Mechanical Behavior and Anaerobic Biodegradation of a Poly(lactic acid) blend containing a Poly(lactic acid)-co-Poly(glycolic acid) Copolymer

Kosar Samadi, Michelle Francisco, Swati Hegde, Vishal Datta, Carlos Diaz, Thomas Trabold, E. Dell and Christopher L. Lewis

Rochester Institute of Technology, Rochester, NY

Abstract

Poly(lactic acid) (PLA) is arguably the most well-known biodegradable plastic. However, its degradation behavior is far from ideal. The goal of this work is to prepare PLA blends that exhibit accelerated biodegradation performance whilst retaining adequate mechanical properties. To accomplish this a copolymer consisting of poly(L-lactic acid) and poly(glycolic acid) (PGA) structural units was synthesized and subsequently melt blended with a commercially available PLA homopolymer. The anaerobic degradation behavior of the polymer blend was greatly enhanced as a result of the incorporation of 20 wt% of the copolymer. A moderate change in mechanical properties including a 20% reduction in stiffness and strength and an 80% increase in elongation to break was also observed.

Introduction

Polylactic acid (PLA) is a commonly used bioplastic due to its excellent biodegradability and diverse range of applications.[1,2] However, PLA takes a prolonged period to degrade completely. Anaerobic degradation of PLA under mesophilic conditions (35-40°C) has been reported to be extremely slow, while up to 90% degradation has been observed in 60 days under thermophilic (50-60°C) conditions.[2] Several approaches including blending[3] and copolymerization[4] have been suggested in the literature as mechanisms to increase PLA's degradation rate. In another approach, the inclusion of components such as a lactate monomer into PLA polymer could act as a mechanism to aid attachment of microbes to polymer surfaces and hence improve biodegradation.[4] Polyglycolic acid (PGA) is structurally similar to PLA except that it lacks a pendant methyl group in its repeat unit and therefore is more hydrophilic. PGA is receiving increased interest because of its biodegradability and environmentally benign degradation products like glycolic acid, which is a natural plant metabolite.[5] Polylactic-co-glycolic-acid (PLGA) polymers exhibit enhanced biodegradation over both PLA and PGA[6] and therefore are used in a wide range of biomedical applications such as biocompatible tissue scaffolds[7] and drug delivery systems.[8]

In this study, a low molecular weight PLGA copolymer was synthesized and melt blended with a commercially available high molecular weight PLA homopolymer (Figure 1). The mechanical and biodegradation behavior of the blend under thermophilic anaerobic conditions is presented and compared to PLA homopolymer.

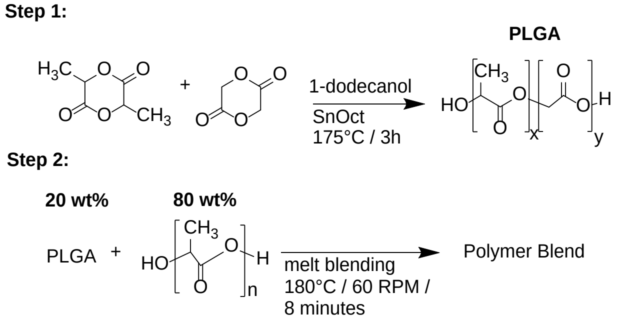

Figure 1. ***Scheme for Preparation of Biodegradable Polymer Blend Examined in this Study.*** *Step #1:* Ring Opening Polymerization (ROP) of L-lactide and glycolide to produce random copolymer bearing approximately 25 mol% glycolic acid. *Step #2:* PLGA melt blended with a commercially available PLA homopolymer.

Experimental

Materials. PLA homopolymer (Ingeo™ Biopolymer 4043D) was supplied by Natureworks LLC (Minnetonka, MN). The PLGA copolymer was synthesized using as-received materials unless otherwise noted. Chloroform (≥99.5%) and anhydrous toluene (99.8%) were obtained from Sigma Aldrich. Tin (II) 2-ethylhexanoate (Total Tin: 28.0 wt%, min) was obtained from Alfa Aesar.

