POLYMER TESTING

Material properties

Hydrolytic degradation of bio-based polyesters: Effect of pH and time

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ABSTRACT

A hydrolytic degradation study of two bio-based polyesters, poly(trimethylene malonate) (PTM) and poly(trimethylene itaconate) (PTI) with bimodal molecular weight distribution, was performed in aqueous solutions adjusted to pH values from ~5.5 to 11. Final weight loss varied from 20 to 37 wt% for PTM and from 7 to 21 wt% for PTI as a function of degradation time and initial solution pH. Fourier transform infrared (FTIR) spectroscopy was used to monitor ester bond concentration of these bio-plastics, and the molecular weights and polydispersity index were obtained by gel-permeation chromatography (GPC). Solutions with lower initial pH values resulted in lower molecular weights for both PTM and PTI after one week of degradation. Degradation especially affected the amorphous region, leading to an increase in crystallinity of PTI samples.

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1. Introduction

Biodegradation is limited to specific temperatures and moisture, oxygen, and nutrient contents where the responsible enzymes can function [1–5]. Polymers that are classified as being biologically degradable by fungal or bacterial enzymes, such as polylactic acid (PLA) and poly(ε-caprolactone) (PCL), may exhibit no degradation and appear biostable due to the lack of any biological activity in the environment. The incorporation of hydrolytically degradable bonds into the backbone of the polymer allow for an addition degradation route besides biologically degradation. Hydrolytically degradable materials require only the presence of (liquid) water.

Several types of hydrolytically degradable polymers, poly(-anhydrides), poly(orthoesters), poly(depsipeptides), poly(ether esters), and poly(esters) are currently being researched as replacements for non-hydrolytically degradable petroleum-based polymers [6]. Poly(esters) have shown the most promise for commercialization and replacement of petroleum-based polymers with the development of poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and poly(ε-caprolactone) (PCL). In the 1960s and 1970s, PGA was the first bio-compatible and hydrolytically degradable synthetic polymers and was commercialized as dissolvable suture material [7]. This advance spurred research into other biocompatible polymers and into other applications for these polymers. However, performance issues encountered with PLA and PGA are poor thermal stability and brittleness [8,9]. In our previous study, we synthesized novel bio-based polyesters, poly(trimethylene malonate) (PTM) and poly(trimethylene itaconate) (PTI), by following green chemistry principals, and these polyesters belong to the polyhydroxyalkanoates (PHAs) family [10].

In general, molecular weight (Mw) and crystallinity have been shown to have the largest impact on polyester degradation. With increasing crystallinity and Mw, the rate of PLA degradation decreases due to a hindrance in water being able to diffuse into the matrix; therefore, water is not in proximity to the polymer backbone and so hydrolysis is hindered [8,9,11–13]. Excess water forces ester hydrolysis to break ester bonds in acidic conditions that are found in polyesters, such as PLA [14–17]. If the system is basic, the driving force for hydrolytic degradation changes to the formation of stable carboxylate anions. Varying the solution pH in which aliphatic polyesters are laced can have a range of effects on degradation. It is generally agreed that pH affects the rate of degradation of bioplastics [18–20]. For polyesters like PLA and PGA, hydrolytic degradation is considered bulk degradation with two steps. The first step is the uptake of water into the polymer. The second step is the ester cleavage, and diffusion of low Mw products out of the polymer [6,21–23]. If the polymer is sufficiently large that degradation product diffusion is slow, the increased number of end groups leads to auto-catalyzation conditions in which the interior of the polymer degrades at a faster rate than the surface of

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the polymer [23].

High degradation rates, complete degradation or substantial loss of mechanical properties, are desirable in only select applications, such as drug release, sensors, and specialty packaging. Polymers exhibiting a controlled degradation and complete degradation or substantial loss of mechanical properties (dependent on application) between 6 and 36 months could be used in a large number of disposable or short-term use product applications. The working assumption is that if the chemical structure of the polymer can be controlled, then the degradation (rate and total time) can be tailored for specific applications.

In this study, the hydrolytic degradation of these bioplastics with bimodal molecular weight distribution was examined under variable pH conditions for up to 10,000 min. Changes in gravimetric weight, molecular weight, chemical functionality, and thermal properties were monitored by gel-permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC). The effects of Mw distribution on hydrolytic degradation were evaluated.

2. Experimental section

2.1. Materials

The PTM sample used for the degradation study was bulk polymerized from 1,3-propane diol (PDO, 98%, Sigma Aldrich) and malonic acid (MA, 99%, VWR) using $AlCl_3$ catalyst (98%, Sigma Aldrich) with a 100:1 monomer to catalyst ratio at 155 °C for 4 h. With a similar way, the PTI sample was bulk polymerized from 1,3-propanediol (PDO, 98%, Sigma Aldrich) and itaconic acid (IA, 99%, VWR) using $AlCl_3$ catalyst (98%, Sigma Aldrich) with a 100: 1 monomer to catalyst ratio at 155 °C for 16 h. Additional details on the PTM and PTI synthesis and characterization was provided previously [10]. KOH (99%) and Optima tetrahydrofuran (+99.9%) were purchased from Fisher Scientific. All chemicals purchased were used as received without further purification.

