Polymer Degradation and Stability xxx (2016) 1–7

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Cardanol derivatives as innovative bio-plasticizers for poly-(lactic acid)

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ARTICLE INFO

Article history:
Received 11 December 2015
Received in revised form
3 February 2016
Accepted 25 February 2016
Available online xxx

Keywords:
Cardanol
Plasticizer
Poly(lactic acid)
Durability

ABSTRACT

This work is aimed to study the suitability of a bio based compound, cardanol acetate (CA), as plasticizing agent of poly(lactic acid) (PLA). Compared to other natural derived plasticizers, cardanol acetate is not obtained from food crops but as a by product of cashew nut extraction. In addition, the cardanol derived plasticizers can be obtained by the use of non toxic and low environmental impact reagents. The plasticizing effectiveness of cardanol acetate was confirmed by the decrease of the glass transition temperature and flexural modulus, which were comparable to those obtained by the use of conventional oil based plasticizers, such as diethylhexyl phthalate (DEHP). In addition, calorimetric analysis revealed that the addition of the plasticizer, both cardanol derived and phthalate, involves a significant increase of the crystallization kinetics. An analysis of the flexural strength and deformation at break indicated that the increase of the crystallization kinetics has more dramatic effects compared to the decrease of the glass transition, particularly at low plasticizer content, finally leading to a decrease of the ductility. At higher plasticizer content, an increase of the ductility is observed, and PLA plasticized by 10% of CA showed a significant higher deformation at break than PLA plasticized by DEHP. In addition, plasticizer migration tests showed a lower weight loss of PLA plasticized by CA compared to DEHP plasticized PLA, which indicates the potential higher stability of properties of the cardanol derived plasticizer.

1. Introduction

Poly (lactic acid) (PLA) emerged in the last years as a biodegradable polymer, being also synthesized from renewable resources, represents a valid alternative to oil based plastics in many industrial applications [1]. PLA is characterized by stiffness and strength comparable to those of polystyrene, making it attractive for packaging applications [2], as well as for others industrial fields [3]. It is processed using extrusion, injection molding, calendering, thermoforming, fiber spinning and rotational molding [4–6], for the production of different items.

Nevertheless, PLA processability and potential applications are severely limited by its brittleness [7]. The most widespread used approach in order to improve polymer ductility, is the use of plasticizers [8,9], potentially able to reduce the glass transition temperature of the polymer. Compared to other approaches, as reactive extrusion, involving for example polymer grafting [10,11], blending with plasticizer represents an easier and faster way to improve PLA mechanical properties. Essential requirements for plasticizers include good miscibility with the polymer and adequate stability. In addition, low volatility and migration of the plasticizer are relevant parameters to ensure the stability of plasticized polymers during their service [12]. Several compounds have been studied as potential PLA plasticizers, such as citrate esters [13], glycerol [14], malonate oligomers, adipates and polyadipates [2], poly (ethylene glycol) (PEG) [15], poly (propylene glycol) (PPG) [16].

However, plasticization in semicrystalline polymers increases the chain mobility and enhances PLA crystallization. The formation of larger and more brittle crystals is particularly critical in processes, such as rotational molding, characterized by slow cooling rates; in such case it was found that plasticized PLA showed a significant embrittlement compared to neat PLA [7]. Another drawback of using these low molecular weight additives is that they can leach out of the PLA matrix, resulting in a brittle plastic over time [17].

Cardanol derivatives have been proven to be efficient plasticizers for poly-vinylchloride PVC [18]. Cardanol is an industrial

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.02.020
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Please cite this article in press as: A. Greco, A. Maffezzoli, Cardanol derivatives as innovative bio-plasticizers for poly-(lactic acid), Polymer Degradation and Stability (2016), http://dx.doi.org/10.1016/j.polymdegradstab.2016.02.020

grade oil obtained by vacuum distillation of "cashew nut shell liquid" (CNSL), which represents a by-product of cashew nut shell industry. In particular, it was shown that acetylation of the cardanol hydroxyl group improves the compatibility with PVC [19]. Such reaction can be performed in quantitative yields using non-toxic reagents and solvents. Cardanol acetate (CA) can be used as secondary plasticizer, in addition to conventional plasticizers, for the production of soft PVC. Nevertheless, the migration of CA is very high compared to the migration of conventional phthalate plasticizers for PVC [20], mainly due to the relatively low compatibility between the PVC and the relatively more polar CA.

The aim of this paper is the analysis of the suitability of cardanol acetate as an effective plasticizer for PLA. Compared to other natural originating plasticizer, cardanol acetate is not obtained from food crops but as a by product of cashew nut extraction. PLA samples plasticized by CA and a conventional phthalate plasticizer were produced by melt blending, and the resultant thermal, mechanical and durability properties were compared.

2. Materials and methods

The PLA used in this study is NatureWorks Ingeo Biopolymer 3251D, specifically designed for injection molding, which, according to the producer technical data sheet, is characterized by a density of 1.24 g cm^{-3} and a Melt Flow Rate (MFR) of 80 g/600 s at 210 °C.

