Supporting Information

3D Printable Polymer Foams with Tunable Expansion and Mechanical Properties Enabled by Catalyst-Free Dynamic Covalent Chemistry

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mol %	Non-dynamic TEGDA	Dynamic DPE
0.00	340 ± 33	
0.05	347 ±8	223 ± 2
0.10	186 ± 12	254 ± 16
0.25	193 ± 6	229 ± 17
0.50	146 ± 8	179 ± 7
0.75	125 ± 2	151 ± 9
1.00	95 ± 3	142 ± 6
1.25	75 ± 3	111 ± 6
1.50	64 ± 9	101 ± 5

Table S1. Foaming relative volume expansion of 3D printed cylinders

Highlighted colors indicate similar foam expansion rate for comparison

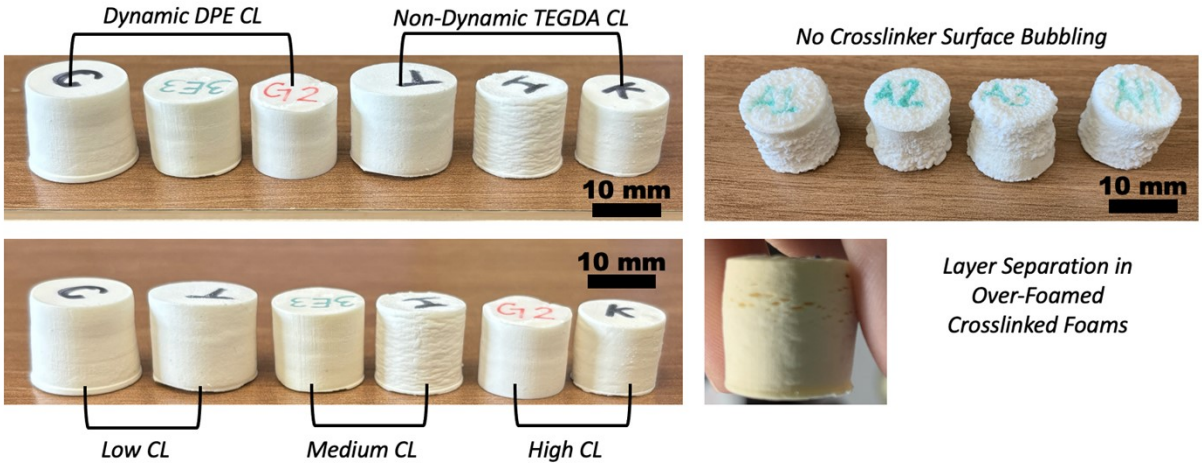

Figure S1. 3D printed foamed dynamic and non-dynamic low, medium, and high showing volume expansion (left) surface bubbling in no crosslinker foams (top right) and layer separation in crosslinked foams (bottom right)

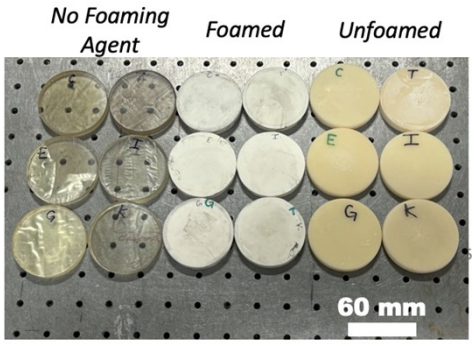

Figure S2. 3D printed no foam, foamed and unfoamed disc samples

Table S2. Density values of unfoamed 3D printed cylinders

mol %	Non-dynamic TEGDA	Dynamic DPE
0.00	1.10 ± 0.01	
0.05	1.09 ± 0.02	1.11 ± 0.01
0.10	1.13 ± 0.00	1.12 ± 0.01
0.25	1.08 ± 0.01	1.10 ± 0.00
0.50	1.13 ± 0.01	1.13 ± 0.01
0.75	1.08 ± 0.01	1.10 ± 0.01
1.00	1.12 ± 0.01	1.09 ± 0.02
1.25	1.12 ± 0.00	1.12 ± 0.01
1.50	1.11 ± 0.00	1.12 ± 0.01

