SUPPLEMENTARY INFORMATION

Hybrid granular hydrogels: combining composites and microgels approaches for extended ranges of material properties

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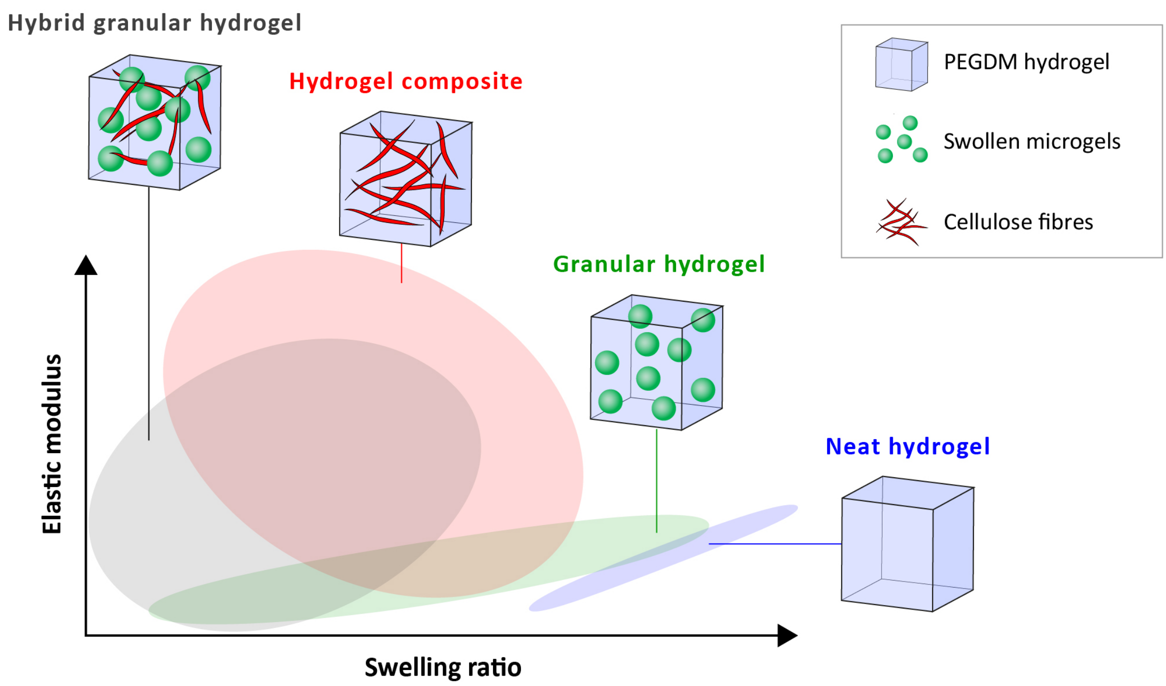


