Supporting Information

Engineering Bio-Based Eutectogels from Casein via 3D Printing

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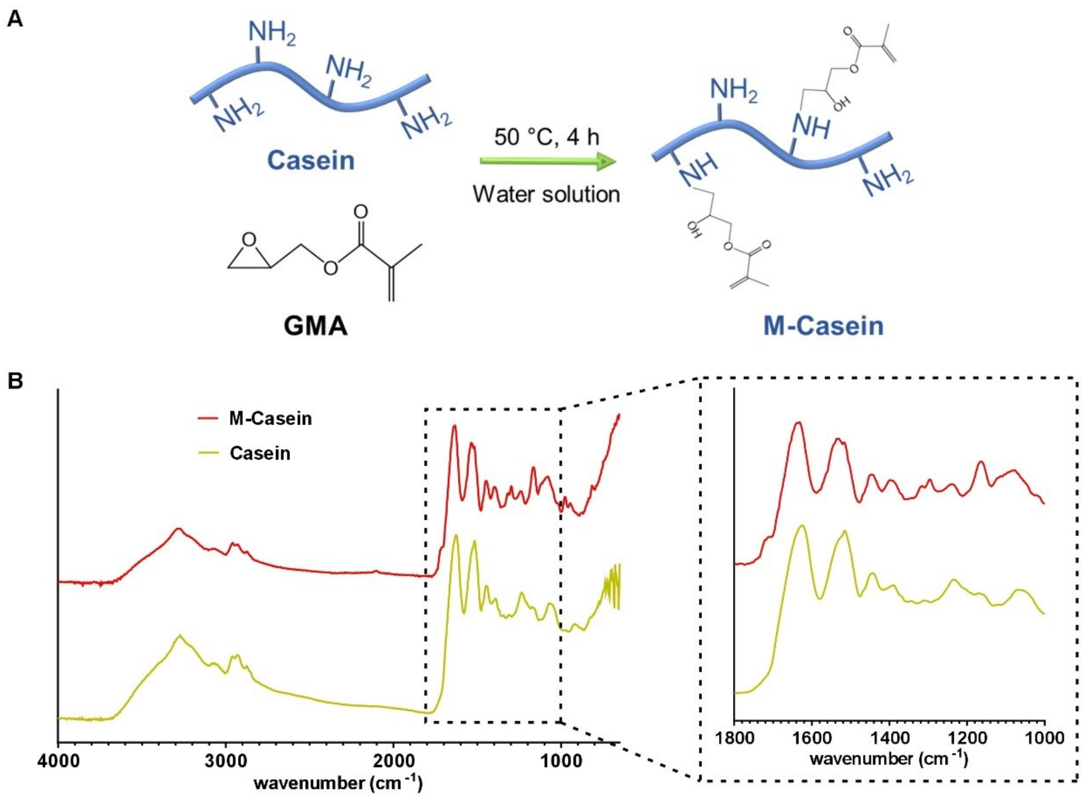


Figure S1. (A) Scheme of the synthesis of M-casein with GMA. (B) ATR-FTIR spectra of casein and M-casein.