Highlighted colors indicate similar foam expansion rate for comparison

Table S3. Density values of foamed 3D printed cylinders

mol %	Non-dynamic TEGDA	Dynamic DPE
0.00	0.261 ± 0.016	
0.05	0.256 ± 0.005	0.340 ± 0.003
0.10	0.385 ± 0.027	0.314 ± 0.013
0.25	0.392 ± 0.005	0.334 ± 0.018
0.50	0.463 ± 0.011	0.401 ± 0.009
0.75	0.504 ± 0.014	0.454 ± 0.012
1.00	0.576 ± 0.011	0.471± 0.019
1.25	0.632 ± 0.006	0.482 ± 0.018
1.50	0.670 ± 0.028	0.527 ±0.038

Highlighted colors indicate similar foam expansion rate for comparison

Figure S3. FT elf-healing, and foamed samples (botto

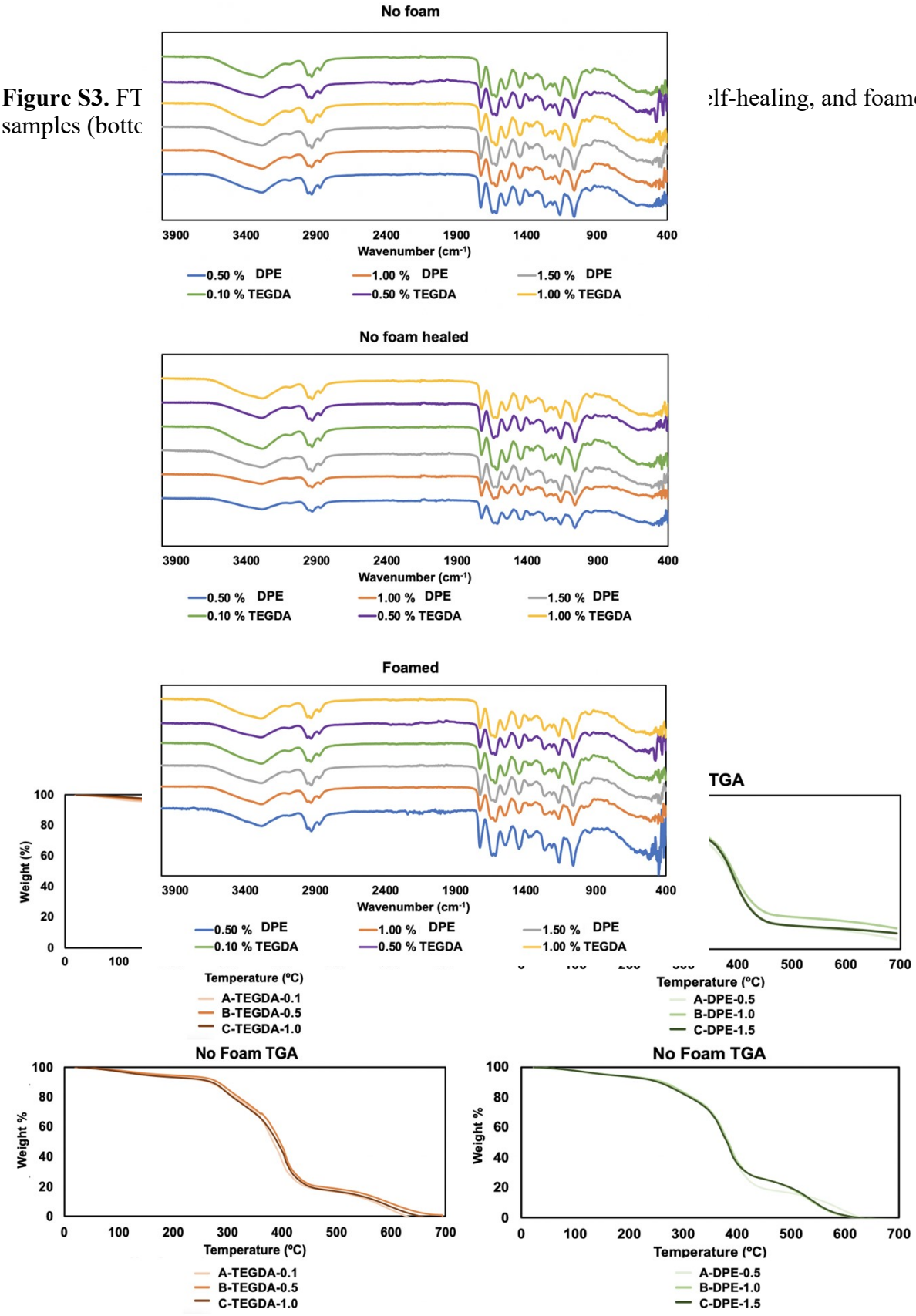

Figure S4. Thermogravimetric analysis of no foam and foamed samples

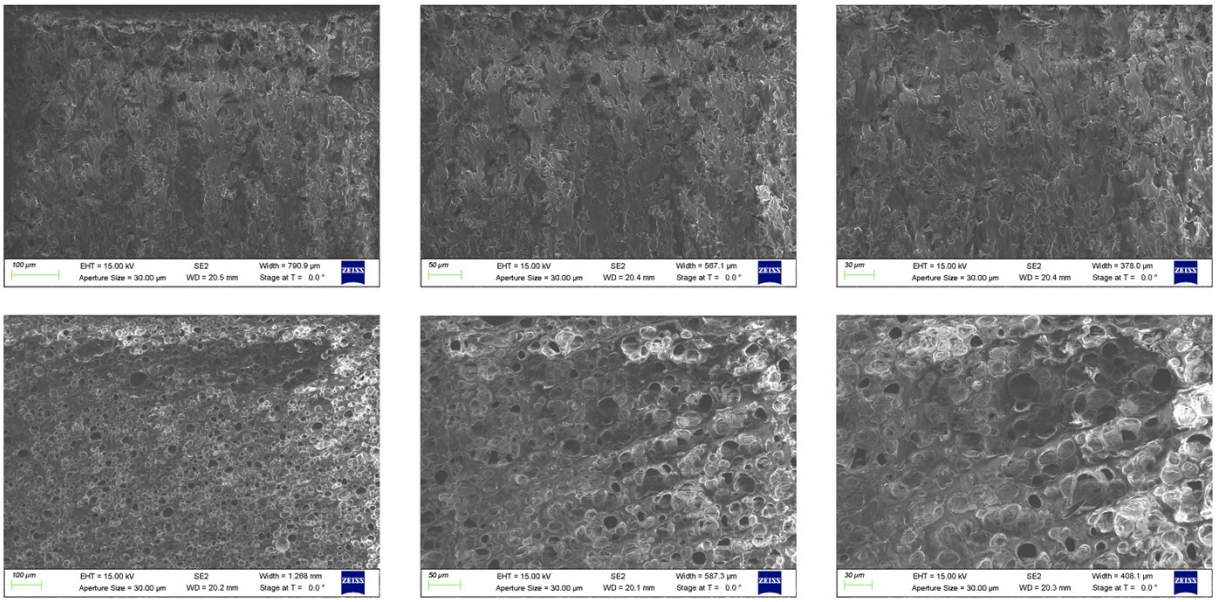

Figure S5. SEMs of non-dynamic A-TEGDA-0.1 unfoamed (top) and foamed (bottom)

