# Formation of Stereocomplex Crystallite in a PLLA/PDLA blend

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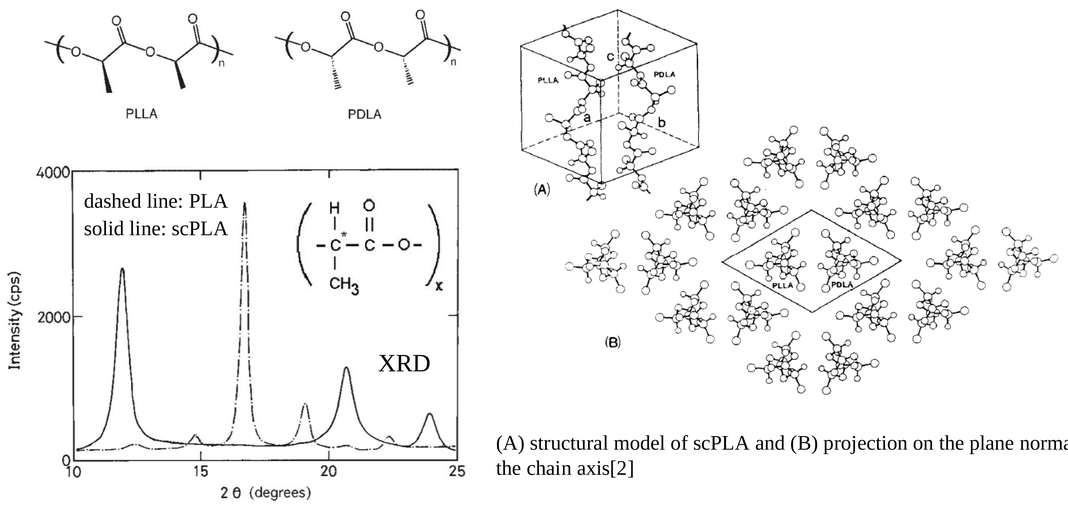
Sharing knowledge...

## 1. Introduction

PLLA / PDLA (50/50, w./w.) blend was prepared by extrusion. The goal of the investigation is to prepare stereocomplex PLA (scPLA) of high crystallinity from high Mn components by choosing suitable processing conditions and thermal treatment. The role of long time isothermal annealing at high temperatures has been discussed.

## 2. Background and motivation




(A) structural model of scPLA and (B) projection on the plane normal to the chain axis[2]

***Scheme 1**: PLLA, PDLA and stereocomplex PLA [1, 2].*

- Poly(L-lactide) (PLLA) and PDLA can form stereocomplex (scPLA) that has Tm about 40-70°C higher than that of the PLA homo-crystallite (~ 175°C) [1]
- The ability to form scPLA decreases as Mn of PLLA and PDLA increases, while to achieve good mechanical properties, high Mn is needed [1]
- High crystallinity is important for hydrolytic stability and mechanical properties [1]

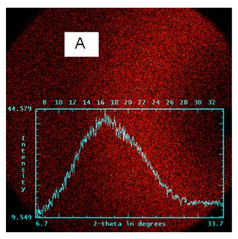
MOTIVATION: to prepare scPLA of high crystallinity from high Mn PLLA and PDLA

## 3. Blending and Characterization

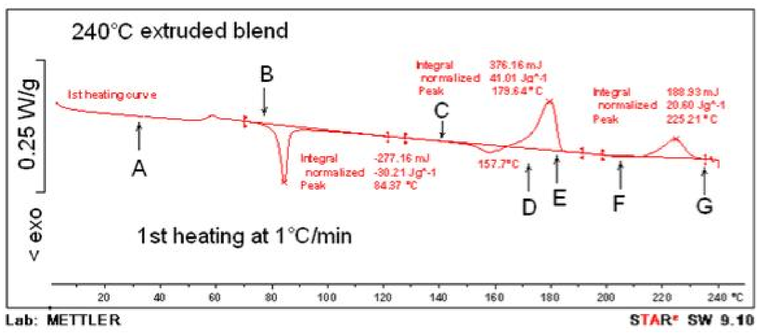
- PLLA with Mn=86kg/mol (Mw/Mn=1.41), and PDLA (high Mn) with Mn=64kg/mol (Mw/Mn=1.85) are provided by Purac. The PLLA/PDLA (high Mn) blend at mass ratio of 50/50 are prepared after extrusion at 240 ° C or 220 ° C for 3 min, and then extruded to room temperature (RT) in the air.
- Differential scanning calorimetry (DSC): first heating at 1 or 10° C/min; after 3 min at 250°C, cooling to RT at 10°C/min and subsequent 2nd heating at 10°C/min. Hot-stage X-ray diffraction (XRD): Bruker D8 Discover, Mettler F82 hot stage, heating at 1°C/min, 1 image/min.