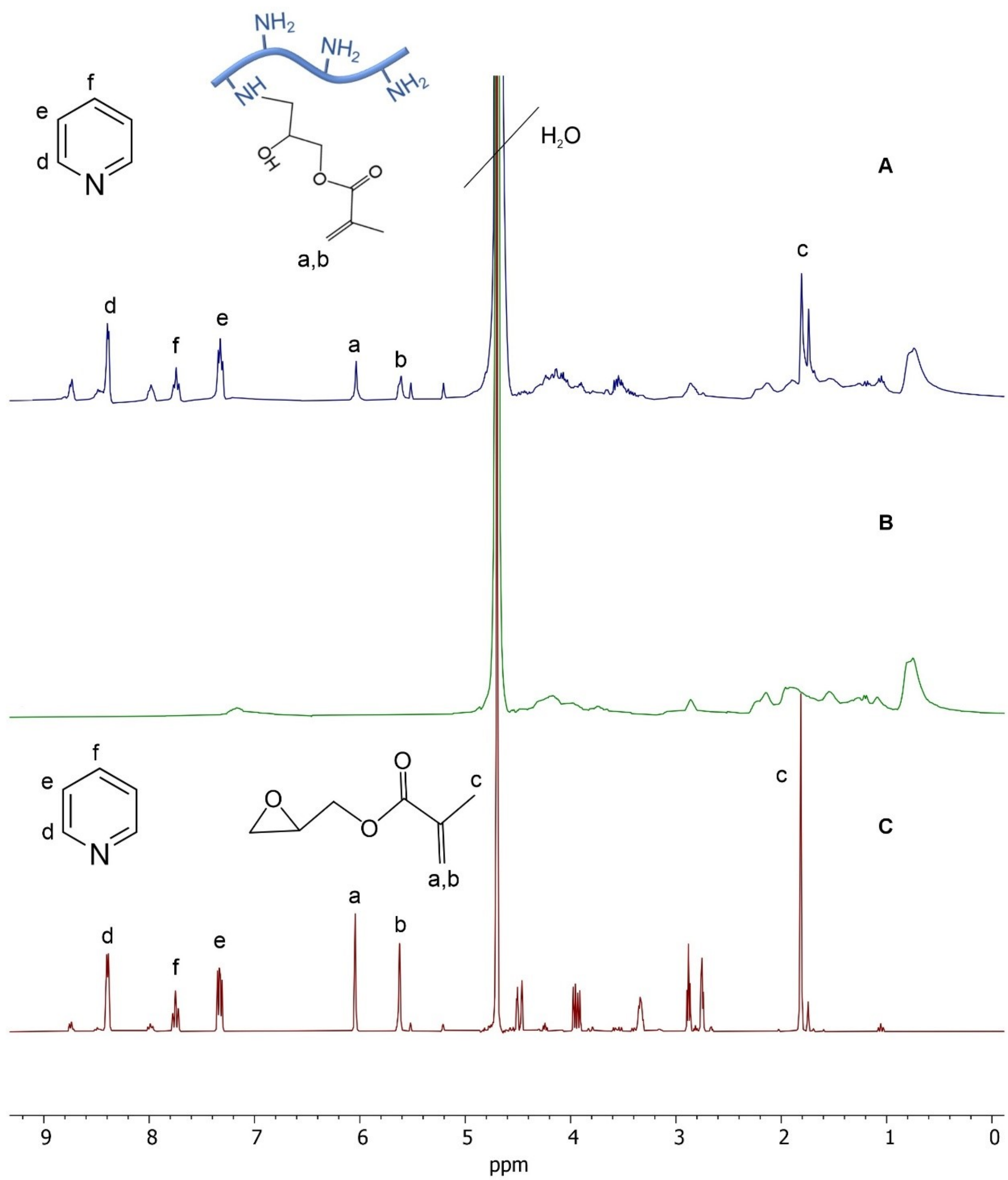


Figure S2. [1]H NMR spectra of M-casein (A), native casein (B) and a mixture of pyridine and GMA used in the calibration curve (C), all of them in D_2O.

