Towards Super-tough Poly(L-lactide) via Constructing Pseudo-crosslink Network in Toughening Phase Anchored by Stereocomplex Crystallites at Interface

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Synthesis of LB-PCL-b-DLA copolymer. LB-PCL-b-DLA copolymer was synthesized through three procedures: ring-opening polymerization of ε-CL with DMPA as initiator, polycondensation of HOOC-PCL-2OH, and ring-opening polymerization of D-LA with LB-PCL as macro-initiator. The ring-opening reaction of ε-CL was carried out in a previously flame-dried and nitrogen purged three-necked flask equipped with a stirrer. The polymerization was then implemented at 120°C for 48 h under nitrogen atmosphere using DMPA with one carboxyl and two hydroxyl groups as initiator and Sn(Oct)$_2$ as catalyst to obtain the two-hydroxyl-terminated PCL precursor with one carboxyl group.
(HOOC-PCL-2OH). The molar ratios of ε-CL:DMPA and ε-CL:Sn(Oct)$_2$ were 60:1 and 2000:1, respectively. The long-chain branched PCL (LB-PCL) was prepared through a two-step polycondensation procedure of HOOC-PCL-2OH: esterification and subsequent polycondensation. Typically, HOOC-PCL-2OH was added into a three-necked flask equipped with Dean-Stark water separator, a mechanical stirrer, and an inlet of dry nitrogen. The esterification reaction was conducted at 200°C for 4 h. Then, the catalyst Ti(OBu)$_4$ (0.2 wt % of total amount of the reactants) was introduced and the condensation polymerization was carried out at 220°C under 70 Pa vacuum for about 2-4 h, depending on when the product started to climb onto the stirring paddle. The LB-PCL was extracted for 72 h with refluxing chloroform in a Soxhlet extractor before used. The PDLA segments were grafted onto LB-PCL to obtain LB-PCL-b-DLA through the ring-opening polymerization of $\text{D}_L$-LA with LB-PCL as a macro-initiator and Sn(Oct)$_2$ as catalyst. Owing to the high melt viscosity of LB-PCL, dried xylene (150 wt % of total amount of the reactants) was added into the system to ensure the reaction proceeding smoothly. The polymerization was conducted at 120°C for 12 h under nitrogen atmosphere in a previously flame-dried and nitrogen purged three-necked flask equipped with a mechanical stirrer, and an inlet of dry nitrogen. The molar ratio of $\text{D}_L$-LA:LB-PCL was 4:6, and the molar ratio of $\text{D}_L$-LA:Sn(Oct)$_2$ was 200:1
Synthesis of PCL-b-DLA copolymer. The synthesis procedures of PCL-b-DLA copolymer were almost the same as the LB-PCL-b-DLA copolymer, only different in the initiator used. As control, glycolic acid with one carboxyl and one hydroxyl groups was used as initiator to prepare PCL-b-DLA copolymer with linear topology. The linear copolymer was also synthesized through three procedures: (1) ring-opening polymerization of \( \varepsilon \)-CL using glycolic acid as initiator to prepare HOOC-PCL-OH precursor; (2) preparation of linear PCL by polycondensation of HOOC-PCL-OH; and (3) preparation of PCL-b-DLA copolymer by ring-opening polymerization of D-LA with linear PCL as macro-initiator.

\(^1\text{H} \) NMR measurement. The chemical structures of HOOC-PCL-2OH, LB-PCL, LB-PCL-b-DLA, HOOC-PCL-OH, linear PCL and PCL-b-DLA were characterized by \(^1\text{H} \)
NMR (Bruker AC-P 400 MHz spectrometer) at room temperature with CDCl$_3$ and tetramethylsilane (TMS) as a solvent and an internal chemical shift standard, respectively. It is clear that the resonance signals of all the characteristic protons can be found in the spectra. Particularly, the signals of the methylene proton connected to terminal hydroxyl groups (-CH$_2$OH) of HOOC-PCL-2OH, LB-PCL, HOOC-PCL-OH and linear PCL were observed at 3.53 ppm but disappeared in LB-PCL-b-DLA and PCL-b-DLA copolymer, meanwhile, the signals of the methine proton connected to terminal hydroxyl groups (-CHOH) of PDLA segments were detected, indicating that the terminal hydroxyl groups of LB-PCL and linear PCL successfully initiated the ring-opening polymerization of D-LA and therefore resulted in LB-PCL-b-DLA and PCL-b-DLA copolymers. The molar ratio of ε-CL and D-LA repeating units in the synthesized copolymers were calculated through the ratio of integral areas of the corresponding peaks. The monomeric unit molar ratio of ε-CL to D-LA obtained from integral area ratios of peak $e$ to peak $f$ were 1.58:1 and 1.35:1 for LB-PCL-b-DLA and PCL-b-DLA copolymers, respectively, which were very close to the feed ratio of 1.5:1.

