Effects of Stereocomplex Nuclei or Spherulites on Crystalline Morphology and Crack Behavior of Poly(L-lactic acid)

Siti Nurkhamidah and Eamor M. Woo
2011/11/16

Department of Chemical Engineering
National Cheng Kung University, Tainan, Taiwan.
Introduction

- **Poly(lactic acid) (PLA) – L/D forms – as green material**

  ![Chemical structures of L-lactic acid (PLLA) and D-lactic acid (PDLA)]

  - **Advantages**: Biodegradable, renewable bio-natural resources, high mechanical property, transparency…
  - **Disadvantages**: Brittleness, low heat resistance, poor processing properties

  ![Cyclic diagram of crack formation](imageURL)

  **Crack formation:**
  - During crystallization
  - During cooling process
  - Contacting with a solvent

**Ref.**
Introduction – Neat PLLA

\( T_c = 120^\circ C^1 \)

Circumferential cracks

\( T_c = 135^\circ C^2 \)

Circumferential cracks

\( T_c = 130^\circ C^3 \)

Circumferential and radial cracks

\( T_c = 130^\circ C^3 \)

Cracks were increasingly less likely to occur with increasing Mw in PLLA

Interspherulitic cracks

\( T_c = 130^\circ C^3 \)

Circumferential and radial cracks

\( T_c = 135^\circ C^2 \)

Circumferential cracks

\( T_c = 120^\circ C^1 \)

Circumferential cracks

\( \checkmark \) upon cooling

\( \checkmark \) crystallized between two glass slides

\( \checkmark \) after being quenched in liquid nitrogen \( \rightarrow \) the crack patterns arise from rhythmic growth and thermal shrinkage.

Ref.

Introduction – Neat PLLA and blend

Neat PLLA

Circumferential cracks

Circumferential and radial cracks

Irregular circumferential cracks

PLLA/PHB (50/50) blend

Radial cracks

The crack patterns and types are highly associated with the lamellar patterns and coarseness in spherulites.

Ref.

Experimental section

Materials

- Poly(L-lactic acid) (PLL), Polyscience, Inc
  \(M_w = 11,000 \text{ g/mol}, T_g = 45^\circ \text{C}, T_m = 155^\circ \text{C}\)

- Poly(D-lactic acid) (PDL), Fluka, Inc
  \(M_w = 124,000 \text{ g/mol}, T_g = 54^\circ \text{C}, T_m = 170^\circ \text{C}\)

Sample Preparations

PLL/PDL (90/10)

Chloroform

Drip casting

Solution (4 wt%)

Thin film

Observation

- Polarized Optical Microscopy (POM)
- Differential Scanning Calorimeter (DSC)
- Wide-angle X-ray Diffraction (WAXD)
- Atomic Force Microscopy (AFM)
**POM morphology of PLLA/PDLA (90/10)**

**Thermal treatment**

- **$T_{max} = 190^\circ C$**
  - sc-PLA nuclei remain unmelted
  - PLLA crystallized in the presence of sc-PLA nuclei

- **$T_{max} = 240^\circ C$**
  - all the sc-PLA nuclei can be erased
  - PLLA and sc-PLA crystallized simultaneously
**PLLA/PDLA (90/10) (240-2-125)**

**Heating process**

- Dendritic spherulites (strong birefringence) → PLLA spherulites
- Ringless spherulites (weak birefringence) → sc-PLA spherulites

**In-situ growth**

- The growth rate of the sc-PLA spherulites is much faster than that of the PLLA spherulites
- PLLA spherulites overlap with the sc-PLA spherulites
PLLA/PDLA (90/10)

PLLA/PDLA (90/10) blend is crystallized at 140 °C. DSC thermograms show similar patterns and only differ in size.

**WAXD patterns**

PLLA and sc-PLA spherulites are observed. sc-PLA spherulites are not only sc-PLA but also PLLA crystals when the PLLA/PDLA (90/10) blend is crystallized at 140 °C.

**Why only sc-PLA spherulites can be observed and whether there are spherulites of PLLA crystals in the crystallized blends...**
Heating process

- PLLA crystals completely melt and the birefringence of the spherulites becomes weak

- PLLA spherulites enhance the birefringence of the sc-PLA spherulites
- PLLA spherulites are trapped in the sc-PLA spherulites
**POM morphology of PLLA/PDLA (90/10)**

190-2-140

In the presence of sc-PLA nuclei

VS

240-2-140 - RT - 190-2-140

In the presence of sc-PLA spherulites

---

No cracks occur when PLLA crystallized in the presence of sc-PLA spherulites. Cracks only occurs in the presence of sc-PLA nuclei.
AFM images of PLLA/PDLA (90/10) 190-2-140

The number of cracks is fewer and the crack depth is less in PLLA crystallized from the PLLA/PDLA (90/10) blend than those in neat PLLA with no sc-PLA crystals.

Unmelted sc-PLA (sc-PLA nuclei) apparently contain protruded crystalline rod-like dots about 150-250nm in diameter.
**AFM images** of PLLA/PDLA (90/10) 240-2-140 –RT-190-2-140

The lamellar arrangement in the presence of sc-PLA spherulites is more compact or denser than that in the presence of sc-PLA nuclei.
Conclusions

1. When PLLA crystals are melted but sc-PLA crystals are not (at $T_{\text{max}}=190$ °C), subsequent holding of the PLLA/PDLA (90/10) blend at $T_c$ results in the PLLA component crystallizing on the presence sc-PLA nuclei and cracks (short-radial cracks but also wrinkles) occur during cooling.

2. Upon crystallization by quenching from $T_{\text{max}}=240$ °C, sc-PLA spherulites and homocrystals of PLLA are crystallized simultaneously from PLLA/PDLA melts, there are no cracks.

3. Cracks are less prone to occur in the more compact spherulites and the sc-PLA crystal reduces and hinders the formation of cracks in PLLA spherulites.
This work has been financially supported by a basic research grant (NSC 96-2221-E-006-099-MY3 and NSC-97- 2221-E-006-034-MY3) for three consecutive years from Taiwan’s National Science Council (NSC).

Funding for attending this conference is supported by NSC and National Cheng Kung University (NCKU).

Thank you for your attention.