



Recycling PLA to multifunctional oligomeric compatibilizers for PLA/starch composites



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ABSTRACT

Simple one-pot valorization of poly(lactic acid) (PLA) to green additives was demonstrated. PLA was thermally recycled in the presence of polyols, which accelerated the degradation process by reacting with PLA chains. As a result low molecular weight oligomers with polyols end-groups were formed. The reaction between PLA and multifunctional alcohols *i.e.* glycerol, sorbitol, glucose and starch were confirmed by FTIR, ¹H NMR, SEC and MALDI-MS. The resulting amphiphilic products were evaluated as compatibilizer candidates for PLA/starch blends. Multiple techniques demonstrated that the obtained oligomers strengthened the interfacial adhesion and improved the compatibility and flexibility of extruded and melt-blended PLA/starch composites. The developed one-pot procedure required no solvent or catalyst offering good possibilities for up-scaling. It was, thus, demonstrated that PLA can be recycled to low molecular weight compatibilizers by simple process of thermal heating in the presence of polyols. This provides profound promise for retaining the material value of old PLA products at the same time as biobased additives are produced.

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1. Introduction

Waste recycling is an important issue for building a sustainable or closed-loop society. Even though we are advancing in recycling and reusing, there is still much place for improvement, especially considering the growing pressure of environmental safety and limited resources on our planet. It is possible to derive more value from waste products that were previously considered useless by leading these waste products back into the loop [1].

Poly(lactic acid) can be derived from agriculture resources and it is among the most promising biobased plastics for packaging and other short term applications. The performances of PLA are in many cases comparable to those of synthetic polymers from fossil fuels [2,3]. How-

ever, PLA is more expensive for disposable or short term applications. It can degrade rather rapidly in suitable environment and PLA products can be biologically recycled [4,5]. However, in many cases it would be beneficial to retain the value by material recycling. Methods for PLA recycling at a temperature higher than 200 °C, *e.g.*, by pyrolysis [6] and hydrolysis in water [7] have been studied. Various types of products, *e.g.* cyclic or linear oligomers, are obtained depending on the experimental conditions. Oligolactic acid, as an example, could be produced under controlled heating conditions [8].

Starch, an inexpensive natural biopolymer, is a strong candidate for preparation of PLA biocomposites to reduce the product cost while maintaining the biodegradability [9,10]. However, this approach generally results in poor interfacial adhesion between hydrophobic PLA and hydrophilic starch granules [11]. The mechanical properties are also significantly reduced with increasing starch content [12,13]. Efforts such as surface modification of starch

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[14–17], or use of compatibilizers or coupling agents [10,18–20] have been made to both improve the compatibility between PLA and starch, and the performance of final PLA/starch composites. Development of green and safe compatibilizers to improve the performance of PLA/starch composite is highly desirable to maintain the green and environmentally friendly nature of PLA/starch blends.

Lactic acid oligomers or oligolactide have been shown to function well as polylactide plasticizers [21–23]. They have the additional advantage of possessing repeating units identical to the PLA chain, and thus they will not lead to any new migrants. Biobased polyols such as glycerol, sorbitol and glucose are compatible with starch and have been proven as effective plasticizers for starch [24–29]. They are also nontoxic and all of them are allowed as food additives.

We hypothesized that polyol ended oligolactic acid additives could be prepared by subjecting PLA to thermal degradative conditions in the presence of glycerol, sorbitol, glucose or starch. The obtained amphiphilic polyol ended oligolactic acids could improve the interfacial adhesions in PLA/starch composites as the oligolactic acid moiety is miscible with PLA, while the hydrophilic polyol end is compatible with the starch component. This would offer an excellent route to biobased compatibilizers through bioplastic recycling.

2. Materials and experimental

2.1. Materials

Poly lactide was NatureWorks PLA (5200D). Glycerol was supplied by VWR International (Leuven, Belgium). Sorbitol and α -D-glucose (anhydrous, 96%) were obtained from Sigma–Aldrich Chemie GmbH (Steinheim, Germany) and used without further purification. Tapioca starch was bought from Ibu Tani, cap anak no. 1, (Bogor, Indonesia). Dichloromethane (HPLC grade) and methanol (HPLC grade) were obtained from Fisher Scientific. 2,5-Dihydroxybenzoic acid (DHB) was purchased from Fluka, (Buchs, Switzerland).

