Supporting information

Incorporating steric hindrance into the additive design enables a robust formulation of alumina ink for extrusion-based 3d printing

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Figure S1. Representative particle size distribution of alumina nanoparticles after addition of additives (here 2 wt. % A25P1 as an example)
Figure S2. General chemical structure of PCEs

Figure S3. Representative H1-NMR of A30P1
Figure S4. H1-NMR of A25P2 with integral values associated with each peak as an example for calculation of molar ratio of building blocks in additives

**Molar ratio calculated by NMR**

The peaks used to calculate the molar ratio of additives are assigned as i) 3.6–3.8 ppm (CH$_2$-CH$_2$-O of PEG side chains, 23 x 4=92 proton, ii) 3.3–3.63 (S–CH$_2$ of AMPS monomer, 2 protons), and iii) 1.9–2.3 (-CH of AA + -CH of AMPS + -CH-CH of MAPEG of side chain, AA monomer.

The molar feed ratio of A25P2 shown in Figure S2 as an example was calculated as following; i) PEG (CH2-CH2-O) with integral value of 13.75 and associated value of 0.149, ii) AMPS (S–CH2) with integral value of 12.72 and associated value of 6.36, iii) AA+AMPS+PEG (-CH) with integral value of 12.52 giving rise to associated value of 12.52-6.36-0.3=5.86 for AA. Thus, side chain density (PEG/AA+AMPS) is 0.149/12.22=0.0122 and AMPS/AA is 6.36/5.86=1.08.
Figure S5. Effect of pH on zeta potential of neat alumina nanoparticles (◊ symbol) and representative zeta potential behavior of alumina nanoparticles in the presence of different amounts of polymers (triangle symbols, A25P1)

Figure S6. a) Sodium and b) calcium hydroxide titration on polymer solutions

Table S1. Characteristic properties of synthesized additives

<table>
<thead>
<tr>
<th>Molar feed ratio (AMPS/AA/PEG)</th>
<th>Acronym</th>
<th>AMPS/AA</th>
<th>PEG/AA+AMPS</th>
<th>mmol anionic sites/mg solid</th>
<th>Mmol bound Ca/mg solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/45/1</td>
<td>A5P1</td>
<td>3.1/10</td>
<td>0.6/100</td>
<td>$4.6 \times 10^{-3}$</td>
<td>$3.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>10/40/1</td>
<td>A10P2</td>
<td>4.2/10</td>
<td>0.5/100</td>
<td>$5.6 \times 10^{-3}$</td>
<td>$2.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>20/30/1</td>
<td>A20P1</td>
<td>7.5/10</td>
<td>0.5/100</td>
<td>$5.8 \times 10^{-3}$</td>
<td>$2.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>30/20/1</td>
<td>A30P1</td>
<td>17/10</td>
<td>0.7/100</td>
<td>$6.2 \times 10^{-3}$</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Figure S7. Zeta potential behavior of alumina nanoparticles in the presence polymers with different molecular weight; a) A20P1 and A30P1 and b) A25P1 at different pH
Figure S8. Viscosity as a function of shear-rate at different particle loadings in the presence of 1.25 wt% polymers: a) A25P0.33, b) A25P1, c) A25P2, and d) A25P5
Figure S9. Representative images of 3D-printed inks prepared by 1.25 wt. % non-optimized additives: a) A25P5 (73 wt. %), b) A25P1 (75 wt. %), c and d) A25P 0.33 (77 wt. %). Numbers in parenthesis show the solid content of the ink and arrow in (d) shows sagging in unsupported regions (Scale bar represents 5 mm.)

Figure S10. Representative images of 3D-printed ink prepared by 1.25 wt. % optimized additive (A25P2) showing the deposited rods a) traversing the gaps in underlying layers with minimal deflection during printing and b) preserving their shapes after drying