Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information for

Unravelling parameter interactions in calcium alginate/polyacrylamide double network hydrogels using a design of experiments approach for the optimization of mechanical properties

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1 Ca-Alg/PAAm DN hydrogel preparation conditions in the literature

Table S 1. Experimental conditions used for Ca-Alg/PAAm DN hydrogel preparation in the literature. *KPS instead of APS, **α-ketoglutaric acid, ***relative to alginate.

Reference	c_{Alg} [wt.%]	c_{AAm} [wt.%]	c_{MBA} [wt.%]	c_{APS} [wt.%]	c_{TEMED} [wt.%]	Ca cross-linker	Ca cross-linker concentration
[1]	0.84 - 4.62	9.38 – 13.16	0.003 - 0.016	?	0,023 - 0,033	$CaSO_4$	13.28 %***
[2]	2	12	0.0036 - 0.0072	?	0.03	$CaSO_4$	?
[3]	1.56	12.44	0.0076	0.012	0.03	$CaCl_2$ solution	0.3 M
[4]	2	44.56	0.15	0.6	0.178	$CaCl_2$ solution	0.9 M
[5]	1 - 5	11.6	0.25	0.24**	-	$CaCl_2$ solution	0.1 M
[6]	1 - 4	12	0.05 - 0.13	0.046*	-	$CaCl_2$ solution	0.18 M
[7]	2.3 - 6.4	16.8	0.01	0.10	0.092	$CaSO_4$ + $CaCl_2$ solution	0.25 - 1.28 %, 1 M
[8]	1.27 - 2.73	12.73 - 27.27	0.0005 - 0.13	0.038 - 0.112	0.015 - 0.045	$CaCO_3$/GDL	0 - 40 wt.%***

2 Calculation of coded parameter values

Experimental values of each parameter were varied between a maximum value x_{max} and a minimum value x_{min}. The actual parameter values x_a were then transformed to the dimensionless coded parameter values x_c by using the equation:

$$x_c = \frac{2 \cdot (x_a - x_{max})}{x_{max} - x_{min}} + 1 \quad \text{(S1)}$$

Thus, x_{min} corresponds to a coded value of -1 and x_{max} to a coded value of +1.

3 Actual and coded parameter settings in this study

Table S 2. The 25 different compositions of solutions used for preparation of Ca-Alg/PAAm DN hydrogels in this study, defined by the alginate concentration c_{alg}, the fraction R_P of long-chain alginate, acrylamide concentration c_{Aam}, and MBA concentration c_{MBA}. The compositions are given in actual parameter values (left) and coded parameter values (right).

Actual parameter values				**Coded parameter values**			
c_{alg} [wt.%]	R_P	c_{AAm} [wt.%]	c_{MBA} [wt.%]	c_{alg}	$R_{Prot/Man}$	c_{AAm}	c_{MBA}
1	0.17	6	0.01	-1	-1	-1	-1
1	0.17	6	0.03	-1	-1	-1	1
1	0.17	19	0.01	-1	-1	1	-1

1	0.83	6	0.01	-1	1	-1	-1
5	0.17	6	0.01	1	-1	-1	-1
1	0.17	19	0.03	-1	-1	1	1
1	0.83	19	0.01	-1	1	1	-1
5	0.83	6	0.01	1	1	-1	-1
1	0.83	6	0.03	-1	1	-1	1
5	0.17	19	0.01	1	-1	1	-1
5	0.17	6	0.03	1	-1	-1	1
1	0.83	19	0.03	-1	1	1	1
5	0.17	19	0.03	1	-1	1	1
5	0.83	19	0.01	1	1	1	-1
5	0.83	6	0.03	1	1	-1	1
5	0.83	19	0.03	1	1	1	1
3	0.5	12	0.02	0	0	0	0
1	0.5	12	0.02	-1	0	0	0
3	0.17	12	0.02	0	-1	0	0
3	0.5	6	0.02	0	0	-1	0
3	0.5	12	0.01	0	0	0	-1
5	0.5	12	0.02	1	0	0	0
3	0.83	12	0.02	0	1	0	0
3	0.5	19	0.02	0	0	1	0
3	0.5	12	0.03	0	0	0	1

4 Experimental results for all tested samples

Table S 3. All parameter settings and characterization data for the samples in this study. The data was collected chronologically in the order of appearance in the table. The samples with grey background were excluded from the data analysis.

