



Post-polymerization modification of poly(lactic acid) via radical grafting with itaconic anhydride

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ABSTRACT

Poly(lactic acid) (PLA) was functionalized via radical grafting with itaconic anhydride (IAH) in melt. Reaction was initiated using 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane (L101). Experiments were achieved in order to determine the relationship between reaction conditions and grafting yield, whereas different concentrations of IAH (0.5–10 wt%) and L101 (0.1–2 wt%) were used for reaction. Reaction temperature 190 °C (calculated according to Arrhenius equation) guaranteed complete decomposition of L101 upon reaction period 6 min. Grafted IAH onto PLA backbone was proved by infrared spectroscopy (FTIR). Structure analysis also proved IAH isomerization to citraconic anhydride (CAH) which affects monomer reactivity at processing temperature. Homopolymerization of IAH was predicted regarding thermal stability of extracted byproducts compared to poly(itaconic anhydride) (PIAH) prepared by radical polymerization in solution. Acid–base titration proved that amount of grafted IAH increases with increasing IAH and L101 concentrations. However, increasing IAH and L101 concentrations lead to higher extent of undesired reactions which were detected by melt flow rate measuring (MFR).

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1. Introduction

PLA is biodegradable, thermoplastic, aliphatic polyester produced from renewable resources, e.g. from corn or sugar cane [1,2]. Monomer (lactic acid) is produced by starch fermentation. Synthetic PLA is obtained by ring opening polymerization of lactide (ROP) which is extensively studied [1,3,4]. Hydrolytic scission represents reversible depolymerization process which allows obtaining lactic acid which can be used for synthesis of high-molecular PLA product [1]. This is the main reason of scientist's interest in PLA which could be alternative to the petroleum-based polymers recycled only by physical degradation.

Functionalized PLA can be prepared in two major ways – ROP of substituted lactides or post-polymerization modification of poly(lactic acid) according to various reaction mechanisms. Synthesis of functionalized poly(lactic acid) according to first mentioned method consists of synthesis of substituted lactides with subsequent ROP which is widely described in the literature. Nevertheless, ROP of substituted lactides has hardly been investigated. For example, Simmons and Baker [5] described synthesis of poly(phenyllactides) via solution polymerization catalyzed using tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) and via melt polymerization. While solution polymerization provided relatively low conversion (~70% after reaction time of 1 week), melt polymerization at 190 °C led to conversion ~90% within 2 h. ROP of several symmetric substituted lactides was described by Yin and Baker [6]. Syntheses were realized by two different methods – condensation of corresponding

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α -hydroxy acids and two-step synthesis of an α -hydroxy acid with a 2-halo-alkanoyl halogenide. Amorphous high molecular weight polymers were prepared with decomposition temperature above 300 °C and polydispersity >1.7. Though mentioned authors prepared substituted polylactides with predictable properties, synthesis of substituted lactides is not easy and requires strict reaction conditions.

Second functionalization method – post-polymerization modifications – is based on preparation of new materials via modification of native polymers without synthesis of new monomers with subsequent polymerization. Blending and grafting are commonly used methods for preparation of new polymeric materials. The interest in post-reactor modification is caused by an effort of wider polymer applicability in industry and for tailoring. Processing technology used for the free-radical grafting (e.g. kneading, extrusion, etc.) supports this technique in industry. Depending on activation mechanism, anionic and radical grafting is mentioned in the literature.

Principle of PLA functionalization by anionic activation is described by Vert et al. [7]. The modification route is based on the formation of carbanion site of a polyester chain by proton extraction on the CH–R groups (R = H or CH₃) in the α -position with regard to the main chain carbonyl. For example Ponsart et al. [8] evaluated anionic activation using lithium N,N-diisopropylamide (LDA) for labeling of PLA with naphthoyl chloride in THF. Authors considered this method extremely versatile and with possible labeling other aliphatic polyesters.

Mostly used functionalization method – free-radical grafting – is a polymer-analogous reaction usually initiated by thermal decomposition of thermolabile compounds with O–O bond. Thus generated primary radicals attack the weakest bond in polymer backbone; in the case of PLA it is usually C–H bond of tertiary carbon. In the next step, monomer is covalently bonded on the radical centre located on the polymer substrate. Termination, as the final reaction of grafting, occurs in the case combination of radical centre and other radical species, disproportionation or scission of backbone. During the free-radical grafting parallel reactions occur upon decreasing grafting yield. Decrease of grafting yield occurs due to undesired side reactions such as cross-linking, β -scission, thermo hydrolysis and recombination of primary radicals. It is necessary to set up reaction parameters (i.e. reaction time and temperature, concentration of reactants) in order to reach high grafting efficiency whereas the effect of monomer and polymer structure cannot be neglected (e.g. polarity, constitution, side chains, etc.).

Introducing new functional groups onto PLA backbone paves the way to prepare new functional materials with potential application in composites, laminates and polymer blends with improved material properties and cost effectiveness. Advantages of the incorporation of polar monomer (especially maleic anhydride) onto PLA backbone are mentioned in several studies [9–11]. In this paper, itaconic anhydride is covalently bonded onto PLA backbone via radical grafting in melt. Unlike many works focused on grafting with maleic anhydride, both PLA and itaconic anhydride can be derived from renewable resources which makes this topic more attractive. In addition, C=C double bond located out of the anhydride ring could make IAH more reactive compared to maleic anhydride. Finally, goal of this study is important to evaluate the influence of reaction conditions on the structure and material properties of modified PLA.

2. Experiments

2.1. Materials

PLA 2003D grade (NatureWorks, Minnetonka, USA) was dried in vacuum oven at 60 °C for 12 h to remove residual moisture and stored according to recommended conditions. Itaconic anhydride (IAH; purity >95%) and initiator 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane (L101) were purchased from Sigma–Aldrich without any treatment as well as other chemicals used for dissolving and precipitation.

2.2. Reaction methodology

2.2.1. Radical grafting of PLA with IAH and samples treatment

The PLA-g-IAH was prepared via grafting reaction between PLA and IAH initiated by L101 in laboratory kneader Brabender (Brabender, Germany) with 50 mL volume of reaction chamber. The reaction parameters used for reaction are summarized in Table 1. Defined amount of PLA was loaded into reaction chamber and plasticized for 2 min. After that

Table 1
Concentration of reactants applied for radical grafting of PLA (based on the PLA mass).

| [IAH] ₀ [wt%] | [L101] ₀ [wt%] | | | | |
|--------------------------|---------------------------|---------|---------|-------|-------|
| | 0 | 0.1 | 0.5 | 1 | 2 |
| 0.5 | 0.5-0 | 0.5-0.1 | 0.5-0.5 | 0.5-1 | 0.5-2 |
| 1 | 1-0 | 1-0.1 | 1-0.5 | 1-1 | 1-2 |
| 5 | 5-0 | 5-0.1 | 5-0.5 | 5-1 | 5-2 |
| 10 | 10-0 | 10-0.1 | 10-0.5 | 10-1 | 10-2 |

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