2.2. Synthesis of PLA with multiple hydroxyl end groups

Oligomeric PLA with multiple hydroxyl terminal groups was produced through transesterification reaction between NatureWorks PLA and multifunctional alcohols. 10 g of PLA and a polyol (glycerol (1.068 g), sorbitol (2.108 g), glucose (2.108 g) or starch (2.108 g)) were added to a 100 mL round bottomed flask equipped with a magnetic stirrer. The mixtures were heated to 180 °C for 2 h until melt and then the reactions were continued at 170 °C for 14 h under a nitrogen atmosphere and with constant stirring. After this, the mixtures were again heated to 180 °C and stirred for 2 h. The produced hydroxyl ended PLAs were named as PLA-GLY, PLA-SB, PLA-GLU and PLA-ST. NatureWorks PLA alone was also thermally treated under the same conditions as above for comparison and labeled as PLA-DEG for degraded PLA. Another degraded glucose ended PLA of lower molecular weight (PLA-GLU-

2) was also produced in order to investigate the effect of molecular weight on the compatibilization efficiency in the PLA/starch composites. This compound was produced in the same way but the reaction time was prolonged by another 3 h at 170 °C. All the resulting PLA degradation products were then dissolved in dichloromethane and precipitated by methanol to purify them. The precipitates were then dried under vacuum.

2.3. Preparation of PLA/starch composites

NatureWorks PLA pellets, PLA-DEG and the synthesized hydroxyl group end functionalized PLAs compatibilizers (PLA-GLY, PLA-SB, PLA-GLU, PLA-GLU-2 and PLA-ST) were milled into powder with high speed mixing. Starch was dried in an oven at 135 °C for 2 h before mixing. PLA/starch composites with different compatibilizers were prepared by mixing the three component powders and then feeding the mixtures into a twin-screw mini-extruder (DSM Xplore 15 micro-compounder, model 2005) at 170 °C 100 rpm for 4 min. The composition ratio of PLA/compatibilizers/starch in the powder mixture was 50/10/40% (w/w). The powder mixture was then shaken in a PP tube for 1 h to get it thoroughly mixed. The prepared composites include PLA/PLA-DEG/starch, PLA/PLA-GLY/starch, PLA/PLA-SB/starch, PLA/PLA-GLU/starch, PLA/PLA-GLU-2/starch, and PLA/PLA-ST/starch. Pure PLA/starch composite (60/40% w/w) without additives was also prepared for comparison. In addition a blend with gelatinized tapioca starch was prepared. Starch was first gelatinized in water at 80 °C and then decanted on a clean petri dish to form a thermoplastic starch film (TPS). The film was dried at room temperature for 7 days and then another 2 days in vacuum oven. It was then cut into small pieces and milled to powder for mixing with PLA-GLY and PLA to extrude a PLA/PLA-GLY/TPS blend. The extruded strips were then pressed into 100 × 100 × 0.5 mm³ sheets using a hot press (Fontijne Press) and cut into tensile bars with 50 mm in length and 5 mm in width. All the samples were stored in desiccator at room temperature until further testing.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of PLA-DEG and multiple hydroxyl group ended PLAs *i.e.* PLA-GLY, PLA-SB, PLA-GLU and PLA-ST were recorded by Perkin Elmer Spectrum 2000 FTIR spectrometer (Nowwalk, CT) equipped with a single reflection attenuated total reflectance (ATR) accessory (golden gate) from Graseby Specac (Kent UK). Spectra were scanned at 2 cm⁻¹ resolution in the 4000–600 cm⁻¹ interval.

2.5. Nuclear Magnetic Resonance (NMR)

PLA, PLA-GLY, PLA-SB, PLA-GLU and PLA-ST were analyzed by Bruker Avance 400 Fourier transform nuclear magnetic resonance spectrometer (FT-NMR) operating at 400 MHz (¹H NMR). The temperature was 25 °C and deuterated chloroform (CDCl₃) was used as a solvent. 10–20 mg of each sample was dissolved in 0.5 mL solvent.

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