1. Synthesis steps of microgels and granular hydrogels

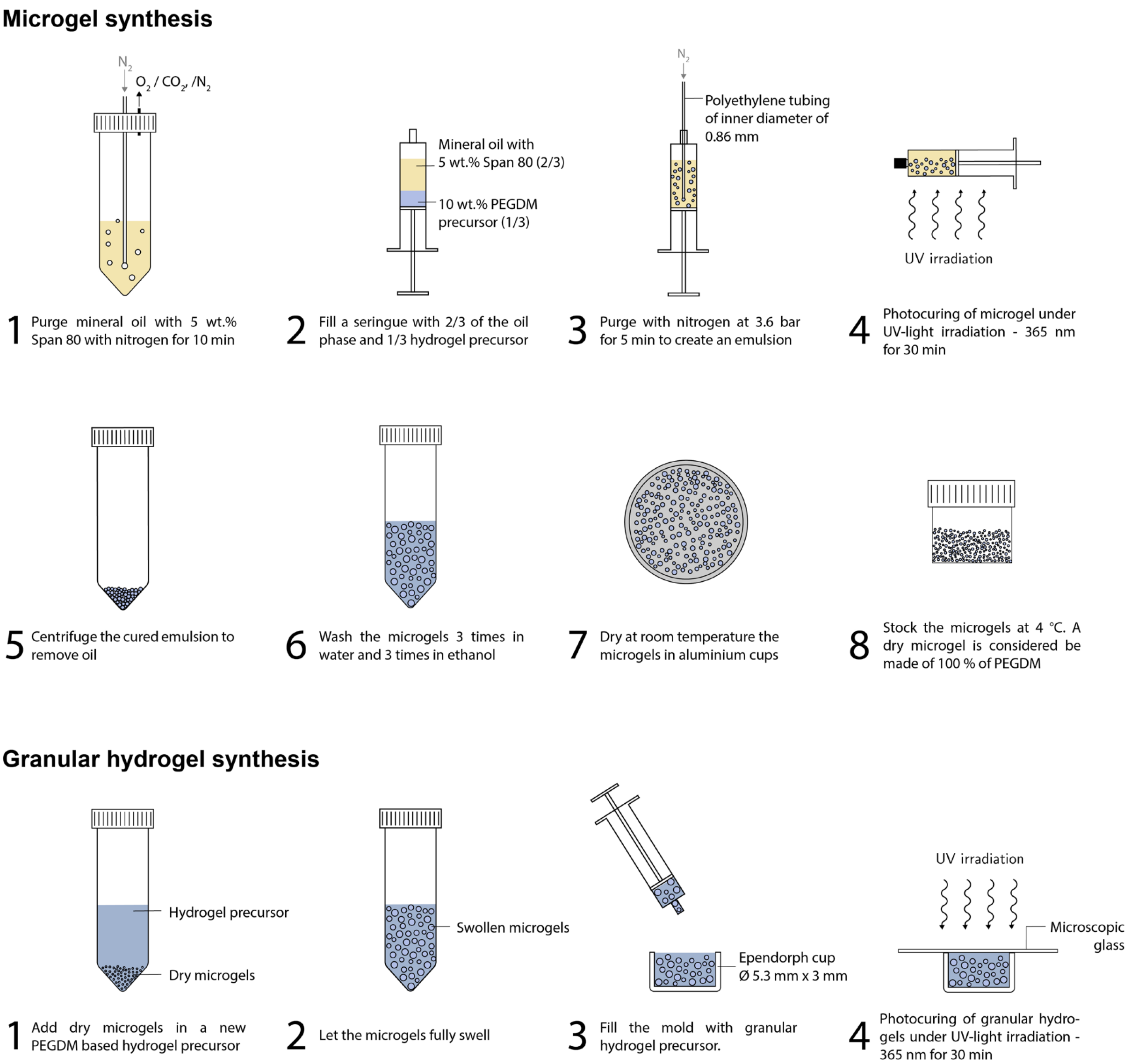


Fig. S1 Synthesis steps of microgels and granular hydrogels based on poly(ethylene glycol) dimethacrylate (PEGDM), note that microgels smaller than 20 um in diameter were removed during centrifuging probably because thermal forces dominated gravitational forces.[23]

2. Microgels size distribution and morphology

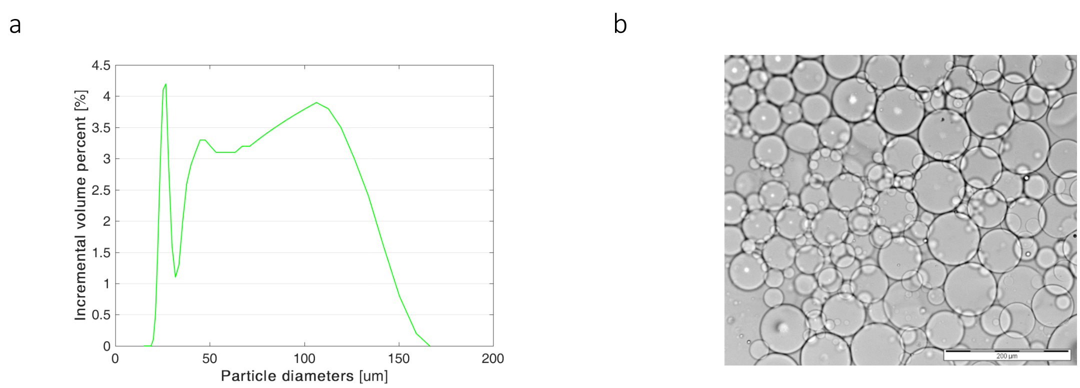
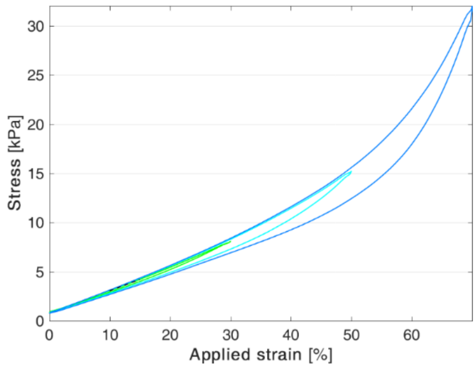
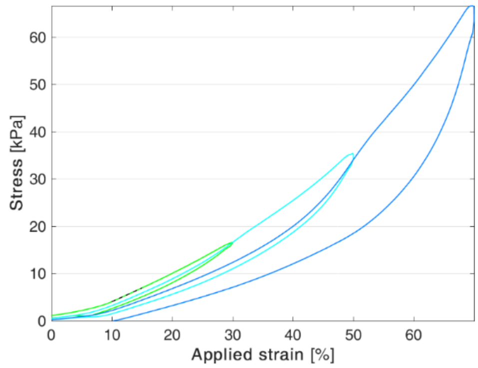


