Biodegradable Silicone-Gelatin Hydrogels

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Electronic Supporting Information (ESI)

Table S1. Recipes for gelatin/silicone copolymers without crosslinking

Product	Mass Silicone (g, mmol)	Mass Gelatin (g)	Volume Water (mL)
T37-67	6.6 (2.2)	3.3	17
T37-50	5.0 (1.7)	5.0	25
T37-33	3.3 (1.1)	6.6	33
T8-50	2.5 (2.3)	2.5	13
T334-50	2.5 (0.1)	2.5	13
P10-50	2.5 (1.4)	2.5	13

Table S2. Young's Modulus of gelatin/silicone copolymers prepared without chemical crosslinking.

Gelatin:Silicone Ratio (Mass)	Young's Modulus (kPa, n = 3)	
	Hydrated	Air-Dried
Gelatin	80.4 ± 15.40	3487 ± 2292
T37-67	32.88 ± 1.995	418.3 ± 28.05
T37-50	47.16 ± 4.525	1924 ± 1218
T37-33	36.90 ± 8.619	2074 ± 299.7

Table S3. Hydration of the as-produced crosslinked gels (data added to Table 4, main text)

Product[a]	Mass Silicone (g, mmol, equiv NH_2)	Mass Gelatin (g)[b]	Equiv. HCHO Relative to NH_2 (mmol)[c]	Volume 37% HCHO Solution (µL)	Mass water[d]	mass other	% water
T37-67	6.60	3.30	1 (4.4)	438.00	16.7	9.9	62.7
			2 (8.8)	876.00	16.8	9.9	63.0
			5 (22)	2190.00	17.3	9.9	63.6
			7.5 (33)	3286.00	17.7	9.9	64.2
			10 (44)	4382.00	18.1	9.9	64.7
T37-50	5.00	5.00	1 (3.3)	332.00	25.1	10.0	71.5
			2 (6.7)	664.00	25.2	10.0	71.6
			5 (17)	1660.00	25.6	10.0	71.9
			7.5 (25)	2490.00	25.9	10.0	72.2
			10 (33)	3320.00	26.2	10.0	72.4
T37-33	3.30	6.60	1 (2.2)	219.00	33.1	9.9	77.0
			2 (4.4)	438.00	33.2	9.9	77.0
			5 (11)	1095.00	33.4	9.9	77.1
			7.5 (17)	1643.00	33.6	9.9	77.2
			10 (22)	2191.00	33.8	9.9	77.4
T8-50	2.50	2.50	5 (28)	2766.00	3.5	5.0	41.3
T334-50	2.50	2.50	5 (1.0)	100.00	2.5	5.0	33.7
P10-50[e]	2.50	2.50	5 (14)	1351.00	13.0	5.0	72.2

[a] The starting silicone is indicated at the beginning of each hydrogel product number. [b] Gelatin dry weight. [c] HCHO concentrations were based on the known quantity of silicone amines. [d] Water:gelatin 5:1 + the water in the formaldedyde solution (37%). [e] This value is for each amine monomer ($MeSi(CH_2)_3NH_2O$:Me_2SiO~1:9 ($Me_3SiO(MeSi(CH_2)_3NH_2O)_3(Me_2SiO)_{27}SiMe_3$); molar mass 2000-3000 g mol^{-1}.

Table S4. Changes in mass after drying on the bench (7 days) or in an oven at 60 °C (24 h) of hydrogels and HCHO crosslinked hydrogels.

Silicone	Equivalents of Formaldehyde	Water Content, Air-Dried (% of original)	Water Content, Oven-Dried (% of original)
T37-67	0	3	<1
	1	7	<1
	2	7	<1
	5	8	<1
	7.5	18	4
	10	12	<1
T37-50	0	5	<1
	1	9	<1
	2	12	<1
	5	11	<1
	7.5	6	<1
	10	18	1
T37-33	0	9	<1
	1	17	<1
	2	18	<1
	5	14	<1
	7.5	20	<1
	10	8	<1

Table S5. Contact angle (°) of air and oven-dried hydrogels produced using varying: gelatin:silicone ratios and amounts of formaldehyde crosslinker.

