

Mechanically strong triple network hydrogels based on hyaluronan and poly(N,N-dimethylacrylamide)

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Supporting Information

Table S1. Preparation conditions and mechanical data of SN and DN hydrogels. $C_1 = 0.02 \text{ g.mL}^{-1}$. DN hydrogels were prepared without and with 0.05 mol % BAAM crosslinker in the 2nd monomer solution. Blue and red rows represent data for SN and DN hydrogels, respectively.

SN hydrogels	DN Hydrogels			Mechanical data		
DM ^a	C ₂ ^b	BAAM % ^c	w ₂₁ ^d	σ _f ^e / MPa	ε _f ^f / %	
4	0	0	0	0.024 (0.005)	43	SN hydrogel
4	0.10	0	13	0.03 (0.01)	38	DN hydrogels
4	0.10	0.05	13	11 (1)	94	
4	0.30	0	29	0.07 (0.01)	36	
4	0.30	0.05	29	12 (2)	93	
14	0	0	0	0.050 (0.002)	45	SN hydrogel
14	0.10	0	6	0.16 (0.03)	40	DN hydrogels
14	0.10	0.05	6	6.2 (0.8)	92	
14	0.30	0	15	0.4 (0.1)	34	
14	0.30	0.05	15	6.7 (0.5)	88	
25	0	0	0	0.026 (0.009)	34	SN hydrogel
25	0.10	0	8	0.1 (0.01)	52	DN hydrogels
25	0.10	0.05	8	3.1 (0.4)	77	
25	0.30	0	15	0.3 (0.05)	53	
25	0.30	0.05	15	9.4 (1)	90	

^a Methacrylation degree of GMHA (in %) formed at various n_{GM}/n_{HA} ratios, ^b DMA concentration in the 2nd monomer solution (in g.mL⁻¹), ^c BAAM concentration in the 2nd monomer solution (in mol %), ^d the mass ratio of the second to the first network units, ^e fracture stress, ^f strain at break. Standard deviations in parentheses.

Table S2. Preparation conditions, mechanical data, and water contents of SN, DN, and TN hydrogels. $C_1 = 0.02 \text{ g.mL}^{-1}$. DN hydrogels were prepared with 0.05 mol % BAAM crosslinker in the 2nd monomer solution. Blue, red, and white rows represent data for SN, DN, and TN hydrogels, respectively.

SN hydrogels	DN hydrogels		TN Hydrogels			Mechanical data		Water content (%)		
	C_2^b	w_{21}^c	C_3^d	BAAM % ^e	$w_{32/1}^f$	σ_f^g / MPa	$\varepsilon_f^h / \%$			
4	0	0	0	0	0	0.024 (0.005)	43	99.5	SN hydrogel	
4	0.10	13	0	0	13	11 (1)	94	95	DN hydrogels	
4	0.10	13	0.10	0.05	29	11.2 (0.7)	93	89	} TN hydrogels	
4	0.10	13	0.30	0.05	101	15 (3)	93	85		
4	0.10	13	0.10	0	27	8.4 (0.8)	95	88		
4	0.10	13	0.30	0	45	8.8 (0.7)	95	83		
4	0.30	29	0	0	29	12 (2)	93	88		DN hydrogels
4	0.30	29	0.30	0.05	106	22 (5)	96	84	} TN hydrogels	
4	0.30	29	0.30	0	115	2 (0.4)	87	84		
14	0	0	0	0	0	0.050 (0.002)	45	99.2	SN hydrogel	
14	0.10	6	0	0	6	6.2 (0.8)	92	90	DN hydrogels	
14	0.10	6	0.10	0.05	22	18 (2)	92	91	} TN hydrogels	
14	0.10	6	0.30	0.05	36	12 (2)	91	82		
14	0.10	6	0.10	0	18	5.6 (0.5)	92	88		
14	0.10	6	0.30	0	27	8.5 (0.7)	95	84		
25	0	0	0	0	0	0.026 (0.009)	34	99.3	SN hydrogel	
25	0.10	8	0	0	8	3.1 (0.4)	77	94	DN hydrogels	
25	0.10	8	0.10	0.05	22	11.1 (1)	92	86	} TN hydrogels	
25	0.10	8	0.30	0.05	46	16.3 (2)	94	80		
25	0.10	8	0.10	0	21	10.7 (1)	94	89		
25	0.30	15	0	0	15	9.4 (0.8)	90	89		DN hydrogels
25	0.30	15	0.10	0.05	26	15.7 (2)	93	85		} TN hydrogels
25	0.30	15	0.30	0.05	65	17.2 (1)	94	81		
25	0.30	15	0.10	0	43	10.1 (1)	92	87		
25	0.30	15	0.30	0	70	8.9 (0.8)	93	78		