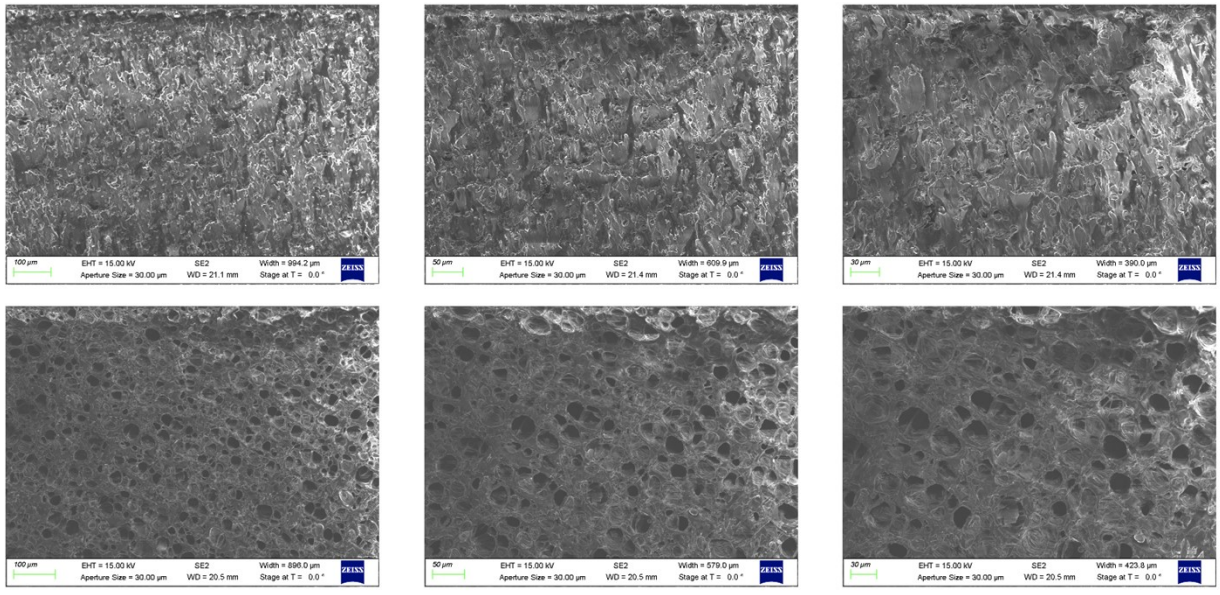

Figure S6. SEMs of dynamic A-DPE-0.5 unfoamed (top) and foamed (bottom)

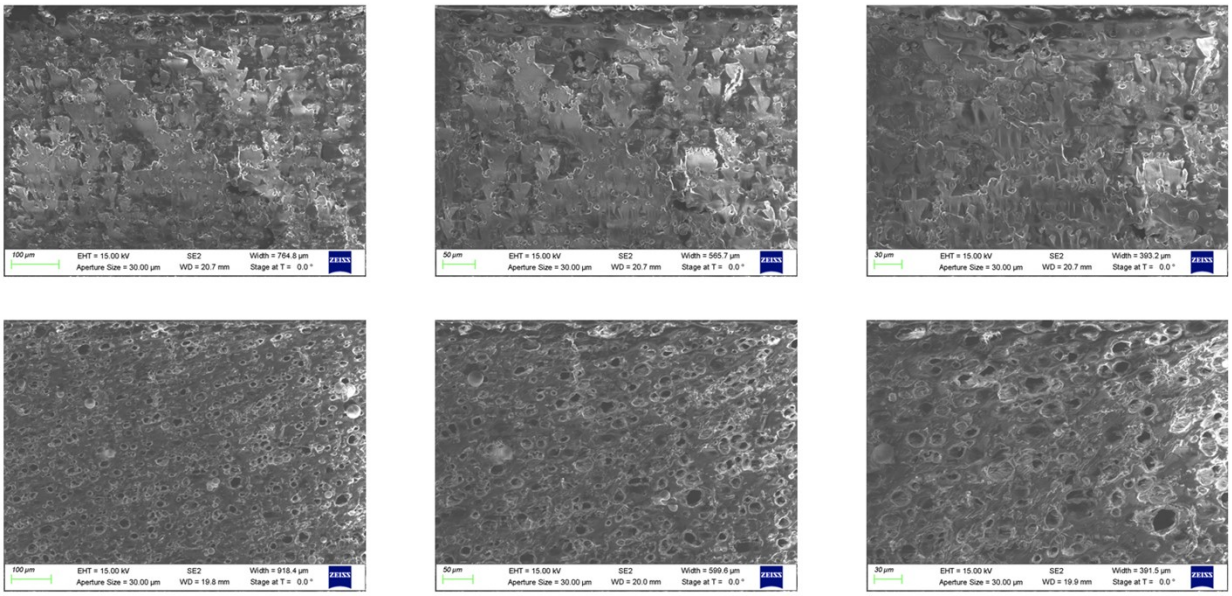

Figure S7. SEMs of non-dynamic B-TEGDA-0.5 unfoamed (top) and foamed (bottom)