Fig. S2 (a) The size distribution of microgels measured with a digital particle size analyser (Saturn DigiSizer II, Micromeritics) and (b) the morphology of microgels observed with an invert optical microscope (Eclipse Ti2, Nikon)

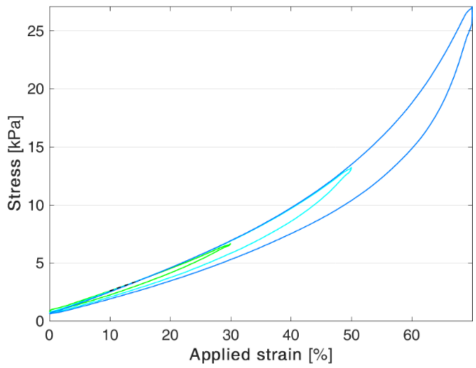
3. Representative stress-strain curves



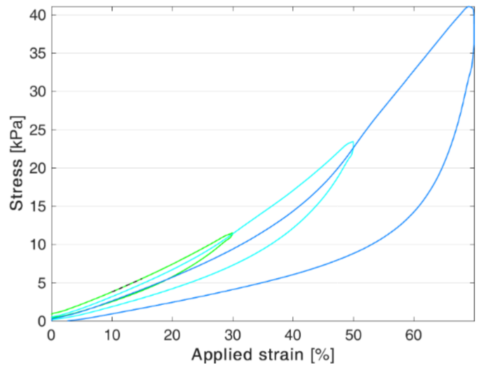
(a) Bulk hydrogel - B_{10}



(b) Hydrogel composite - $C_{10}^{0.5}$



(c) Granular hydrogel - $6G_4$



(d) Hybrid granular hydrogel - $6H_4^{0.5}$

Fig. S3 Representative cyclic compression loadings of (a) neat, (b) composite, (c) granular and (d) hybrid granular hydrogels. Neat and granular hydrogels fully recovered, while composite structures showed characteristics similar to the Mullins effect: they becomes softer after the first loading cycles.

4. Representative curve of viscosity – oscillating strain

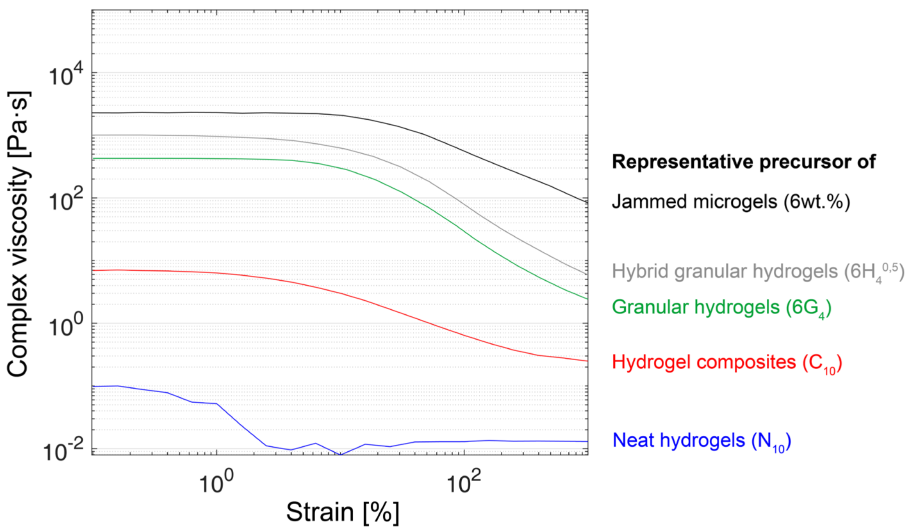


Fig. S4 Representative behaviour of precursors' viscosities measured with a parallel plate rheometer (TA Instruments AR2000ex) under an oscillating strain sweep at 0.5Hz at room temperature. All precursors except that of neat hydrogels showed obvious shear-thinning behaviour.

