



# Mechanical, aging, optical and rheological properties of toughening polylactide by melt blending with poly(ethylene glycol) based copolymers



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## ABSTRACT

Two novel biodegradable copolymers, including poly(ethylene glycol)-succinate copolymer (PES) and poly(ethylene glycol)-succinate-*l*-lactide copolymer (PESL), have been successfully synthesized via melt polycondensation using SnCl<sub>2</sub> as a catalyst. The copolymers were used to toughen PLA by melt blending. The DSC and SEM results indicated that the two copolymers were compatible well with PLA, and the compatibility of PESL was superior to that of PES. The results of tensile testing showed that the extensibility of PLA was largely improved by blending with PES or PESL. At same blending ratios, the elongation at break of PLA/PESL blends was far higher than that of PLA/PES ones. The elongation maintained stable through aging for 3 months. The moisture absorption of the blends enhanced due to the strong moisture absorption of PEG segments in PES or PESL molecules, which did not directly lead to enhance the hydrolytic degradation rate of the PLA. The PLA blends containing 20–30 wt% PES or PESL were high transparent materials with high light scattering. The toughening PLA materials could potentially be used as a soft biodegradable packaging material or a special optical material.

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## 1. Introduction

Advanced technology in the field of petroleum-based polymers has brought large benefits to mankind. At the same time, the ecosystem is considerably disturbed and damaged as a result of the non-degradable plastic materials for disposable items [1]. In recent years, the biodegradable polymeric materials derived from renewable resources have attracted more attention due to the daily increasing environmental consciousness and sustainability issues associated with the continuously reduced amount of petroleum resources [2,3]. In a large number of the biodegradable materials, polylactide (PLA) derived from renewable resources has attracted more and more attention due to its high biocompatibility and good biodegradability and mechanical properties [4–7], and thus PLA

has a broad application prospect in the fields of biomedical materials and general plastics [8–13]. For a long time, PLA holds tremendous promise as an alternative to the ubiquitous petroleum-based materials. In recent decades, the advances in the polymerization technology have significantly reduced the production cost and have contributed to make PLA economically competitive with the petroleum-based polymers. However, the inherent brittleness of PLA severely limits its more widespread implementation [10,14]. Considerable efforts have been made to toughen PLA, such as copolymerizing lactide with other monomers or macromolecules to produce PLA-based random or block copolymers, blending PLA with other flexible polymers and modifying it with biocompatible plasticizers. Copolymerization of PLA has been extensively investigated as a powerful means to obtain desired polymer materials with properties unattained by homopolymers [15–19]. However, sometimes the copolymerization of PLA with other monomers is not economically practical for its applications. Compared with copolymerization, blending modification for PLA is more economical and more suitable for industrialized production. In order to keep the biodegradability of PLA materials, blending PLA with other flexible biodegradable materials has been extensively investigated.

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The flexible biodegradable materials are mainly some aliphatic polyesters, such as poly( $\epsilon$ -caprolactone) (PCL) [20–29], poly(butylene succinate) (PBS) [30–34], poly(butylene adipate-co-terephthalate) (PBAT) [35–41], Poly(butylene succinate-co-L-lactate) (PBSL) [42–44], Polyamide elastomer (PAE) [45], and poly(ether urethane) (PU) elastomer [46]. These aliphatic polyesters are fully biodegradable and thus ideal polymers for toughening PLA. Unfortunately, these polyesters are commonly immiscible with PLA and thus could not remarkably improve the flexibility of the end materials. On the other hand, the sold prices of the polyesters are much higher than that of PLA. In order to overcome the immiscibility of PLA with toughening modifiers to achieve enhanced mechanical properties, the suitable blocks or the graft copolymers that are either premade or *in situ* formed during reactive compatibilization are added in. Plasticizing PLA to improve its toughness also has received extensive attention. However, the low molecular weight plasticizers often trend to migrate from PLA matrix, resulting in the gradual loss of the toughness of PLA materials with aging time [47,48]. In order to overcome the migration of plasticizers to the surface of materials, oligomeric plasticizers have been widely studied [48–52]. Poly(ethylene glycol) (PEG) has a good compatibility with PLA [53,54]. PEGs with different molecular weights are all good plasticizers for PLA [54–56], but the relatively lower molecular weight PEGs could slowly migrate to the material surface with aging time, in order to overcome this defect, the higher molecular weight PEGs as plasticizers for PLA have been used to improve the flexibility of PLA, but the crystallization of the PEGs can a little occur in the process of cooling from the melting PLA blends [57] and the embrittlement of blends renewly occurs with aging time because the crystallization of PEGs leads to the phase separation between PLA and PEG at room temperature [55,56,58–60].

In this work, in order to overcome the phase separation of PEGs from PLA matrix leading to the renew embrittlement of materials, due to the migration of lower molecular weight PEGs toward the material surface and the crystallization of higher molecular weight PEGs with aging time, and obtain PLA materials of performance stability, two types of linear copolymers based on poly(ethylene glycol), including poly(ethylene glycol)-succinate copolymer (PES) and poly(ethylene glycol)-succinate-L-lactide copolymer (PESL), were synthesized, and were used as plasticizers to toughen PLA. PES and PESL could not migrate to the surface from PLA matrix, due to their high molecular weight. PESL, as an amorphous material, could not lead to the phase separation with PLA because of itself crystallization. And the PEG segments in PES and PESL have good compatibility with PLA. Therefore, these two copolymers are expected to the good compatibility and the phase morphology stability with PLA, thus retaining the properties of toughened PLA for long and obtaining high performance PLA composites. The effect of the PES or PESL content on the tensile properties of the blends was discussed in details, and at the same time the effect of aging on the tensile properties of the blends was also evaluated. The phase morphology, rheological behavior, optical properties, moisture absorption and hydrolytic degradation of the blends were also investigated.

