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New development on plasticized poly(lactide): Chemical grafting of citrate on PLA by reactive extrusion

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ABSTRACT

New plasticization ways based on low molecular plasticizers from citrates family were investigated to improve the ductility of poly(lactide) (PLA). Grafting reactions between anhydride-grafted PLA (MAG-PLA) copolymer with hydroxyl-functionalized citrate plasticizer, i.e. tributyl citrate (TbC), were so-carried out through reactive extrusion. Tributyl*O*-acetylcitrate (ATbC) was used as a non-functionalized reference. Both plasticizers drastically decreased the T_g of PLA. However, the grafting reaction of TbC into MAG-PLA revealed a shift of PLA T_g toward higher values. After 6 months of aging, no phase separation was observed. However, plasticizer leaching was noticed in the case of PLA/ATbC materials, leading to the shift of T_g toward lower temperatures. In contrast, no major leaching phenomenon was noticed in PLA/TbC and PLA/MAG-PLA/TbC blends, indicating that the mobility restriction derived from the hydrogen bonding that can occur between PLA and TbC as well as the grafting reaction of TbC into MAG-PLA enabled to reduce leaching phenomena.

1. Introduction

Poly(lactide) has received much attention in the research of alternative biodegradable polymers [1–3]. Its low toxicity, along with its environmentally benign characteristics, has made PLA an ideal material for food packaging and film wrap, as well as for other consumer products [4–6]. PLA is characterized by excellent optical properties and high tensile-strength but unfortunately, it is rigid and brittle at room temperature due to its glass transition temperature (T_g) close to 55 °C [2]. Previous works suggested that the brittleness of PLA is due to the low entanglement density (*Ve*) and the high value of characteristic ratio (C_∞), a measure of chain stiffness [7,8], limiting its melt-processability and its end-use mechanical performance. In the frame of packaging materials a high ductility at room temperature is required and thus, there is no tolerance for the polymer film tearing or cracking when subjected to stresses during package manufacturing or use [2,9]. For such application, other requirements include transparency and low crystallinity. To improve the ductility of PLA-based materials, a large number of investigations have been performed to modify PLA properties *via* plasticization. However, an enormous number of variables, i.e. the nature of the PLA matrix, the type and optimal percentage of plasticizer, the thermal stability at the processing temperature, etc. must be taken into account. Unfortunately, poor mechanical properties are often reported and the relationships between the thermo-mechanical properties and the molecular parameters are far from being elucidated. In this paper, we focus on the plasticizer type that is believed to predominantly influence the final thermo-mechanical properties of the modified PLA. Rather than lactide, many kinds of ester-like plasticizers for PLA have been studied such as bishydroxymethyl malonate (DBM) [10], glucose

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monoesters and partial fatty acid esters, citrates [11], etc. However, the low molecular weight plasticizers have the problem of migrating, owing to their high mobility within the PLA matrix. Therefore, plasticizers with rather high molecular weight and low mobility are suitable such as poly(ethylene glycol) (PEG) [11–13], poly(propylene glycol) (PPG) [14], atactic poly(3-hydroxybutyrate) (a-PHB) [15,16] and oligoesteramide (DBM-oligoesteramide) [10,17,18]. On the other hand, the choice of plasticizer used as a modifier for PLA is limited by the legislative or technical requirements of the application, and in this context, its selection becomes more difficult [10,18]. In fact, the plasticizer used for PLA has to be biodegradable, non-toxic for food contact (for packaging) and/or biocompatible (for medical applications). In general, amounts ranging from 10 to 20 wt.% of plasticizers are required to provide both a substantial reduction of T_g of the PLA matrix and adequate mechanical properties. In sustainable issues, the preferred plasticizer for PLA is biodegradable/bioresorbable, sufficiently non-volatile, with a relatively low molecular weight to produce the desired decrease of the Young's modulus value and increase of the impact strength. Moreover, the addition of more that 20–30% (depending on the plasticizer) of plasticizers into the PLA matrix leads to a phase separation. The plasticization is thus limited by the amount of plasticizer to be blended with PLA. Recently, we have developed new ways of plasticizing PLA with low molecular poly(ethylene glycol) (PEG) to improve the ductility of PLA while maintaining the plasticizer content at maximum 20 wt.% PLA [19]. The *in situ* reactive grafting of hydroxy terminated poly(ethylene glycol) (PEG) plasticizer onto the maleic anhydride modified PLA in PLA/PEG blends lowered significantly the glass transition temperature compared to the blends where no grafting could occur (neat PLA + PEG) and had a positive impact on the mechanical properties. Indeed, absence of yield peak was observed for PLA + 10% MAG-PLA + 20% PEG. In the present work, we applied the same strategy developed for the *in situ* reactive grafting of hydroxy terminated poly(ethylene glycol) (PEG) plasticizer into PLA to graft citrate plasticizers. The objectives of the present study is to verify if the strategy consisting in the grafting of a fraction of the plasticizer can be applied to citrate family (tributyl*O*-acetylcitrate and tributyl citrate) to further improve the PLA ductility compared to what is done so far, while maintaining the plasticizer content at a maximum of 20 wt.% (to avoid phase separation). The strategy chosen consists in grafting a fraction of hydroxyl-functionalized citrate plasticizer (tributyl citrate) onto a PLA backbone by reactive extrusion in order to create more interactions between the functionalized polyester matrix and the remaining fraction of non-grafted plasticizer.