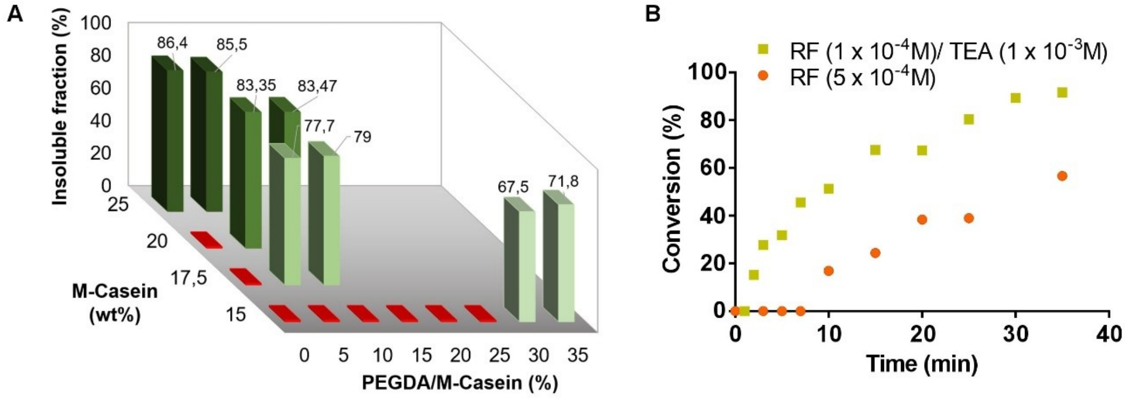


Figure S3. (A) Insoluble fraction for different formulations containing variable concentration of M-casein and PEGDA, photo-polymerized during 20 min in bulk using RF (5 x10^{-4} M) as photo-initiator. Formulations without gel formation are indicated in red. (B) Photo-polymerization kinetics given by % vinyl groups of M-casein and PEGDA conversion vs irradiation time (min) for the formulation with 17.5 wt% of M-casein and 30% of PEGDA, using different photoinitiator systems.

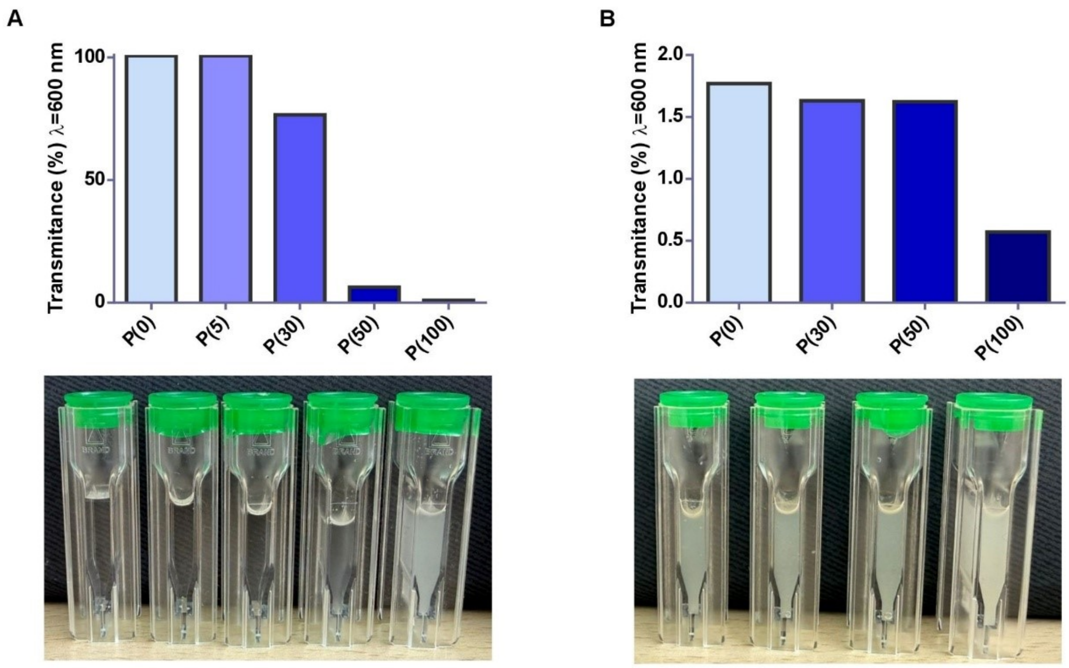


Figure S4: Transmittance at 600 nm of precursor solutions (water/D_1, 50/50) containing different PEGDA contents, in the absence (A) and presence (B) of 12.5 wt% M-casein, along with photographs of the corresponding mixtures.