^a Methacrylation degree of GMHA (in %) formed at various n_{GM}/n_{HA} ratios, ^b DMA concentration in the 2nd monomer solution (in g.mL⁻¹), ^c the mass ratio of the second to the first network units, ^d DMA concentration in the 3rd monomer solution (in g.mL⁻¹), ^e BAAM concentration in the 3rd monomer solution (in mol %), ^f the mass ratio of the second and third to the first network units, ^g fracture strain, ^h strain at break. Standard deviations in parentheses while for water contents; they are less than 5 %.

Table S3. Equilibrium swelling ratio m_{rel2} of DN hydrogels in water and DMA solutions. The hydrogels were prepared at various w_{21} ratios. SN hydrogels were prepared from GMHA of various methacrylation degrees (DM) indicated. Standard deviations for DM values are given in the parenthesis, while for the swelling ratios; they are less than 10 %.

DM %	w_{21}	m_{rel2}		
		water	10% DMA	30% DMA
4 (1)	13	1.4	2.0	1.6
	29	2.4	2.4	2.4
8 (2)	11	1.8	-	-
	24	2.4	-	-
14 (2)	6	1.4	1.8	1.5
	15	2.1	-	-
25 (4)	8	1.8	2.2	2.1
	15	2.7	2.9	2.6

Table S4. Equilibrium swelling ratio m_{rel3} of TN hydrogels in water. The hydrogels were prepared at various w_{21} and $w_{32/1}$ ratios. SN hydrogels were prepared from GMHA of various methacrylation degrees (DM) indicated. Standard deviations for DM values are given in the parenthesis, while for the swelling ratios, they are less than 10 %.

DM %	w_{21}	$w_{32/1}$	m_{rel3}
4 (1)	13	29	1.8
		101	2.6
4 (1)	29	60	1.6
		106	3.1
14 (2)	6	22	1.9
		36	2.7
25 (4)	8	22	1.5
		46	2.5
25 (4)	15	26	1.4
		65	2.6