Silicone	Equivalents of Formaldehyde	**Water Contact Angle (°, n = 3)** Hydrated	Oven-Dried	Air-Dried
Gelatin (Control)	0	79.6 ± 15.0	102.6 ± 5.7	99.7 ± 27.0
	5 (rel. to **T37**)	92.1 ± 11.0	98.4 ± 8.8	95.4 ± 5.7
T8-100 (Control)	1	-	-	96.3 ± 12.3
T8-50	5	81.9 ± 6.4	102.8 ± 16.4	99.0 ± 16.4
T37-100 (Control)	1	-	-	106.3 ± 16.3
T37-67	0	67.3 ± 6.4	59.9 ± 4.1	82.3 ± 10.7
	1	72.5 ± 8.8	103.7 ± 19.2	91.9 ± 21.1
	2	82.1 ± 1.2	118.2 ± 4.4	109.5 ± 3.9
	5	71.7 ± 10.5	79.0 ± 8.0	102.8 ± 6.5
	7.5	88.0 ± 13.0	102.1 ± 20.0	88.3 ± 7.5
	10	86.0 ± 24.1	77.3 ± 6.4	97.6 ± 2.9
T37-50	0	89.7 ± 16.7	96.0 ± 8.1	93.0 ± 14.5
	1	77.1 ± 8.0	91.5 ± 9.3	87.3 ± 7.9
	2	86.9 ± 5.4	100.6 ± 7.6	90.2 ± 14.0
	5	69.2 ± 5.4	101.7 ± 13.2	87.7 ± 16.6
	7.5	77.7 ± 9.2	104.5 ± 4.2	94.7 ± 22.1
	10	68.4 ± 4.1	101.0 ± 19.8	102.1 ± 7.6
T37-33	0	60.1 ± 6.9	79.6 ± 22.0	82.5 ± 8.6
	1	89.0 ± 6.4	102.9 ± 5.2	92.4 ± 21.7
	2	82.9 ± 12.1	111.3 ± 1.1	105.1 ± 8.1
	5	84.6 ± 5.9	114.0 ± 9.4	109.4 ± 6.1
	7.5	75.7 ± 7.2	104.8 ± 3.7	101.6 ± 8.7
	10	90.6 ± 0.7	98.4 ± 18.1	103.6 ± 16.2
T334-100 (Control)	1	-	-	106.8 ± 8.7
T334-50	5	92.3 ± 10.9	110.7 ± 8.6	108.5 ± 4.3
P10-100 (Control)	1	-	-	94.6 ± 6.3
P10-50	5	83.1 ± 18.9	115.9 ± 1.8	106.9 ± 10.2

