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Plasticizing effect of a degradable baroplastic copolymer on polylactide

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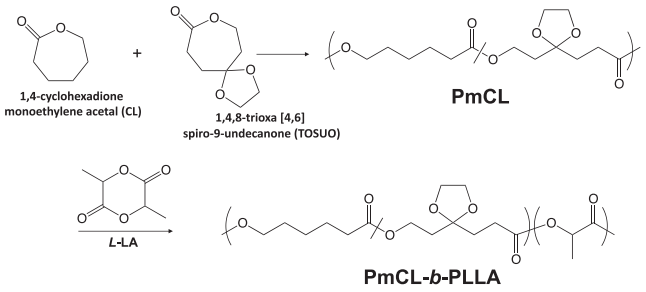
Introduction

Polylactides, a widely used degradable polymer, are processed at 210-220°C, which causes thermal degradation of the backbone of the polymer with limiting the recyclability. To address this issue, in the current study, we propose an idea to use baroplastic block copolymers as a pressure-responsive plasticizer, which would reduce the processing temperature of PLLA. Baroplastics used in this study is poly(ε-caprolactone-*r*-5ethyleneketal ε-caprolactone)-*b*-poly(L-Lactide) (PmCL-*b*-PLLA) synthesized by a two-step ring-opening polymerization of the corresponding lactones and then L-lactide (Scheme 1). In general, baroplastics are a two-component copolymer system with a low-T_g (glass transition temperature) soft segment and a high-T_g hard segment. These block copolymers flow under applied pressure at temperatures as low as room temperature[1]. It was reported these polymers could be processed multiple times without any significant degradation in their thermal and physical properties[2]. The addition of the block copolymers would suppress the thermal degradation of PLLA by reducing the processing temperature under pressure.



Scheme 1. Ring-opening polymerization of PmCL-*b*-PLLA.

Experimental, Results & Discussion

The synthesized PmCL-*b*-PLLAs had different ratios of two segments (40 to 60 wt% of PLLA) in the block copolymers. The block copolymers were mixed with PLLA (M_w: 74.6 kDa) in different ratios by dissolving in chloroform followed by reprecipitation in methanol. First, rheological properties of the polymeric specimens were measured on a capillary rheometer (Shimadzu CFT 500EX). Under 50 MPa, PLLA flowed above 160 °C, while block copolymers PmCL-*b*-PLLA40, 50 and 60 did above 2, 14 and 40°C, respectively. Further, the PmCL-*b*-PLLA/PLLA mixtures (by the weight ratio of 1/9, 2/8, 3/7, 4/6 and 1/1) were processed at lower temperatures than the that of neat PLLA as shown in the Figure 1. The flow temperature of PLLA was decreased by 100°C at most when mixed with PmCL-*b*-PLLA40 or 50, suggesting plasticization of the block copolymers. Later, the effect of these block copolymers on the tensile properties of PLLA was measured. In addition, mechanism behind the plasticizing effect of developed copolymers was investigated. In conclusion, plasticizing effect of baroplastics could be a breakthrough step in lowering the processing temperature/energy and also enhancing the recyclability of PLLA.

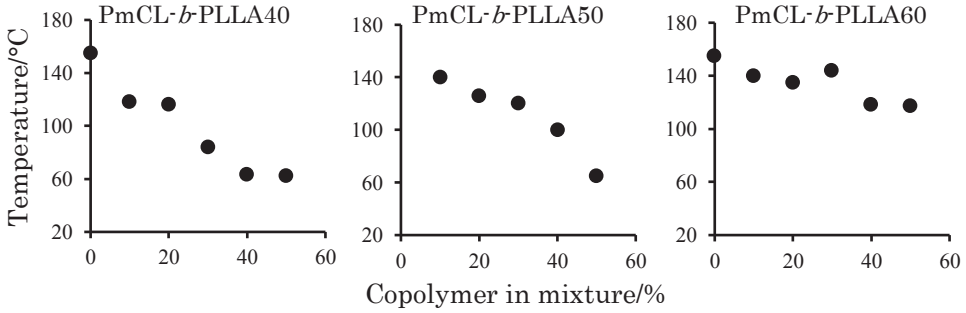


Figure 1. Flow temperature of the polymeric mixtures of PmCL-*b*-PLLA 40, 50, 60/PLLA at 1/9, 2/8, 3/7, 4/6 and 1/1 weight ratio, processed at 50 MPa.

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References:

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