Run	c_{alg} [wt.%]	R_P	c_{AAm} [wt.%]	c_{MBA} [wt.%]	EDS	E [kPa]	ε_{max} [%]	σ_{max} [kPa]	U_T [kJ m^{-3}]
1	3	0.5	12.5	0.02	7.98	182.1	541.1	313.1	1148.8
2	1	0.17	19	0.01	6.22	4.0	996.2	74.6	306.3
3	3	0.5	19	0.02	7.40	108.4	586.4	251.5	875.8
4	5	0.83	19	0.03	4.98	455.7	462.2	844.4	2494.7
5	1	0.83	19	0.03	6.79	20.9	506.8	76.2	219.0
6	5	0.83	19	0.03	5.92	398.1	407.3	672.4	1765.1
7	5	0.83	6	0.01	9.23	816.0	67.1	547.6	200.5
8	3	0.83	12.5	0.02	5.55	659.6	83.5	570.2	254.4
9	5	0.5	12.5	0.02	5.74	381.5	380.1	467.8	1263.2
10	1	0.17	19	0.01	4.94	3.4	928.3	48.9	221.7
11	1	0.83	19	0.01	5.39	21.4	1430.9	125.4	988.3
12	3	0.5	12.5	0.03	4.67	171.8	475.1	313.1	981.1
13	5	0.5	12.5	0.02	6.84	447.7	337.2	544.3	1331.0
14	5	0.17	19	0.03	6.81	133.9	398.7	208.1	524.5
15	1	0.83	6	0.01	7.68	80.1	596.1	101.8	434.8
16	3	0.5	6	0.02	5.99	340.8	173.5	367.1	602.5

17	3	0.5	12.5	0.02	6.10	180.5	422.2	246.3	728.9
18	5	0.17	6	0.01	6.31	268.4	28.3	78.7	14.8
19	1	0.83	6	0.01	5.26	94.1	497.5	122.4	460.2
20	5	0.17	19	0.03	7.30	126.8	444.7	214.8	597.0
21	1	0.17	6	0.03	5.29	21.8	373.8	46.7	110.7
22	1	0.5	12.5	0.02	5.68	20.8	550.8	72.4	226.3
23	5	0.17	6	0.01	5.50	230.1	30.5	106.5	20.2
24	3	0.5	12.5	0.03	5.84	166.7	368.1	217.8	569.8
25	5	0.83	6	0.03	6.42	537.4	140.9	740.1	587.8
26	5	0.83	6	0.01	5.80	687.7	59.1	411.0	124.2
27	3	0.5	6	0.02	7.63	292.5	176.1	319.8	473.2
28	1	0.83	19	0.03	5.58	18.8	430.5	68.6	168.7
29	5	0.83	6	0.03	5.88	93.8	378.0	163.9	417.6
30	3	0.5	19	0.02	4.72	636.6	125.3	800.0	541.6
31	1	0.17	6	0.03	7.48	21.4	524.0	48.2	156.1
32	3	0.5	6	0.02	7.45	59.2	458.0	78.1	255.2
33	1	0.17	19	0.03	5.14	123.3	405.3	179.9	469.4
34	3	0.17	12.5	0.02	5.23	90.9	561.2	148.8	531.9
35	1	0.17	19	0.03	5.58	8.4	405.1	42.8	99.1
36	1	0.17	6	0.01	6.04	22.7	596.3	37.7	185.1
37	1	0.17	19	0.03	5.58	9.8	406.6	48.5	111.5
38	5	0.17	6	0.03	6.43	315.7	222.8	255.2	474.1
39	3	0.5	12.5	0.03	6.06	182.7	371.9	238.1	616.5
40	3	0.5	12.5	0.01	5.05	239.9	431.5	202.9	736.1
41	3	0.83	12.5	0.02	5.40	245.1	441.3	387.9	1241.0
42	5	0.17	6	0.01	4.88	354.3	36.4	141.4	29.5
43	1	0.17	6	0.01	5.29	19.5	598.0	27.9	121.4
44	3	0.5	12.5	0.02	5.18	184.4	736.4	346.0	1703.3
45	5	0.17	19	0.01	6.58	126.4	710.1	187.5	854.7
46	1	0.83	6	0.03	5.77	71.3	494.0	127.0	420.0
47	5	0.83	6	0.03	5.53	647.0	104.8	649.6	400.1
48	1	0.83	6	0.03	5.64	66.5	481.5	132.0	434.3
49	5	0.83	19	0.01	7.51	362.3	449.2	574.3	1932.9
50	5	0.17	19	0.01	5.70	104.8	815.5	216.5	1053.0
51	1	0.83	6	0.03	7.45	79.3	495.5	147.0	488.9
52	1	0.83	19	0.01	6.20	19.1	1147.8	208.2	910.3
53	1	0.83	19	0.01	6.29	16.6	1269.0	165.9	858.0
54	1	0.17	19	0.01	5.61	4.0	1106.0	76.4	360.4
55	1	0.83	19	0.03	5.77	18.2	439.1	73.5	181.8
56	5	0.17	6	0.03	6.27	299.2	208.2	232.9	427.5
57	5	0.83	6	0.01	7.78	797.0	86.0	682.5	311.3
58	1	0.83	6	0.01	6.03	84.0	901.6	166.6	984.1
59	3	0.5	12.5	0.01	6.23	219.7	569.6	288.4	1183.1
60	5	0.17	19	0.03	5.96	128.9	440.2	195.9	555.0
61	5	0.5	12.5	0.02	5.51	471.2	387.9	521.1	1444.0
62	1	0.5	12.5	0.02	5.91	24.1	264.4	40.6	77.5
63	3	0.83	12.5	0.02	6.55	266.2	428.6	380.4	1187.0
64	3	0.5	12.5	0.01	6.18	197.6	672.6	270.5	1282.3
65	5	0.17	19	0.01	4.91	145.8	1008.2	250.2	1527.2