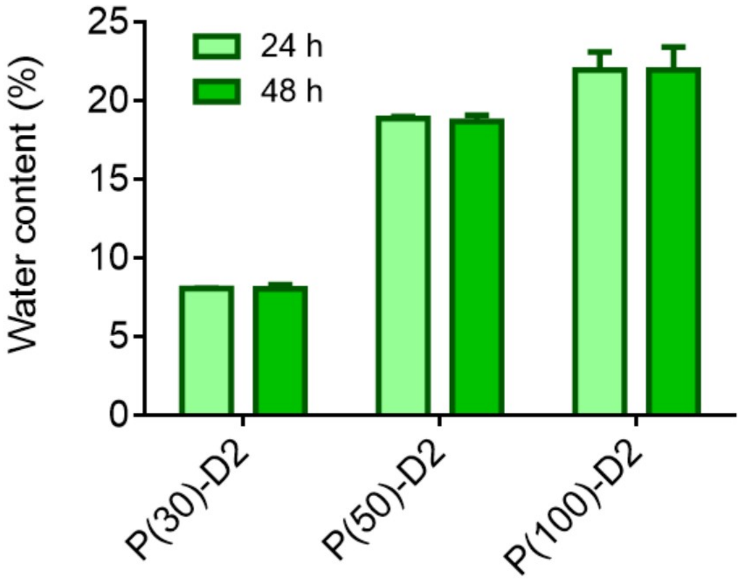


Figure S5: Equilibrium water content (wt% relative to the initial water content, Eq. 3) of D_2-based gels with different PEGDA content after being exposed to a controlled humidity and temperature atmosphere (75% RH at 25 °C) for 24 h and 48 h.

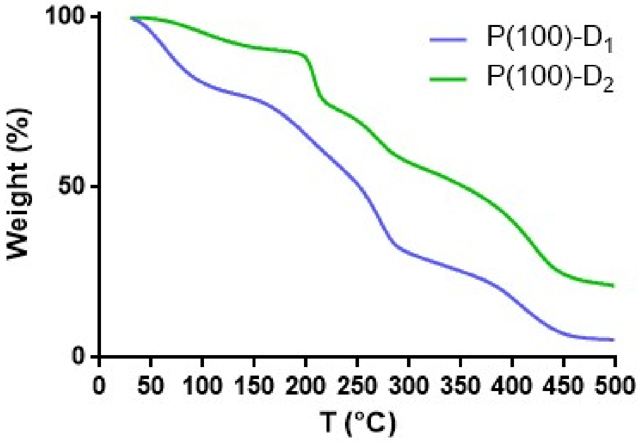


Figure S6: TGA results for P(100)-D_1 (A) and P(100)-D_2 (B) formulations.

Table S1: Eutectogel composition based on M-Casein after synthesis (initial formulation) and after being exposed to 75% RH at 25 °C for 24 h (equilibrium content).

Formulation	Initial/final stage	M-casein	PEGDA (wt relative to M-Casein)	DES (wt relative to M-Casein)	Water (wt relative to M-Casein)
P(30)-D_1	Initial formulation	1.00	0.30	2.85	2.85
	Equilibrium content	1.00	0.30	2.86	2.09
P(50)-D_1	Initial formulation	1.00	0.50	2.85	2.85
	Equilibrium content	1.00	0.50	2.85	2.24
P(100)-D_1	Initial formulation	1.00	1.00	2.85	2.85
	Equilibrium content	1.00	1.00	2.85	2.08
P(30)-D_2	Initial formulation	1.00	0.30	2.85	2.85
	Equilibrium content	1.00	0.30	2.86	0.23
P(50)-D_2	Initial formulation	1.00	0.50	2.85	2.85
	Equilibrium content	1.00	0.50	2.86	0.54
P(100)-D_2	Initial formulation	1.00	1.00	2.85	2.85
	Equilibrium content	1.00	1.00	2.86	0.63

