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Thermo-mechanical characterization of plasticized PLA: Is the miscibility the only significant factor?

Isabelle Pillin *, Nicolas Montrelay, Yves Grohens

Université de Bretagne Sud, Laboratoire Polymères, Propriétés aux Interfaces et Composites, Rue de St Maudé, BP 92116, 56321 Lorient Cedex, France

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Abstract

PLA is a widely used polymer which has received much attention in the last decade because of its originating from renewable resources and its potential biodegradability. PLA fulfils the packaging industry's requirements for most of the rigid objects but the polymer needs to be plasticized to be used as soft films. In this work, agreed plasticizers for food contact were melt mixed with L-PLA and then, the glass transition, melting, crystallization and mechanical properties of the blends were investigated. The experimental results were compared to the predicted results found through empirical interaction parameters and Fox equations. Molecular scale miscibility is assumed in the amorphous phase whatever the plasticizer. The mobility gained by the PLA chains in the plasticized blends yields crystallization, which is the driving force for various scale phase separations.

Keywords: PLA; Plasticization; Mechanical properties

1. Introduction

Research in biodegradable polymers has received increased attention in recent years because of their wide application in environmental friendly packaging. The most popular and biodegradable polymers are aliphatic polyesters, such as polylactic acid (PLA), polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT) and polyhydroxybutyrate (PHB).

PLA has a number of interesting properties including biodegradability, good mechanical properties, and processability. For these reasons PLA is an interesting candidate for producing biodegradable packaging materials. However, low deformation at break and high modulus have limited applications of PLA to the rigid thermoformed packaging industry [1]. One important requirement for packaging materials such as films is high flexibility at room temperature, transparency, and low crystallinity. Barrier properties are also relevant for these applications.

So, attempts to improve the mechanical properties for packaging applications have focused on food contact agreed plasticizers or polymers. PLA has been blended with a number of polymers such as poly(hydroxybutyrate) [2,3], poly(vinylacetate) [4], poly(ethylene oxide) [5–9] and polysaccharides [10–13]. These polymer blends generally exhibit phase separation in the whole or part of the composition range.

Plasticizers are widely used to improve processability, flexibility and ductility of polymers. In the case of semi-crystalline polymers like PLA, an efficient plasticizer has to reduce the glass transition temperature but also to depress the melting point and the crystallinity [9]. Lactide monomer, for instance, is a good candidate to plasticizing PLA but it tends to migrate to the material's surface causing a stiffening of the films in time. The most common plasticizers used for PLA are poly(ethyleneglycol) [9,14–20] and citrate [21–24].

Among the more representative results, Younes and Cohn [9] showed that microphase separation occurs at a given composition depending on the molecular weight of PEG (1500 and 35,000 g/mol). Hu et al. [18] demonstrated that the glass transition temperature of PLA–PEG (8000 g/mol) followed the empirical Fox equation but the blends were not stable in time and phase separation was observed. Another work described PEG (1500 g/mol), glucosemonoesters and partial fatty acid esters blended with PLA at 2.5, 5, and 10 wt%. It was claimed that fatty acid ester is a good plasticizer with a strong hindrance of the crystalline phase development [17]. Nijenhuis et al. [15] explained that the poor long-term stability of blends between PLA and PEG was due to slow crystallization of PEG.

* Corresponding author.
E-mail address: isabelle.pillin@univ-ubs.fr (I. Pillin).

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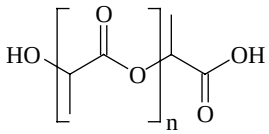
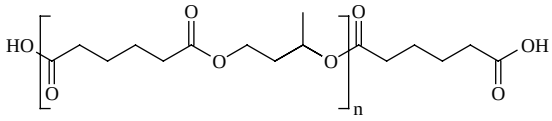
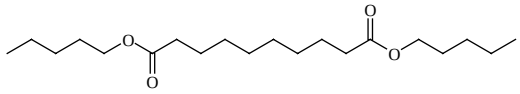
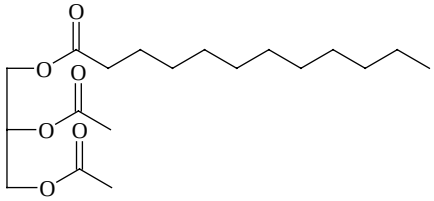
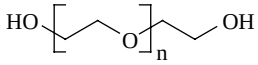
Table 1
Chemical formula of PLA and plasticizers

Name		M_w (g mol^{-1})	Chemical formula
Poly(lactic acid)	PLA	74,000	
Poly(1,3-butanediol)	PBOH	2100	
Dibutyl sebacate	DBS	314	
Acetyl glycerol monolaurate	AGM	358	
Poly(ethyleneglycol)	PEG	200 400 1000	

Plasticization of PLA with citrate provides materials, which exhibit the same properties as those with PEG, and long-term phase separations have also been observed [22,24]. Moreover, the choice of plasticizers to be used as modifiers for PLA is limited by technical and legislative [European directive 2002-72-CE] requirements of the application in food packaging.

The objectives of the present study are to determine thermal and mechanical properties of PLA with PEG and several other oligomeric plasticizers that can be used in food packaging. Moreover, glass transition and melting behavior are discussed in light of traditional polymer blend approaches and the mechanical performances assessed for blends containing 10, 20, and 30% of plasticizers.

2. Materials and methods

2.1. Materials

PLA 4042D was purchased from Cargill-Dow, and consists of 92% L-lactide and 8% D-lactide units. The molecular weight is 74,000 g mol^{-1} with polydispersity index of 2 and a density of 1.25 g cm^{-3}. Its glass transition temperature is about 54 °C and melting temperature 155 °C (Table 1).

All the plasticizers were chosen for their being food-contact approved. PBOH was obtained from Bayer. AGM, DBS and the PEGs (molecular weight 200, 400, and 1000 g mol^{-1}) were purchased from Sigma–Aldrich.

2.2. Blending conditions

The plasticizers were blended to PLA at 10, 20, and 30% w/w. Higher plasticizer content was studied but the results are not reported here since the mechanical properties are only very poor. An opened mixer (Brabender, 50 EHT) controlled by a Lab-Station driven by the BRABENDER Software Winmix was used. Blending temperature was 180 °C and blending time 15 min and blade rotation speed was 30 rpm. The blends were then extracted from the blender and molded into plates of 20×20×0.8 cm^3 from which tensile test samples were cut.

2.3. Differential scanning calorimeter

Thermograms were obtained from a Perkin–Elmer Pyris 1 differential scanning calorimeter (DSC) using the Pyris V 3.0 software under Windows NT 4.0 for data collection and treatment. Calibration was done with indium and tin in the temperature range [+15 to +350 °C]. The base line was checked every day. Aluminum pans with holes were used and the samples' mass was approximately 10 mg. All samples were first heated to 200 °C for 5 min to get rid of thermal history. All the temperatures measured at the peak maximum (T_c, T_m) are determined with an accuracy of less than ±0.5 °C. Non-isothermal crystallization and melting temperatures, respectively, T_c and T_m, and glass transition temperature T_g, were determined at ±20 °C min^{-1} heating/cooling rates. Melting enthalpies were determined using constant integration limits.

2.4. Mechanical measurements

The static tensile experiments were performed on the MTS Synergie RT1000 testing apparatus for comparing with the above tensile impact results. The loading speed was 1 mm min^{-1} for pure PLA and 10 mm min^{-1} for plasticized PLA.