Cracks and Lamellar Patterns in co-Crystallized Poly(L-lactic acid) with Poly(ethylene oxide)

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Crack patterns of PEO/PLLA blends crystallized at 110 °C with a top cover:

- (A) 10/90
- (B) 20/80
- (C) 50/50
- (D) 80/20

What is the mechanism for these different crack patterns formation?

### Materials and Procedure

#### PLLA
- Biodegradable, biocompatible polyester
- Brittleness, low heat resistance

#### PEO
- Water soluble polyether
- Low toxicity in biomedical applications

<table>
<thead>
<tr>
<th>Polymer blend</th>
<th>$M_w$ (g/mol)</th>
<th>Phase behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO/PLLA</td>
<td>$M_w$ of PLLA $&lt; 150,000$ with low $M_w$ PEO</td>
<td>Miscible</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Materials</th>
<th>Structure</th>
<th>$M_w$ (g/mol)</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA</td>
<td><img src="image" alt="PLLA structure" /></td>
<td>11,000</td>
<td>45</td>
<td>155</td>
</tr>
<tr>
<td>PEO</td>
<td><img src="image" alt="PEO structure" /></td>
<td>20,700</td>
<td>-60</td>
<td>64</td>
</tr>
</tbody>
</table>

Materials and Procedure

Sample preparation

- PEO+PLLA were dissolved in CHCl₃ to form 4 wt% solution
- Cast on a glass slide to form a thin film (7-14 μm)
- Melt-crystallized at T_c=110 °C then quenched to RT with top cover (Two steps crystallization)

- Top cover: glass slide or polyimide film
- Etching agent: deionized water

Physical etching process for showing 3-D lamellar morphology
The crack patterns are affected by the compositions of the blends.

Dual spherulite types and cracks in PEO/PLLA (80/20) blend crystallized at $T_c=110 \degree C$ then cooled to ambient temperature.
Three conditions must be met for occurrence of cracks in the PEO/PLLA blend:

1) samples are **confined in a limited space**;
2) the later-grown PEO spherulites are **overlapped** with the earlier-grown PLLA crystals (which could be either large ring-banded spherulites or tiny non-banded PLLA crystal);
3) **impingement** of the PEO polymer.
Results and Discussion

PEO/PLLA blends (water-etched sample)

50/50

OM & POM

80/20

SEM

The PLLA lamellae → seaweed patterns

Lenticular-shaped Inter-lamellae void

Results and Discussion

PEO/PLLA (50/50) blend

unetched

water-etched

~10 μm

fractured surface

~7 μm

fractured surface

~10 μm

fractured surface

Scheme for crack formation mechanism in the PEO/PLLA (50/50) blend

Top view

ridge

valley

PEO crystallized

cross section

Top cover

Substrate

inter-lamellae void

valley

top surface

ridge

top surface

fractured surface

fractured surface

inter-lamellae void

inter-lamellae void

Top cover

Substrate

void

void
RESULTS AND DISCUSSION

PEO/PLLA blends

- 40/60
  - 20 µm

- 30/70
  - 20 µm

PEO/PLLA (80/20) blend

- Top view
  - irregular crack

- Cross section
  - PEO crystallized


directional crack + irregular crack
Three conditions must be met for occurrence of cracks in the PEO/PLLA blends under two-steps crystallization:

a) samples are **confined in a limited space**;
b) the later-grown PEO spherulites are **overlapped** with the earlier-grown PLLA crystals (which could be either large spherulites or tiny polymer crystal);
c) **impingement** of the PEO polymer.

The crack patterns are correlated with the lamellae morphology of the earlier-grown PLLA. These PEO-induced cracks are caused by the volume reduction due to the PEO crystallization process.
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Thank You for Your Listening~