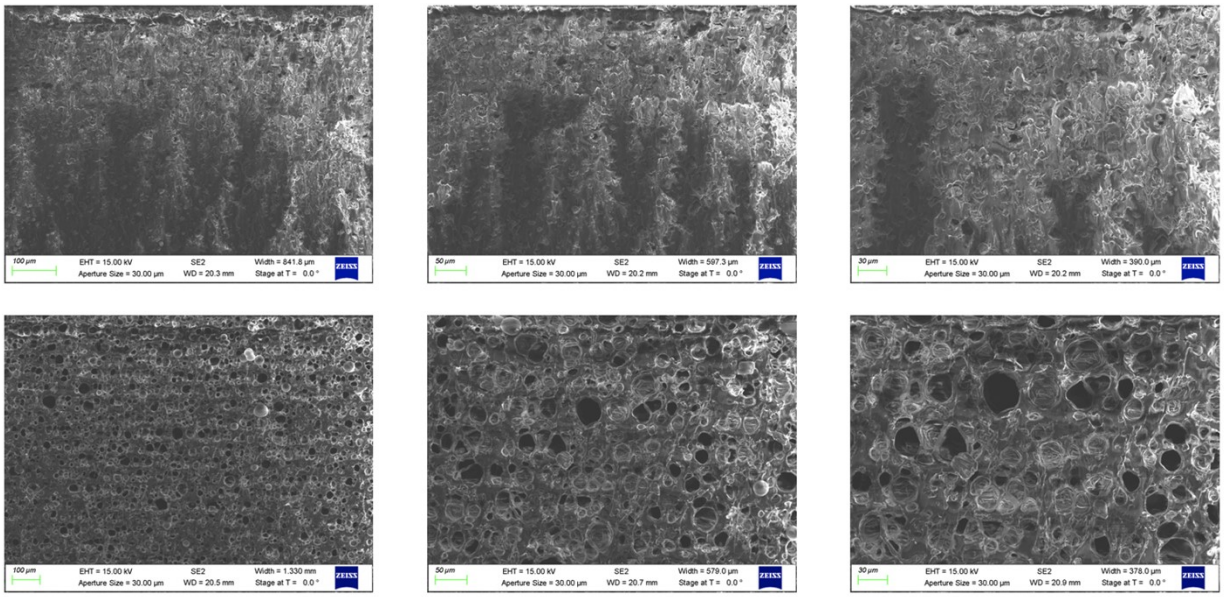

Figure S8. SEMs of dynamic B-DPE-1.0 unfoamed (top) and foamed (bottom)

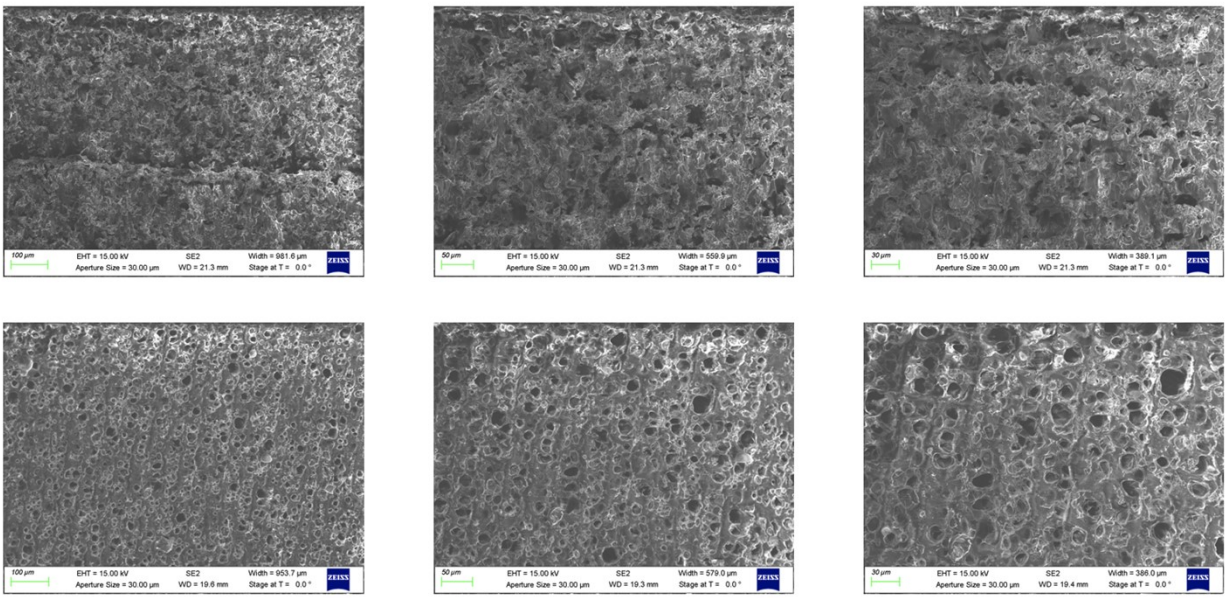

Figure S9. SEMs of non-dynamic C-TEGDA-1.0 unfoamed (top) and foamed (bottom)