**Gel Permeation Chromatography with Multiangle Laser Light Scattering (GPC-MALLS).** A Waters GPC, which was equipped with a 1515 pump, a Waters model 717 autosampler, and a 2414 refractive index detector was used for determining the molar mass ($M_n$) and dispersity ($Đ$) of samples with Chloroform as the eluent. The flow rate of eluent and the concentration of sample were 1.0 mL/min and 0.25 mg/mL, respectively. The experiments were carried out at 35°C. A MiniDAWN (Wyatt Technology) multiangle laser light scattering (MALLS) detector equipped with 690 nm semiconductor laser was connected
between the gel permeation columns and a Wyatt Optilab DSP differential refractometer. CHCl$_3$ was used as a mobile phase at a flow rate of 1.0 mL/min. A 100 µL sample of a 0.2 mg/mL solution, which was filtered through a 45 µm Whatman filter prior to use, was injected for all measurements. The software Astra (ver. 4.90.04, Wyatt Technology) was used to compute the calibration curves and the molecular weights distribution. The calibration of detectors was achieved using polystyrene standards of narrow molecular weight distribution with known molecular weights. The ratio of the mean-square radius of gyration of the given hyperbranched polymer to that of its linear analogue, termed as branching ratio, $g$, provides a mean to characterize the branching structure:$^{S1}$

$$g = \frac{\langle R_g^2 \rangle_{\text{branched}}}{\langle R_g^2 \rangle_{\text{linear}}}$$ (S1)

The molecular weights of copolymers significantly increased compared with precursors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio of CL:LA$^a$</th>
<th>$M_n^b$ (g/mol)</th>
<th>$M_w^b$ (g/mol)</th>
<th>PDI$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOOC-PCL-2OH</td>
<td>-</td>
<td>$5.2 \times 10^3$</td>
<td>$1.1 \times 10^4$</td>
<td>2.1</td>
</tr>
<tr>
<td>LB-PCL</td>
<td>-</td>
<td>$2.1 \times 10^4$</td>
<td>$5.5 \times 10^4$</td>
<td>2.6</td>
</tr>
<tr>
<td>LB-PCL-b-DLA</td>
<td>1.58:1</td>
<td>$5.4 \times 10^4$</td>
<td>$1.1 \times 10^5$</td>
<td>2.1</td>
</tr>
<tr>
<td>PCL-b-DLA</td>
<td>1.35:1</td>
<td>$6.8 \times 10^4$</td>
<td>$1.0 \times 10^5$</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^a$ calculated from $^1$H NMR;

$^b$ The $M_n$, $M_w$ and PDI were obtained from GPC-MALLS.
Table S2. Molecular architecture parameters of LB-PCL and commercial PCL measured by GPC-MALLS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mₙ (g/mol)</th>
<th>Mₘ (g/mol)</th>
<th>PDI</th>
<th>Rₙ (nm)</th>
<th>Rₘ (nm)</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOOC-PCL-2OH</td>
<td>5.2×10³</td>
<td>1.1×10⁴</td>
<td>2.1</td>
<td>57.3</td>
<td>77.2</td>
<td>-</td>
</tr>
<tr>
<td>LB-PCL</td>
<td>2.1×10⁴</td>
<td>5.5×10⁴</td>
<td>2.6</td>
<td>37.4</td>
<td>50.6</td>
<td>0.65–0.74</td>
</tr>
<tr>
<td>commercial PCL</td>
<td>8.5×10⁴</td>
<td>1.5×10⁵</td>
<td>1.8</td>
<td>51.0</td>
<td>68.7</td>
<td>-</td>
</tr>
</tbody>
</table>
### Tensile properties of neat PLLA and the blends

Table S3. Tensile properties of neat PLLA and the blends.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA</td>
<td>77.6±2.5</td>
<td>9.0±1.2</td>
</tr>
<tr>
<td>PLLA/9%LB-PCL</td>
<td>66.7±1.3</td>
<td>34.6±4.7</td>
</tr>
<tr>
<td>PLLA/15%LB-PCL-b-LLA</td>
<td>66.8±2.2</td>
<td>25.0±1.1</td>
</tr>
<tr>
<td>PLLA/15%LB-PCL-b-DLA</td>
<td>56.0±0.4</td>
<td>24.3±2.9</td>
</tr>
<tr>
<td>PLLA/15%PCL-b-DLA</td>
<td>61.6±0.4</td>
<td>41.8±5.1</td>
</tr>
<tr>
<td>non-annealed PLLA/15%LB-PCL-b-DLA</td>
<td>58.5±0.8</td>
<td>347.4±10.9</td>
</tr>
</tbody>
</table>

*All samples had been annealed at 100°C for 30 min before testing besides the last one.*
Comparison of mechanical properties of toughened PLLA reported in the literature

Figure S3. A comparison of mechanical properties (A) and additive content (B) of toughened PLLA with different protocols; the solid symbols represent literatures reporting toughened PLLA with SC crystallites constructed at the interfaces.
Crystallization of PLLA

The intrinsic degree of crystallinity ($\chi_{c,PLL A}$) of PLLA matrix in the injection-molded samples was calculated according to the following equation:\textsuperscript{S17}

$$
\chi_{c,PLL A}(\%) = \frac{\Delta H_{m, hc} + \Delta H_{m, sc} - \Delta H_{cc}}{w_f \Delta H_{m(\text{blend})}^0} \times 100\%
$$

