_w/M_n) of PHBV (2 mg/mL in $CHCl_3$) were determined by SEC. Separation was achieved using a Jordi DVB linear mixed bed column (78 mm × 300 mm) at 40 °C on elution with $CHCl_3$ (1 mL/min) and detected with triple detector array (refractive index, Waters model 2478), low- and right-angle laser light scattering, and differential viscometer (Viscotek model 270, Viscotek Corporation). The system was calibrated using a narrow polystyrene standard (Viscotek, M_w = 98 946 g/mol).

The average number of chain scission per macromolecule was estimated using the method described by Sadi et al. [22]:

$$No.of\ scissions = M_n^0 \big/ M_n^t \qquad (1)$$

where M_n^0 and M_n^t are the M_n of unweathered and weathered PHBV after time t (h), respectively.

2.3.3. Monomeric composition by GCMS

PHBV samples were methanolyzed at 100 °C for 4 h in acidified methanol (3% v/v H_2SO_4, 2 mL) and $CHCl_3$ containing benzoic acid as internal standard (2 mL). The methyl ester derivatives were analyzed by GCMS (Finnigan PolarisQ, Thermo Electron Corp.) in positive electron impact mode. Separation was achieved on a ZB1 capillary column (30 m × 0.25 mm Ø, Phenomenex) using a temperature program from 40 °C (2 min) ramped to 200 °C at 5 °C/min. The compounds were confirmed by their retention times and mass spectra. The HV and hydroxybutyrate (HB) mol% was quantified relative to an internal standard and a commercial PHBV standard (22 mol% HV, Tianan, China) with a calibration curve ($R^2 > 0.97$).

2.3.4. FTIR spectroscopy

The surface chemistry of weathered PHBV samples was examined by FTIR spectroscopy using a Nicolet iS5 FTIR spectrometer (Thermo Scientific) with an attenuated total reflection (ATR) iD5 probe (ZnSe). The absorbance spectra of vacuum dried unweathered controls and weathered sample surfaces (in triplicate) were averaged and baseline corrected using Omnic v9.0 software (Thermo Scientific).

For the quantitative analysis, the spectra were normalized and curve-fitted using IGOR Pro 6.03 software (WaveMetrics). The area (A) of each band found by curve fitting was integrated by the software. In order to estimate the crystallinity changes due to weathering, the crystallization index ($I_{C=O}$) was calculated as the ratio of the areas (A) under carbonyl (C=O) bands between 1800 and 1680 cm^{-1} [33−36]:

$$I_{C=O} = A_{1720}/A_{1740} \qquad (2)$$

where A_{1720} and A_{1740} are the areas of the peaks at 1720 (crystalline portion of PHBV) and 1740 cm^{-1} (amorphous portion of PHBV), respectively.

The concentrations of the carbonyl (C=O) and vinyl groups (C=C) present in the WPC were determined using the Beer−Lambert equation with some assumptions [27]:

$$A = \varepsilon bc \qquad (3)$$

where A is the absorbance of the band obtained from FTIR spectra, c is the molar concentration in mol/L (M) relative to the functional group, ε is the molar absorptivity (L/mol/cm), and b is the path length of the sample (i.e., optical path of the beam through the sample, cm). Molar absorptivity ε values used in this study were taken from the literature [37] using model compounds esters (C=O, 1720 cm^{-1}) and vinyl (C=C, 910 cm^{-1}) groups were 590 and 121 L/mol/cm, respectively.

Optical path length b was considered to be the effective path-length (I). Effective path-length can be calculated from the following equation:

$$I = d_p \times N \qquad (4)$$

where d_p is the depth of penetration of the radiation and N represents the number of total internal reflections that occurred in the ATR crystal. However, for the ATR crystal used in this study, N = 1 (single bounce). Therefore, equation (4) can be rewritten into

$$I = d_p \qquad (5)$$

According to Averett [38], I is twice the d_p for a polarized ZnSe ATR crystal. Thus,