Support Information

Solvent-Free and Photocurable Polyimide Inks for 3D Printing

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Table S1 GPC results of polyimide oligomer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn</th>
<th>Mw</th>
<th>Mz</th>
<th>Mz/Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-g-GMA</td>
<td>6973</td>
<td>16715</td>
<td>40913</td>
<td>2.447757</td>
</tr>
</tbody>
</table>

Table S2 Thermal properties of polyimide oligomer

<table>
<thead>
<tr>
<th>polyimide</th>
<th>T_g</th>
<th>T_5</th>
<th>T_10</th>
<th>T_max</th>
<th>CR(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>273</td>
<td>428.21</td>
<td>466.11</td>
<td>472</td>
<td>36.06</td>
</tr>
<tr>
<td>Pi-g-GMA</td>
<td>272</td>
<td>407.14</td>
<td>459.74</td>
<td>469</td>
<td>37.08</td>
</tr>
</tbody>
</table>

T_g and T_10: Temperature at a 10% or 20% weight loss
T_max: Temperature at the maximum degradation
CR: Char Residual at 800 °C in nitrogen

![Graph showing viscosity vs. shear rate]
Fig. S1 Viscosity curves of photo-curing polyimides inks: PI-2, PI-3 and PI78, PI78 is defined as the content of LMA and PEG400DA is 7 and 8.

![Viscosity curves of photo-curing polyimides inks](image)

Fig. S2 The typical load-displacement curve of the UV-cured polyimides ink.

![Load-displacement curve](image)

Table S3 mechanical behaviors of UV cured polyimide inks

<table>
<thead>
<tr>
<th>Materials</th>
<th>Hardness (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-0</td>
<td>167.82±14.74</td>
<td>5.83±0.81</td>
<td>5.29±5.85</td>
<td>2.61±0.20</td>
</tr>
<tr>
<td>PI-1</td>
<td>109.84±28.51</td>
<td>9.63±1.41</td>
<td>7.70±1.60</td>
<td>1.37±0.07</td>
</tr>
<tr>
<td>PI-2</td>
<td>150.13±2.93</td>
<td>16.13±3.10</td>
<td>5.10±2.29</td>
<td>2.48±0.07</td>
</tr>
<tr>
<td>PI-3</td>
<td>165.12±27.09</td>
<td>24.93±3.13</td>
<td>5.43±1.08</td>
<td>2.16±0.10</td>
</tr>
<tr>
<td>PI-4</td>
<td>183.30±11.23</td>
<td>19.55±2.40</td>
<td>5.04±0.71</td>
<td>3.17±0.06</td>
</tr>
<tr>
<td>PI-5</td>
<td>170.17±1.27</td>
<td>11.99±2.43</td>
<td>11.85±3.22</td>
<td>2.14±0.02</td>
</tr>
</tbody>
</table>
Fig. S3 SEM images of a tensile fracture surface of the UV cured polyimide inks:
(a) PI-0, (b) PI-1, (c) PI-2, (d) PI-3, (e) PI-4, (f) PI-5.

Table S4 Thermal properties of UV cured polyimide inks

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T_a$</th>
<th>$T_{10}$</th>
<th>$T_{\text{max}}$</th>
<th>CR(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI-0</td>
<td>335.97</td>
<td>367.17</td>
<td>443.56</td>
<td>28.32</td>
</tr>
<tr>
<td>PI-1</td>
<td>349.23</td>
<td>374.02</td>
<td>432.77</td>
<td>24.73</td>
</tr>
<tr>
<td>PI-2</td>
<td>350.45</td>
<td>375.85</td>
<td>434.36</td>
<td>24.69</td>
</tr>
<tr>
<td>PI-3</td>
<td>351.16</td>
<td>376.75</td>
<td>434.56</td>
<td>25.23</td>
</tr>
<tr>
<td>PI-4</td>
<td>354.25</td>
<td>379.75</td>
<td>444.66</td>
<td>25.87</td>
</tr>
<tr>
<td>PI-5</td>
<td>354.26</td>
<td>379.76</td>
<td>428.56</td>
<td>25.87</td>
</tr>
<tr>
<td>Commercial ink</td>
<td>141.9</td>
<td>262.1</td>
<td>358.6</td>
<td>0</td>
</tr>
</tbody>
</table>

Table S5 Effect of exposure energy on the cured layer thickness at exposure 3 s

<table>
<thead>
<tr>
<th>n</th>
<th>$E_0$ (mJ/cm²)</th>
<th>ln $E_0$</th>
<th>$C_d$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>66.96</td>
<td>4.20</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>83.16</td>
<td>4.42</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>102.40</td>
<td>4.63</td>
<td>0.27</td>
</tr>
<tr>
<td>4</td>
<td>122.40</td>
<td>4.81</td>
<td>0.30</td>
</tr>
<tr>
<td>5</td>
<td>141.60</td>
<td>4.95</td>
<td>0.33</td>
</tr>
<tr>
<td>6</td>
<td>159.60</td>
<td>5.07</td>
<td>0.34</td>
</tr>
<tr>
<td>7</td>
<td>180.00</td>
<td>5.19</td>
<td>0.36</td>
</tr>
<tr>
<td>8</td>
<td>198.00</td>
<td>5.29</td>
<td>0.38</td>
</tr>
<tr>
<td>9</td>
<td>222.00</td>
<td>5.40</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>242.40</td>
<td>5.49</td>
<td>0.41</td>
</tr>
<tr>
<td>11</td>
<td>268.80</td>
<td>5.59</td>
<td>0.42</td>
</tr>
<tr>
<td>12</td>
<td>291.60</td>
<td>5.68</td>
<td>0.44</td>
</tr>
<tr>
<td>13</td>
<td>320.40</td>
<td>5.77</td>
<td>0.45</td>
</tr>
<tr>
<td>14</td>
<td>337.20</td>
<td>5.82</td>
<td>0.47</td>
</tr>
<tr>
<td>15</td>
<td>380.40</td>
<td>5.94</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Fig. S4 The contrast of high temperature resistant oil performance between PI-3 ink and commercial ink at (a) 200°C, 30 min, (b) 250°C, 30 min and (c) 300°C, 30 min.