Characterization of injection molded polylactide stereocomplexes blended with thermoplastic starch and chain extender

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Abstract. Polylactide (PLA) is an interesting biodegradable polymer but has limited application because of its low thermal stability and brittleness. Both weaknesses of PLA were solved by stereocomplexes (ST) blended with thermoplastic starch (TPS). In this work, 15% and 30% TPS and 2% chain extender were blended with poly(L-lactide) (PLLA)/poly(D-lactide) (PDLA) (50/50) in an internal mixer. The blended materials were then injection molded into tensile specimens. Differential scanning calorimetry demonstrated that despite the added starch, the stereocomplex structures were still formed and stereocomplex crystallinity decreased with increasing starch content. Compared to neat PLLA, the melting temperature of the stereocomplex and its starch blends was about 55°C higher. The starch enhanced the elongation at break of the stereocomplex samples. Furthermore, stereocomplex and starch compatibility was improved by extending the chains, which in turn improved the stereocomplex and starch blend mechanical properties.

1. Introduction

Derived from natural sources, polylactide (PLA) also degrades naturally and has good optical, mechanical and barrier properties [1] and two enantiomers, poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA). To enhance mechanical and thermal properties and resistance to hydrolysis PLA-based materials, PLLA and PDLA can be blended leading to a stereocomplex, with a 220°C melting temperature or ~50°C greater than either homocrystallized enantiomer [2,3]. The molecular weight, optical purity and chain structure (linear or branched) affect the degree of the stereocomplex formation [4].

This study aimed to improve thermal stability and toughness of PLA, hypothesizing that the stereocomplex would enhance thermal stability and thermoplastic starch (TPS) would improve the toughness. Further, it confirmed that adding chain extenders (CE) is an effective way to improve the compatibility of the blended materials. Equal quantities of PLLA and PDLA, with varying amounts
of added starch, were melt blended and injection moulded. In the blend, stereocomplexes were formed, which significantly altered the PLLA properties, already studied with added starch [5]. Differential scanning calorimetry was used to evaluate and measure stereocomplex formation in the blends. Moreover, mechanical properties and morphologies were studied.

2. Experiments

2.1 Materials
PLLA (trade name L175) and PDLA (trade name D120) was obtained from Total Corbion PLA (Thailand) Ltd. Native rice starch was purchased from Thai Flour Industry, Thailand. Glycerin (Green Global Chemical, Thailand, purity 99.5%) was used as a plasticizer. To join the chains, we used a styrene acrylic copolymer (oligomeric coupling agent), equipped with epoxy functional groups (BASF Corporation Joncryl ADR4370).

2.2 Processing
For TPS preparation, native rice starch and glycerin (content 25wt%) were manually mixed and stored at 25 ± 2°C for 24 h. The resulting blends were mixed in a rheometer or mixer (HAAKE Polylab OS system) at 60 rpm and 200°C for 4 min.

PLLA or ST was then mixed with 15 or 30wt% TPS with the 0 and 2wt% chain extender using the same mixer at 60 rpm and 200°C for 4 min. Tensile bars were formed in an injection molding machine (ING-58T, Chareon Tut Co., Ltd) following ASTM D638 Type I. The neat stereocomplex (PLLA: PDLA 50:50), neat PLLA and TPS were injection moulded and used as reference materials.

2.3 Material Characterization

2.3.1 Differential Scanning Calorimetry (DSC). Melting temperatures of the homo, \( T_{m1} \), and stereocomplexes, \( T_{m2} \), and enthalpies of both structures were determined with a differential scanning calorimeter (Perkin–Elmer DSC4000, Massachusetts, USA). Samples were heated at 10°C/min from 0 to 250°C in an \( \text{N}_2 \) gas flow.

2.3.2 Scanning Electron Microscopy (SEM). The samples were frozen in liquid \( \text{N}_2 \) and then quickly impact fractured, after which an (≈20 nm) Au layer was sputter-coated on them. SEM images of the fracture surfaces were acquired with a Hitachi SU-1500 electron microscope, operated at 3 kV.

2.3.3 Mechanical Testing. Tensile properties of the injection moulded specimens were measured with an NRI-TS501 universal testing instrument at a constant 10 mm/min crosshead speed.

