# Recyclable 3D Printable Single Network Granular Hydrogels

Gaia De Angelis[a,b], Gaia Dupont[a], Lorenzo Lucherini[a], and Esther Amstad[a,b,*]

[a]Soft Materials Laboratory, Institute of Materials, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne (Switzerland).

[b]Bioinspired Materials National Center of Competence in Research (NCCR), Fribourg. Email address: esther.amstad@epfl.ch

*Corresponding author

## Supplementary Information

## Hydrophobic interactions

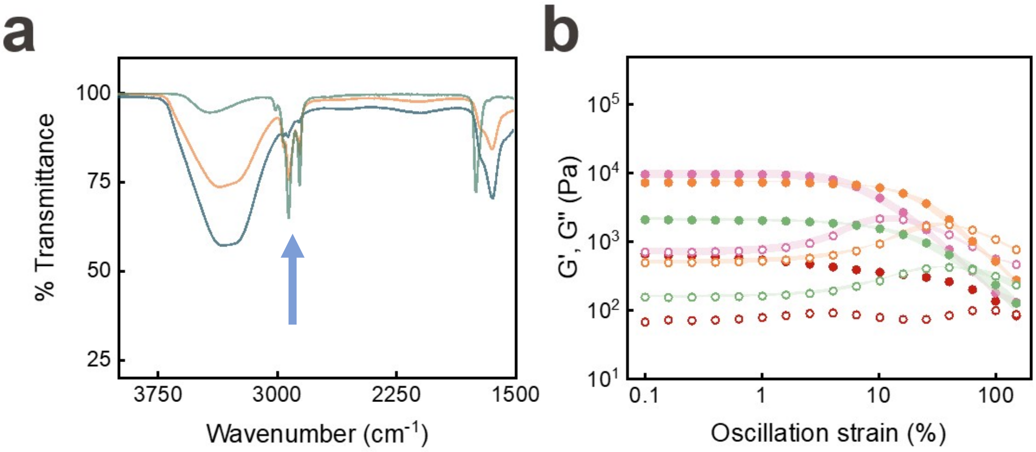

**Figure S1**: (a) FTIR spectra of (●) Span80, (●) washed microgels, and (●) microgels that have only been mildly washed once such that they still contain Span80 at their surfaces. (b) Influence of the jamming on the rheological properties of PAA microgels. Storage (●) and loss (○) moduli extracted from oscillation strain measurements of jammed PAA microgels. Microgels have been jammed through centrifugation (●), centrifugation followed by an additional removal of the oil using a filter paper in the absence of any other additives (●) and in the presence of 2 wt% lauryl acrylate in the oil (●). Paste composed of jammed microgels where only 80% of the excess oil has been removed (●). Each experiment was repeated three times.

A comparison of the FTIR spectra performed on washed microgels and those made on microgels which have only been mildly washed reveals clear differences. Peaks around 2750-3000 cm$^{-1}$ are present in spectra of Span80 and those of mildly washed microgels but absent in spectra of washed microgels, as shown in **Figure S1a**. We assign these peaks to C-H stretches of the hydrophilic tail of Span80, indicating that mildly washed microgels indeed contain Span80 at their surfaces.

To assess the influence of the jamming protocol on the rheological properties of PAA microgels, we jam microgels whose surfaces contain Span80 surfactants. Other PAA microgels whose surfaces contain Span80 surfactants are jammed through centrifugation and additionally dried with a filter paper. The additional removal of oil with a filter paper does not significantly influence the rheological properties of the microgels. However, removing only 80% of the oil or adding 2 wt% lauryl acrylate decreases the storage and loss moduli of the paste, as shown in **Figure 1b** in the main paper. These results indicate that the dynamic mechanical properties of the paste can be adjusted with hydrophobic additives.