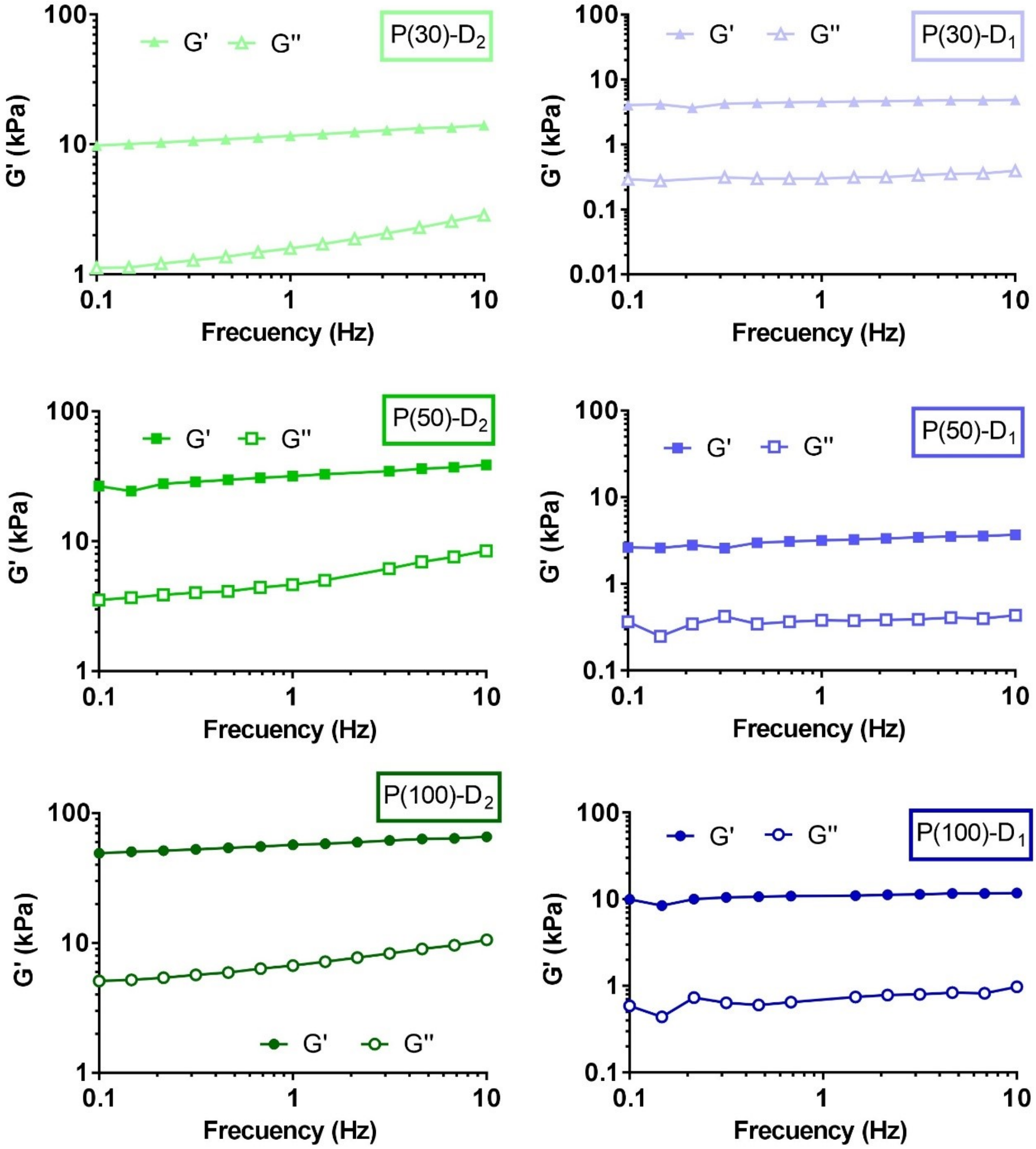


Figure S7: Frequency sweep test of each eutectogel formulation.