3. Results and Discussions

3.1 Thermal Properties
Figure 1. shows DSC thermograms of PLLA blended with TPS. PLA had three thermal steps: (1) a glass transition temperature \( (T_g) \) ~60°C, (2) a cold crystallization step in the range 95-120°C, and (3) an endothermic fusion step (melting peak, \( T_m \)) with a maximum at 155-175°C. On the other hand, TPS is an amorphous polymer. When PLLA and TPS were mixed, the melting enthalpy decreased with increasing TPS content (see Figure 1). Thus, dispersing TPS into the blends reduced the crystallization. When the chain extender was added to the blends, the resulting longer chains decreased PLLA chain mobility and melting enthalpy of the blended materials.

Figure 2. shows the DSC thermogram of the stereocomplex blends (PLLA: PDLA 1:1) with varying amounts of TPS. The blended materials had a similar glass transition temperature \( (T_g) \) ~60°C but the endothermic peaks of all blends, observed from 208 to 230°C, were assigned to the melting of
stereocomplex crystallites, which were \( \approx 50^\circ \text{C} \) higher than that of PLLA blends, confirming almost complete formation of stereocomplex crystallites.

![Figure 1. Thermograms of PLLA and TPS blends with CE contents, 0 and 2wt.%.](image1)

![Figure 2. Thermograms of ST and TPS blends with CE content 0 and 2wt.%.](image2)

### 3.2 Morphology

Since the morphology of the PLLA/TPS/CE blends and the ST/TPS/CE blends was similar, only those of ST/TPS/CE blends are shown. SEM images of the stereocomplex blends are in Figure 3. They reveal the microstructure and the fractures of the specimens. The fracture surfaces of the stereocomplex and starch were relatively smooth and consistent with brittle fracture following freezing (Figure 3a and 3b), whereas the ST+15%TPS (Figure 3(c)) and ST+30%TPS (Figure 3(d)) clearly showed distinct phases. With chain extended added, compatibility between the stereocomplex and the starch TPS improved and the dispersed phase size reduced (Figure 3(e) ST+15%TPS+2%CE and (f) ST+15%TPS+2%CE). Similar behaviour was reported in blending PLLA/TPS and chain extender was used as compatibilizer [6].

![SEM images](image3)
Figure 3. Scanning electron micrographs: raw stereocomplex (a) ST and starch (b) TPS; stereocomplex with added starch (c) ST+15%TPS (d) ST+30%TPS; and with added chain extender (e) ST+15%TPS+2%CE and (f) ST+30%TPS+2%CE.

3.3 Tensile Properties
Stress-strain curves were acquired for PLLA (Figure 4.) and stereocomplex (Figure 5.) specimens; blended with starch and chain extender. Figure 4 shows that the PLLA tensile stress decreased but strain-at-break increased with starch content, indicating the toughening effect of starch in the PLLA. Przybytek et al. (2018) incorporated thermoplastic starch (TPS) in the PLLA matrix and found that it increased the flexibility and reduced the tensile strength [5]. In our study, the chain extender enhanced this effect: elongation at break steadily increased with added chain extender, reaching 46%.

The influence of the starch on mechanical properties of stereocomplex specimens is shown in Figure 5. Adding both starch and chain extended led to tougher specimens: the strain for the stereocomplex with 30 wt.% starch increased from 1% to 10%. However, the tensile strength and elongation-at-break of stereocomplex specimens was slightly lower than those of PLLA samples. We believe that a higher density of links between chains for the stereocomplex samples led in shrinkage and warp and caused lower mechanical properties.

![Stress-strain curves of PLLA and starch blends with CE content of 0 and 2wt.%](image1)

![Stress-strain curves of stereocomplex and starch blends with CE content of 0 and 2wt.%](image2)

4. Conclusions
In this article, the PLLA and PDLA with various amounts of thermoplastic starch were injection molded. The PLLA/PLDA blends almost completely formed stereocomplex crystallites - verified by DSC. We showed that adding the starch to the stereocomplex PLA improved toughness and expanded potential applications of stereocomplex PLA. The chain extender improved compatibility between stereocomplex and the starch and further improved the mechanical properties of the blended materials.

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