The commercial oil derived plasticizer was bis-(2-ethylhexyl) phthalate (DEHP) from Huls, characterized by a molar mass of 390 g mol^{-1}. Technical cardanol, characterized by a purity of 95% and molar mass 300 g mol^{-1}, was purchased by Oltremare (Bologna, Italy). Hexahydrate zinc perchlorate and acetic anhydride were purchased by Aldrich Chemicals, and used as received. In order to be used as plasticizer for PLA, cardanol was subjected to an acetylation reaction, for the production of cardanol acetate (CA). The batch esterification process, involving the conversion of the cardanol hydroxyl group to an acetate group, as reported in Fig. 1, was performed by mixing 1 mol of cardanol (304.00 g) with 1.5 mol of acetic anhydride (153.13 g), using 0.015 mol (5.58 g) of hexahydrate zinc perchlorate as catalyst without any solvent used during the reaction. The mixture was stirred for 24 h at room temperature, after which the cardanol derivative was washed with water to eliminate the traces of hexahydrate zinc perchlorate [16]. The cardanol acetate obtained is characterized by a molar mass about 342 g mol^{-1}.

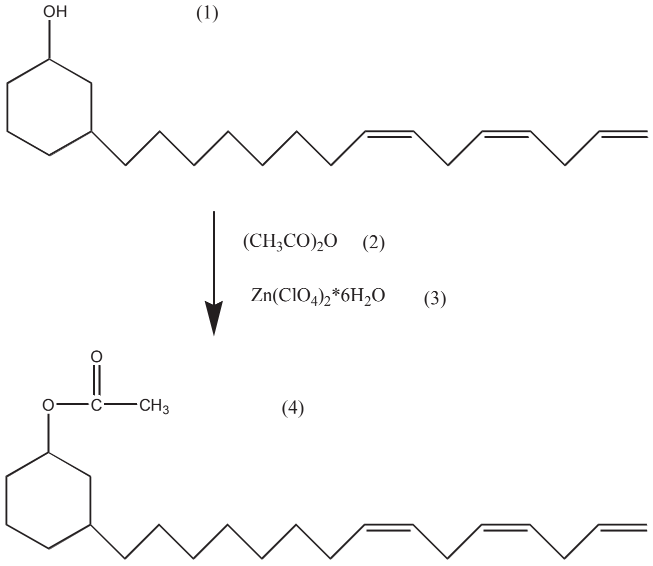

Fig. 1. Scheme for cardanol acetylation: cardanol (1) is modified to cardanol acetate (CA) (4) though acetylation by acetic anhydride (2) in the presence of hexahydrate zinc perchlorate (3).

Plasticized PLA was produced at different plasticizer contents by a HAAKE RHEOMIX 600/610 mixer, at 180 °C for 15 min under nitrogen flux, with a rotor speed of 60 rpm. The temperature and the time of mixing were chosen in order to reduce degradation phenomena of PLA polymer. In facts, in a previous work [6] it was shown that a temperature of 180 °C involves a negligible variation of the viscosity of the material, which is considered an indication of a stable molecular weight of the polymer.

The nomenclature and composition of the different samples investigated are reported in Table 1.

Differential scanning calorimetry (DSC) was performed using a Mettler Toledo 822 under a nitrogen flux of 30 mL min^{-1} applying a cooling scan from 210 to 30 °C at 10 °C min^{-1}, followed by a heating scan between 30 °C and 210 °C at 10 °C min^{-1}. The maximum temperature attained during DSC scans was chosen as a value higher than the equilibrium melting temperature of PLA, in order to delete the previous thermal history of the sample.

Samples for mechanical characterization, about 3 mm thick, were produced by a Campana (Italy) hot press, pre-heating the material in a forced convection oven up to 210 °C, followed by compression molding under 300 MPa pressure, with hot plates at 130 °C. Samples for plasticizer migration tests, about 0.4 mm thick, were produced by the same equipment.

Flexural tests were performed on a Lloyd LR5K dynamometer according to ASTM D790 standard, using a crosshead speed of 1 mm min^{-1}.

Ageing tests were performed holding the samples for 3 weeks in a forced convection oven at 105 °C. Weight loss of the samples was periodically measured.

3. Results and discussion

DSC analysis on neat PLA is reported in Fig. 2. During cooling at 10 °C min^{-1}, no evidence of crystallization is observed, which indicates that, once cooled down at room temperature, the neat PLA is completely amorphous. Therefore, as expected, upon subsequent heating, the PLA shows a broad cold crystallization peak, at about 120 °C, followed by the melting peak, at 167 °C, as also summarized in Table 2. The crystallization and melting enthalpies reported in Table 2 are substantially equivalent, which indicates that melting is only associated to the cold crystallization phenomena, and therefore an amorphous glassy polymer is obtained at room temperature. Quenched PLA is also characterized by a glass transition temperature (T_g) at about 59 °C, characterized by a $\Delta c_p = 0.598$ J/gK. On the other hand, the cooling curve of sample CA10, also reported in Fig. 2, clearly shows a crystallization peak, which is indicative of an enhanced crystallization kinetic brought by the addition of plasticizer.

Table 1
Composition of the different samples produced and investigated.

Sample	% Plasticizer	Type of plasticizer
PLA	0	//
CA	100	Cardanol acetate
CA3	3	Cardanol acetate
CA5	5	Cardanol acetate
CA10	10	Cardanol acetate
DEHP3	3	bis-(2-ethylhexyl) phthalate
DEHP10	10	bis-(2-ethylhexyl) phthalate

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