66	1	0.5	12.5	0.02	5.85	23.0	645.5	69.6	270.6
67	5	0.83	19	0.01	4.96	425.7	394.2	548.6	1681.9
68	5	0.83	19	0.01	5.87	401.3	460.0	532.3	1816.0
69	5	0.83	19	0.03	6.38	388.7	441.0	612.4	1794.1
70	1	0.17	6	0.03	5.26	23.3	408.8	43.8	119.0
71	3	0.5	19	0.02	5.70	465.7	417.0	562.8	1769.7
72	3	0.17	12.5	0.02	5.81	22.5	653.5	83.5	302.9
73	5	0.17	6	0.03	5.62	244.9	487.5	417.4	1453.3
74	3	0.17	12.5	0.02	6.26	198.8	575.7	253.9	1207.6
75	1	0.17	6	0.01	6.95	135.9	726.0	180.4	909.4

5 Representative photo of sample for tensile tests

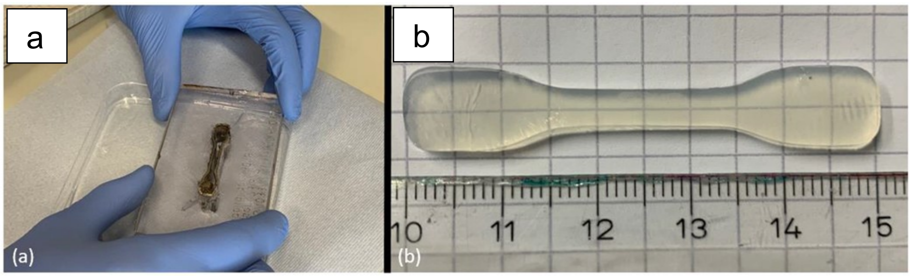

Figure S 1. Photography of the punching knife (a) and of an S3A tensile test specimen (b).

6 Clamping tool for tensile tests

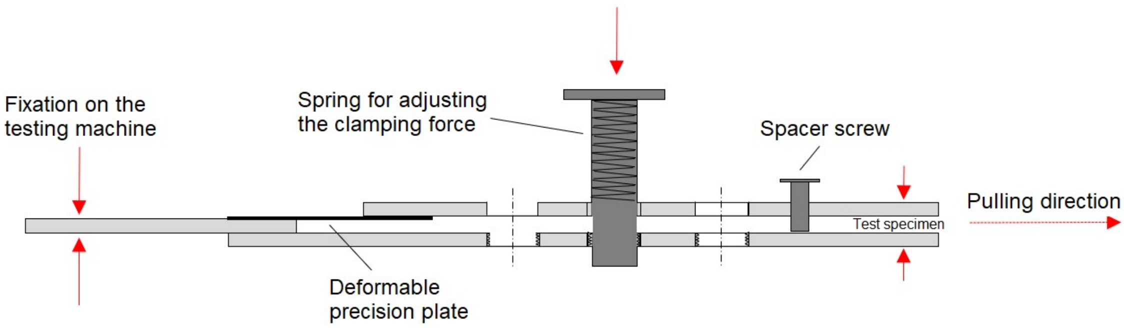

Figure S 2. Schematic illustration of the clamping tool used for the tensile tests.