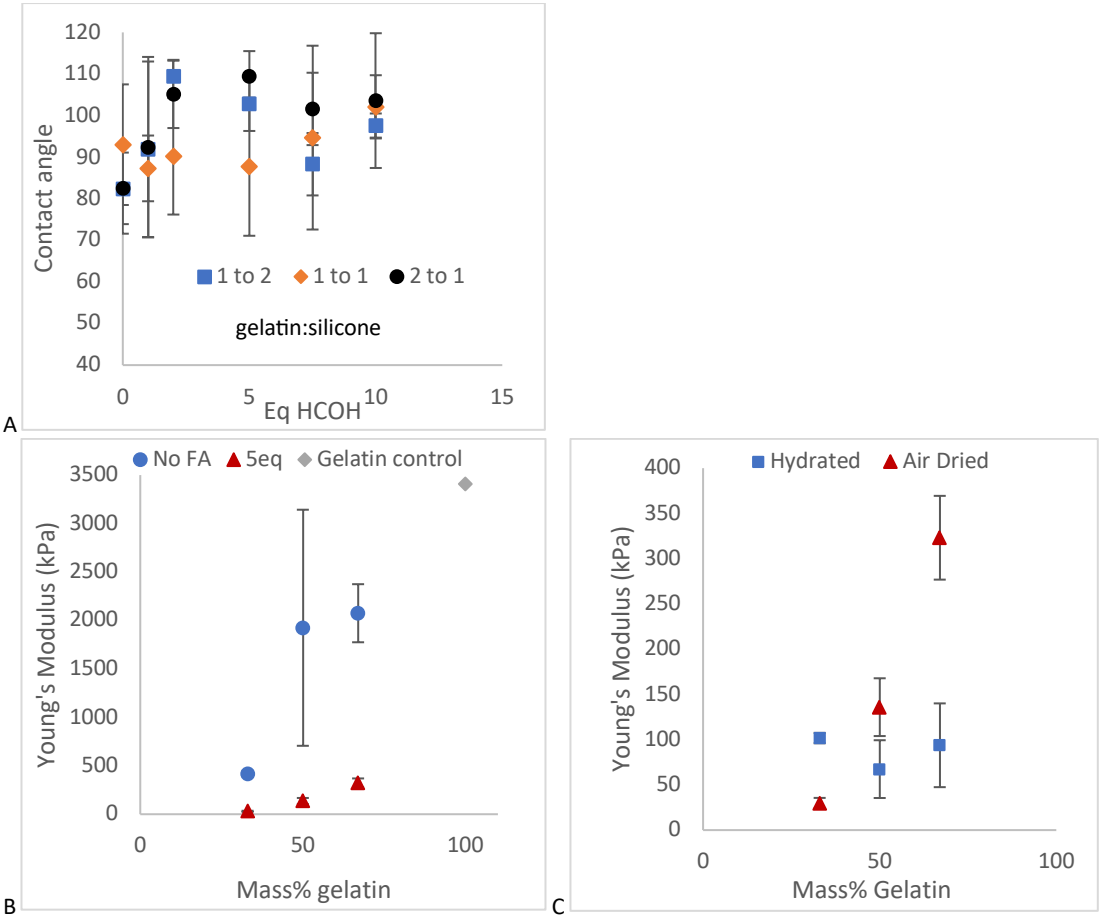


Figure S1 A) Contact angle of air-dried gelatin/silicone hydrogels crosslinked with various amounts of formaldehyde: **T37-33, T37-50** and **T37-67**. B) Young's moduli of gelatin/**T37** optionally crosslinked with HCHO (5 equiv). C) The crosslinked hydrated and air-dried samples are compared (the data from Figure 4 is plotted showing only the crosslinked polymers).

Table S6. Young's Modulus of HCHO crosslinked gelatin/silicone copolymers.

Gelatin: Silicone Ratio (Mass)	**Equivalents of Formaldehyde**	**Young's Modulus (kPa, n = 3)** Hydrated	Air-Dried
Gelatin	5	10.92 ± 3.818	2010 ± 979.2
T37-67	1	68.32 ± 16.33	635.4 ± 254.4
	5	101.7 ± 12.44	588.6 ± 179.8
T37-50	1	39.81 ± 10.38	1151 ± 349.0
	5	67.39 ± 12.50	135.9 ± 31.93
T37-33	1	22.86 ± 4.313	3620 ± 66.64
	5	94.59 ± 21.28	323.1 ± 46.29
T334-50	5	59.18 ± 15.43	929.3 ± 331.2
P10-50	5	35.21 ± 11.96	204.5 ± 122.4

Table S7. Extraction efficiency of gelatin/silicone polymers

Silicone	HCHO	Initial Mass (g)	Mass after H_2O extraction (g)	%swelling	Mass after IPA extraction (g)	%sol
T8-50	5	0.571±0.04	0.502±0.04	136.0%	0.502±0.04	12.2±1.0
T37-33	1	0.262±0.06	0.253±0.06	165.3%	0.251±0.06	4.04±2.0
	10	0.452±0.06	0.434±0.06	166.8%	0.432±0.06	4.46±1.0
T37-50	5	0.367±0.03	0.348±0.03	148.8%	0.346±0.03	5.72±0.73
T37-67	1	0.623±0.14	0.554±0.11	125.2%	0.550±0.10	11.1±2.6
	10	0.590±0.16	0.534±0.13	132.9	0.512±0.12	11.8±5.6
T334-50		0.350±0.04	0.341±0.04	116.9%	0.331±0.04	5.43±0.95
P10-50		0.515±0.14	0.457±0.11	123.5%	0.456±0.11	10.3±3.7
CONTROLS (Gelatin)						
Gelatin	0	0.236	0.202	136.0%	0.198	16.18±3.38
	5	0.316	0.251	159.0%	0.251	21.20±2.57
CONTROLS (No HCHO)						
T8-50		0.265±0.03	0±0	116.3%	0±0	79.62±2.34
T37-50		0.256±0.10	0.053±0.03	121.0%	0.051±0.02	100±0
T334-50		0.351±0.14	0.197±0.14	110.5%	0.190±0.14	46.57±33.0
P10-50		0.230±0.02	0.008±0.01	106.8%	0.003±0.01	98.48±2.15