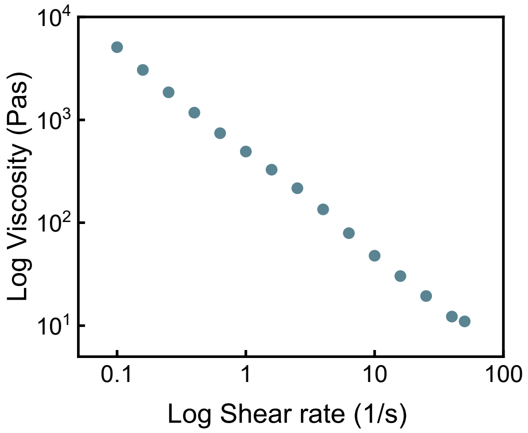

**Figure S2:** Shear thinning behaviour of jammed PAA microgels whose surfaces are modified with hydrophobic tails originating from the Span80 surfactant, which has been used to stabilise the emulsions prior to their conversion into microgels.

Rheological measurements show the shear thinning behaviour of jammed PAA microgels whose surfaces are modified with hydrophobic tails, making them well-suited for 3D printing.

## Influence of PD incubation time

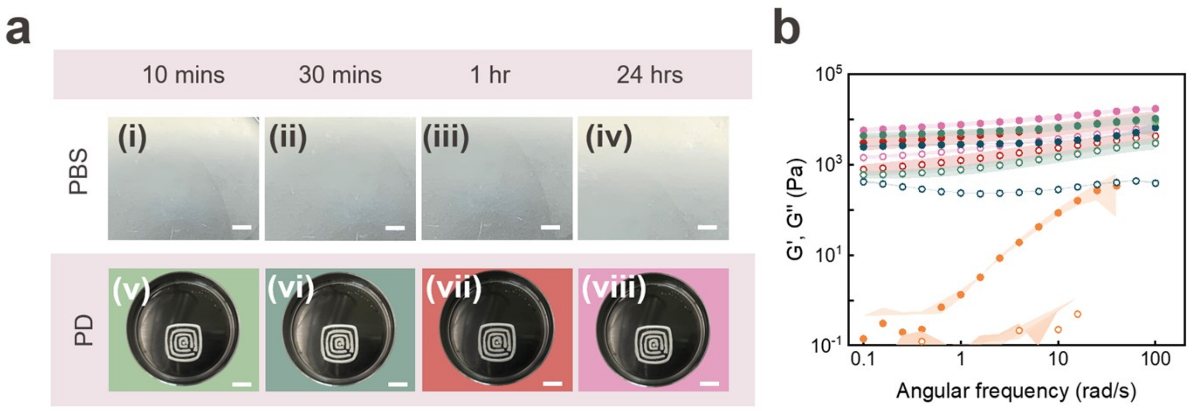

**Figure S3:** Influence of incubation time on rheological properties of electrostatically reinforced granular hydrogels. (a) Storage (●) and loss (○) moduli measured as frequency sweeps performed on jammed PAA microgels printed in air without any interfacial reinforcement (●), printed into PBS (●) and samples that have been reinforced by incubating them in an aqueous solution containing 1 wt% PD for (●) 10 min, (●) 30 min, (●) 1 hour, and (●) 24 hours. Each experiment was repeated 3 times. (b) Photographs of 3D printed structures incubated in PBA (top, i-iv) and an aqueous solution containing 1 wt% PD for (v) 10 min, (vi) 30 min, (vii) 1 hour, and (viii) 24 hours. Scale bar 1 cm.

Jammed PAA microgels disassemble if 3D printed in PBS, as shown in **Figure S3a(i)-(iv)**. By contrast, they retain structural integrity if they are incubated in a 1 wt% PD aqueous solution for up to 24 hours, as shown in **Figure S3a(v-viii).** Frequency sweep measurements of jammed PAA microgels 3D printed in air, PBS, and an aqueous solution containing PD at different time points indicate that an incubation time of 10 minutes in an aqueous solution containing 1 wt% PD is sufficient to stabilise the printed structures, as shown in **Figure S3b**.

