



# Toughening modification of diglycerol-based polylactide networks by incorporating poly(propylene sebacate) segments



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## ABSTRACT

The reactions of a diglycerol-based 4-armed L-lactide oligomer (DG4LAO) with a degree of polymerization ( $n = 10.5$ ) per arm, a hydroxy-terminated propylene sebacate oligomer (H2PSeO,  $n = 6.7$ ) and methylenediphenyl 4,4'-diisocyanate (MDI) produced bio-based polyester-urethanes (PEU-LAO/PSeOs) with feed DG4LAO/H2PSeO weight ratios, 100/0, 75/25, 50/50, 25/75 and 0/100. The FT-IR analysis and chloroform extraction experiment revealed that polymer networks by urethane crosslinkages were certainly formed for all of the polymers except for PEU-LAO/PSeO 0/100 which is a linear polymer. Scanning electron microscopic analysis revealed that the oligolactate (LAO) and propylene sebacate oligomer (PSeO) segments are compatibilized for all of the copolymer networks. The differential scanning calorimetric analysis of PEU-LAO/PSeOs revealed that LAO segments did not crystallize but PSeO segments crystallized, and that melt crystallization efficiency of PSeO segments was much enhanced by the presence of LAO segments. The polarized optical microscope analysis revealed that PEU-LAO/PSeO 25/75 possessed the fastest melt-crystallization rate among all of the PEU-LAO/PSeOs. The elongation at break and tensile toughness for PEU-LAO/PSeOs 100/0–25/75 significantly increased with increasing PSeO fraction, even though those of PEU-LAO/PSeO 0/100 were very low.

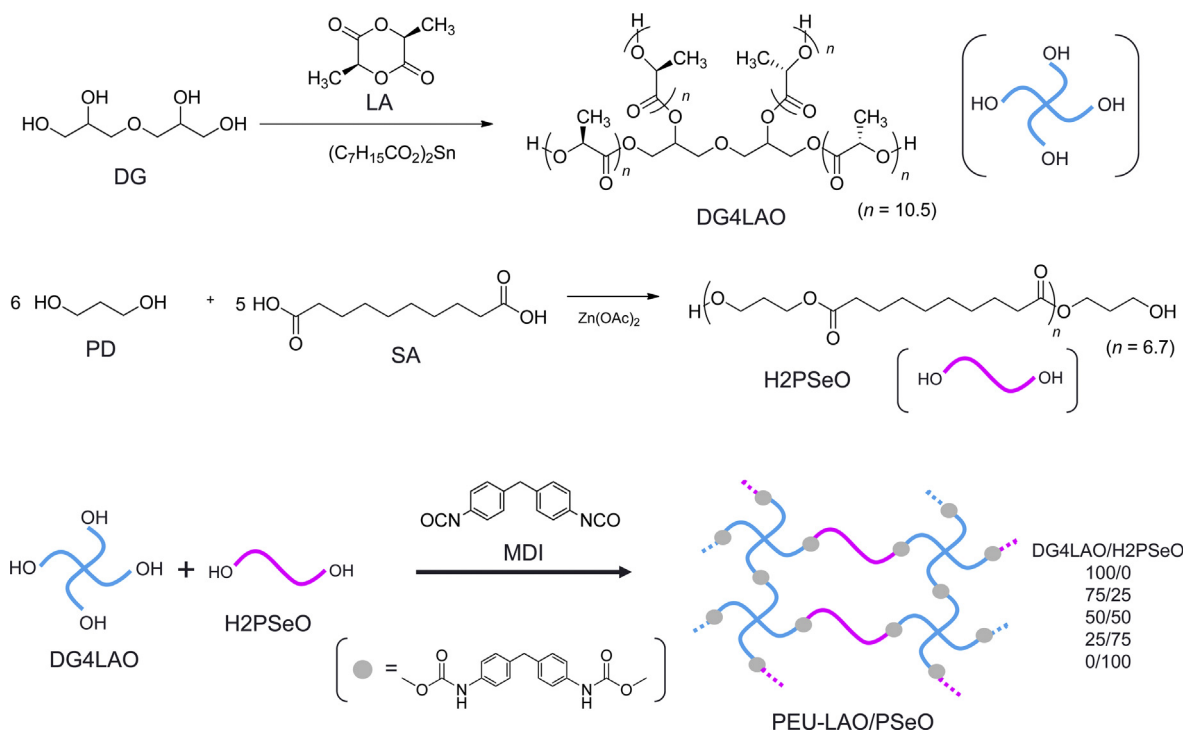
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## 1. Introduction