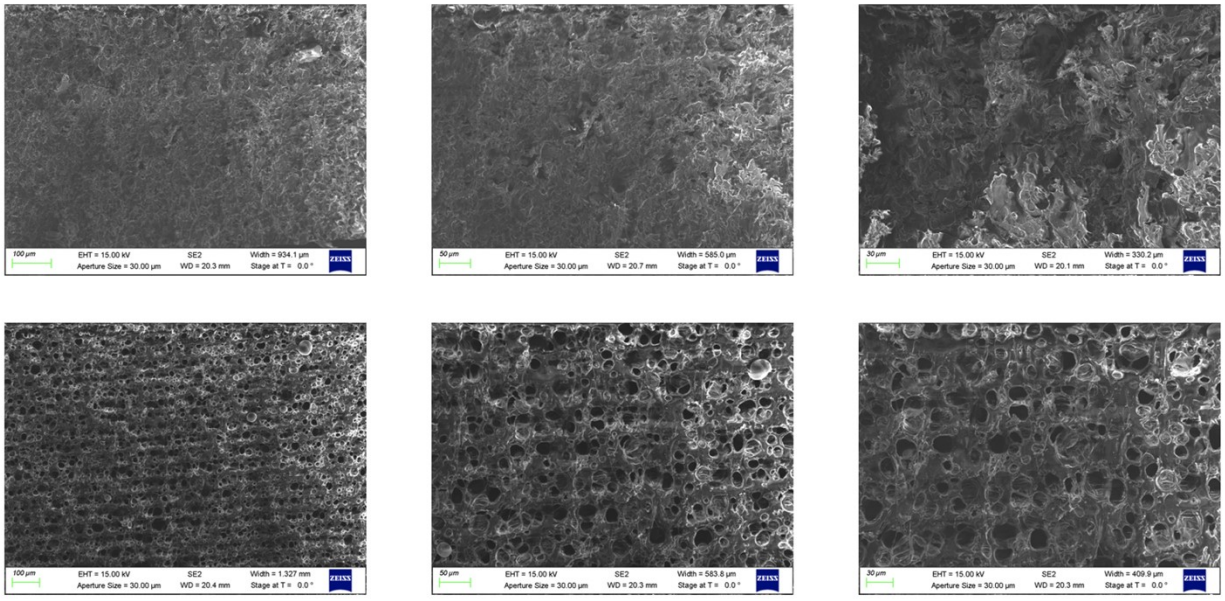

Figure S10. SEMs of dynamic C-DPE-1.5 unfoamed (top) and foamed (bottom)