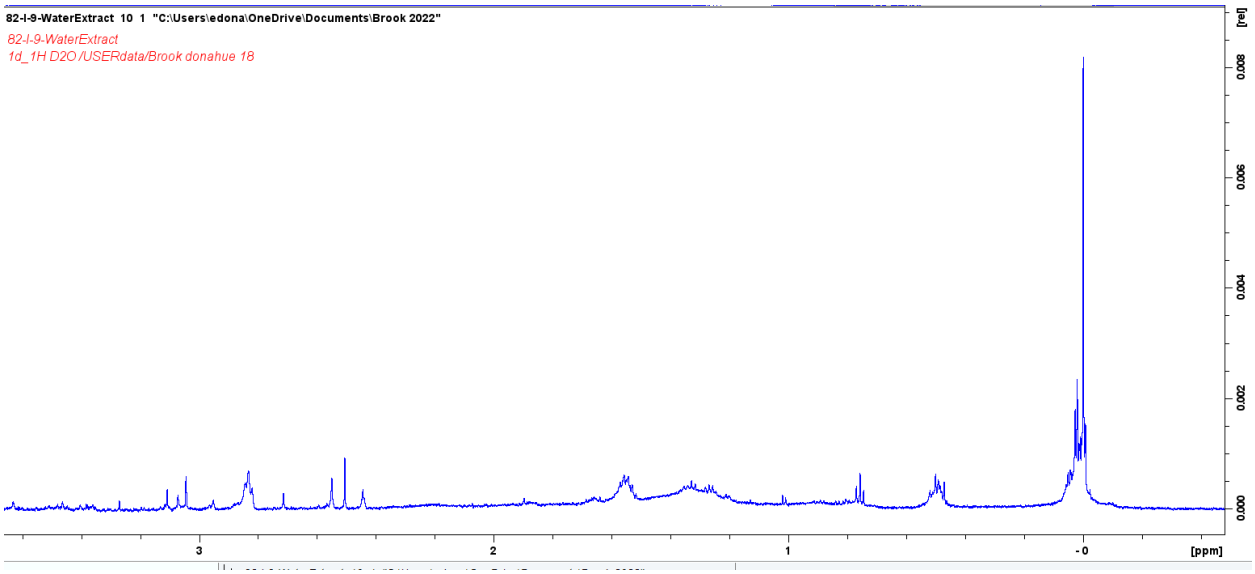
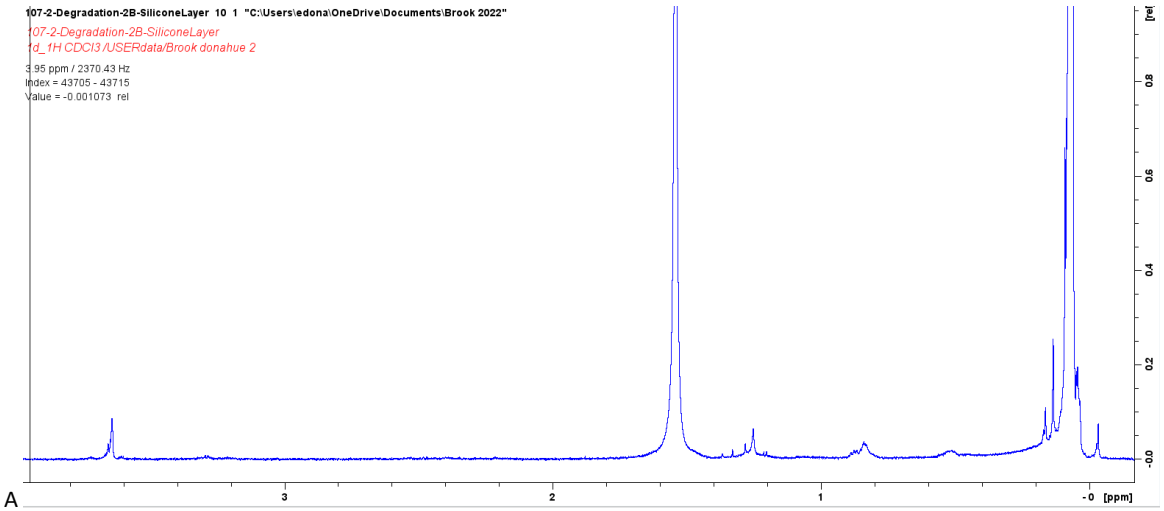