5. Data summary

Table S1 Data overview of swelling ratios, viscosities and mechanical properties measurements

		Swelling ratios		Viscosities [Pa·s] - Oscillation strain of					Mechanical properties			
		SR [wt.%]	SR [vol.%]	0.1 [%]	1 [%]	10 [%]	100 [%]	1000 [%]	E [kPa] - cycle 1	E [kPa] - cycle 2	G [kj/m²] - 50 % strain	Ɛ [%]
Neat hydrogels	B_7	127.7 ± 1.5	128.2 ± 1.9	0.07	0.01	0.01	0.01	0.01	9.7 ± 0.4	10.1 ± 0.2	11.9 ± 0.8	96.7 ± 0.6
	B_8	136.7 ± 1.1	138.4 ± 0.8	0.09	0.05	0.01	0.01	0.01	14 ± 0.8	14.9 ± 0.7	17.2 ± 3.1	95.3 ± 4.6
	B_9	144.8 ± 2	146.1 ± 1.5	0.08	0.03	0.01	0.01	0.01	18.1 ± 1.6	18.9 ± 1.4	20.7 ± 2.8	89.7 ± 0.6
	B_{10}	154.3 ± 1.6	156.1 ± 1.9	0.09	0.01	0.01	0.02	0.02	21.6 ± 0.5	22.7 ± 0.8	20.7 ± 3.3	92.7 ± 4.6
	B_{11}	161.6 ± 1.8	164.4 ± 1.8	0.09	0.05	0.02	0.02	0.02	25.4 ± 0.9	26.7 ± 0.7	27.5 ± 3.1	92.7 ± 4.6
Hydrogel composites	$C_7^{0.1}$	110.6 ± 2.8	111.8 ± 2.4	0.12	0.07	0.10	0.05	0.03	12.7 ± 1.6	13 ± 1.5	39.2 ± 1.1	98 ± 0
	$C_7^{0.3}$	89.1 ± 2.2	89.7 ± 1.4	2.05	2.03	1.01	0.21	0.08	22.1 ± 1.5	21.4 ± 1.2	87 ± 5.5	98 ± 0
	$C_7^{0.5}$	77.1 ± 0.8	78 ± 0.8	9.01	8.26	3.80	0.63	0.18	31.8 ± 1.3	30 ± 1.2	132.3 ± 4.6	98 ± 0
	$C_8^{0.1}$	116 ± 3.5	117.6 ± 3.3	0.11	0.06	0.08	0.05	0.03	20.4 ± 0.6	20.9 ± 0.6	47.7 ± 2.3	98 ± 0
	$C_8^{0.3}$	93.4 ± 1.3	95.1 ± 2.1	1.77	1.74	1.08	0.26	0.08	32.1 ± 1.2	30.6 ± 1.2	122.8 ± 9.8	98 ± 0
	$C_8^{0.5}$	78.6 ± 2.3	79.5 ± 2.3	11.82	10.86	5.54	0.98	0.24	41.3 ± 2.4	38.7 ± 2	164.8 ± 11.8	98 ± 0
	$C_9^{0.1}$	120.9 ± 2.5	122.5 ± 3	0.15	0.12	0.10	0.06	0.03	25.6 ± 0.5	26.4 ± 0	59.1 ± 3.4	93.7 ± 4
	$C_9^{0.3}$	97.7 ± 1.8	99.3 ± 2	2.15	1.98	1.23	0.29	0.10	38.6 ± 0.8	37 ± 0.5	127.9 ± 5.3	94.3 ± 4
	$C_9^{0.5}$	83.8 ± 1.2	83.4 ± 1.4	10.50	10.12	5.36	0.96	0.26	53.2 ± 0.6	50 ± 0.7	226.6 ± 9.7	98 ± 0
	$C_{10}^{0.1}$	129.7 ± 1.1	131.8 ± 1.3	0.23	0.19	0.12	0.06	0.03	33.1 ± 0.1	33.3 ± 0.1	65.7 ± 3.3	91.7 ± 2.9
	$C_{10}^{0.3}$	101.8 ± 0.3	103.6 ± 1.2	2.21	2.15	1.17	0.25	0.10	47.3 ± 1.2	45.6 ± 1.2	153 ± 11.9	98 ± 0
	$C_{10}^{0.5}$	83.4 ± 0.8	84.9 ± 0.7	6.96	6.35	2.99	0.64	0.25	67.2 ± 3.7	61.1 ± 3.4	287.7 ± 5.2	98 ± 0
Microgels	2M	N/a	N/a	2.13	2.50	0.38	0.06	0.03	N/a	N/a	N/a	N/a
	3M	N/a	N/a	205.85	196.32	93.84	9.36	1.02	N/a	N/a	N/a	N/a
	4M	N/a	N/a	966.41	995.36	634.45	71.57	14.81	N/a	N/a	N/a	N/a
