European Polymer Journal 67 (2015) 213–223

Contents lists available at ScienceDirect

European Polymer Journal

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

Modification of poly(lactic acid) using itaconic anhydride by reactive extrusion

K.I. Ku Marsilla, C.J.R. Verbeek *

Department of Engineering, School of Science and Engineering, University of Waikato, Hamilton 3204, New Zealand

ARTICLE INFO

Article history:
Received 12 January 2015
Accepted 24 March 2015
Available online 3 April 2015

Keywords:
PLA
Free radical grafting
Itaconic anhydride
Crystallinity
Reactive extrusion

ABSTRACT

Itaconic anhydride (IA) was grafted onto poly(lactic acid) (PLA) using dicumyl peroxide (DCP) as radical initiator using free-radical grafting. Different concentrations of monomer (2–6 wt.%) and initiator (0.5–0.75 wt.%) at 180 and 200 °C were used for chemical modification. Grafting was confirmed using titration and the highest degree of grafting was 0.75%. The degree of grafting increased gradually with increasing IA and DCP concentration, with minimal chain scission. Reaction kinetics showed that the initial rate of reaction was between 0.024 and 0.03 $(\text{l/mol s})^{1/2}$, depending on temperature. Grafted PLA showed a significant change in enthalpy of crystallization, enthalpy of fusion as well as increased tensile strength and elongation at break accompanied by a reduction in stiffness.

1. Introduction

Poly(lactic acid) (PLA) is one of the most promising biodegradable thermoplastics and has received considerable attention because of its glossy optical appearance, high tensile strength and good barrier properties toward carbon dioxide, oxygen and water. PLA is used in compostable packaging materials such as bags, food packaging and disposable tableware, as well as in medical applications such as ligament reconstruction, suture, tissue engineering, and controlled release systems [1]. It is also used in blends with other polymers, but may require chemical modification to improve compatibility. However, PLA lacks reactive side-chain groups, which make surface and bulk modification challenging.

PLA can be modified using techniques such as plasticization, chemical modification or melt blending with flexible polymers. High molecular mass plasticizers such as, polyethylene glycol (PEG), poly(propylene glycol) (PPG), atactic poly(3-hydroxybutyrate (a-PHB), polyester diol (PED), poly(diethylene adipate) (PDEA), tributyl citrate-oligo-ester (DBM-oligoester) and oligoesteramide (DBM-oligoesteramide) have been reported to be miscible with PLA and are efficient plasticizers, while acetyl triethyl citrate and triethyl citrate were shown to be the most effective plasticizers [2,3]. Although plasticization is well known, the high amount required (10–20 wt.%) to reduce the T_g and improve ductility is not always cost effective [4].

Among chemical modification methods used, free radical grafting is probably the most successful and cost effective treatment for improving adhesion efficiency and preparing compatibilizers for polymer/polymer blends. It can be carried out either in solution or during a melt-compounding process. Maleic anhydride (MA) is by far the most commonly used monomer for grafting reactions due to its availability and low propencity for homopolymerization. Grafting MA onto polyolefins is an established technique, however, MA grafted onto PLA (PLA-g-MA) is not commercially available.

Carlson et al. and Mani et al. first reported grafting MA onto PLA using twin-screw extrusion, achieving a 0.5 wt.% degree of grafting [5,6]. However, the grafting efficiency

---

* Corresponding author. Tel.: +64 7 8384947; fax: +64 7 8384835.
E-mail addresses: marsyilla@yahoo.com (K.I. Ku Marsilla), jverbeek@waikato.ac.nz (C.J.R. Verbeek).

http://dx.doi.org/10.1016/j.eurpolymj.2015.03.054
0014-3057/

was low compared to other polyesters due to PLA's limited reactivity [7]. This is due to poor activity of MA toward macro-radicals resulting from a low-density electron around —CH=CH— bonds and PLA's structural symmetry [8]. The competition between monomer and initiator suggests that there is an optimum radical concentration that depends on the peroxide/monomer ratio to promote grafting efficiency before termination reactions and chain scission become predominant [6]. Zhu reported an improved grafting yield when using an electron-donating monomer styrene as a co-monomer [9]. Grafting decreased the T_g, crystallinity (X_c) and thermal stability of PLA. The physical properties of PLA were affected because of new regular structures forming after grafting.

