Supplementary Information for

Intrinsic flame retardant phosphonate-based vitrimers as a recyclable alternative for commodity polymers in composite materials

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Additional Results

Calculation of fibre mass content (fmc)

Table S1. Equations used for the calculation of fibre mass content.

\[
\begin{align*}
\frac{w_{\text{char, GFRP}}}{\%} & \quad \text{Char yield of the GFRP at 800 °C determined by TGA} \\
w_{\text{combustible, GFRP}} = 100 - \frac{w_{\text{char, GFRP}}}{\%} & \quad \text{Combustible fraction of the GFRP} \\
\frac{w_{\text{char}, P}}{\%} & \quad \text{Char yield of the neat polymer at 800 °C determined by TGA} \\
\frac{w_{\text{non-combustible polymer, GFRP}}}{\%} = \frac{w_{\text{char}, P} \cdot (100 - w_{\text{char, GFRP}})}{100} & \quad \text{Non-combustible fraction of the polymer in the GFRP} \\
\frac{w_{F, GFRP}}{\%} = 100 - w_{\text{combustible, GFRP}} - w_{\text{non-combustible polymer, GFRP}} & \quad \text{Fibre mass fraction in the GFRP}
\end{align*}
\]

GFRP: Glass-fibre reinforced plastic

Table S2. Char yield of the Glass-fibre reinforced plastic (GFRP) and the neat polymer determined by TGA at 800 °C in an oxygen atmosphere.

<table>
<thead>
<tr>
<th></th>
<th>( w_{\text{char, GFRP}} ) / %</th>
<th>( w_{\text{char, P}} ) / %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Standard Deviation</td>
<td>Values</td>
</tr>
<tr>
<td>Poly-1</td>
<td>71.3</td>
<td>0.5</td>
<td>24.1</td>
</tr>
<tr>
<td>Poly-2</td>
<td>66.1</td>
<td>3.6</td>
<td>19.3</td>
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</tbody>
</table>

Table S3. Fibre mass fraction in the Glass-fibre reinforced plastic (GFRP).

<table>
<thead>
<tr>
<th></th>
<th>( w_{\text{combustible, GFRP}} ) / %</th>
<th>( w_{\text{non-combustible polymer, GFRP}} ) / %</th>
<th>( w_{F, GFRP} ) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-1</td>
<td>28.7</td>
<td>9.1</td>
<td>62.2</td>
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<tr>
<td>Poly-2</td>
<td>33.9</td>
<td>7.5</td>
<td>58.6</td>
</tr>
</tbody>
</table>
Additional Characterization Data

Figure S1. $^1$H-NMR (300 MHz in CDCl$_3$ at 298 K) of 1a.

Figure S2. $^1$H-NMR (300 MHz in CDCl$_3$ at 298 K) of 1.
Figure S3. $^{31}$P $\{H\}$-NMR (121 MHz in CDCl$_3$ at 298 K) of 1.

Figure S4. Mass loss (bottom) and mass loss rate (top) curves of vitrimers poly-1 and poly-2 in nitrogen via TGA. Heating rate: 10 K min$^{-1}$.

Table S4. LOI and UL-94 results of the vitrimers.

<table>
<thead>
<tr>
<th></th>
<th>UL-94 rating</th>
<th>LOI [% O$_2]$ ± 0.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-1</td>
<td>V-2</td>
<td>21.3</td>
</tr>
<tr>
<td>Poly-2</td>
<td>N.R.</td>
<td>26.1</td>
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</table>
Figure S5. Total heat released (THR) measured by cone calorimetry.

Figure S6. Carbon monoxide production (COP) from cone calorimetry.
Figure S7. Amount of smoke release (SPR) during combustion processes measured by cone calorimetry.

Figure S8. Silicone mold used for the preparation of the composites.
Figure S9. Prepregs after curing in the convection oven. Top: poly-1, Bottom: poly-2.
Figure S10. Preparation of a vitrimer in a heated glass-reactor.

Figure S11. Poly-1 after polycondensation and released from the glass-reactor.
**Figure S12.** Poly-1 after Curing.

**Figure S13.** Poly-1 after shredding with a blender (Bestek BTBL1193).
**Figure S14.** Preparation of 12 x 12 mm² cone plates: Poly-1 powder in a steel mold.

**Figure S15.** Preparation of 12 x 12 mm² cone plates: Poly-1 cone plate after releasing from the mold.
Figure S16. Microscope image after hot pressing two prepreg layers of poly-2 with a 0.3 mm gap at 150 °C and 10 kN for 1 h.
**Figure S17.** IR spectrum of poly-1.

**References**