	5M	N/a	N/a	1653.25	1702.84	1450.80	218.87	49.38	N/a	N/a	N/a	N/a
	6M	N/a	N/a	2269.43	2290.89	2070.67	466.71	71.23	N/a	N/a	N/a	N/a
	7M	N/a	N/a	2788.65	2722.86	2509.71	708.61	92.10	N/a	N/a	N/a	N/a
Granular hydrogels	$3G_4$	98.2 ± 1.7	99.3 ± 2.7	3.92	4.69	3.47	0.92	0.09	9 ± 0.5	10.1 ± 0.6	20.3 ± 0.9	89.7 ± 0.6
	$3G_5$	114.8 ± 2.6	116.1 ± 3.2	3.43	3.80	2.34	0.76	0.09	12.3 ± 0.1	13.4 ± 0.2	26.3 ± 1.2	88.7 ± 0.6
	$3G_6$	123.3 ± 1.4	125.1 ± 0.4	2.81	2.79	2.06	0.30	0.08	16.1 ± 0.5	17.5 ± 0.5	25.4 ± 2.4	89.3 ± 0.6
	$3G_7$	136.3 ± 2.7	139.9 ± 3.9	2.10	2.08	1.53	0.37	0.03	18.8 ± 1.3	19.8 ± 1.1	28.5 ± 4.7	89.7 ± 0.6
	$4G_3$	79.1 ± 2.2	80.6 ± 2	191.97	189.77	84.50	6.18	0.61	8.7 ± 0.5	9.1 ± 0.5	23.7 ± 2	88.7 ± 9
	$4G_4^{*}$	90.9 ± 3.3	92.7 ± 2.8	95.06	97.97	46.50	4.12	0.39	11.7 ± 0.8	12.3 ± 0.9	20.2 ± 0.7	84.7 ± 0.6
	$4G_5$	119.6 ± 1.2	121.6 ± 1.8	39.87	19.77	8.56	1.37	0.32	17 ± 0.4	18.9 ± 0.3	32.1 ± 1.5	89 ± 0
	$4G_6$	133.9 ± 1.4	136.2 ± 1.6	15.48	11.28	2.72	0.74	0.16	18.2 ± 1	18.7 ± 1.1	26.2 ± 1.7	89.3 ± 0.6
	$5G_2^{**}$	68.7 ± 1.3	70.2 ± 1.6	592.65	589.88	370.95	31.46	3.27	9.8 ± 1.1	10.1 ± 1.1	46.9 ± 10.3	61.3 ± 2.1
	$5G_3^{*}$	96.7 ± 3.8	98.5 ± 4.8	307.81	314.53	180.82	14.14	1.41	12.7 ± 0.4	13 ± 0.3	21.1 ± 1.2	81.7 ± 6.4
	$5G_4$	117.7 ± 0.4	119.5 ± 1.1	171.42	178.10	104.10	7.14	0.65	18.3 ± 1.6	19.1 ± 1.7	30 ± 7	89.7 ± 0.6
	$5G_5$	129.9 ± 2.9	132.8 ± 3.2	143.26	142.39	68.17	5.11	0.59	18.9 ± 0.7	19.8 ± 0.6	34.4 ± 3.7	89.3 ± 0.6
	$5G_6$	142.6 ± 1.2	145.6 ± 0.7	120.65	128.57	42.38	3.28	0.57	22.3 ± 1.2	22 ± 1.7	47.3 ± 7.2	90 ± 0
	$6G_2^{**}$	84.6 ± 3.7	85.5 ± 3.9	1006.82	985.38	664.37	68.54	6.86	11.6 ± 1.3	11.3 ± 1.8	37.1 ± 5	64.7 ± 3.1
	$5G_3^{*}$	109 ± 2.2	111.1 ± 1.3	819.37	835.12	577.59	51.25	5.91	15.8 ± 1.1	17.1 ± 1.4	43.4 ± 5.2	84 ± 4
	$6G_4$	135.7 ± 2.7	135.7 ± 1.3	426.43	421.53	283.18	21.94	2.39	19.5 ± 1.2	20.1 ± 0.9	39.1 ± 1.6	89.7 ± 0.6
	$6G_5$	146.5 ± 5.1	151 ± 3.7	351.11	361.87	221.00	15.86	1.87	23.2 ± 0.8	24.7 ± 1.3	46.7 ± 3.1	90 ± 0
Hybrid granular hydrogels	$3H_4^{0.1*}$	88.2 ± 2.4	90.7 ± 0.7	3.70	3.50	1.56	0.24	0.16	10.5 ± 2.1	11.3 ± 2.6	34.4 ± 2.2	84.7 ± 8.4
	$3H_4^{0.3}$	74.4 ± 3.6	76.5 ± 3.6	46.41	41.16	17.18	1.58	0.54	17.2 ± 1.6	17.4 ± 1.4	81.3 ± 6.5	90 ± 0
	$3H_4^{0.5}$	65.8 ± 1.3	67.5 ± 1.3	109.55	99.09	40.88	3.61	0.73	25.2 ± 0.6	23.6 ± 0.5	123 ± 7.2	90 ± 0