Renewable resources-derived polymers (bio-based polymers) have become more important in recent years for reduction of greenhouse gas emissions and fossil resource-saving [1–4]. Polylactide (PLA) is one of the most promising bio-based polymers, which is produced from lactic acid derived from corn, potato, and sugarcane, etc. [5]. It exhibits great potential in a wide variety of applications from biomedical materials to industrial packaging materials due to its renewability, biodegradability, biocompatibility, good mechanical strength and easy processability. However, the industrial applications are limited at present due to its inherent brittleness. Therefore, a great deal of efforts has been made to toughen PLA and PLA-incorporating polymers in both industry and academia [6,7]. The most practical method for toughening PLA is to blend with flexible polymers and elastomers. Poly( $\epsilon$ -caprolactone) (PCL) was the earliest flexible polymer investigated for toughening PLA [8–12]. However, as PLA and PCL are not compatible, the morphology of a simple PLA/PCL blend becomes coarse with poor adhesion between the two phases. Consequently, the resulting mechanical properties are not those expected. In order to improve the compatibility of PLA and PCL, various strategies such as the addition of a compatibilizer [13–15], reactive compatibilization [16,17], copolymerization [18–20], crosslinking [21–24], and semi-interpenetrating polymer networks

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**Scheme 1.** Synthesis of DG4LAO, H2PSeO and PEU-LAO/PSeOs (100/0, 75/25, 50/50, 25/75 and 0/100).

[25,26] of PLA and PCL chains had been investigated in past studies. Much recently, we reported that polyester-urethane copolymer networks (MH4(LA/CL) $O_n$ ,  $n = 3, 5$  or  $10$ ) composed of pentaerythritol-based 4-armed star-shaped oligomers of  $\iota$ -lactide (LA) and  $\epsilon$ -caprolactone (CL) with a degree of polymerization ( $n$ ) per arm, 3, 5 or 10 exhibited a much higher tensile toughness than the corresponding PLA/PCL blend did as a result of the compatibilization of the lactide oligomer (LAO) and  $\epsilon$ -caprolactone oligomer (CLO) segments [27]. However, these PCL-based toughening modifiers were not renewable polymers. A recent trend for developing biodegradable and biocompatible polymers with excellent toughness is to adopt fully renewable polymers. As bio-based flexible polyesters for toughening PLA, poly(butylene succinate) [28–30], poly(hydroxyalkanoates) [31,32], a bioelastomer prepared from renewable diols and dicarboxylic acids [33], etc. have been investigated in past studies. For example, Zhang et al. reported that a PLA blend with 11.5 vol% of the bioelastomer prepared by the condensation reaction of itaconic acid, succinic acid, 1,3-propanediol (PD), sebacic acid (SA) displayed much higher tensile toughness than PLA did [33]. Poly(propylene sebacate) (PPSe) is a promising bio-based and biodegradable polyester [34,35], because its two monomers, PD and SA are produced from glycerol [36,37] and castor oil [38] using microbial and chemical processes, respectively. However, published works on utilization of PPSe itself or its derivatives as a toughening modifier for PLA are scarce, probably because the elongation at break PPSe itself is not so high ( $\sim 8\%$ ) in spite of the presence of the long alkylene chain [39].

In this study, bio-based polyester-urethanes (PEU-LAO/PSeOs) were prepared by reactions of a diglycerol-based 4-armed  $\iota$ -lactide oligomer (DG4LAO) with a degree of polymerization ( $n = 10.5$ ) per arm, a hydroxy-terminated propylene sebacate oligomer (H2PSeO,  $n = 6.7$ ) and methylenediphenyl 4,4'-diisocyanate (MDI), and thermal and mechanical properties of PEU-LAO/PSeOs with various compositions were investigated (Scheme 1). Our attention is focused on the improvement of flexibility and tensile toughness of the PLA network by incorporating the PSeO segment.

## 2. Experimental

### 2.1. Materials

Sebacic acid (SA) and 1,1,2-trichloroethane (TCE) were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). Methylenediphenyl 4,4'-diisocyanate (MDI) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan).  $\alpha,\alpha'$ -Diglycerol (DG) was supplied from Sakamoto Yakuin Kogyo, Co. Ltd. (Osaka, Japan). 1,3-Propanediol (PD), zinc acetate ( $Zn(OAc)_2$ ) and chlorobenzene were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Tin (II) bis(2-ethylhexanoate) ( $Sn(Oct)_2$ ) was purchased from KISHIDA CHEMICAL Co. Ltd. (Osaka, Japan).  $\iota$ -Lactide (LA,  $>99\%$ ) was purchased from Musashino Chemical Laboratory, Ltd. (Tokyo, Japan). All the reagents were used without further purification.

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