## Presence of PD within the PAA structures

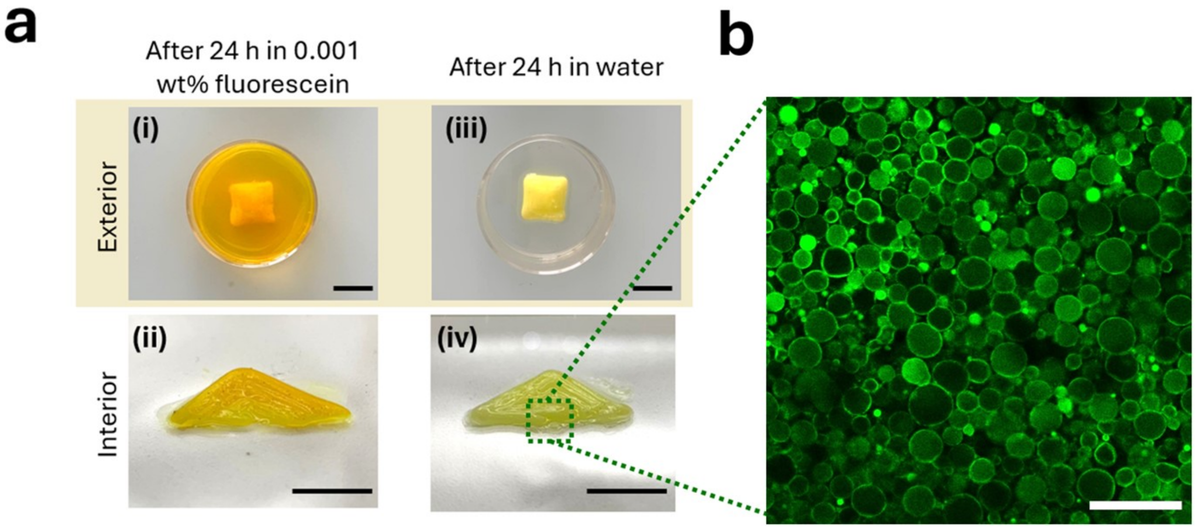

**Figure S4**: (a) 3D-printed PAA structure soaked in PD for 10 minutes. The structures are soaked in a 0.001 wt% fluorescein containing aqueous solution for 24 hours. Photographs of the structure if (i) incubated in the fluorescein-containing aqueous solution and (ii) transferred into air, (iii) incubated in deionized water and (iv) transferred again into air. Scale bar 10 mm. (b) Confocal microscopy image showing how fluorescein is preferentially localised at the microgel surface. Scale bar 50 µm.

To visualise the distribution of PD, we 3D-printed PAA microgel structures with dimensions of 10 x 10 x 5 mm$^3$. These structures were soaked in an aqueous solution containing PD for 10 minutes before being transferred to an aqueous solution containing 0.001 wt% fluorescein disodium salt. Fluorescein, which bears a negative charge at pH > 6, binds electrostatically to PD. After 24 hours of soaking, fluorescein has penetrated the structure, as shown in **Figure S4a(i-ii)**. To ensure that the fluorescein influx is not due to osmotic pressure differences between the interior and exterior of the structure, we replace the fluorescein-containing solution with DI water. After another 24 hours of incubation, fluorescein remains bound to the PD within the structure, as demonstrated in **Figure S4a(iii-iv)**, confirming our hypothesis that PD is present within the structure even after only 10 minutes of soaking. To visualize the distribution of PD, we performed confocal microscopy on the sample in **Figure S4a(iv).** Indeed, fluorescein and hence, PD is closely associated with the microgels, as shown in **Figure S4b**. These results suggest that PD is homogeneously distributed.