1-dodecanol was obtained from TCI America in a minimum of 99% purity. Methanol was obtained from VWR-BDH in a minimum of 99.8% purity. Lactide monomer (PURALACT L, 99% minimum S/(R+S) chirality) was kindly supplied by Total Corbion PLA (Gorinchem, Netherlands). This pure monomer (assay min 99 %w/w) was supplied in moisture-proof bags and used as-received. Any unused lactide monomer was promptly vacuum sealed in moisture-proof bags and stored at 6°C. Glycolide was obtained from Sigma Aldrich and crystallized three times in anhydrous toluene prior to usage. Any unused monomer was stored under dry nitrogen.

Synthesis. The ring opening polymerization (ROP) of L-lactide and glycolide monomers was performed to produce PLGA copolymer containing both repeat units. The synthetic procedure to prepare the copolymer was based on an approach similar to that outlined by Erbetta et al[9] except that our copolymers were made using L-lactide (instead of D,L lactide). In our work, the molar proportion of lactide to glycolide in the feed was maintained at 75:25. Briefly, L-lactide (11.34 g, 78.68 mmol) and glycolide (3.05 g, 26.28 mmol) were added to a dried 3-neck round bottom flask, sealed and subsequently purged with dried nitrogen. 2.01 mg of 1-dodecanol (0.01 mmol) and 4.3 mg of tin (II) 2-ethylhexanoate (0.01 mmol) were dissolved in 1 ml of anhydrous toluene and injected into the flask through a rubber septum. The flask was placed under vacuum and then lowered into a silicon oil bath set at 175°C for 3 hours. The product was purified by dissolving in chloroform followed by precipitation in methanol under mechanical stirring (3x). The product was collected using vacuum filtration. The final product was collected in the form of a white powder (yield 65%). The chemical composition of the copolymer was determined using ^{1}H-NMR (Bruker DRX-300). The weight average molecular weight (M_w) was determined to be 15,600 g/mol with a polydispersity index of 1.8 as measured by size exclusion chromatography (Agilent 1100 series equipped with G1362A RID detector and Zorbax PSM 60S and PSM 1000S GPC columns) using THF as an eluent (30°C) and calibrated using polystyrene standards. The material was determined to be amorphous as indicated by the absence of a melting peak and the glass transition temperature (T_g) was determined to be approximately 38°C (TA Instruments Q100 Differential Scanning Calorimeter (DSC), heat/cool/heat cycle over range 0-200°C, 10°C min^{-1}).

Sample preparation. In this study, the PLA/PLGA blend was prepared by melt blending followed by compression molding. First, a dry mix consisting of 20 wt% PLGA and 80 wt% PLA was compounded using a melt mixer (CWB Brabender Intelli-torque Plasticorder torque rheometer with a 60cc 3-piece mixing head). The temperature and screw speed were maintained at 180 °C and 60 rpm, respectively, for 8 minutes. This time was found to be sufficient to reach a plateau in the torque. Materials were dried in a convection oven for 24 hours at 50°C prior to the mixing step. The blend was then compressed through a hand-operated hot press (12 ton hydraulic manual Carver laboratory) at a load of about 3 tons and temperature of 210 °C. Cooling was assisted by running cold water through the press platens. Finally, sheets with a nominal thickness of 0.3 mm were obtained using Teflon sheets and cut using an ASTM D638 Type 5 dog-bone shaped sample cutting die.

Mechanical Characterization. Tensile testing of the blend was carried out using an Instron Universal Testing Machine model 5567 at a crosshead speed of 12.5 mm/min. At least five specimens of each sample were tested according to ASTM D638. Samples were conditioned at room temperature for at least 24 hours prior to mechanical testing.

Anaerobic Biodegradation. PLA and the PLA/PLGA blend were cut into approximately 1 cm square pieces to obtain uniform particle size for degradation. The total solids (TS) and volatile solids (VS) content of the samples were determined according to a standard protocol.[10]