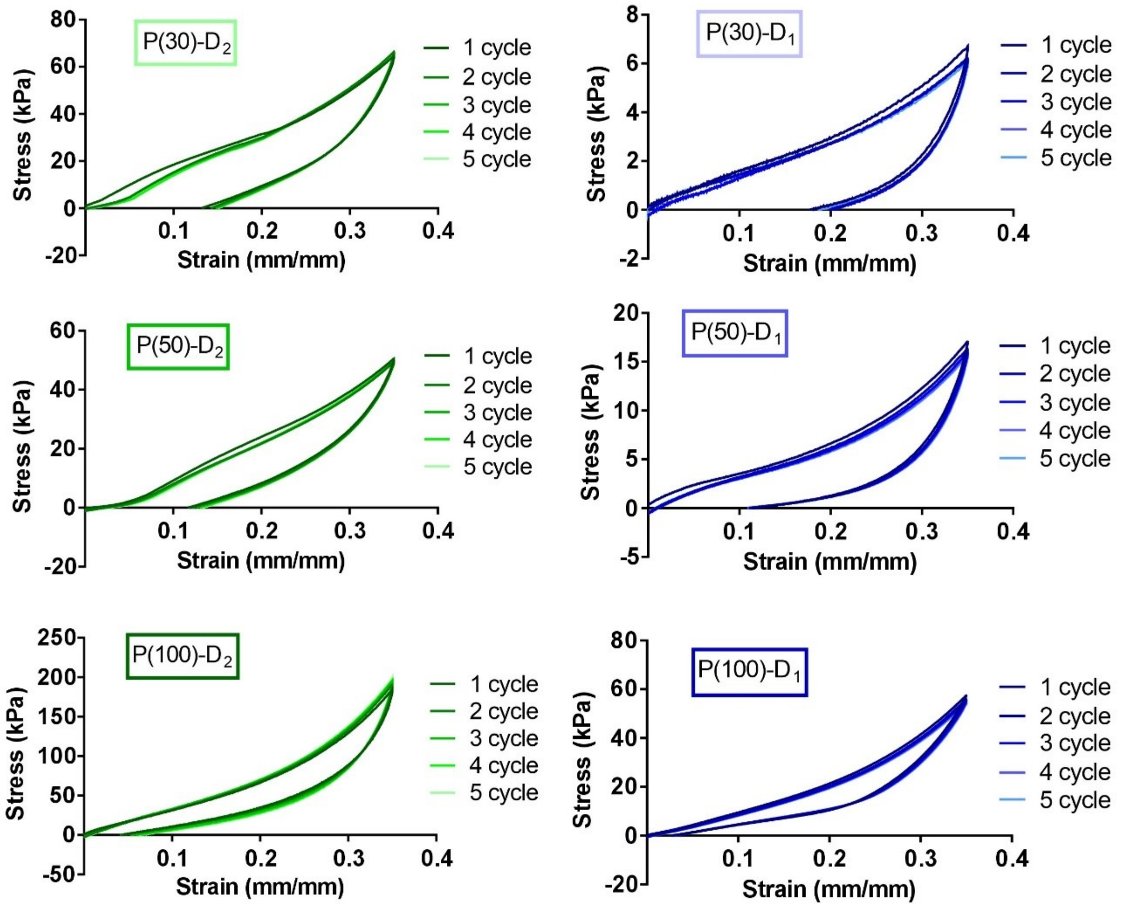
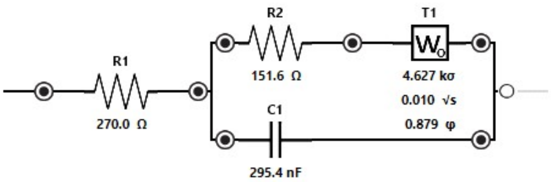
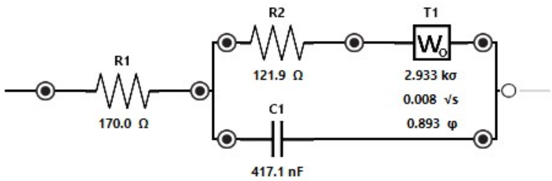