7 Model equation for regression of responses

All responses R were fitted with a linear model including interaction terms:

$$R = r_0 + a_{Alg} \cdot c_{Alg} + a_R \cdot R_P + a_{AAm} \cdot c_{AAm} + a_{MBA} \cdot c_{MBA} + b_{Alg,R} \cdot c_{Alg} \cdot R_P + b_{Alg,AAm} \cdot c_{Alg} \cdot c_{AA}$$
$$\cdot c_{Alg} \cdot c_{MBA} + b_{R,AAm} \cdot R_P \cdot c_{AAm} + b_{R,MBA} \cdot R_P \cdot c_{MBA} + b_{AAm,MBA} \cdot c_{AAm} \cdot c_{MBA}$$

(S2)

8 Correlation between Young's modulus and strength

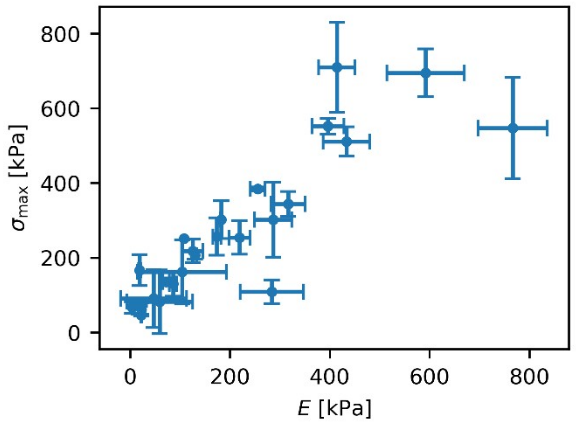

Figure S 3. Young's modulus E plotted against the strength σ_{max}.

9 Correlation between Young's modulus and strain at break

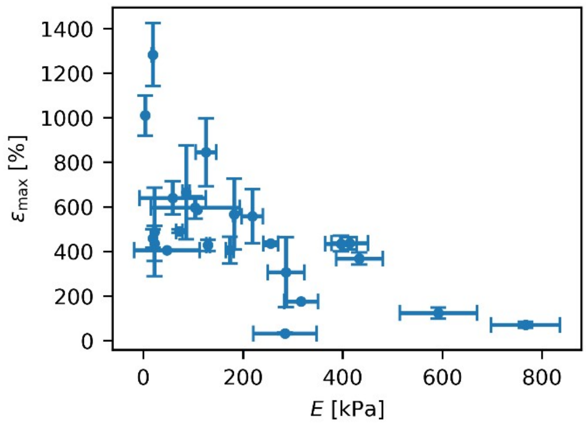

Figure S 4. The strain at break ε_{max} plotted against the Young's modulus E.

