Polymer Degradation and Stability 95 (2010) 1387–1393

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Chemical recycling of poly(lactic acid)-based polymer blends using environmentally benign catalysts

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ARTICLE INFO

Article history:
Received 14 December 2009
Received in revised form
15 January 2010
Accepted 15 January 2010
Available online 25 January 2010

Keywords:
Chemical recycling
Polymer blends
Lipase
Montmorillonite
Poly(L-lactic acid)
Polyethylene

ABSTRACT

Typical poly(L-lactic acid) (PLLA)-based polymer blends, PLLA/polyethylene (PE) and PLLA/poly(butylene succinate) (PBS), were degraded into each repolymerizable oligomer using environmentally benign catalysts, clay catalysts and enzymes, with the objective of developing a selective chemical recycling process. Two routes to selective chemical recycling of PLLA/PE blend were tested. One is the direct separation of PLLA and PE first by their different solubilities in toluene, followed by the chemical recycling of PLLA using montmorillonite K5 (MK5). The other is the selective degradation of PLLA in the PLLA/PE blend by MK5 in a toluene solution at 100 °C for 1 h forming the LA oligomer with a molecular weight of $M_n = 200–300$ g/mol, which is the best M_n for repolymerization. Thus regenerated PLLA had a M_w of greater than 100,000 g/mol. The PE remained unchanged and was quantitatively recovered by the reprecipitation method for material recycling. In a similar procedure, chemical recycling of PLLA/PBS blend was also carried out and compared by two routes. One is the direct separation of PLLA and PBS by solubility in toluene. The other route is the sequential degradation of PLLA/PBS blend using a lipase first to degrade PBS into cyclic oligomer, which was then repolymerized to produce a PBS. Next, PLLA was degraded into repolymerizable LA oligomer by MK5. The former procedure was carried out using a single solvent; however, the latter required mixed solvents, which decreased the efficient recycling use of solvents.

1. Introduction

Poly(L-lactic acid) (PLLA) is a compostable and commodity plastic and has been highlighted as a bio-based and hard-type plastic because of its availability from agricultural renewable resources. Recently, the petroleum-derived biodegradable and soft-type plastic, poly(butylene succinate) (PBS), has been produced using succinic acid and butane-1,4-diol. Succinic acid is produced by a fermentation process and butane-1,4-diol is produced by some biological processes, such as hydrogenation of succinic acid and chemical derivation of furfural produced by the pyrolysis of cellulose. Thus, PBS can be regarded as a potentially bio-based plastic. Both PLLA and PBS show characteristic physicochemical properties as plastics, used both alone and as a polymer blend. Typical examples are PLLA/polyethylene (PE) and PLLA/PBS blends. With PLLA and PBS, carbon dioxide is removed from the atmosphere when growing the feedstock crop, and returned to the Earth when such bio-based plastics are degraded and mineralized. However, their production and processing require a considerable amount of energy, thus even biodegradable and bio-based plastics should be recycled as much as possible. With repetitive chemical recycling, production costs and energy will be reduced and a significant amount of bio-based plastics will be accumulated in our society, thus contributing to the establishment of a sustainable chemical industry. From the standpoint of sustainable chemical recycling, biodegradable polyesters show excellent properties, such as enzymatic degradability and hydrolytic degradability. These properties can be applicable for sustainable chemical recycling processes, degradation and repolymerization. Kobayashi et al. and Matsumura et al. reported the enzymatic hydrolytic degradation of aliphatic polyesters in organic solvents. The degradation of polycaprolactone took place using lipase CA as a catalyst in toluene at 60 °C to produce an enzymatically repolymerizable oligomer with a molecular weight of less than 500 [1,2].