Figure S2. ^{1}H NMR: **w**ater extract of sample containing 1:1 **T37**: gelatin with 5 equivalents formaldehyde. Both silicone and protein moieties are present, suggesting that cross coupling has occurred.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2
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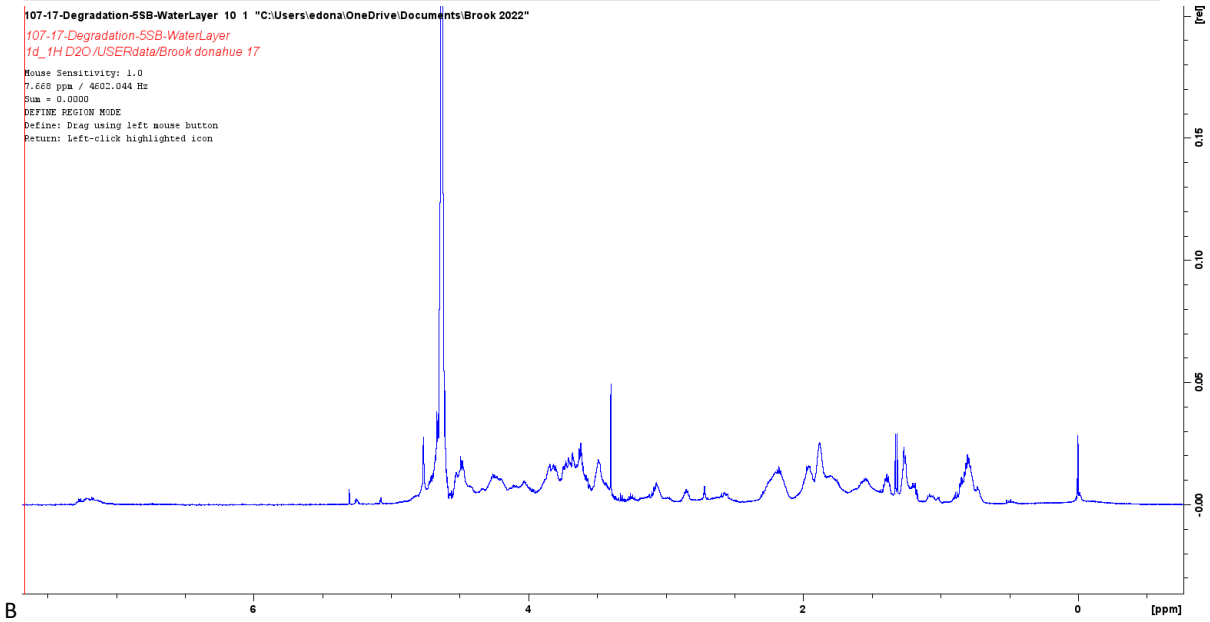