To this end, a reactive blending of maleic anhydride-grafted PLA (MAG-PLA) copolymer with hydroxyl-functionalized TbC was performed. Physico-chemical, thermal and mechanical properties of the extruded blends were studied in order to assess the compatibility of the plasticizer with the PLA. Tributyl*O*-acetylcitrate was used as a reference as this plasticizer does not possess any reactive group able to react with anhydride functions in melt temperature.

2. Experimental part

2.1. Materials

Poly(lactide) (PLA) was provided by NatureWorks LLC under the reference 4042D. (i) 2,5-Dimethyl-2,5-di-(tert-butylperoxy)hexane organic peroxide (Lupersol 101), (ii) maleic anhydride (MA) and (iii) tributyl*O*-acetylcitrate 98% (ATbC) were purchased from Sigma–Aldrich. Tributyl citrate 99 + %(TbC) was provided by Acros Organics. The properties of the used plasticizers are listed in Table 1 [20].

2.2. Processing

All melt (reactive) blending were performed on a Leistritz corotating intermeshing twin-screw extruder ($L/D = 45$). The temperature profile was 160/180/180/180/180/180/180/180/180/180 from the feed throat to the die, and the melt temperature was 181 °C. The employed screw speed was 80 rpm. A two-hole filament die, 3 mm in diameter and equipped with a cooling sleeve, was assembled to the extruder. PLA was dried overnight at 40 °C in a vacuum oven before processing. Dry TbC and ATbC were used with any particular precaution.

Maleation of poly(lactide) (MAG-PLA) was carried out by reactive extrusion. PLA, MA and Lupersol 101 (L101) were hand-mixed together before extrusion.

The percentage of Lupersol added is based on a PLA weight (0.5 wt.%), while 2 wt.% of MA (PLA basis) is chosen for this maleation procedure [21]. Neat PLA and PLA + 10 wt.% MAG-PLA are mixed, added at a rate of 2.0 kg/h to the feed zone and submitted to extrusion using the same conditions than the grafting step. TbC or ATbC plasticizers are introduced to the extruder using a calibrated pump. The contents of plasticizer (TbC and ATbC) are chosen to be 10 and 20 wt.%, based on the total weight of the mixture. Table 2 summarizes the composition of each formulation.

For the mechanical study (tensile tests and dynamical mechanical analysis), 110 × 110 × 4 mm^3 plates of PLA were compression-molded using a Carver laboratory press and a specific rectangular mold. The procedure utilized was as follows: (i) extruded PLA was first heated at 190 °C for 3 min, (ii) PLA was then compressed during 30 s with a pressure of 15 MPa and (iii) under the same pressure (15 MPa) PLA was cooled by means of a room temperature water circulation.

2.3. Characterization

Fourier transform infrared (FTIR), Nuclear Magnetic Resonance (NMR), potentiometric titration and soxhlet

Table 1
Properties of the used plasticizers [20].

Plasticizer	Molecular weight ($g\ mol^{-1}$)	Density ($g\ mL^{-1}$)	Solubility parameters $(J cm^3)^{1/2}$
Tributyl citrate (TbC)	360	1.104	18.8
Tributyl*O*-acetylcitrate (ATbC)	402	1.046	18.7