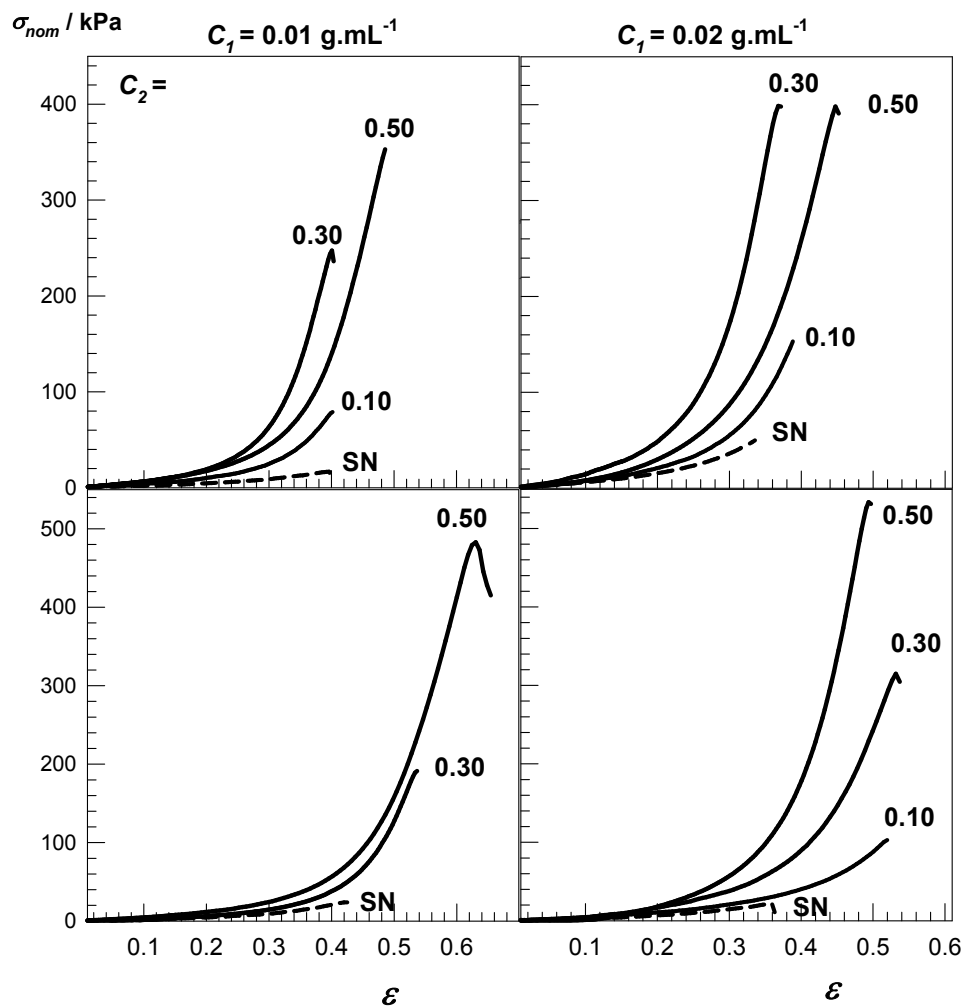


Fig. S1. Compressive stress-strain curves of SN and DN hydrogels formed from 14 (upper panel) and 25% methacrylated HA (bottom panel). $C_1 = 0.01$ (left) and 0.02 g.mL^{-1} (right). DN hydrogels were prepared without use of a chemical cross-linker in DMA solutions at a concentration (C_2) of 0.10, 0.30, and 0.50 g.mL^{-1} , as indicated.