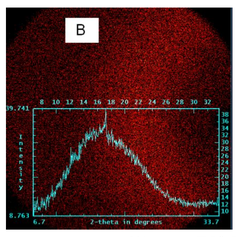
## 4. Results and Discussion

•The 240°C as-extruded blend is amorphous. The observed melting of PLA and scPLA crystallites on DSC are formed during the heating scan. It is noticed that at the T interval between 181°C and 214°C, continuous formation of scPLA is accompanied by a weak exothermal signal.

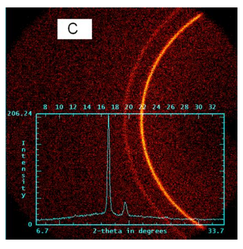



A: 240°C as-extruded blend is amorphous

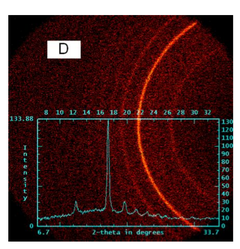



start to crystallize at 76°C

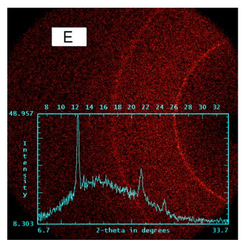


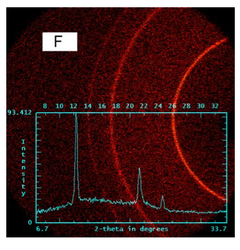

C: homo-crystallites formed at 138°C




D: mixture of two crystallites at 171°C

E: mixture of scPLA crystallite and amorphous melt at 181°C




F: at 204°C, the scPLA crystallizes further (till 214°C), although there is no obvious signal

G: melting of scPLA crystallite at 236°C

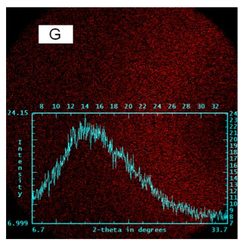
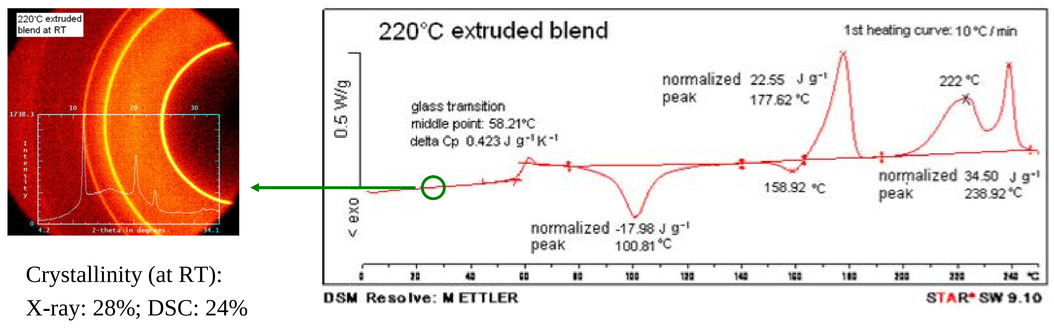



***Fig. 1**: DSC and hot-stage XRD on 240°C as-extruded 50/50 blend.*

## 5. Results and Discussion (Continued)

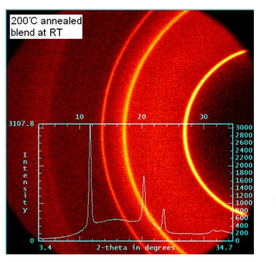
- The 220°C as-extruded blend is semi-crystalline scPLA (Fig. 2, XRD). The presence of these scPLA crystals result in melting of sc PLA at 222 ° C.
- However, the amorphous phase inside the blend almost exclusively crystallizes into PLA homo-crystallites during the heating (Fig. 2, DSC).