The original protocol described by Owen et al.[11] was used to test biochemical methane potential (BMP). The inoculum originated from the effluent of a commercial digester that co-digests industrial food waste with cow manure. The effluent was separately pre-incubated in a BOD incubator for 7-9 days at 52°C to develop the inoculum for thermophilic digestion experiments. The samples for degradation studies were prepared to obtain an inoculum-to-substrate ratio of 2 (g VS inoculum: g VS substrate added). An Automated Methane Potential Testing System (AMPTS II, Bioprocess Control, Lund, Sweden) was used to perform BMP assays. The AMPTS II system continuously records the biomethane production at regular time intervals (Figure 2). The reactors were incubated at 52 ± 2°C, with mixing at 160 rpm, with an 'ON' cycle of 10 seconds and 'OFF' cycle of 50 seconds. Commercial cellulose powder (Sigma-Aldrich) was used as a positive control sample. Cellulose is the most widely accepted standard in the literature for anaerobic degradation because its degradation kinetics are very well studied. Before starting the data acquisition, the reactors were purged with nitrogen gas to create an anaerobic environment by displacing residual oxygen. Methane production was recorded on a daily basis using the online flow cell detector array shown in Figure 2.

Biomethane potential (BMP) is defined as the volume of methane produced per unit mass of volatile solids (VS) added in a defined period. Volatile solids (VS) represent the biodegradable fraction of a material and varies for different materials. Therefore, BMP is used to normalize methane production for comparison purposes.

$$\text{BMP}\left(\frac{\text{mLCH4}}{\text{gVS}}\right) = \frac{m_t - m_b}{VS_{total}} \qquad (1.)$$

In equation 1, m_t and m_b are the volume of methane (expressed in mL) produced by the test and blank respectively and VS_{total} is the total grams of volatile solids added.

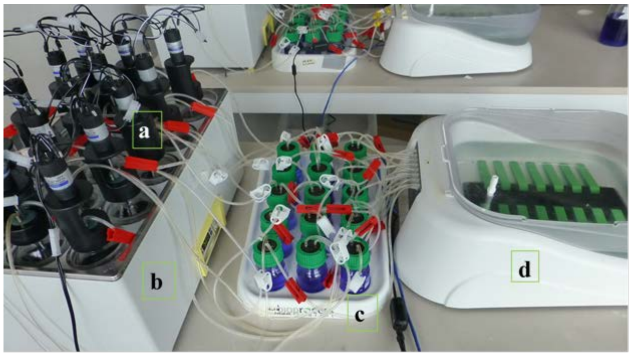

Figure 2. ***AMPTSII system used in studying degradation of bioplastic materials under anaerobic conditions.*** A water bath incubator (b) set at the desired temperature helps to maintain the optimum temperature of reactors (a). A carbon dioxide fixing unit (c) connects to the biogas outlet tubing of the reactors. Biogas mainly contains methane and CO_2; the fixing unit absorbs CO_2 from the biogas and methane passes through a flow cell detector (d). The flow cell detector continuously records methane production at regular intervals.

Discussion

PLA homopolymer is commercially available over a wide range of viscosities and in both amorphous and semi crystalline versions. The PLA compound chosen for this study (Natureworks 4043D) is semi-crystalline owing to its relatively low D-isomer content (~2%) and is marketed for 3D printing and film applications.[12]

It is well-known that the hydrolysis and in-vivo degradation of PLGA random copolymers can be manipulated by altering comonomer content, polymer molecular weight and stereochemistry of the lactide monomer.[13] Many commercially available PLGA copolymers contain both D- and L-isomers and are therefore amorphous except at high glycolic acid contents.[14] On the other hand, PLGA copolymers based on L-lactide are semi-crystalline at concentrations up to ~20mol% glycolide content.[15] We elected to synthesize our own PLGA copolymer based on L-lactide units as it enables control over important variables such as polymer crystallinity and hydrophobicity. This level of control over the copolymer, along with the blending ratio, is anticipated to enable greater tuning of the mechanical, thermal and degradation behavior of the blend.

In this study a low molecular weight copolymer bearing nearly the maximal concentration of L-lactide units whilst still obtaining an amorphous material was prepared. Figure 3 shows the ^{1}H-NMR (solvent: $CDCl_3$) for the PLGA copolymer. As shown, peaks associated with both PLA and PGA were observed. These results indicate approximately 27% incorporation of glycolide monomer which is in good agreement with the 25% feed composition. The reactivity of the glycolide monomer is known to be greater than that of the lactide monomer which may explain the slightly higher concentration of PGA units in the final copolymer.[15]