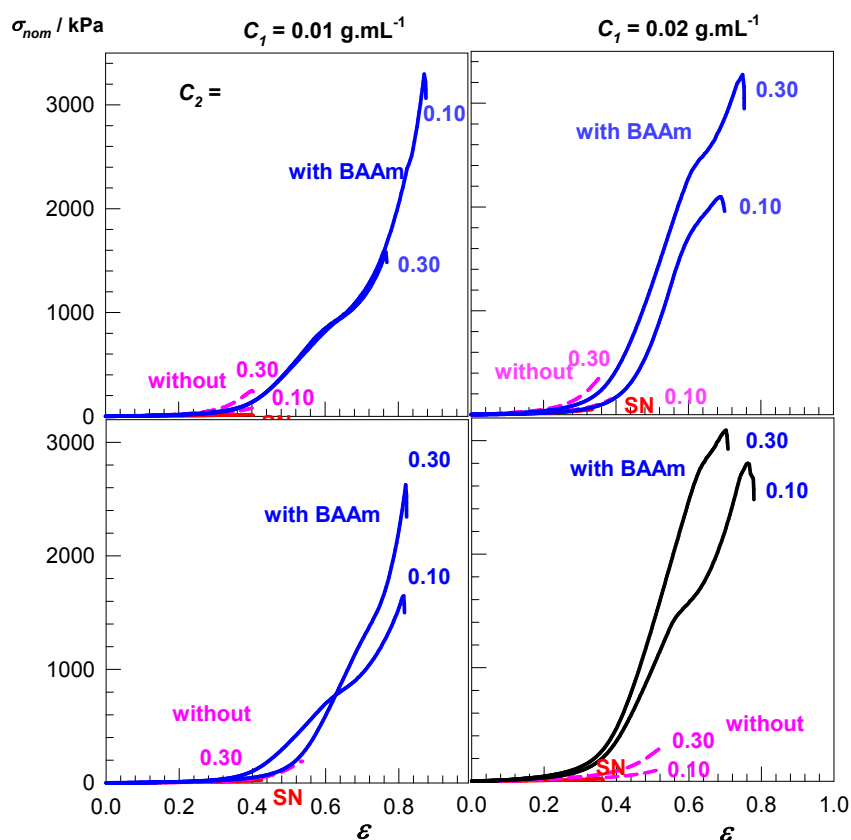


Fig. S2. Compressive stress-strain curves of SN and DN hydrogels formed from 14 (upper panel) and 25% methacrylated HA (bottom panel). $C_1 = 0.01$ (left) and 0.02 g.mL^{-1} (right). DN hydrogels were prepared without and with 0.1 mol% BAAm cross-linker in in DMA solutions at a concentration C_2 of 0.10 and 0.30 g.mL^{-1} , as indicated.

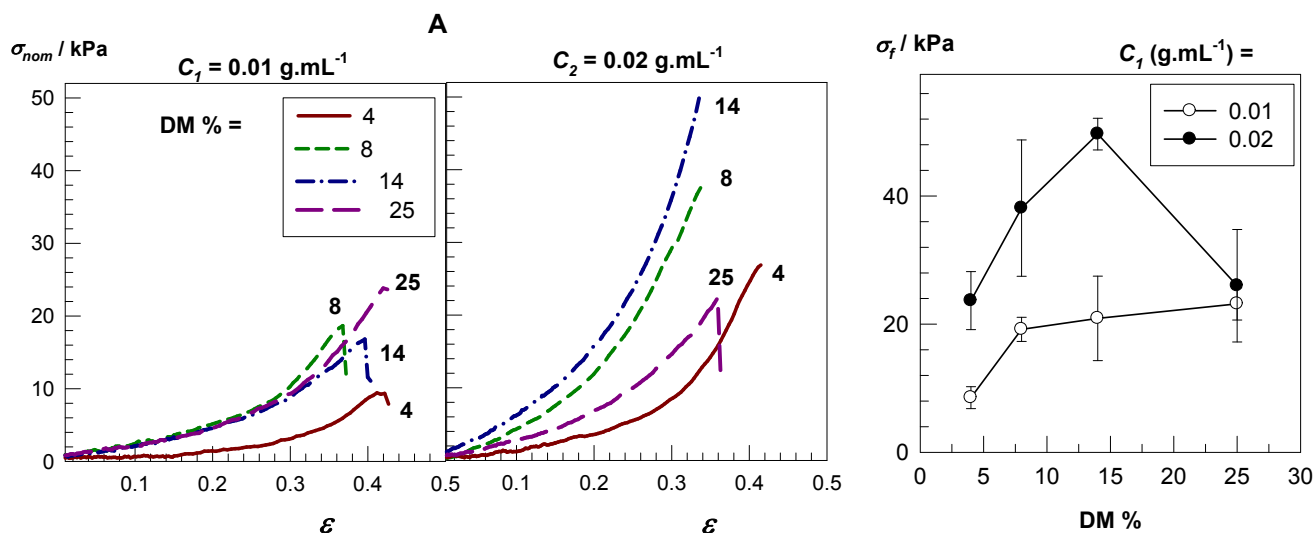


Fig. S3. (A): Compressive stress-strain curves of SN hydrogels formed GMHA macromer of various methacrylation degrees DM as indicated. $C_1 = 0.01$ (left) and 0.02 g.mL^{-1} (right). **(B):** Fracture stress of SN hydrogels plotted against the degree of methacrylation DM of the macromer.