	$3H_5^{0.1}$	98.8 ± 1.6	99.7 ± 0.2	4.57	4.28	2.02	0.33	0.17	15 ± 0.9	16.2 ± 0.5	36.9 ± 5.2	90 ± 0
	$3H_5^{0.3}$	85.8 ± 0.5	87.6 ± 1.4	46.45	40.83	15.81	1.24	0.49	21.2 ± 0.9	21.2 ± 1.2	88.4 ± 5.2	90 ± 0
	$3H_5^{0.5}$	73.3 ± 4.1	75.3 ± 4.5	68.11	60.98	25.84	2.74	0.78	31.3 ± 2.7	29.4 ± 2.6	137.3 ± 3.6	90 ± 0
	$4H_3^{0.1}$	72.1 ± 1.3	74.2 ± 1.1	61.69	55.48	21.81	1.82	0.58	11 ± 0.5	12.1 ± 0.5	44.7 ± 4.8	86 ± 6.9
	$4H_3^{0.3}$	66.7 ± 3.5	67.9 ± 3.2	217.27	197.85	87.46	7.29	0.78	13.5 ± 0.2	13.6 ± 0.6	60.2 ± 3.5	88.3 ± 2.9
	$4H_3^{0.5}$	60.2 ± 0.6	61.8 ± 0.6	430.20	384.57	183.98	15.40	1.12	17.8 ± 1.1	17 ± 1.3	99.4 ± 5.5	77 ± 3
	$4H_5^{0.1}$	105 ± 1.4	106.7 ± 1.1	41.31	21.34	9.02	1.90	0.42	21.6 ± 0.3	22.9 ± 0.3	64.6 ± 2	90 ± 0
	$4H_5^{0.3**}$	92 ± 1.4	93 ± 0.8	172.26	140.84	70.01	5.83	1.05	31.5 ± 1.1	30.5 ± 1.3	118 ± 3.7	90 ± 0
	$4H_5^{0.5}$	78.4 ± 2.6	80.2 ± 2.1	379.94	247.04	178.96	12.57	1.53	45.4 ± 1.1	42.2 ± 0.8	194.2 ± 4.3	86 ± 1.7
	$4H_6^{0.1}$	112.8 ± 1.6	114.5 ± 1.4	17.69	15.57	5.78	1.88	0.33	25.1 ± 0.6	25.7 ± 0.9	69.1 ± 4.2	86.7 ± 5.8
	$4H_6^{0.3}$	100 ± 0.1	102 ± 0.3	121.87	110.67	42.19	3.58	0.86	36.5 ± 2	35.3 ± 1.6	128.1 ± 10	88.3 ± 2.9
	$4H_6^{0.5*}$	87.7 ± 3	90.3 ± 4.1	361.94	332.28	144.59	10.97	2.28	53 ± 2.4	48 ± 1.6	225.1 ± 17.7	84.7 ± 4.2
	$5H_3^{0.1}$	85.4 ± 0.6	86.9 ± 0.7	247.53	235.15	92.95	7.57	1.16	14.8 ± 0.7	16.1 ± 0.7	52.9 ± 1.6	90 ± 0
	$5H_3^{0.3*}$	77.7 ± 3.5	78.6 ± 3.1	281.21	257.97	132.97	12.75	1.40	20 ± 0.5	20.8 ± 0.6	87.7 ± 7.3	83 ± 1.7
	$5H_3^{0.5*}$	72.3 ± 3.7	73.6 ± 3	565.90	531.83	294.05	24.24	2.47	27.2 ± 0.9	26.9 ± 0.7	129.9 ± 4	83.3 ± 5
	$5H_4^{0.1}$	101.6 ± 3.4	102.8 ± 2.9	39.14	38.83	17.96	1.94	0.73	21.9 ± 0.1	23 ± 0.2	64 ± 1.2	90 ± 0
	$5H_4^{0.3}$	89.1 ± 2.6	91 ± 1.8	178.88	162.12	74.44	7.42	1.66	25 ± 0.5	25 ± 1.1	101.2 ± 4.9	90 ± 0
	$5H_4^{0.5*}$	79.1 ± 1.6	79.4 ± 1.5	479.22	841.27	440.89	36.64	3.56	32.9 ± 0.5	31.6 ± 1	143.8 ± 2.2	84 ± 1.7
	$6H_4^{0.1}$	107.2 ± 1.7	108.4 ± 1.8	253.14	252.22	130.47	10.47	1.79	25.5 ± 2	26.8 ± 2	77.5 ± 6	90 ± 0
	$6H_4^{0.3}$	97.3 ± 4.3	98.2 ± 4.4	529.26	498.11	253.78	21.39	2.45	31.8 ± 1	31.7 ± 1.1	115.3 ± 7.8	86.3 ± 1.5
	$6H_4^{0.5*}$	85.9 ± 3.6	88 ± 3.7	1004.69	954.73	602.15	52.80	5.74	41.7 ± 0.7	40.3 ± 1.3	171.3 ± 4.2	82 ± 3.6