A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Sum = 0.0000
DEFINE REGION MODE
Define: Drag using left mouse button
Return: Left-click highlighted icon
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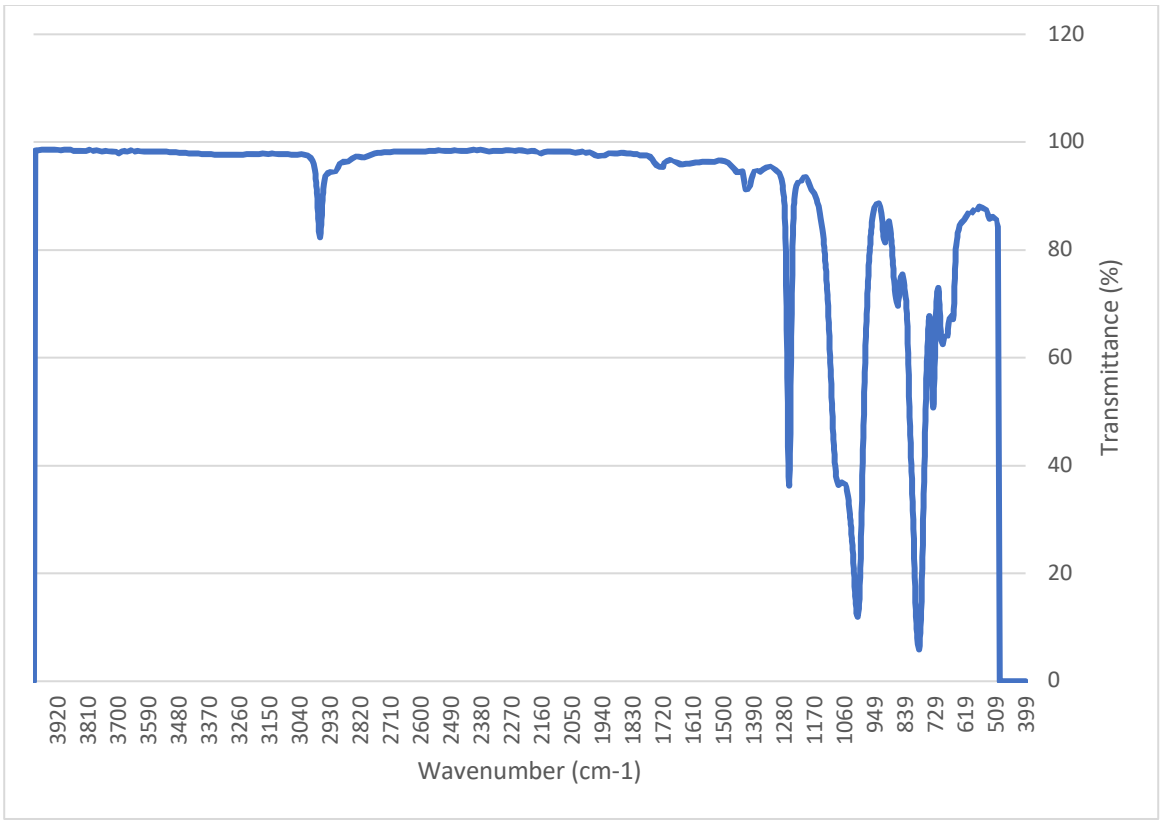
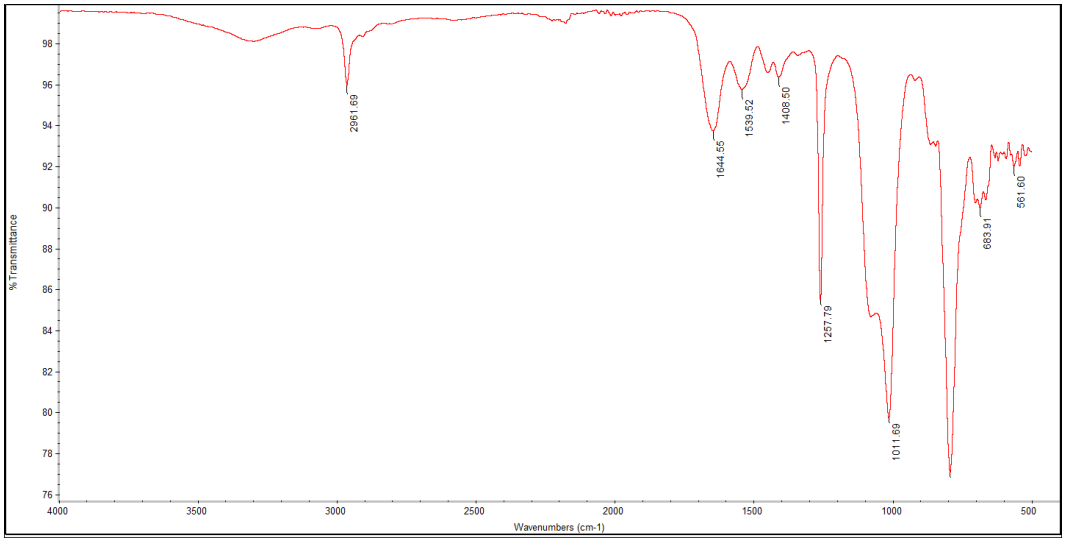
-0.00
6
4
2
0
[ppm]