(S2)

where $\Delta H_{m, hc}$ and $\Delta H_{m, sc}$ are the experimental melting enthalpies of $\alpha$ form of homopolymer crystals and $\beta$ form of the stereocomplex crystals, respectively. $\Delta H_{cc}$ is the cold crystallization enthalpy and $w_f$ is the weight fraction of PLA component in the blends. $\Delta H_{m(\text{blend})}^0$ is the theoretical value of melting enthalpy for perfect crystals, which can be postulated in the following manner:

$$
\Delta H_{m(\text{blend})}^0 = \Delta H_{m, hc}^0 \cdot f_{hc} + \Delta H_{m, sc}^0 \cdot f_{sc}
$$

(S3)

where $\Delta H_{m, hc}^0$ and $\Delta H_{m, sc}^0$ are the theoretical enthalpy values for polylactide $\alpha$ form homopolymer crystallites (93.6 J/g) and $\beta$ stereocomplex crystallites (142 J/g), respectively. $f_{hc}$ and $f_{sc}$ are the relative amounts of homo and stereocomplex crystallites, respectively, developed during processing under nonisothermal conditions, and can be calculated as follows:

$$
f_{hc}(\%) = \frac{\Delta H_{m, hc}}{\Delta H_{m, hc} + \Delta H_{m, sc}} \times 100\%
$$

(S4)

$$
f_{sc}(\%) = \frac{\Delta H_{m, sc}}{\Delta H_{m, hc} + \Delta H_{m, sc}} \times 100\%
$$

(S5)

The crystallinity degree of stereocomplex crystals ($\chi_{sc}$) of sc-PLA was obtained from the following equation:

$$
\chi_{sc}(\%) = \chi_c \times f_{sc} \times 100\%
$$

(S6)
By contrast, the crystallinity degree of injection-molded PLLA without sc crystallites was calculated according to the following equation:

\[
\chi_c(\%) = \frac{\Delta H_{m,sc} - \Delta H_{cc}}{w_f \Delta H_{m,sc}^0} \times 100\%
\]  

(S7)

Isothermal crystallization

\[
1 - \chi(t) = \exp(-kt^n)
\]  

(S8)

where \(n\) is known as the Avrami index, \(k\) is the overall rate constant including nucleation and crystal growth, and \(\chi(t)\) is the relative crystallinity. We defined \(t_{1/2}\) as the half-crystallization time, so that:

\[
1/2 = 1 - \chi(t) = \exp(-kt^n)
\]  

(S9)

that is

\[
t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n}
\]  

(S10)

with

\[
(t_{1/2})^{-1} = \tau_{1/2} = G
\]  

(S11)

where \(G\) is defined as the crystallization rate, so \(\tau_{1/2}\) directly reflects the magnitude of the crystallization rate at different crystallization temperatures. (7) could also be expressed as

\[
\log[-\ln(1 - \chi(t))] = \log k + n \log t
\]  

(S12)
Table S4. Thermal characteristics obtained from the DSC heating scan of the PLLA blends.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCL</th>
<th>HCs</th>
<th>SCs</th>
<th>( \chi_{c,hc} )</th>
<th>( \chi_{c,sc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_{m1} )</td>
<td>( \Delta H_{m1} )</td>
<td>( T_{m2} )</td>
<td>( \Delta H_{m2} )</td>
<td>( T_{m3} )</td>
</tr>
<tr>
<td>PLLA</td>
<td>-</td>
<td>-</td>
<td>169.1</td>
<td>38.4</td>
<td>-</td>
</tr>
<tr>
<td>PLLA/9%LB-PCL</td>
<td>51.4</td>
<td>1.7</td>
<td>169.1</td>
<td>32.6</td>
<td>-</td>
</tr>
<tr>
<td>PLLA/15%PB-PCL-b-LLA</td>
<td>-</td>
<td>-</td>
<td>168.6</td>
<td>36.2</td>
<td>-</td>
</tr>
<tr>
<td>PLLA/15%PB-PCL-b-DLA</td>
<td>-</td>
<td>-</td>
<td>168.8</td>
<td>31.1</td>
<td>213.1</td>
</tr>
<tr>
<td>non-annealed PLLA/15%PB-PCL-b-DLA</td>
<td>-</td>
<td>-</td>
<td>167.8</td>
<td>34.9</td>
<td>213.5</td>
</tr>
<tr>
<td>PLLA/15%PB-PCL-b-DLA</td>
<td>51.9</td>
<td>1.1</td>
<td>167.5</td>
<td>28.7</td>
<td>219.2</td>
</tr>
</tbody>
</table>

Figure S4. The crystallization of non-annealed PLLA/15\%PB-PCL-b-DLA and PLLA/15\%PB-PCL-b-DLA samples.
Figure S5. POM images showing the changes of crystalline morphologies as time increasing for PLLA (A1, A2, and A3), PLA/9%LB-PCL (B1, B2, and B3), PLA/15%LB-PCL-b-LLA (C1, C2, and C3), and PLA/15%LB-PCL-b-DLA (D1, D2, and D3).
SUPPORTING REFERENCES


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