Crosslinking of PBT by reactive extrusion using Zn(II) epoxy-vitrimer chemistry

Adrien Demongeot,† Ramon Groote,‡ Han Goossens,† Theo Hoeks,‡ François Tournilhac,*,† Ludwik Leibler*,†

† Matière Molle et Chimie, UMR 7167 CNRS ESPCI Paris, PSL Research University, 10 rue Vauquelin 75005 Paris, France.
‡ SABIC T&I, Plasticslaan 1, 4612 PX Bergen op Zoom, the Netherlands.

Supplementary Information

Synthesis of bisphenol A bis(2,3-dihydroxypropyl) ether

Scheme 1 Synthesis of bisphenol A bis(2,3-dihydroxypropyl) ether.

In a 500 mL two necks round bottom flask attached to a condenser, a solution of sodium hydroxide (7.26 g, 0.18 mol) in water (120 mL) was placed. With stirring, bisphenol A (10.3 g, 45 mmol) were added. The mixture was heated to 80 °C under a nitrogen atmosphere. Then, 3-chloro-1,2-propanediol (11.4 mL, 0.14 mol) was slowly added dropwise with a purged syringe. Stirring was continued for 16 hours at 80 °C. Subsequently, the solution was allowed to cool down to room temperature. After cooling, a solution of hydrochloric acid (16.0 mL, 0.18 mol) in water (120 mL) was added and the mixture stirred at 80 °C for an hour. Again the solution was allowed to cool down to room temperature. The mixture was decanted and the organic phase was extracted in ethyl acetate. This solution was washed three times with NaCl-saturated water (80 mL) and distilled water (80 mL), dried over anhydrous magnesium sulfate, and filtered. The obtaining solid was purified by
chromatography eluting with ethyl acetate. The product was dried in vacuum at 50 °C for 16 hours. The final product is a white crystalline solid (MP=86-87°C).

**Figure S1** Determination of [COOH] and [OH] end-group concentration by IR spectrometry. (A) FTIR spectrum of dried PBT (black) and PBT after immersion in D₂O (B) FTIR signal difference.

**Figure S2** Determination of epoxy consumption during kinetic experiments with model molecules. Example of ATR-IR spectra showing the epoxy-acid addition catalyzed by Zn (acac)₂ at 200 °C. Spectra were taken every 5s.
Figure S3 Variation of [COOH] end-group content as a function of extrusion time for PBT of two different molar masses with and without the presence of Zn(acac)$_2$ at [Zn(II)]/([OH] + [COOH]) molar ratio of 10%.

Figure S4 Visual aspect of an unswollen specimen of compound 4c (A) and the same after swelling in TCB (B).
Figure S5 Effect of cross-linking through epoxy vitrimer chemistry on crystallization. Thermal analysis data of compounds 4a-4d as a function of the epoxy quantity: (A) crystallization temperature, (B) melting temperature, (C) melting enthalpy (integral between 75 and 232°C) measured on 2nd heating, (corresponding degree of crystallinity, compound 1: $\chi_c = 23.0\%$, compound 4a: $\chi_c = 25.6\%$, compound 4b: $\chi_c = 24.2\%$, compound 4c: $\chi_c = 23.7\%$, compound 4d: $\chi_c = 21.1\%$) and (D) glass transition temperature.
**Table S1** Characteristics of model compounds investigated.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Function</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-heptyl benzoic acid</td>
<td>acid</td>
<td><img src="image1" alt="Structure of 4-heptyl benzoic acid" /></td>
</tr>
<tr>
<td>bisphenol A bis(2,3-dihydroxypropyl) ether</td>
<td>alcohol</td>
<td><img src="image2" alt="Structure of bisphenol A bis(2,3-dihydroxypropyl) ether" /></td>
</tr>
<tr>
<td>diglycidyl ether of bisphenol-A (epoxy n=0.03)</td>
<td>[OH] &lt;&lt; [epoxy]</td>
<td><img src="image3" alt="Structure of diglycidyl ether of bisphenol-A (epoxy n=0.03)" /></td>
</tr>
<tr>
<td>oligo(bisphenol A-co-epichlorhydrin) (epoxy n=2.4)</td>
<td>[OH] = 1.2 [epoxy]</td>
<td><img src="image4" alt="Structure of oligo(bisphenol A-co-epichlorhydrin) (epoxy n=2.4)" /></td>
</tr>
</tbody>
</table>

**Figure S6** Kinetics of model molecules with 2-MI. The reaction is performed at 200°C in bulk between heptyl benzoic and phenyl glycidyl ether in the presence of 5 mol% of 2-MI. Addition takes place within a few minutes, further evolution is analyzed by gas chromatography. The plot shows the time dependance of \( \text{b-hydroxy-ester (mixture of isomers, black squares) and diester (red disks) concentrations.} \)