10 Model diagnosis graphs

10.1 Actual values versus predicted values

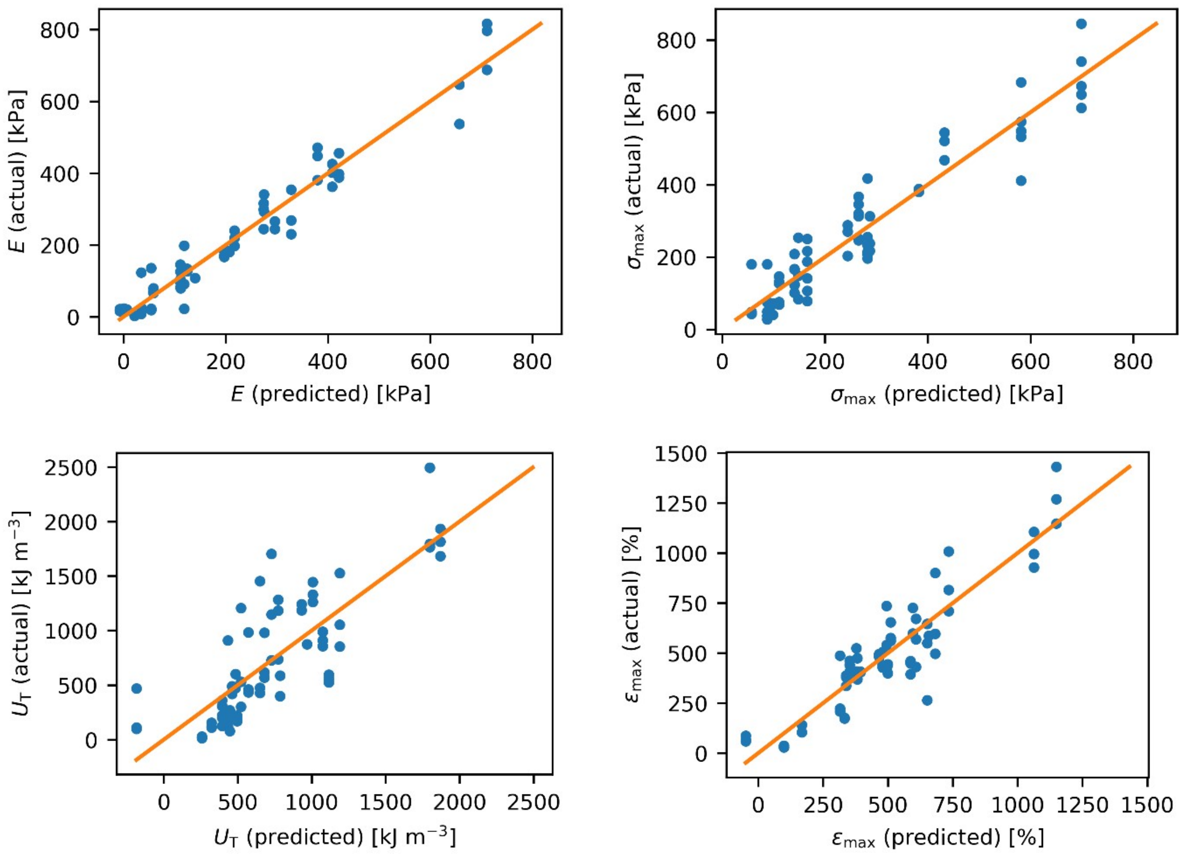

Figure S 5. Plots of experimental response values (actual values) against response values predicted by the regression model fitted to the data.

