Supporting Information

Enabling Free-Standing 3D Hydrogel Microstructures with Micro-Reactive Inkjet Printing

Mei Ying Teo,[†] *Seyoung Kee,*[‡] *Narrendar RaviChandran,*[†] *Logan Stuart,*[†] *Kean C. Aw,*[†] *Jonathan Stringer**[†]

[†]Department of Mechanical Engineering, The University of Auckland, Auckland 1010, New Zealand

[‡]School of Chemical Sciences, The University of Auckland, Auckland 1010, New Zealand

Corresponding Author

* Email: j.stringer@auckland.ac.nz; Phone: +64 9 923 707

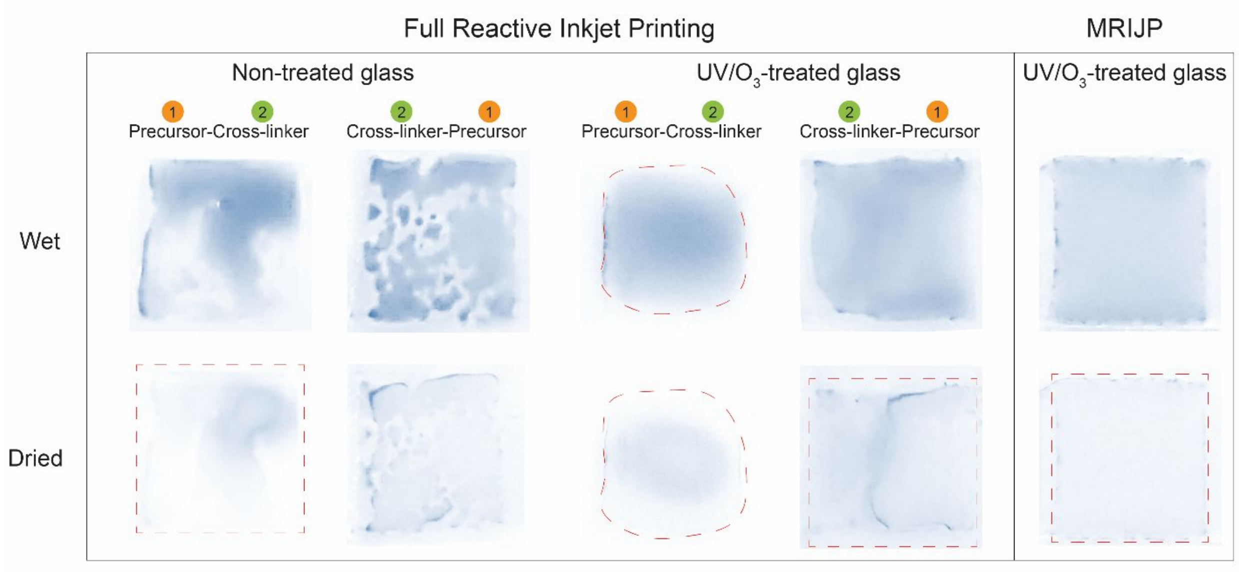

Figure S1. Wet and dried alginate hydrogel printed on non-treated and UV/O_3 treated glass substrates by different inkjet printing techniques (food dye was added for better visualization of hydrogel structures).