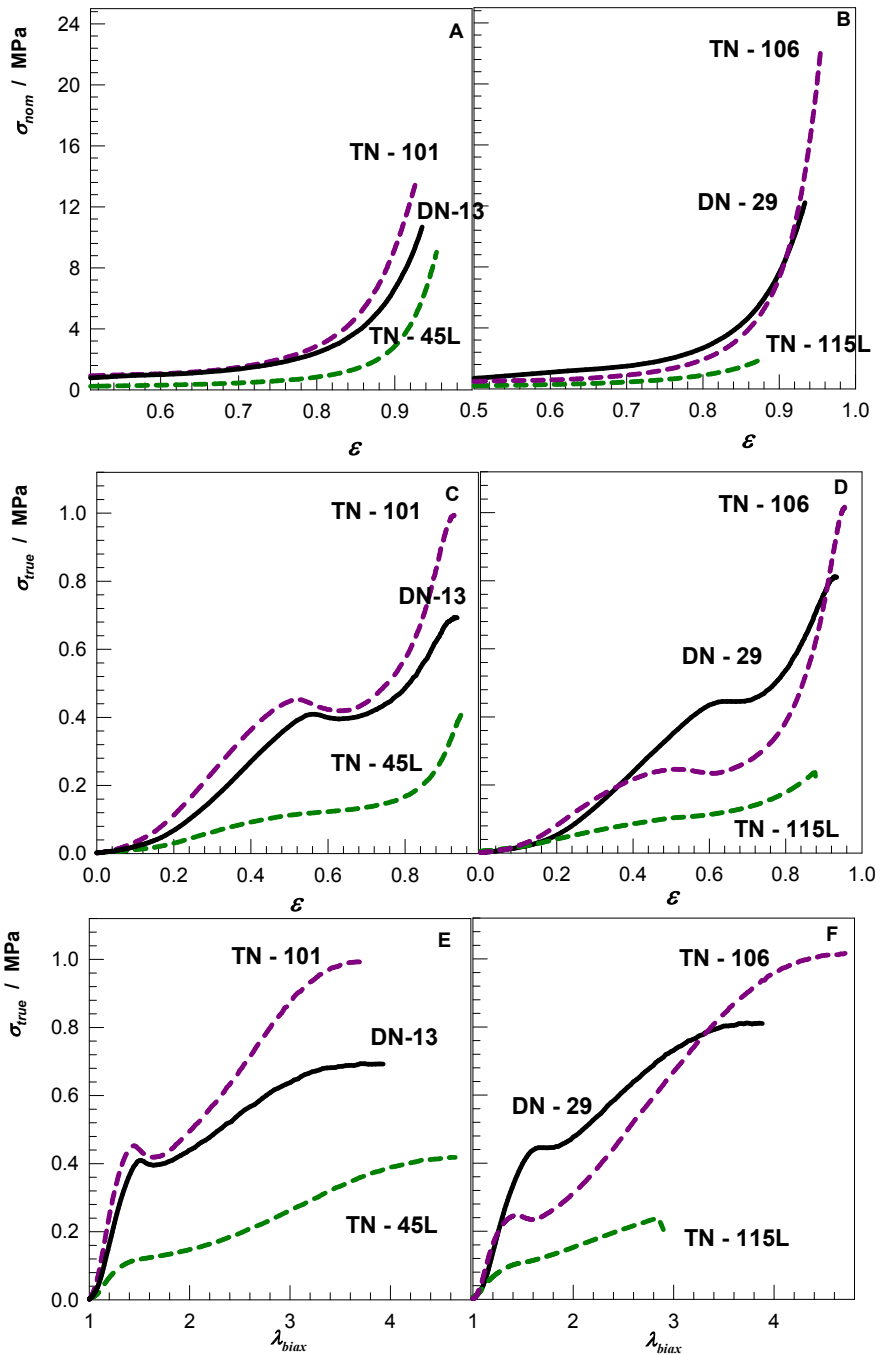


Fig. S4. (A, B): σ_{nom} vs. ϵ plots for DN (solid curves) and TN hydrogels (dashed curves) formed from 4% methacrylated HA. DNs were prepared in DMA solutions at $C_2 = 0.10$ (A) and 0.30 g.mL^{-1} (B), both containing 0.05 mol% BAAM. TNs were obtained in DMA solutions at $C_3 = 0.30 \text{ g.mL}^{-1}$ without and with 0.05 mol% BAAM. The letter L at the end of this abbreviation indicates that no cross-linker was used in TN preparation. $C_1 = 0.02 \text{ g.mL}^{-1}$. Hydrogel samples are denoted in the figures as DN-x or TN-y, where x and y are w_{21} and $w_{32/1}$ ratios, respectively. (C-F): σ_{true} vs. ϵ (C,D) and σ_{true} vs. λ_{biax} plots derived from the curves given in A and B, respectively.