10.2 Residual versus run

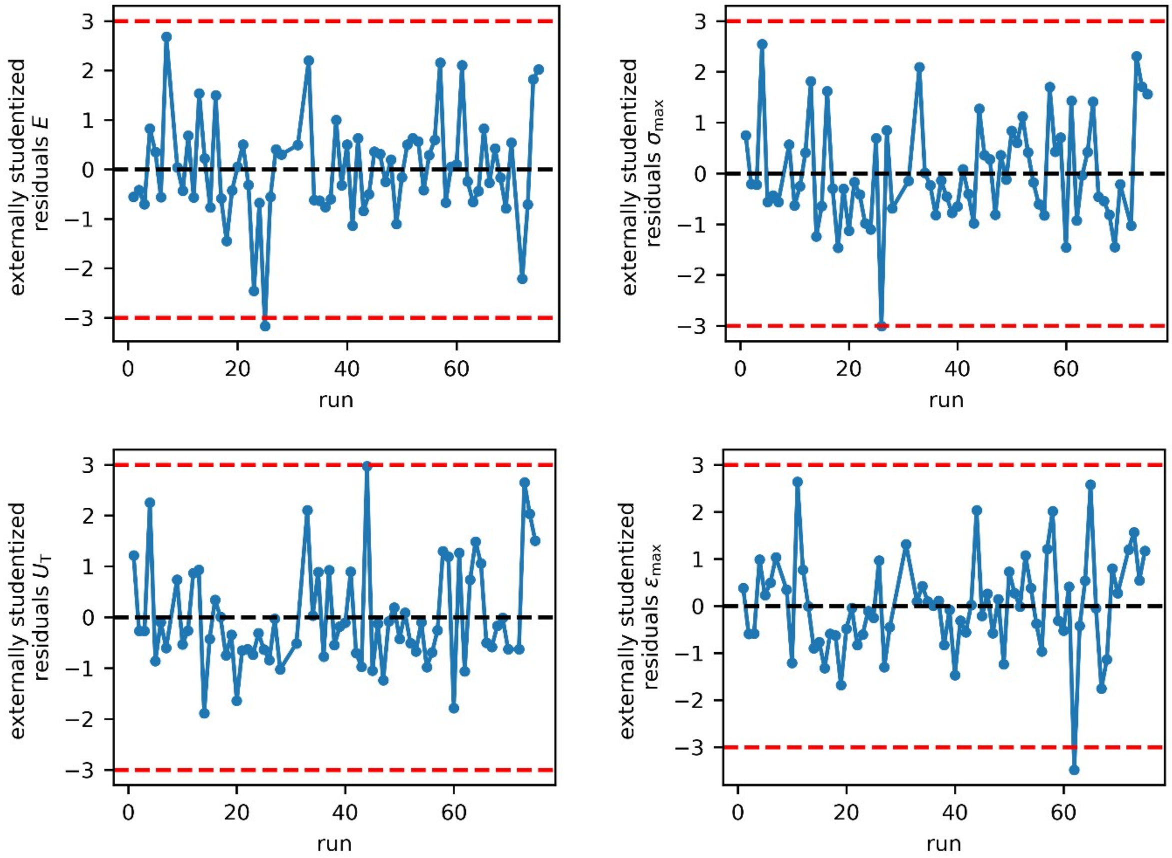

Figure S 6. Plots of externally studentized residuals against the run number. The run number gives the chronological order of sample preparation.