The chemical recycling of PLLA has been extensively studied with respect to the thermal degradation to lactide [3–5], alkaline hydrolysis and hydrothermal depolymerization into the lactic acid monomer [6]. Thermal degradation and hydrothermal depolymerization generally require a temperature above 200 °C, thus consuming a considerable amount of energy and often causing

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doi:10.1016/j.polymdegradstab.2010.01.019

isomerization. We previously reported the degradation of PLLA into repolymerizable oligomers using a solid acid, montmorillonite K10 (MK10) [7]. Recently, we found that the MK5 was more active for the hydrolytic degradation of PLLA when compared to MK10 [8]. We also reported that PBS was degraded into repolymerizable cyclic butylene succinate (BS) oligomers by lipase CA [8–10]. Furthermore, we reported the sequential degradation of PLLA/PBS blend by a lipase and MK5 using mixed solvents [8]. In a practical application of such recycling system, direct separation of two polyesters using a single solvent may be effective. For the practical use of bio-based plastics, polymer blends may become important tools in order to obtain the desired physicochemical and mechanical properties. Until now, polymer blends have only been recycled for material recycling. The direct and selective chemical recycling of a polymer blend has not yet been extensively studied. Therefore, developments for sustainable and selective chemical recycling for such polymer blends will now be needed.

In this report, typical PLLA-based polymer blends, PLLA/PE and PLLA/PBS, were evaluated with respect to direct and selective chemical recycling. Each polymer component of PLLA/PE and PLLA/PBS was separately recycled using the environmentally benign catalysts, MK5 and lipase CA, with the objective of developing a repetitive chemical recycling of PLLA-based plastics.

2. Experimental

2.1. Materials and measurements

PLLA with a $M_w = 151{,}000$ g/mol was purchased from Sigma–Aldrich Corp. (St. Louis, MO, USA). The polymer was purified by the reprecipitation method using chloroform as a solvent and reprecipitated by methanol. High-density polyethylene (HDPE, $M_w = 125{,}000$) and low-density polyethylene (LDPE, $M_w = 50{,}000$ g/mol) were purchased from Acros Organics (Geel, Belgium). Ethylene-glycidyl methacrylate (E-GMA) copolymer (Bondfast®, Sumitomo Chemical Co., Ltd.) was used as a compatibilizer. Commercially available PE and E-GMA copolymers were each dissolved in toluene at 100 °C and stirred 30 min at room temperature to precipitate the polymer. The soluble oligomeric fraction was removed by filtration to remove any low-molecular-weight fractions. PBS with a $M_w = 110{,}000$ g/mol was supplied by Showa Highpolymer Co., Ltd. (Tokyo, Japan). Immobilized lipase from *Candida antarctica* [lipase CA: Novozym 435 (triacylglycerol hydrolase + carboxylesterase) having 10,000 PLU/g (propyl laurate units: lipase activity based on ester synthesis)] was supplied by Novozymes Japan, Ltd. (Chiba, Japan). The enzyme was dried under vacuum over P_2O_5 at 25 °C for 2 h before use. Montmorillonite K5 (MK5) was purchased from Fluka Chemie GmbH (Germany). Molecular sieves 4A were purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan), and were dried at 150 °C for 2 h before use.

A typical PLLA/PE blend was prepared by mixing the same weight of PLLA, HDPE and LDPE in an *o*-xylene solution. In this report, a mixture of HDPE and LDPE (1:1, wt/wt) was used as a PE sample. PLLA (5.0 g), HDPE (5.0 g) and LDPE (5.0 g) were dissolved in *o*-xylene (100 mL) at 130 °C for 30 min, then the solvent was evaporated using a rotary evaporator to obtain a film-like polymer blend. In a similar way, a polymer blend comprised of PLLA and PBS was prepared by mixing chloroform solutions of PLLA and PBS. The polymer blends were dried in vacuo at 60 °C for 12 h before use.

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) for the polymers were measured by size exclusion chromatography (SEC) using SEC columns (Shodex K-804L + K-800D, Showa Denko Co., Ltd., Tokyo, Japan) with a refractive index detector. Chloroform was used as the eluent at 1.0 mL/min. The SEC system was calibrated with polystyrene standards having a narrow molecular weight distribution. The molecular weight was also measured by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) with a Bruker Ultraflex mass spectrometer equipped with a nitrogen laser. The detection was in the reflectron mode.