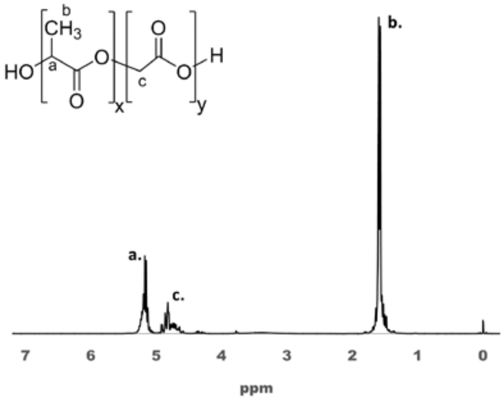

Figure 3. ***Nuclear magnetic resonance (^{1}H-NMR) of PLGA copolymer.*** Proton NMR spectroscopy indicates successful incorporation of both lactide and glycolide monomers. Results indicate incorporation of approximately 27mol% glycolide monomer which agrees well with reactant feed ratios.

Representative mechanical behavior of the polymer blend is presented in Table 1 alongside that of PLA homopolymer. The tensile properties of pure PLA are comparable to that reported by other investigators.[16-18] The incorporation of 20 wt% amorphous PLGA copolymer resulted in a decrease in stiffness and tensile strength of about 20% and an increase in ductility (~80% increase in breaking strain).

Table 1: ***Summary of Mechanical Behavior of PLA and PLA-PLGA blend.***

Material	Young's Modulus (GPa)	Breaking Stress (MPa)	Breaking Strain (%)
PLA	2.7	67.6	6.4
PLA/PLGA Blend	2.1	56.2	11.6

Anaerobic degradation of PLA has been studied previously[2,19], but to the best of our knowledge there are no known studies on the anaerobic degradation of PLGA. The degradation rate of the blend was higher than the PLA homopolymer, indicating a synergistic effect. A biomethane potential of 275 mL/gVS was observed for the blend containing PLGA copolymer over 26 days whereas the PLA homopolymer resulted in a BMP of 187 mL/gVS over that same time frame (Figure 4). The volatile solid content for PLA and PLGA is 100%, and therefore 1g volatile solids are equivalent to 1g bioplastic material. The blend started to degrade faster than the PLA homopolymer and biomethane production was observed by the 2nd day. As suspected, PLA homopolymer exhibited a lag phase (5 days) before any biomethane production was observed.

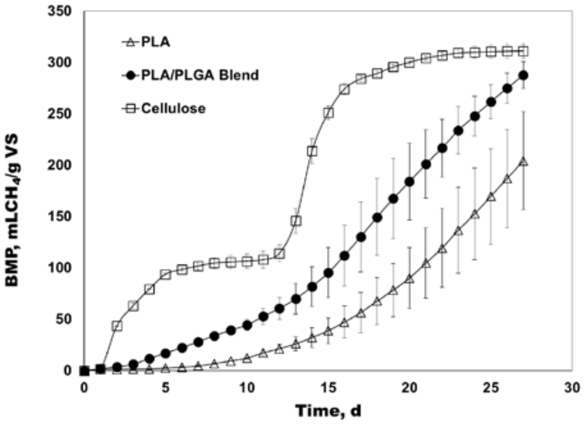

Figure 4. ***Daily biomethane potential normalized to volatile solid content.*** As shown, the PLA-PLGA blend exhibits improved degradation as compared to both PLA and commercial cellulose powder.

As anticipated, the presence of the comonomer unit exhibits a predictable change in the thermal properties of the copolymer. Whereas the homopolymer is reported by the manufacturer as being semicrystalline with T_g=55-60°C and T_m=145-160°C, the PLGA copolyester was determined to be amorphous with T_g~38°C. This was taken to indicate that the placement of PGA units are sufficiently random to suppress crystallinity at this concentration. This is in good agreement with that reported by Gilding and Reed in their exhaustive compositional study of PLGA copolyesters.[15] As such, it is suspected that our polymer blend exhibited enhanced degradation kinetics when subjected to anaerobic degradation as a result of the inclusion of our PLGA copolyester due to its fully amorphous structure, lower T_g and enhanced hydrophilicity.