6. Supplementary movies

Movie 1: Swelling of dry microgels in real time: *"Movie_1-microgel_swelling.mp4"*

Movie 2: Injectability of representative neat hydrogel precursor (N_{10}) through a needle with an inner diameter of 0.133 mm: *"Movie_2-Injectability_of_neat_hydrogel_precursor. mp4".*

Movie 3: Injectability of representative hydrogel composite precursors (C_{10}) through a needle with an inner diameter of 0.133 mm:
"Movie_3-Injectability_of_hydrogel_composite_precursor. mp4".

Movie 4: Injectability of representative granular hydrogel precursors of lower viscosity ($3G_7$) through a needle with an inner diameter of 0.133 mm:
"Movie_4-Injectability_of_granular_hydrogel _precursor-lower_viscosity.mp4".

Movie 5: Injectability of representative granular hydrogel precursors of higher viscosity ($6G_4$) through a needle with an inner diameter of 0.133 mm:
"Movie_5-Injectability_of_granular_hydrogel _precursor-higher_viscosity.mp4".

Movie 6: Injectability of representative hybrid hydrogel precursors of lower viscosity ($4H_6^{0.5}$) through a needle with an inner diameter of 0.133 mm:
"Movie_6-Injectability_of_hybrid_granular_hydrogel _precursor-lower_viscosity.mp4".

Movie 7: Injectability of representative hybrid hydrogel precursors of higher viscosity ($6H_4^{0.5}$) through a needle with an inner diameter of 0.133 mm:
"Movie_7-Injectability_of_hybrid_granular_hydrogel _precursor-higher_viscosity.mp4".