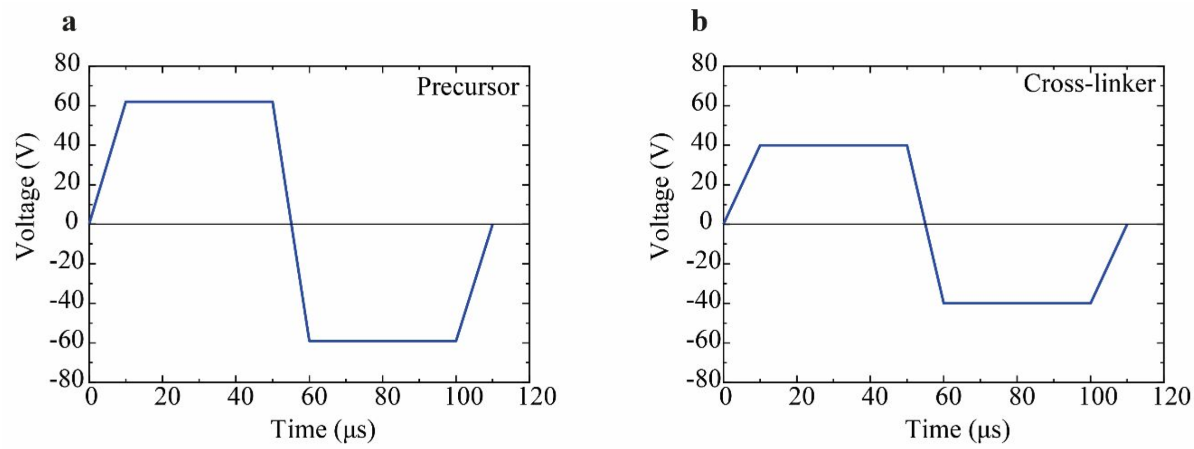

Figure S2. Jetting waveform for (a) Precursor and (b) Cross-linker used in the micro-reactive inject printing system.

Table S1. Ohnesorge and Z number parameters for all precursor and cross-linker ink formulations.

	Viscosity	**Surface tension**	**Density**	**Ohnersorge number**	**Z**
	η (cP)	γ (mN m^{-1})	ρ (kg m^{-3})	Oh -	1/Oh -
Ink 1					
0.8 wt% alginate	3.38	78	1000	0.049	20.24
1.0 wt% alginate	4.24	78	1000	0.062	16.13
1.5 wt% alginate	6.14	78	1000	0.090	11.14
2.0 wt% alginate	11.4	78	1000	0.167	6.00
2.5 wt% alginate	20.98	78	1000	0.307	3.26
Ink 2					
3.0 wt% $CaCl_2.6H_2O$	1.27	80	1000	0.018	54.55

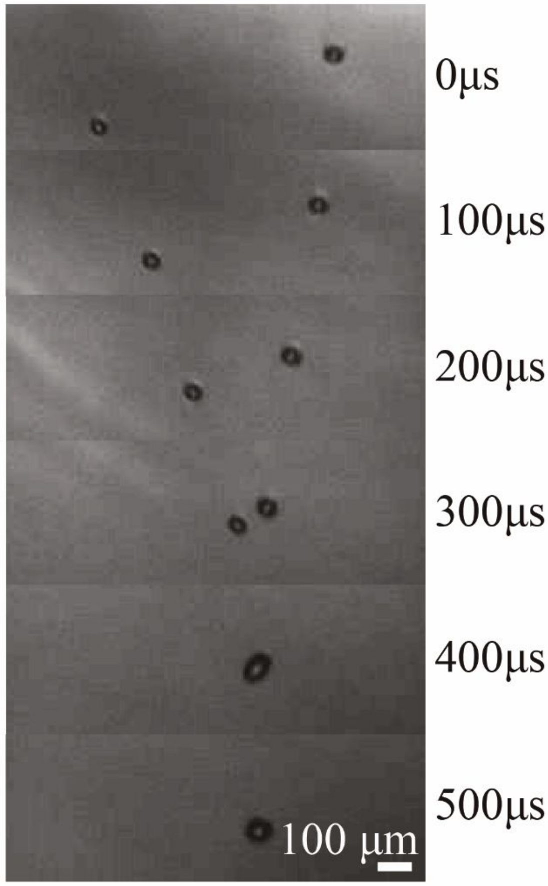

Figure S3. Stroboscopic images demonstrating the in-air coalescence of precursor and cross-linker droplets taken at 500 Hz.