## 2. Experimental

### 2.1. Materials

Poly(lactide) (PLA) was manufactured by Zhejiang Hisun Biomaterials Co., Ltd., Taizhou, Zhejiang, China. Poly(ethylene glycol)-succinate copolymer (PES), and Poly(ethylene glycol)-succinate-L-lactide copolymer (PESL) were prepared by our laboratory. The number-average and weight-average molecular weights ( $M_n$  and

$M_w$ ) and polydispersity index ( $PDI = M_w/M_n$ ) of the polymers were evaluated by gel permeation chromatography (GPC).  $M_n$ ,  $M_w$ , PDI, optical L-lactate unit content (L%) and glass temperature ( $T_g$ ) of PLA are  $M_n = 9.9 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 1.53 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ ,  $PDI = 1.54$ , L% = 89.5% and  $T_g = 58.3 \text{ }^\circ\text{C}$ , respectively.  $M_n$ ,  $M_w$ , PDI and  $T_g$  of PES are  $M_n = 1.23 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 2.30 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ ,  $PDI = 1.87$  and  $T_g = -45.6 \text{ }^\circ\text{C}$ , respectively.  $M_n$ ,  $M_w$ , PDI and  $T_g$  of PESL are  $M_n = 1.27 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 2.36 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ ,  $PDI = 1.86$  and  $T_g = -44.0 \text{ }^\circ\text{C}$ , respectively. Poly(ethylene glycol) (PEG-400), succinic anhydride (SA) (AR grade) and tin(II) chloride dehydrate ( $\text{SnCl}_2$ ) (98%) were purchased from Aladdin Chemistry Co., Ltd. L-lactide (L% > 99.0%) was supplied by Zhejiang Hisun Biomaterials Co., Ltd., Taizhou, Zhejiang, China. ADR (JONCRYL<sup>®</sup>ADR-4370-S) was bought from BASF- The Chemical Company.  $M_w$  and epoxy equivalent weight of ADR are  $6800 \text{ g}\cdot\text{mol}^{-1}$  and  $285 \text{ g}\cdot\text{mol}^{-1}$ .

### 2.2. Preparation of PES and PESL

Poly(ethylene glycol)-succinate copolymer (PES) was prepared by melt polycondensation of poly(ethylene glycol) (PEG) and succinic anhydride (SA). Poly(ethylene glycol)-succinate-L-lactide copolymer (PESL) was prepared by melt polycondensation of PEG, SA and L-lactide (LA). PEG-400 was dried under high vacuum at 120–130 °C for 4 h before using. When PES was prepared, PEG and SA at an equimolar ratio were charged in a 1000 mL three-necked round-bottomed flask, and  $\text{SnCl}_2$  with 0.3 mol% based on the amount of SA was added in. When PESL was prepared, PEG and SA at an equimolar ratio, and LA with 5 wt% based on the total amount of PEG and SA, were charged in a 1000 mL three-necked round-bottomed flask, and  $\text{SnCl}_2$  with 0.3 mol% based on the total amount of SA and LA was added in. Firstly, the reaction mixture was heated and controlled at 90 °C for 16 h at atmospheric pressure, in order to completely react between PEG and SA or among PEG, SA and LA. Secondly, for removing the water formed during this condensation reaction, the reaction temperature was steadily increased up to 130 °C and kept for 24 h under high vacuum. Thirdly, in order to further improve the molecular weight of end products, the reaction temperature was increased to 150 °C and kept for 4–12 h under high vacuum and the weight-average molecular weights of PES and PESL were controlled at 15–25 kg mol<sup>-1</sup> (GPC). At last, the resulting products of PES and PESL were placed in a glass flask and sealed to prevent moisture absorption.

### 2.3. Preparation of PLA blends

PLA and PES or PESL were mixed together in a molten state at various ratios in the presence of ADR in 0.4 parts per hundred of resin (phr) as a stabilizing agent for processing. The blending process was performed by a Torque Rheometer (XSS-300) with a rotor speed of 32 rpm at 190 °C for 8 min. PLA were dried under high vacuum at 80 °C for 12 h before melt-mixing. The obtained blends were pre-heated for about 2 min at 190 °C and then were compressed into flat sheets with approximately 1.0 mm thickness by a laboratory compression-molding machine at 190 °C under 10 MPa for 40 s. Then the sample was subsequently cooled at room temperature in another compression-molding machine for further characterizations.

### 2.4. Measurements

#### 2.4.1. GPC testing

Gel permeation chromatography (GPC) was performed at 25 °C on Waters-410 equipped with Waters Styragel HR4 and HR2 columns, and Waters 2414 RI Detector. Chloroform (HPLC grade) was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup>. Conventional calibrations were performed using polystyrene standards (PS).

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