Figure S8. Cycles of loading-unloading compression test of D_1-based eutectogels (right) and D_2-based eutectogels (left)

P(30)-D1		
Element	**Fitted Value**	**Unit**
R 1	270.0	Ω
R 2	151.6	Ω
T 1	4627	σ
T 1	0.010	√s
T 1	0.879	φ
C 1	2,95E-04	F
Chi-Squared: 0.0611	Iterations: 28	

P(50)-D1		
Element	**Fitted Value**	**Unit**
R 1	170.0	Ω
R 2	121.9	Ω
T 1	2933	σ
T 1	0.008	√s
T 1	0.893	φ
C 1	4,17E-04	F
Chi-Squared: 0.1138	Iterations: 15	





P(100)-D1		
Element	**Fitted Value**	**Unit**
R 1	396.7	Ω
R 2	210.3	Ω
T 1	5319	σ
T 1	0.011	√s
T 1	0.872	φ
C 1	1,99E-04	F
Chi-Squared: 0.0931	Iterations: 20	

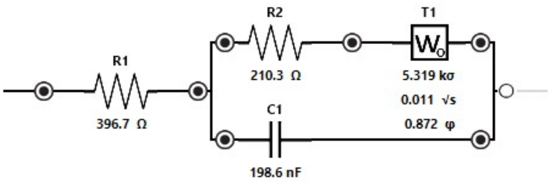


Figure S9. Fitted parameters from the Nyquist plot of different D_1 formulations accompanied by the Randles circuit with the fitting parameters. The elements included in this circuit are: the resistor Rgel (R1) in series with the others elements, which defines the resistance between the electrolyte and the electrode; the resistor Rct (R2), representing the charge transfer resistance, in parallel with the capacitor Cdl (C1), which describes the double layer capacitance present in the gel-electrode interface; and finally, the Warburg impedance Zw (composed of three different elements T1) , which accounts for impedance produced for the ion diffusion within the gel electrolyte.

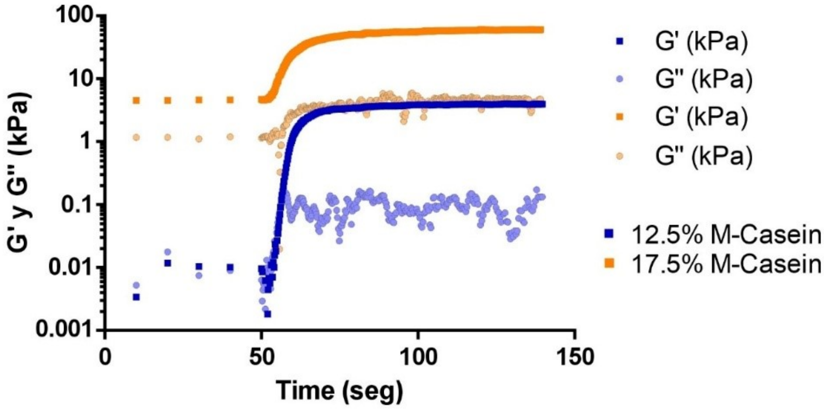


Figure S10: Photorheology comparing the use of LAP as a photoinitiator in formulation containing 12.5 wt% of M-casein and 17.5 wt% of M-casein (30% PEGDA).

Table S2: Ionic conductivity of P(30)-D_1-12.5 and P(40)-D_1-12.5 formulations from EIS measurements performed at different AC voltage amplitudes.

