



## Material properties

## Tough crystalline blends of polylactide with block copolymers of ethylene glycol and propylene glycol



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## ABSTRACT

The effect of crystallinity of polylactide (PLA) on the structure and properties of tough PLA blends with PEG-b-PPG-b-PEG block copolymers was studied. PLA was melt blended with a set of the copolymers with varying ratio of the hydrophilic (PEG) and hydrophobic (PPG) blocks. Although the blend phase structure depended on the copolymer molar mass and PEG content, as well as on the copolymer concentration in the blend, crystallinity also played an important role, increasing the copolymer content in the amorphous phase and enhancing phase separation. The influence of crystallinity on the thermal and mechanical properties of the blends depended on the copolymer used and its content. The blends, with PLA crystallinity of 25 ÷ 34 wt%, exhibited relatively high glass transition temperature ranging from 45 to 52 °C, and melting beginning above 120 °C. Although with a few exceptions crystallinity worsened the drawability and toughness, these properties were improved with respect to neat crystalline PLA in the case of partially miscible blends, in which fine liquid inclusions of the modifier were dispersed in PLA rich matrix. About 20-fold increase of the elongation at break and about 4-fold increase of the tensile impact strength were reached at a small content (10 wt%) of the modifier. Moreover, crystallinity decreased oxygen and water vapor transmission rates through neat PLA and the blend, and the barrier property for oxygen of the latter was better than that of neat polymer.

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## 1. Introduction

Poly lactides (PLAs), linear aliphatic thermoplastic polyesters, have gained enormous attention, especially as they can nowadays be produced on industrial scale from annually renewable resources (agricultural products and side products of food production) [1,2], are biocompatible, biodegradable, compostable and recyclable [3–5]. Nevertheless, the stiffness and brittleness of PLAs, due to relatively high glass transition temperature,  $T_g \approx 55 \div 60$  °C, hinder their application in fields requiring a high level of flexibility, drawability or impact resistance. Toughening of PLA can be achieved by plasticization or blending with other polymers immiscible with PLA via a route termed “rubber toughening” [6–16]. To improve ductility of PLA by plasticization, a decrease of  $T_g$  to at least 35 °C is necessary [17]. Moreover, one of the drawbacks of plasticized PLAs is ageing, which involves migration of plasticizer, phase separation, crystallization of plasticizers and PLA [18–20], and results in a change of the physical properties. Optically pure poly(L-

lactide) (PLLA) and poly(D-lactide) are crystallizable polymers but a decrease of optical purity decreases crystallizability of PLAs. Crystallinity further diminishes the ability of PLA to deform plastically, and slows down biodegradation but enhances the barrier properties and broadens the temperature range of applicability. Slowly crystallizing PLAs can be quenched to the glassy state without crystallization and subsequently cold-crystallized during heating. Usually, the cold crystallization temperature of plasticized PLA, which reflects its ability to crystallize, decreases in parallel with  $T_g$ . In general, although crystallization of PLA in a blend with a plasticizer can be advantageous for the barrier properties and can broaden the application temperature range, it is often accompanied by redistribution of the plasticizer [21,22], which can lead to its accumulation between PLA spherulites, weakening the material and decreasing its ultimate mechanical properties. Excessive local accumulation of the plasticizer can also result in phase separation, detrimental to drawability and toughness, particularly when it is accompanied by crystallization of the plasticizer. Thus, the crystalline PLAs with plasticized amorphous phase frequently exhibit relatively low elongation at break, especially if compared to amorphous materials with the same composition. Moreover, an

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increase of plasticizer content in the amorphous phase caused by crystallization can result in a decrease of elastic modulus despite the presence of stiff crystalline phase [23,24]. After crystallization, PLA blends plasticized with poly(propylene glycol) (PPG) exhibited better drawability than those with poly(ethylene glycol) (PEG) owing to PPG inability to crystallize and its more uniform distribution in the PLA amorphous phase [22].

Immiscible PLA blends with other polymers also exhibit improved ductility, and their elastic modulus and yield strength are less decreased than in the case of plasticization, and  $T_g$  of PLA matrix is practically unaffected. However, the presence of the dispersed phase results in loss of transparency. In addition, in order to improve the dispersion, and thus to enhance the ductility and impact resistance, compatibilization is often required. The properties of PLA blends with not only amorphous but also crystalline matrix have been studied. Liu et al. [25] reported a very minor effect of poly(ethylene/butylenes succinate) dispersed phase on mechanical performance of crystalline PLA. Similarly, improvement of drawability of PLLA/poly(3-hydroxy-butyrates-co-3-hydroxyvalerate) blends with respect to neat PLA was weak [26]. However, Pezzin et al. [27] found improvement of drawability by blending PLLA with 20 wt% of poly(para-dioxanone). Better results were obtained for PLLA/poly( $\epsilon$ -caprolactone), especially compatibilized with the copolymer of both components [28]. Anderson et al. [29] reported toughening of crystalline PLLA with linear low density polyethylene. Interestingly, toughening of amorphous PLA was achieved only when PLLA–PE block copolymer was used as a compatibilizer. Toughening of crystalline PLA with ethylene/acrylate copolymer led to better results than in the case of amorphous PLA [30]; debonding of the modifier particles from PLA matrix facilitated shear yielding of the latter.