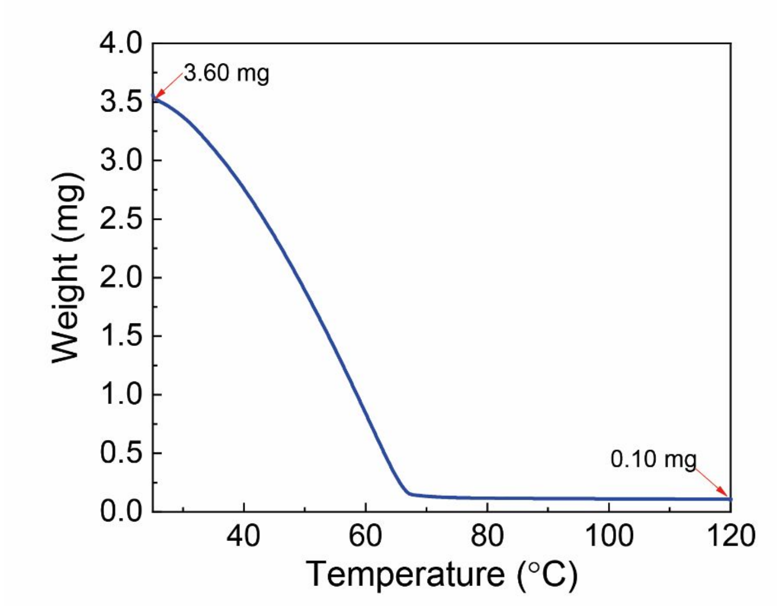

Figure S4. Thermal gravimetric analysis (TGA) of a printed alginate hydrogel. The weight loss of hydrogel at 120 ºC was used to evaluate the water content of the hydrogel.

Derivation of evaporation rate for alginate hydrogel pillar

When the water evaporates from the alginate hydrogel, the evaporation rate of the cone can be described as $I_{cone} = -\pi r\sqrt{h^2 + r^2}D\frac{dc}{dr}$; where *r, h, D, c* are radius, height, diffusion coefficient, and concentration, respectively. At an infinite distance from the cone, the following boundary conditions were imposed: $c = c_\infty$ when $r = \infty$ and $c = c_0$ when $r = r_1$, where r_1 is the radius of the cone. Hence, the evaporation rate of a cone is $I_{cone} = \frac{2\pi Dh_1(c_0 - Hc_0)}{\ln\left|\frac{\sqrt{h_1^2 + r_1^2} + h_1}{h_1}\right| - \ln\left|\frac{\sqrt{h_1^2 + r_1^2} - h_1}{h_1}\right|}$ Similarly, the evaporation rate of the cylinder can be defined as $I_{cylinder} = -2\pi rhD\frac{dc}{dr}$ with the boundary conditions $c = c_\infty$ when $r = \infty$ and $c = c_0$, where r_2 is the radius of the cone at infinite distance. Therefore, the evaporation rate of a cylinder is $I_{cylinder} = -\frac{2\pi Dh_2(c_0 - Hc_0)}{\ln|r_2|}$.

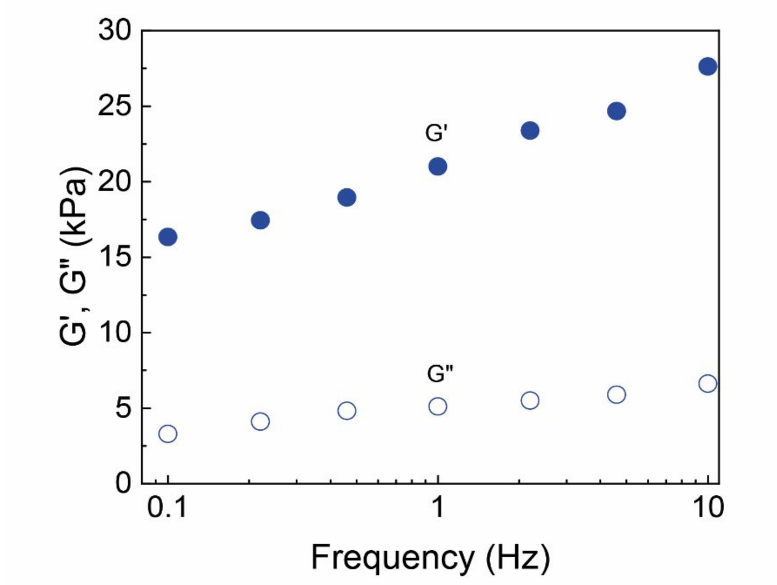

Figure S5. Viscoelasticity of printed alginate hydrogels showing storage modulus G' and loss modulus G" as a function of frequency.

Movie S1

Full-reactive inkjet printing of hydrogel.

Movie S2

Micro-reactive inkjet printing of hydrogel.

Movie S3

A hydrogel pillar printed using the micro-reactive inkjet printing technique.

Movie S4

Shrinkage of a fine hydrogel pillar after printing.

Movie S5

A hydrogel thin film printed using the micro-reactive inkjet printing technique.

Movie S6

A hydrogel hollow tube printed using the micro-reactive inkjet printing technique.