B



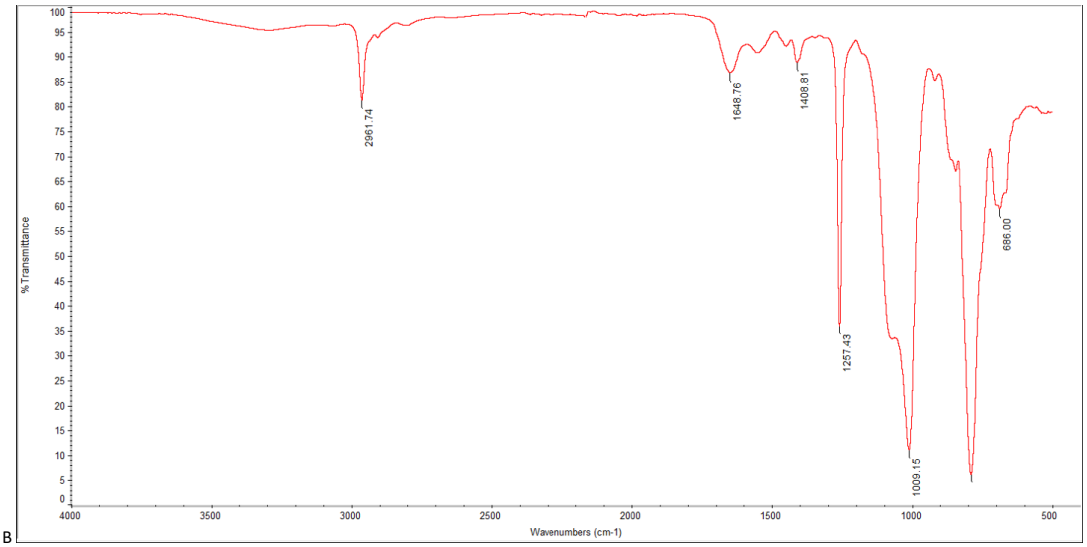
C

Figure S3. Degradation data from material containing 2:1 **T37**:gelatin and crosslinked with 5 equivalents of HCHO : ^{1}H NMR spectrum of A) silicone fraction (aminal linkage at ~3.65 ppm); B) aqueous fraction and C) IR spectrum of recovered rubber, showing very little protein content.



A

B


% Transmittance
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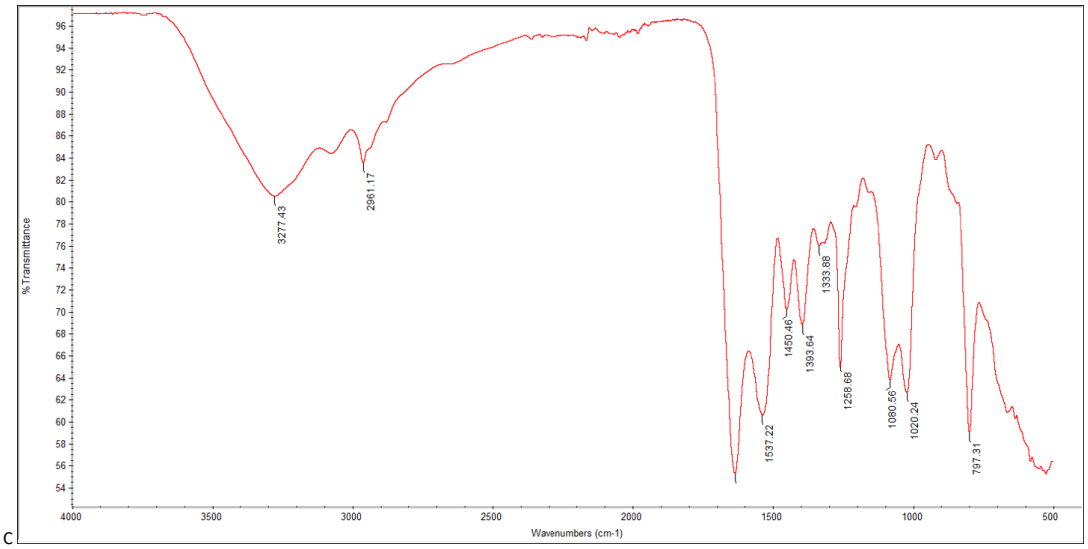
1257.43
1009.15
686.00