In our previous work, PLA was melt blended with PEG-b-PPG-b-PEG block copolymers with varying ratio of the hydrophilic (PEG) and hydrophobic (PPG) blocks. Miscibility of the copolymers with PLA depended on their molar mass,  $M$ , and PEG content,  $P_c$ . Owing to synergy between partial miscibility of the components and the presence of phase separated liquid inclusions, the partially miscible blends exhibited the best drawability and toughness (37-fold increase of the elongation at break and up to about 1.5-fold increase of the tensile impact strength with respect to neat PLA at low copolymer content of 10 wt%), while retaining relatively high  $T_g$ , nearly 50 °C, and also transparency. The current study focuses on the influence of crystallinity on the properties of those materials. Cold crystallization was selected as a crystallization method because it leads to finer spherulitic structure, which can be beneficial for mechanical properties [31]. Although, with a few exceptions, crystallinity worsened the drawability and toughness of the blends, these properties were improved with respect to neat crystalline PLA. About 20-fold increase of the elongation at break and about 4-fold increase of the tensile impact strength were reached at a small content, 10 wt%, of the modifier.

## 2. Experimental

### 2.1. Materials

The study utilized PLA 2002D with density of 1.24 g·cm<sup>-3</sup> and melt flow index of 5–7 g·10 min<sup>-1</sup> (210 °C, 2.16 kg), produced by NatureWorks LLC (Minnetonka, MN). The L-lactide and D-lactide contents, 97.5% and 2.5%, respectively were determined by specific optical rotation measurements whereas weight average molar mass,  $M_w = 104$  kg·mol<sup>-1</sup>, and dispersity,  $M_w/M_n = 1.4$ , of the PLA were measured by size-exclusion chromatography (SEC) with multi-angle laser light scattering (MALLS) detector in dichloromethane.

A range of biodegradable PEG-b-PPG-b-PEG copolymers (Plurionics) provided by BASF (Ludwigshafen, Germany) and Sigma Aldrich (Steinheim, Germany) differing in  $M$  and  $P_c$  were used: group A comprising the copolymers with  $M$  ranging from 2000 to 3500 g·mol<sup>-1</sup> and  $P_c$  of 10 wt%, and group B comprising the copolymers with  $M$  of 2450–4400 g·mol<sup>-1</sup> and  $P_c$  from 20 to 40 wt%. The copolymers used are listed in Table 1, whereas their thermal properties as well as  $M$  measured by a matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) technique are described in Ref. [32]. The copolymers are referred to as, for example, P2000-10, where 2000 denotes nominal  $M$  of the copolymer and 10 stands for percent  $P_c$ .

### 2.2. Blend and sample preparation

PLA and the copolymers were dried under reduced pressure at 100 °C for 4 h and then blended in a Brabender mixer (Duisburg, Germany) operating at 190 °C for 15 min at 60 rpm. The copolymer contents in blends, 5 and 10 wt%, were selected based on preliminary experiments. Neat PLA was processed under the same conditions as a reference material. For further studies, 0.5 mm and 1 mm thick films were compression molded at 180 °C for 3 min in a hydraulic press and quenched between metal blocks kept at room temperature (RT). The films prepared in such a way were amorphous [32]. To crystallize, the films were sandwiched between metal blocks and heated at a rate of about 8–10 °C min<sup>-1</sup> from RT to 120 °C, kept at this temperature for 2–3 min, and quenched to RT. This protocol was chosen based on DSC studies. The blends are referred to as, for example, cPLA10P2450-20, where “c” denotes a crystalline blend and 10 stands for P2450-20 content in wt%.

### 2.3. Characterization

Thermal properties of the materials were examined during heating at 10 °C min<sup>-1</sup> from –50 to 190 °C under nitrogen flow using a DSC 2920 (TA Instruments, New Castle, DE).

Dynamic mechanical thermal analysis (DMTA) was carried out on rectangular specimens, 28 × 10 mm<sup>2</sup>, cut from 1 mm thick films, in dual cantilever bending mode using a Mk III DMTA apparatus (Rheometric Scientific, Epsom, UK), at a frequency of 1 Hz, during heating at 2 °C min<sup>-1</sup> from –100 to 140 °C.

Cryo-fracture surfaces of all the blends were sputtered with gold and examined using a scanning electron microscope (SEM), Jeol 5500LV (Tokyo, Japan).

Tensile measurements were carried out on an Instron machine (High Wycombe, UK) at 20 °C, at a rate of 50 %min<sup>-1</sup> on at least five specimens of each material cut from 0.5 mm thick films, conforming to ISO-527 type 1BA, with 25 mm gauge length. The elastic modulus was determined from the stress-strain plots in the linear range.

Tensile impact tests were conducted on 8–10 specimens of each

**Table 1**

Characteristics of PEG-b-PPG-b-PEG copolymers supplied by BASF<sup>(B)</sup> and Sigma Aldrich<sup>(S)</sup>.  $M$  (calculated from OH number) and  $P_c$  according to the information provided by the suppliers.

Trade name	$M$ (g mol <sup>-1</sup> )	$P_c$ (wt%)	Code
Group A			
PE6100 <sup>(B)</sup>	2000	10	P2000-10
PE8100 <sup>(B)</sup>	2600	10	P2600-10
PE10100 <sup>(B)</sup>	3500	10	P3500-10
Group B			
PE6200 <sup>(B)</sup>	2450	20	P2450-20
L64 <sup>(B)</sup>	2900	40	P2900-40
L121 <sup>(S)</sup>	4400	30	P4400-30

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