Supporting Information

For

Food-safe Glycidyl-free Chain Extenders for Polylactide

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Synthesis of 9-(oxiran-2-yl) nonyl methacrylate (EAT) and 8-(3-octyloxiran-2-yl) octyl methacrylate (EAI)

EAT and EAI were synthesized in two steps from their unsaturated long-chain alcohol using our recently reported method.¹,² Details on synthesis and characterization can be found in the Supporting Information.

Step 1: Epoxidation of unsaturated long chain alcohol: Following our recently reported method,¹,² a 250 mL one-neck round-bottom flask was charged with undec-10-en-1-ol or cis-9-octadecen-1-ol (50 mmoL) in chloroform. Then this was reacted with 3-chloroperbenzoic acid (1.3 equiv.), which was added portion-wise at 0 °C over a period of 20 min. The reaction temperature was brought to 25 °C for 48 h, was extracted with K₂CO₃ solution (100 mL, 10 % (g/L) water solution). The organic layer was removed, and chloroform was removed by rotary evaporator under pressure of 20 Pa at 50 °C for 60 min to yield compound epoxidized long chain alcohols.
Step 2: Acrylation of epoxidized long chain alcohol: Methacrylic anhydride (1.4 equiv.) was added dropwise into epoxidized long chain alcohol dissolved in ethyl acetate (1.0 equiv.). The reaction mixture was stirred at room temperature for 48 h. Ethyl acetate was removed under pressure of 20 Pa at 60 ºC for 60 min. Then, a solution of sodium hydroxide (100 mL, 10%(g/L)) and potassium carbonate (100 mL, 10%(g/L)) was added dropwise, and the reaction mixture was stirred for 5 h. The product was extracted with chloroform (200 mL), dried over anhydrous MgSO₄, and filtered off. Chloroform was removed by rotary evaporator under pressure of 20 Pa at 50 ºC for 60 min to afford EAT and EAI. The products were purified by silica gel column chromatography over chloroform as the eluent.
Fig. S1: FT-IR spectra of EAT and EAI.
Fig. S2: $^1$H-NMR spectra of compound 1 and EAT

Fig. S3: $^1$H-NMR spectra of compound 2 and EAI.
**Fig. S4:** DSC cooling thermograms (i) and second DSC heating thermograms (ii) of neat PCL (a), PCL-g-EAT 95/5 (b), PCL-g-EAT 90/10 (c), PCL-g-EAI 95/5 (d), and PCL-g-EAI 90/10 (e).

**Fig. S5:** TGA (i) and DTG (ii) thermograms of neat PCL (a), PCL-g-EAT 95/5 (b), PCL-g-EAT 90/10 (c), PCL-g-EAI 95/5 (d), and PCL-g-EAI 90/10 (e).
Fig. S6: GPC curves of neat PLA (a), PLA/Joncryl ADR (b), PLA/PCL-g-EAT 95/5 (c), PLA/PCL-g-EAT 90/10 (d), PLA/PCL-g-EAI 95/5 (e), and PLA/PCL-g-EAI 90/10 (f).
A) Model reaction between epoxidized sunflower oil and stearic acid.

**Scheme S1:** Reaction between epoxidized plant oil and stearic acid.

**Fig. S7:** $^1$H NMR analysis of stearic acid (bottom); epoxidized sunflower oil (middle); and the product formed by the reaction between stearic acid and epoxidized sunflower oil (top).
B) Model reaction between 1,2-epoxy octane and stearic acid.

\[
\begin{align*}
\text{1,2-epoxy octane} & \quad \text{(1 equiv, 2 gm)} \\
\text{Stearic acid} & \quad \text{(1 equiv, 4.44 gm)} \\
\end{align*}
\]

210 °C/ 5 min
Free solvent

Scheme S2: Reaction between stearic acid and 1,2-epoxy octane.

Fig. S8: \textsuperscript{1}H NMR analysis of: stearic acid (bottom); 1,2-epoxy octane (middle); and the product formed by the reaction between stearic acid and 1,2-epoxy octane (top).
C) Model reaction between 1,4-butanediol diglycidyl ether and stearic acid.

Scheme S3: Reaction between 1,4-butanediol diglycidyl ether and stearic acid.

Fig. S9: $^1$H NMR analysis of stearic acid (bottom); 1,4-butanediol diglycidyl ether (middle); and the product formed by the reaction between stearic acid and 1,4-butanediol diglycidyl ether (top).
Fig. S10: Optical photographs of neat PLA (a), PLA/Joncryl ADR (b), PLA/PCL-g-EAT 95/5 (C), PLA/PCL-g-EAT 90/10 (d), PLA/PCL-g-EAI 95/5 (e), and PLA/PCL-g-EAI 90/10 (f).

Fig. S11: TGA (i) and DTG (ii) thermograms of neat PLA (a), PLA/PCL-g-EAT 95/5 (b), PLA/PCL-g-EAT 90/10 (c), PLA/PCL-g-EAI 95/5 (d), and PLA/PCL-g-EAI 90/10 (e).
**Table S1:** Mechanical properties of PLA with various chain extenders*

<table>
<thead>
<tr>
<th>Name</th>
<th>Tensile strength at break ((\sigma_Y, \text{MPa}))</th>
<th>Tensile modulus ((Et, \text{MPa}))</th>
<th>Elongation at break ((\varepsilon_Y, %))</th>
<th>Impact strength, notched ((\text{kJ/m}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>49.9 ± 1.29</td>
<td>3240 ± 470.8</td>
<td>5.7 ± 0.86</td>
<td>2.48 ± 0.53</td>
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<tr>
<td>PLA/ADR</td>
<td>55.0 ± 2.36</td>
<td>3450 ± 243.3</td>
<td>37.7 ± 25.86</td>
<td>2.53 ± 0.09</td>
</tr>
<tr>
<td>PLA/1 phr PCL</td>
<td>48.3 ± 2.85</td>
<td>4260 ± 494.8</td>
<td>6.1 ± 0.59</td>
<td>2.61 ± 0.21</td>
</tr>
<tr>
<td>PLA/PCL-g-EAT 95/5</td>
<td>53.2 ± 2.58</td>
<td>3800 ± 384.7</td>
<td>77.8 ± 12.35</td>
<td>2.65 ± 0.22</td>
</tr>
<tr>
<td>PLA/PCL-g-EAT 90/10</td>
<td>54.66 ± 1.89</td>
<td>4048 ± 264.5</td>
<td>75.4 ± 12.05</td>
<td>2.41 ± 0.17</td>
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<tr>
<td>PLA/PCL-g-EAI 95/5</td>
<td>53.6 ± 2.75</td>
<td>4433 ± 325</td>
<td>69.3 ± 5.51</td>
<td>2.70 ± 0.03</td>
</tr>
<tr>
<td>PLA/PCL-g-EAI 90/10</td>
<td>52.3 ± 1.85</td>
<td>4338 ± 386</td>
<td>61.8 ± 3.69</td>
<td>2.68 ± 0.27</td>
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</tbody>
</table>

*) The samples contain 1 phr chain extender.

**References:**