## Influence of PD molecular weight and concentration on structures' rheological properties

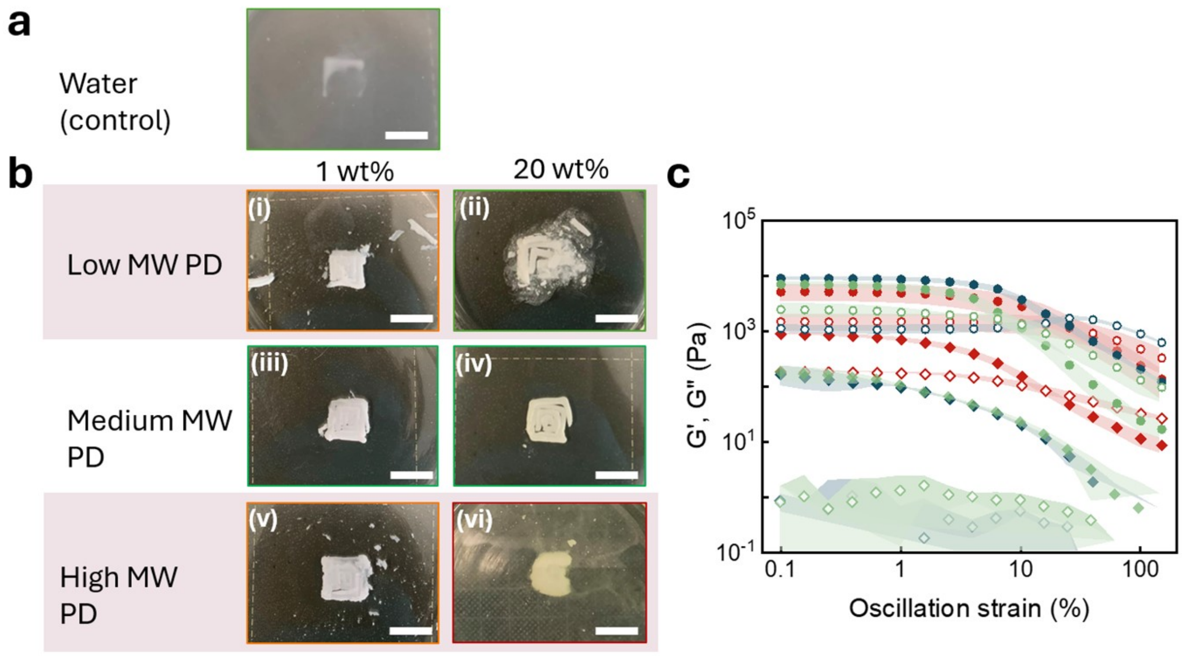

**Figure S5:** (a) Photograph of jammed PAA microgels that have been 3D printed into (a) water and (b) an aqueous solution containing 1 wt% (left) and 20 wt% (right) PD with a low <100 kDa (top) medium 250 kDa (middle) and high 450 kDa (bottom) molecular weight. Scale bar is 1 cm. (b) Storage (●, ◆) and loss (○, ◇) moduli measured from oscillation sweeps of jammed PAA microgels printed in an aqueous solution containing 1 wt% (●) and 20 wt% (◆) PD with molecular weights of <100 kDa (**blue**), 250 kDa (**red**), and 450 kDa (green). Each experiment was repeated 3 times.

When 3D printed in water, jammed microgels instantaneously disassemble, as shown in **Figure S5a**. We assign the disassembly of the microgels to the reduction of inter-particle friction and the electrostatic repulsion of equally charged microgels upon immersion in aqueous solutions. By contrast, if the same ink is printed into an aqueous solution containing PD, the granular hydrogels remain stable for at least one month even if incubated in aqueous solutions containing high salt concentrations. These results highlight the importance of PD for the structural stability of the granular PAA microgel-based hydrogel. To assess the influence of the PD molecular weight we vary this parameter from < 100 kDa to 450 kDa. Granular hydrogels reinforced with PD with a molecular weight of 250 kDa are most stable, as qualitatively illustrated in the photographs in Figure S4b(iii)-(iv).

To quantitatively assess the impact of the PD molecular weight, we perform rheological measurements on all 3D printed samples. Surprisingly, the PD molecular weight does not measurably influence the storage and loss moduli, as shown in **Figure S5c**. To assess the influence of the PD concentration on the dynamic mechanical properties of electrostatically reinforced granular hydrogels, we vary this parameter from 1 to 20 wt%. Interestingly, a higher concentration of PD leads to the disassembly of microgels, as shown in **Figure S5b(ii)**, likely due to an electrostatic repulsion between adjacent microgels whose surfaces are entirely covered with PD. Based on the rheology results and visual observations, we fix the molecular weight of PD to 250 kDa and its concentration in the reinforcing solution to 1 wt% PD for the remaining experiments.