Conclusion

In this work, we have shown that blending PLA with 20 wt% of a PLGA random copolymer comprised of ~25 mol% glycolic acid units yields a material that exhibits somewhat similar mechanical properties to PLA but with enhanced biodegradation characteristics under thermophilic, anaerobic conditions. Not surprisingly, the PLGA copolymer is amorphous and it is likely that this, along with the increased hydrophilicity and reduced T_g, gives rise to the enhanced degradation of the blend. Moreover, a reduction in stiffness and strength coupled with an increase in elongation at break was observed and future work will be aimed to better understand this result.

While this preliminary study focused on a blend containing a copolymer of one composition our ability to tailor the PLGA copolymer grants us with several degrees of freedom with respect to comonomer content, molecular weight, and PLA isomer type. Moreover, it is anticipated that altering the blend ratio will provide yet another opportunity for property modification. Future work is intended to understand how changing these variables influences the blend morphology, mechanical, thermal and biodegradation behavior of blends under anaerobic conditions.

This work is part of a greater effort to understand the influence of adding a fast-degrading PLGA copolymer to a commercially available PLA. Such an approach, where PLGA copolymers are incorporated as an additive, would enable the tuning of both mechanical properties and biodegradation rate to meet the needs for a particular application. Ideally these materials would be used as part of a larger strategy where difficult to separate, mixed waste streams such as paper, food and plastics are anaerobically co-digested.

Support: Funding provided by the NYS Pollution Prevention Institute through a grant from the NYS Department of Environmental Conservation. Any opinions, findings, conclusions or recommendations expressed are those of the authors and do not necessarily reflect the views of the Department of Environmental Conservation.

References

1. J. J. Kolstad, E. T. Vink, B. De Wilde, L. Debeer, *Polymer Degradation and Stability* **2012**, 97, 1131-1141.

2. H. Yagi, F. Ninomiya, M. Funabashi, M. Kunioka, *International journal of molecular sciences* **2009**, 10, 3824-3835.

3. Y. Tokiwa, B. P. Calabia, C. U. Ugwu, S. Aiba, *International journal of molecular sciences* **2009**, 10, 3722-3742.

4. J. C. Lee, J. H. Moon, J.-H. Jeong, M. Y. Kim, B. M. Kim, M.-C. Choi, J. R. Kim, C.-S. Ha, *Macromolecular Research* **2016**, 24, 741-747.

5. E. Göktürk, A. G. Pemba, S. A. Miller, *Polymer Chemistry* **2015**, 6, 3918-3925.

6. R. A. Miller, J. M. Brady, D. E. Cutright, *Journal of Biomedical Materials Research Part A* **1977**, 11, 711-719.

7. A. Shibata, S. Yada, M. Terakawa, *Scientific reports* **2016**, 6, 27884.

8. H. K. Makadia, S. J. Siegel, *Polymers* **2011**, 3, 1377-1397.

9. C. D. A. C. Erbetta, R. J. Alves, J. M. Resende, R. F. de Souza Freitas, R. G. de Sousa, *Journal of Biomaterials and Nanobiotechnology* **2012**, 3, 208.

10. U.S. Environmental Protection Agency, "METHOD 1684: Total, Fixed, and Volatile Solids in Water, Solids, and Biosolids," *EPA-821-R-01-015*, 2001. [Online]. Available: https://www.epa.gov/sites/production/files/2015-07/documents/method_1684_volatile_solids_jana_2001.pdf.

11. W. Owen, D. Stuckey, J. Healy, L. Young, P. McCarty, *Water research* **1979**, 13, 485-492.

12. J. Mulligan, M. Cakmak, *Macromolecules* **2005**, 38, 2333-2344.

13. F. Alexis, *Polymer International* **2005**, 54, 36-46.

14. K. Avgoustakis, *Encyclopedia of biomaterials and biomedical engineering. New York: Informa Healthcare USA, Inc* **2008**, 2259-2269.

15. D. Gilding, A. Reed, *Polymer* **1979**, 20, 1459-1464.

16. K. Chavalitpanya, S. Phattanarudee, *Energy Procedia* **2013**, 34, 542-548.

17. C. A. Diaz, H. Y. Pao, S. Kim, *Journal of Applied Packaging Research* **2016**, 8, 4.

18. A. López-Rubio, J. M. Lagaron, *Polymer Degradation and Stability* **2010**, 95, 2162-2168.

19. P. Šmejkalová, V. Kužníková, J. Merna, S. Hermanová, *Water Science and Technology* **2016**, 73, 2386-2393.