Formulation	Amplitude (mV)	Ionic conductivity (S/cm)
P(30)-D_1-12.5	5	1.81E-02
	10	1.80E-02
	20	1.79E-02
P(40)-D_1-12.5	5	1.20E-02
	10	1.17E-02
	20	1.15E-02

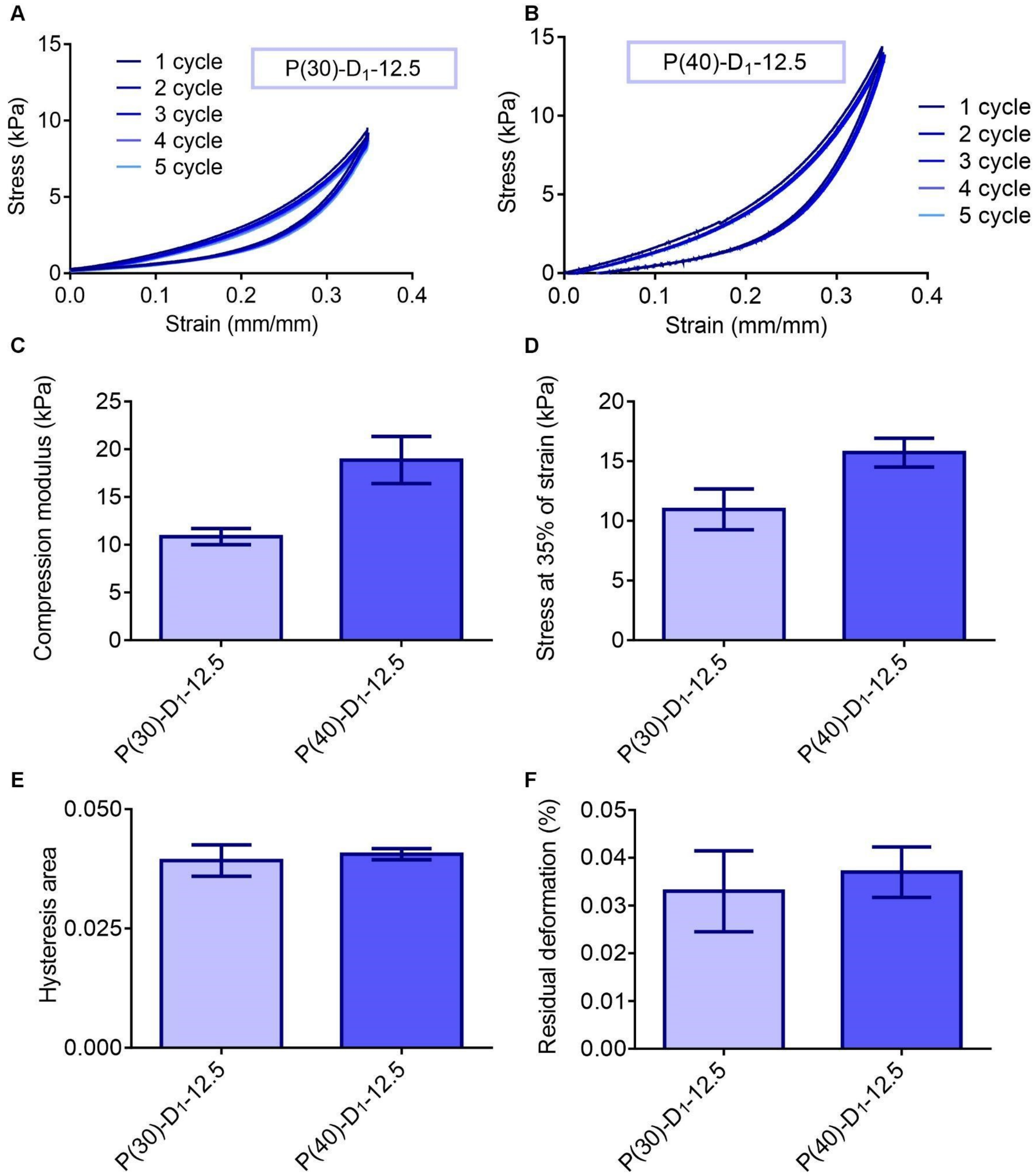


Figure S11: Loading and un-loading repeated compression cycles (A and B). Compression modulus (C), stress at 35% of strain (D), Hysteresis area (E) and residual deformation (F) calculated from compression test of 3D printing formulation.