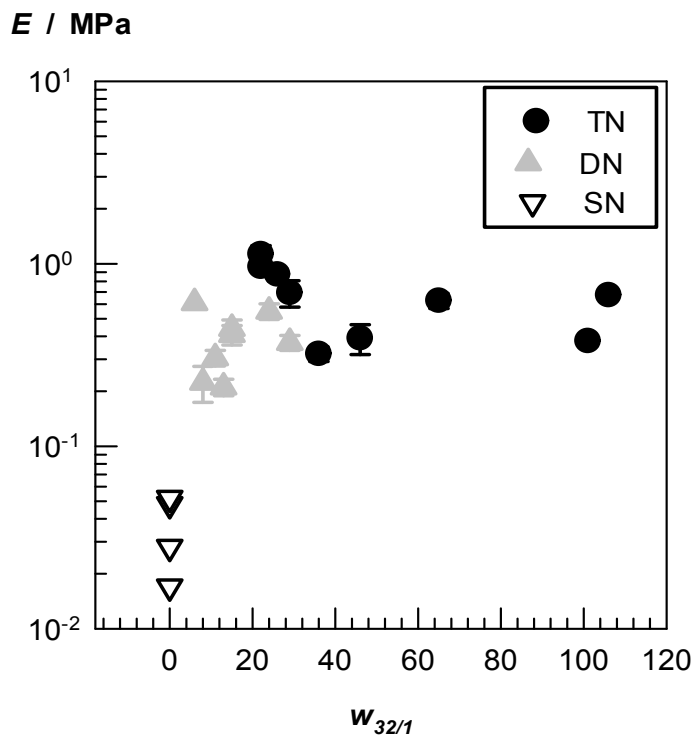


Fig. S5. Young's moduli E of SN, DN, and TN hydrogels plotted against $w_{32/1}$ ratio.

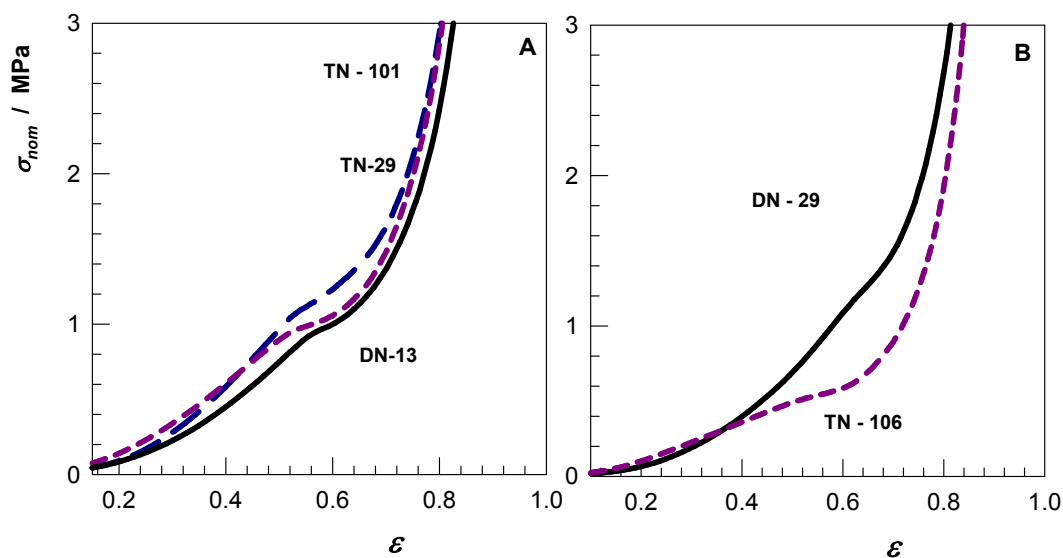


Fig. S6. σ_{nom} vs. ϵ plots for DN (solid curves) and TN hydrogels (dashed curves) formed from 4% methacrylated HA. DNs were prepared in DMA solutions at $C_2 = 0.10$ (A) and 0.30 g.mL^{-1} (B), both containing 0.05 mol% BAAM. TNs were obtained with 0.05 mol % BAAM. $C_1 = 0.02 \text{ g.mL}^{-1}$.