## Ionic interactions

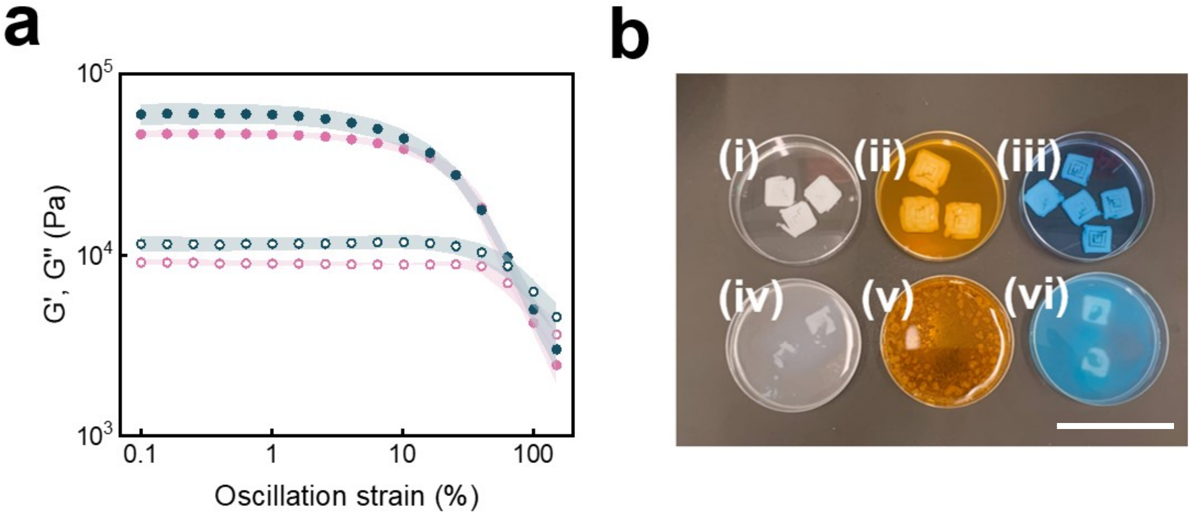

**Figure S6:** Influence of the incubation time on the mechanical properties of electrostatically reinforced granular hydrogels. (a) Oscillation strain measurements of 3D printed granular PAA hydrogels that have been soaked in an aqueous solution containing 1 wt% PD + 0.01 M $Cu^{2+}$ at pH = 9 for (●) 1 h, and (●) 24 h. We do not observe any significant difference of the storage (●) and loss (○) moduli, indicating that the interfacial reinforcement is completed within 1 h of incubation. Each experiment was repeated three times. (b) Photographs of 3D printed squares with side lengths of 3 mm that have been incubated in an aqueous solution containing (i) 1 wt% PD + 0.01 M $Ca^{2+}$ at pH 9, (ii) wt% PD + 0.01 M $Fe^{3+}$ at pH 9, and (iii) wt% PD + 0.01 M $Cu^{2+}$ at pH 9, (iv) $Ca^{2+}$ at pH 9, (v) $Fe^{3+}$ at pH 9, and (vi) $Cu^{2+}$ at pH 9. These results demonstrate the importance of PD for the stability of the granular hydrogels.

To assess if we can further reinforce our PD-stabilized granular hydrogels, we incubate jammed PAA microgels in an aqueous solution containing 1 wt% PD and different cations, as shown in **Figure S6b**. Only structures 3D printed in a solution containing PD and ions maintain structural integrity, highlighting that ionic interactions alone are not strong enough.

To assess the influence of the incubation time on the reinforcement of the granular hydrogel, we incubate jammed PAA microgels in a PD and $Cu^{2+}$-containing aqueous solution for 1 and 24 hours. We cannot measure any significant difference in the plateau storage and loss moduli, as shown in **Figure S6a**. These results indicate that the electrostatic reinforcement of the granular hydrogel is completed within 1 h of incubation.

## Microgel disassembly in water

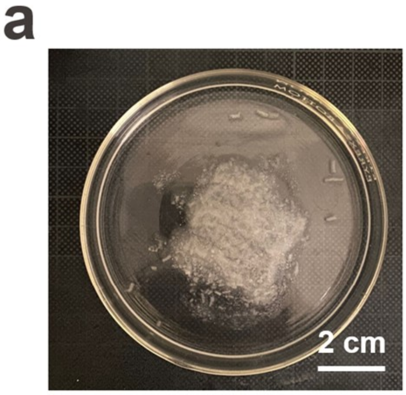

**Figure S7:** (a) Photograph of a 3D printed grid composed of jammed PAA microgels that are surrounded by Span20 incubated in a PD containing aqueous solution for 1 minute.