2.2. Hydrolytic degradation

PTM was compression molded into a 12 cm × 12 cm × 0.159 cm sheet using a Carver 15 ton floor stand press at 6.9 MPa for 10 min at 30 °C. The sheet was cut into 1 cm × 0.318 cm × 0.318 cm samples, and each sample was placed into individual vials. PTI was ground by hand into a powder using a mortar and pestle until all particles could easily sift through 18 × 18 mesh stainless steel wire cloth. Hydrolysis was performed in DI water and in basic aqueous solutions formed by adjusting the pH of DI water (pH 5.4) to pH 7, 9, and 11 using a concentrated DI-KOH solution. DI water was chosen as a control, and pH 7, 9, and 11 were chosen since bioplastics had faster hydrolysis rates at basic pHs. For the PTM hydrolysis experiment, the samples were initially placed under vacuum at room temperature for 24 h to remove excess water. Vials were then prepared containing one compression molded PTM coupon or 0.75 g of PTI powder along with 10 mL of the aqueous solutions. One set of vials had no liquid added as an 'air' control, to attempt to take into account any changes due to aging alone. All of the sealed sample vials were then placed into a 25 °C water bath for 10, 100, 1000, and 10,000 min. At each pre-designated time, the samples were removed from solution and gently blotted with a KimWipe®. They were then vacuum dried (25 torr) at room temperature for 24 h. All degradation samples were run in triplicate.

The weight change was calculated according to the following equation:

$$weight\ change(\%) = \frac{w_0 - w_t}{w_0} * 100 \tag{1}$$

where w_0 and w_t represent the initial weight and the weight at time t, respectively.

2.3. Characterization

The PTM polymer samples were characterized by attenuated total reflectance (ATR) FTIR spectroscopy at discrete times during the degradation study using a Thermo Electron 6700 instrument (DTGS detector, room temperature, dry air purge, ZnSe crystal with a 60° angle of incidence). The PTI polymer samples were characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Thermo Electron 6700 instrument with a He-Ne laser, liquid nitrogen-cooled MCT-A* detector, and EasyDiff accessory (Pike Technologies) at room temperature using a dry air purge. Samples were mixed with KBr powder at 5 wt% PTI and 100% KBr was used for the sample spectra background. The peaks were fitted with PeakSolve in Thermo Scientific Omnic 8.1.10. Gaussian peaks were fitted at specific wavenumbers to minimize standard error. A peak height ratio (PHR) calculation was used in the quantitative analysis of FTIR spectra. PHR uses the height of the C-C rocking at 1465 cm^{-1} as the denominator and the height of the peak of interest as the numerator to form a ratio. Gel permeation chromatography (GPC) data was collected with a Waters GPC with RI detector, 4E and 5E (polystyrene-divinylbenzene, 4.6 × 300 mm) Styragel® columns, Optima THF as the effluent at 0.3 mL/min, and a ten-point polystyrene calibration. A TA Instruments Q-2000 modulated DSC (mDSC) with a nitrogen purge was used for thermal analysis with the TA Universal Analysis 2000 software (v4.7A). mDSC samples were analyzed from −90 to 250 °C (at 5 °C/min) under 50 mL/min of nitrogen.

3. Results and discussion

3.1. Synthesis and characterization

PTM was produced by the melt polycondensation of PDO with MA. The maximum yield (~78 ± 5 wt%) was obtained at the reaction conditions of 155 °C and 4 h with the product having a bimodal weight average molecular weight of ~63 kDa (with 1.82 PDI and 1.6 wt%) and ~1.8 kDa (with 1.83 PDI and 98.4 wt%). PTM with a glass transition, −57 °C is a linear polymer composed of ester and ether backbone bonds. However, PTI is a branched copolymer that is a rigid semi-crystalline material with possible load bearing application. The maximum yield (78 ± 8 wt%) and ester concentration were obtained at 155 °C and 16 h reaction conditions. For the THF-soluble PTI material, the measured weight average molecular weight was ~51 kDa (with 1.71 PDI and 1.5 wt%) and ~1.4 kDa (with 1.78 PDI and 98.5 wt%), and a cold crystallization temperature was found at ~160 °C.

3.2. Hydrolytic degradation

Degradation of PTM and PTI was carried out in aqueous solutions adjusted by KOH to pH 7, 9, and 11, DI water with an initial pH of 5.4, and a control with no fluid referred to as air at 25 °C for 10, 100, 1000, and 10,000 min. All samples do not show significant weight loss during the first 10 min of degradation, Fig. 1. Even though there is a significant weight loss rate initially, it appears that there is an induction period before degradation products can diffuse out of the polymer and cause a significant change in DI and pH 7's dry weight.