10.3 Residual versus predicted values

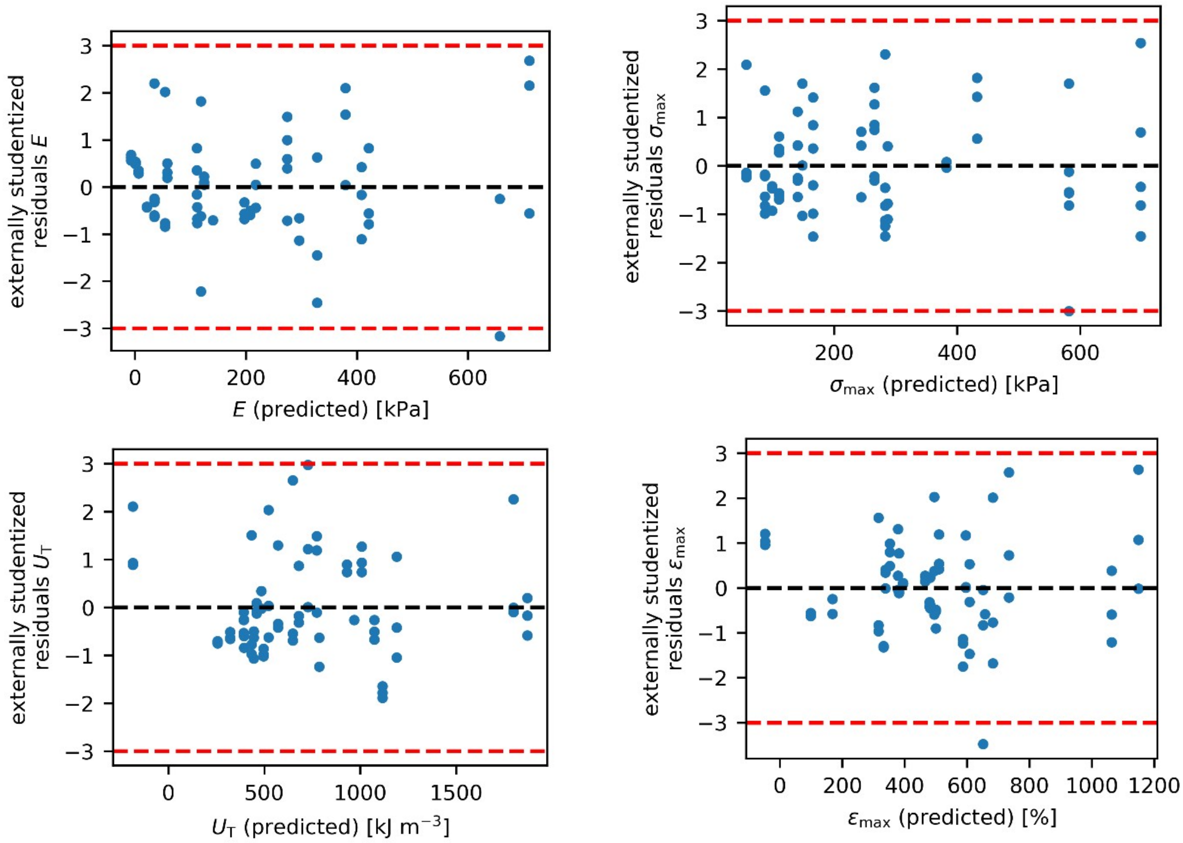

Figure S 7. Plots of externally studentized residuals against response values predicted by the regression model fitted to the data.

10.4 Normal probability plots

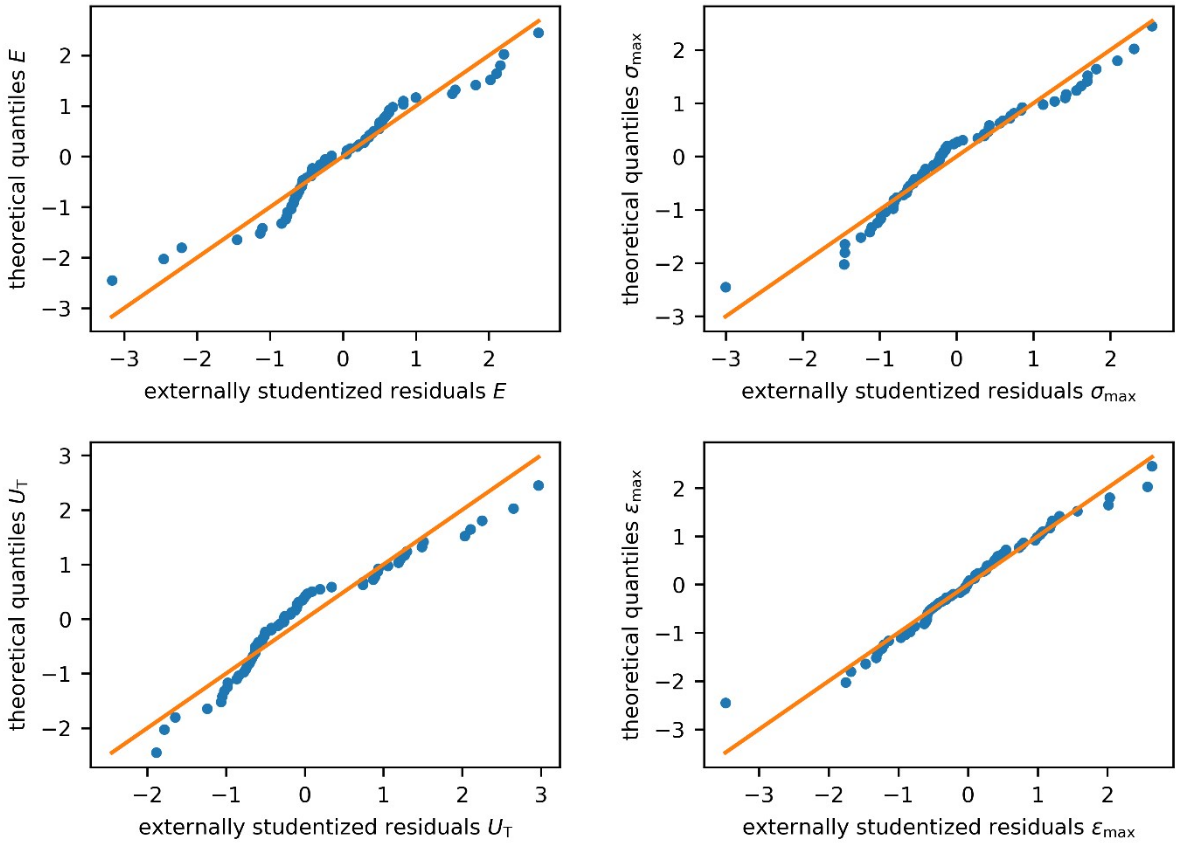

Figure S 8. Normal probability plots for the four responses investigated in this study.

11 References

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