The mechanical properties of grafted PLA were not changed significantly [10] but were improved when blended with other polymers. Improved interfacial adhesion was observed between granular starch and PLA using PLA-g-MA [5]. PLA-g-MA also improved tensile strength and elongation at break of soy protein/PLA composites and finer domain sizes of soy protein concentrate (SPC) were observed suggesting improved dispersion [11]. Addition of 3 parts per hundred (phr) and 5 phr PLA-g-MA to PLA/wheat straw-based composites resulted in a significant improvement in tensile strength (20%) and flexural strength (14%) of the composites [12].

Although MA grafted polymers have shown great importance as compatibilizers their reaction with proteins may result in unstable amide bonds that can easily be hydrolyzed. Itaconic anhydride (IA) is less harmful compared to MA and is extremely stable when reacted with proteins and can used also be used for acetylating lysine, tyrosine and cysteine [13]. IA is a very reactive monomer in free radical grafting as it can produce tertiary radicals [14]. Owing to its chemical similarity to MA, it can be an alternative to MA, but it has not been studied extensively. IA has been used as a renewable monomer for the synthesis of biobased (PLA)-graft copolymers via conventional copolymerization and has potential as bio-based polymer [15]. IA also has been successfully grafted onto polyethylene with a high degree of grafting [16].

Side reactions such as chain scission, branching and crosslinking are common and depend on the nature of the macro-radicals and the polymer backbone [5]. Excessive chain scission usually leads to lower molecular weight and poor performance of the polymer, while crosslinking may lead to formation of insoluble polymers [9]. For polyethylene (PE), crosslinking during grafting reactions reduced the melt flow index and elongation at break whilst improving the impact strength and creep resistance and not affecting the tensile strength [17]. Maleation of propylene (PP) with maleic anhydride (MA) led to degradation rather than crosslinking due to rapid peroxide decomposition [18].

In this study, free radical grafting of IA onto PLA was carried out using dicumyl peroxide (DCP) as initiator in a twin-screw extruder. The effect of grafting parameters on the degree of grafting, thermal and mechanical properties was studied. Grafted PLA can be used as compatibilizer in blends of thermoplastic proteins and PLA, resulting in a blend that could potentially be 100% bioderived.

2. Methodology

2.1. Materials

Poly(lactic acid) was purchased from NatureWorks Ltd in pellet form (3051D). Analytical grade itaconic anhydride (IA), dicumyl peroxide (DCP), chloroform, acetone, potassium hydroxide, hydrochloric acid and phenolphthalein were purchased from Sigma Aldrich and were used as received.

2.2. Sample preparation

2.2.1. Extrusion

PLA was dried at 80 °C for 4 h to remove moisture. Itaconic anhydride (IA) and dicumyl peroxide (DCP) were dissolved in 20 mL dehydrated acetone and mixed with 300 g dried PLA according to the specifications in Table 1. After the acetone evaporated completely, the mixtures were reactively compounded using a LTE-20-44 twin-screw co-rotating extruder with a *L*/*D* of 44:1 and a screw diameter of 20 mm. The extruder barrel temperature was set to 145, 145, 165, 165, 180, 180, 180, 180, 160, 160, 155 °C (feed to die) and the screw speed was maintained at 100 rpm. A vacuum pump was connected to the vent at the 7th heating zone on the barrel to remove vapor generated during extrusion. The extrudate was collected in a water bath and pelletized. Pellets were dried in a convection oven at 80 °C for 12 h before further analysis.

2.2.2. Compounder mixer

To determine reaction kinetics, samples were prepared using a twin blade compounder mixer equiped with a torque sensor (Kistler) and motor unit (Flex 4 M). The mixing chamber diameter was 40 mm. The temperature was set to selected temperatures (180 and 200 °C) with a rotor speed of 100 rpm. PLA was first melted until the torque was constant (around 3 min) before DCP and IA were added. Samples were collected at different time intervals between 10 and 320 s.

2.3. Sample purification

2.5 g grafted PLA was dissolved in 40 mL chloroform and 0.75 mL, 1 M hydrochloric acid solution were added to hydrolyze the anhydride functional groups into carboxylic acids at room temperature. The solution was stirred vigorously for 30 min. The grafted sample was further purified by drop-wise precipitating into cold

Table 1
Formulations used in grafting reactions.

	DCP (%)			
IA (%)	0	0.5	0.75	1
0	PLA	–	–	–
2	–	PLA1	PLA6	PLA11
3	–	PLA2	PLA7	PLA12
4	–	PLA3	PLA8	PLA13
5	–	PLA4	PLA9	PLA14
6	–	PLA5	PLA10	PLA15