The chirality of lactic acid was measured by HPLC using a chiral HPLC column [ChiralPak MA(+), Daicel Chemical Industries, Ltd., Osaka, Japan] with a UV detector (254 nm). 2 mM $CuSO_4$ was used as the eluent. ^1H NMR spectra were recorded with a JEOL Model Lambda 300 spectrometer (JEOL, Ltd., Tokyo, Japan) operating at 300 and 75 MHz, respectively.

2.2. General degradation of PLLA blend and repolymerization procedures

PLLA or PLLA/PE blend was dissolved in toluene and MK5 was added and then stirred. After the reaction, the reaction mixture was poured into acetonitrile with stirring, and the precipitated PE and insoluble MK5 were collected by filtration. The filtrate was evaporated to obtain the lactic acid (LA) oligomer as the degradation product. The LA oligomer was analyzed by ^1H NMR, SEC and MALDI-TOF MS. The M_n of the LA oligomer was calculated by the ratios of the two ^1H NMR peak areas of the terminal hydroxy methine (δ 4.4) and inner methine (δ 5.2) groups [11].

LA oligomer: ^1H NMR (300 MHz, $CDCl_3$): δ 1.58–1.66 (3H, d, $J = 7.0$, CH_3), 4.38 (1H, q, $J = 6.6$, C*H*OH), 5.16 (1H, m, CH_3CH).

The general repolymerization procedure of LA oligomer was carried out using $SnCl_2$/*p*-toluenesulfonic acid (*p*-TSA) essentially according to the method by Fukushima et al. [12]. 800 mg of the LA oligomer was polymerized in a melt using 0.5% $SnCl_2$/*p*-TSA (molar ratio 1:1) at 175 °C for 6 h at 10 mmHg. The solidified reactants were then granulated and further reacted for crystallization at 105 °C for 2 h at 3 mmHg and finally at 150 °C for 20 h at 3 mmHg. After the reaction, the crude polymer was dissolved in chloroform (0.2 mL) and reprecipitated by methanol (30 mL) to give PLLA with a M_W of 173,000 g/mol and $M_W/M_n = 1.7$ with a 67% yield.

PLLA: ^1H NMR (300 MHz, $CDCl_3$): δ 1.58–1.66 (3H, d, $J = 7.0$, CH_3), 5.16 (1H, q, $J = 6.6$, C*H*).

2.3. Sequential degradation of the PLLA/PBS blend by lipase and MK5

A typical procedure for the degradation of PBS in the PLLA/PBS blend using lipase CA was carried out according to our previous report [8]. The PLLA/PBS blend (2.0 g) was dissolved in toluene (440 mL) and lipase CA (3.0 g) was added and stirred at 100 °C for 24 h. After the reaction, the reaction mixture was diluted with chloroform and the insoluble lipase CA was removed by filtration. The filtrate was evaporated, and the residue was dissolved in chloroform and then slowly added to methanol with stirring for the precipitation of PLLA. The cyclic BS oligomer was obtained by the evaporation of the filtrate.

Cyclic BS oligomer: ^1H-NMR (300 MHz, $CDCl_3$): δ 1.58–1.80 (4H, m, $-OCH_2$ C*H*$_2$), 2.55–2.71 (4H, m, $-OOCCH_2CH_2COO-$), 4.04–4.24 (4H, m, $-CH_2O-$).

The obtained cyclic BS oligomer was subjected to ring-opening polymerization by lipase CA according to the method described in a previous report [8]. The polymerization was carried out in a vial with molecular sieves 4A placed at the top of the vial. A mixture of the cyclic oligomer with a M_W of 300 g/mol (30 mg), lipase CA (12 mg) and toluene (0.6 mL) was stirred at 100 °C for 24 h. After the reaction, the reaction mixture was dissolved in chloroform, and the insoluble enzyme was removed by filtration. The solvent was then evaporated under reduced pressure to quantitatively obtain PBS with a M_W of 68,000 g/mol.