Crystallinity (at RT):
X-ray: 28%; DSC: 24%

***Fig. 2**: 220°C as-extruded 50/50 blend. DSC at 10°C/min, and XRD at RT.*

- The 220°C extruded blend, after annealing at 200°C overnight, is semi-crystalline scPLA with slight increase in crystallinity (Figs. 2 and 3). The amorphous phase inside the blend after this annealing, however, crystallizes exclusively into scPLA (during cooling) that leads to a high crystallinity (56%, Fig. 3B). This is in contrast to both as-extruded blends (e.g. 220°C extruded blend, in Fig. 3C).




Crystallinity (at RT):
X-ray: 33%; DSC: 28%

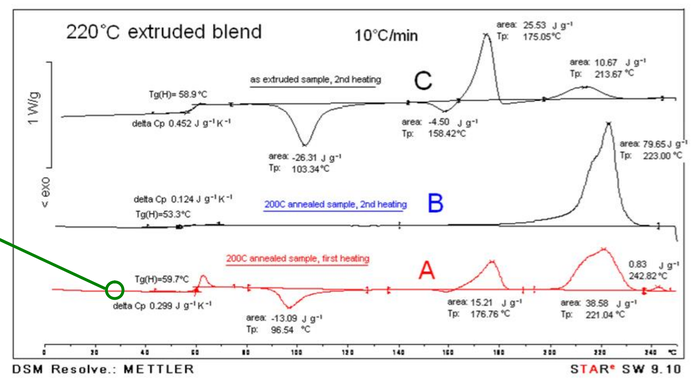



***Fig. 3**: DSC curves for the 220°C extruded blend, 10°C/min. (A+B) after annealing at 200°C overnight, 1st and 2nd heating curves; (C) as-extruded sample, 2nd heating curve.*

### • Role of annealing

There are two possible consequences for the annealing: formation of i) H-bonded precursor to form scPLA, or / and ii) tiny scPLA crystallites as nuclei. For possibility i) one could observe status of the sample after the annealing by IR, e.g. similar peak shift as shown in *Fig. 4* [3]. For possibility ii), several temperature-time cycles are now in trial on DSC.

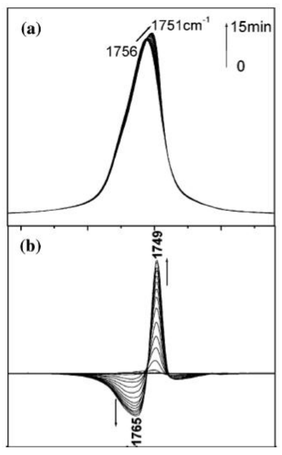



***Fig. 4**: (a) time-resolved IR spectra for scPLA crystallized at 220 °C; (b) difference spectra.*

### • More questions, e.g.:

What are the factors that limit final crystallinity of scPLA? Is it possible to have both fast crystallization and high crystallinity?

## 6. Conclusions and outlook

- scPLA of high crystallinity could be formed from high Mn PLLA and PDLA, in choosing suitable processing conditions and thermal treatment
- Combinatorial approach is helpful for a better understanding
- Further exploration is needed for understanding the mechanism and transformation of the knowledge into application. Estimation of the crystal growth rate by hot-stage optical microscopy (OM) at different temperatures could give more insight.

## 7. References

[1] H. Tsuji. Macromol. Biosci. 2005, 5, 569–597;
[2] T. Okihara, et al. J. Macromol. Sci. Phys. 1991, B30, 119-140;
[3] J. Zhang, et al. Macromolecules 2005, 38, 1822-1828.