Jammed PAA microgels disperse if immersed in water, if they are only connected through hydrophobic inter-particle interaction, as illustrated in **Figure S7**. These results demonstrate that weak Van-der-Waals interactions are insufficient to overcome the loss of friction and the repulsive electrostatic interactions between negatively charged PAA microgels.

## Energy damping

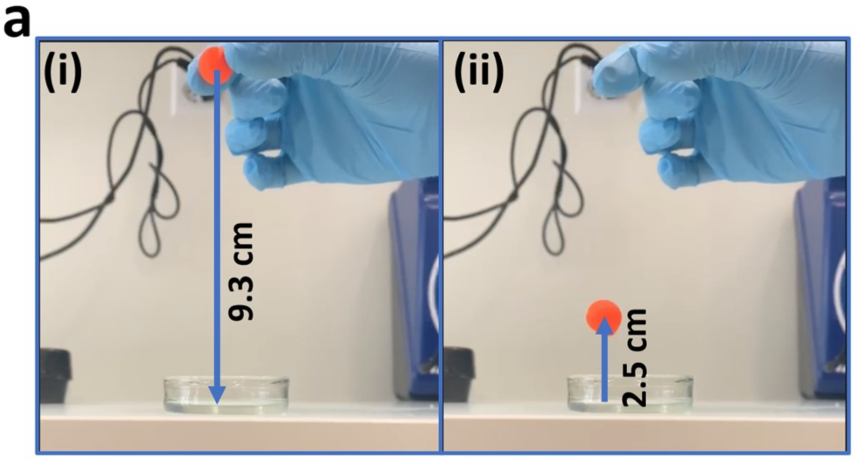

**Figure S8:** (a) Control experiment for underwater dampers. (i, ii) Time-lapse photographs of a ball composed of polyethylene terephthalate glycol (PETG) with a diameter of 1.4 cm dropped from a height of 9 cm into a Petri dish half-filled with water.

A control experiment shows that water only absorbs 40 ± 2 % of the potential energy of the ball, as shown in **Figure S8**. As a result of the limited damping property of water, the ball bounces back to 2.5 cm when dropped on water.

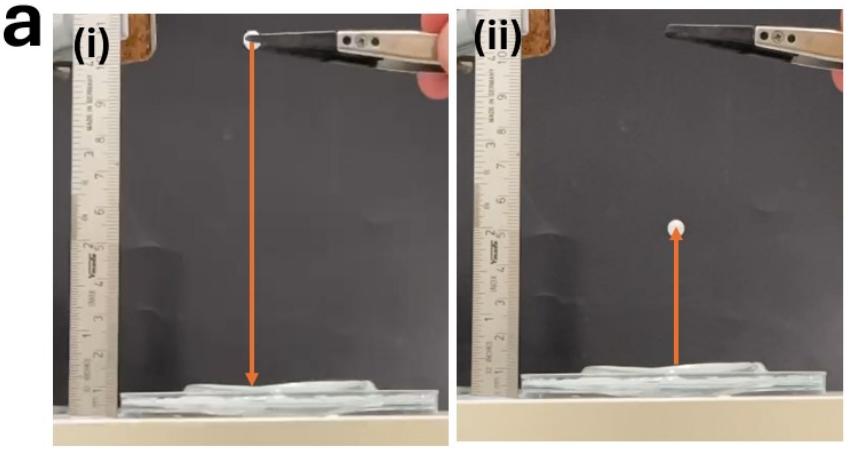

**Figure S9:** (a) Control experiment for bulk PAA hydrogel (i, ii) Time-lapse photographs of a ball composed of polyethylene terephthalate glycol (PETG) with a diameter of 1.4 cm dropped from a height of 8 cm onto a bulk PAA gel contained in a Petri dish half-filled with water.

A positive control experiment shows that a sample of bulk PAA hydrogel submerged in water only absorbs 62 ± 3 % of the potential energy of the ball, as shown in **Figure S9**.