C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Wavenumbers (cm-1)
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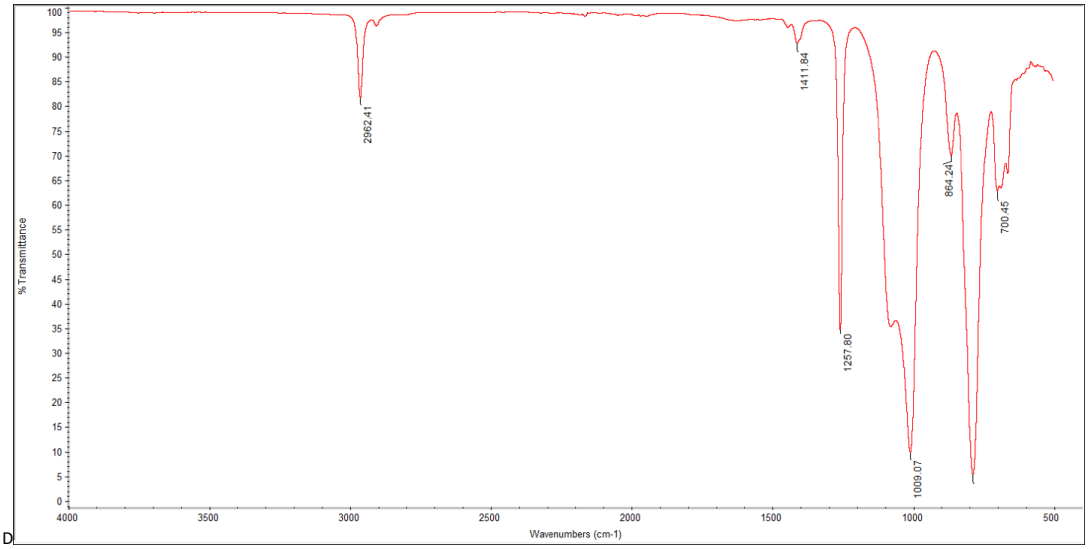
D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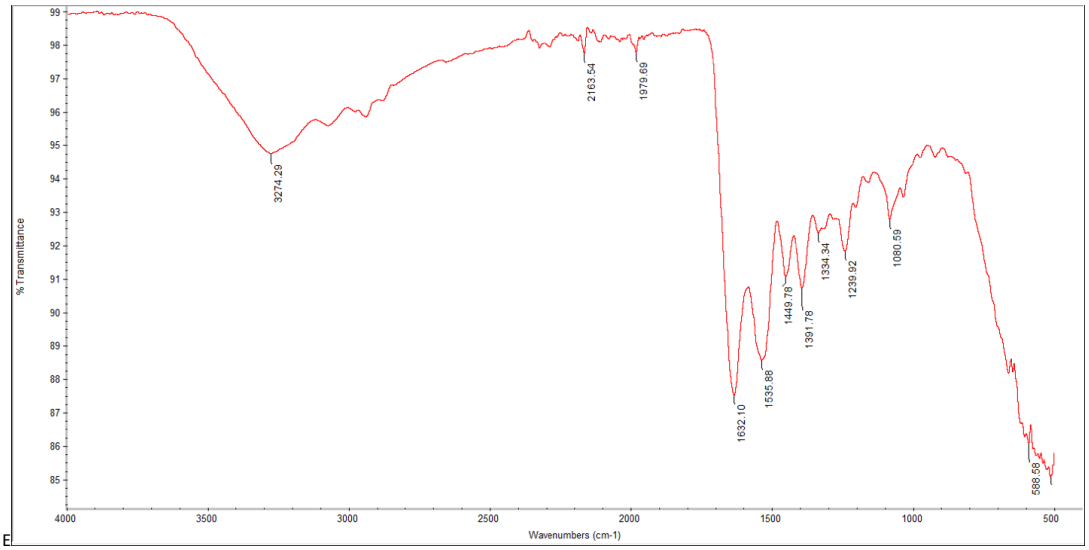

E

Figure S4. FTIR spectrum of chemically crosslinked **P10-50** A) as prepared, after degradation with bromelain B) silicone fraction, C) aqueous fraction. FTIR spectrum of chemically crosslinked **T670-50** D) as prepared, E aqueous fraction.

Table S8. Summary of degradation outcomes.

		Fraction degraded after 7 Days (%)		
Hydrogel	Equiv HCHO	Deionized Water (Control)	0.1% Bromelain	1.0% Bromelain
T37-67	1	3	99	95
	2	6	19	72
	5	8	2	12
	7.5	6	26	53
	10	2	95	47
T37-50	1	2	7	99
	2	4	95	52
	5	7	53	93
	7.5	10	93	20
	10	9	93	70
T37-33	1	3	95	99
	2	6	93	99
	5	8	49	95
	7.5	6	95	99
	10	2	15	44