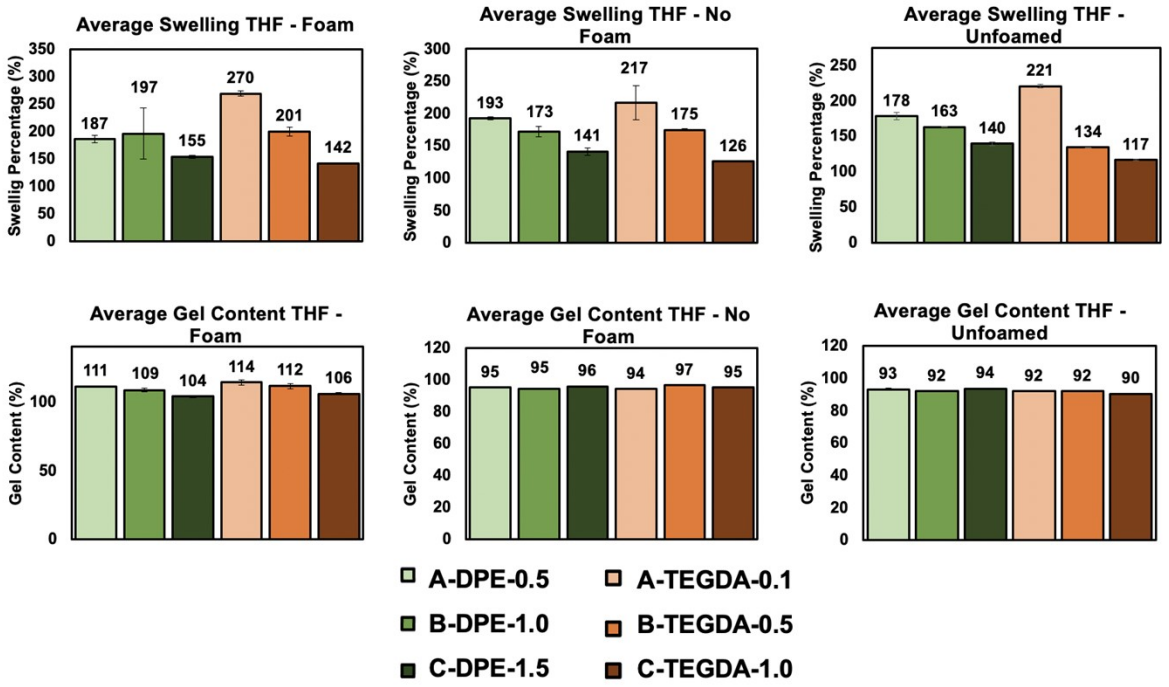

Figure S11. Charts of average swelling and gel content for foam, no foam and unfoamed samples in THF

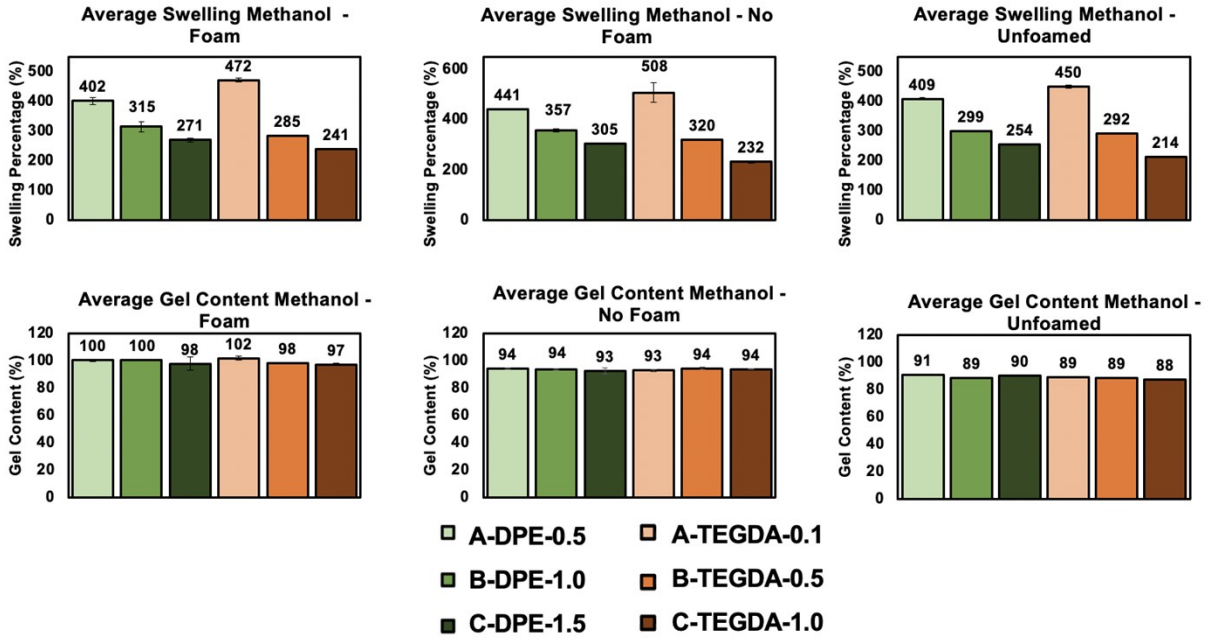

Figure S12. Charts of average swelling and gel content for foam, no foam and unfoamed samples in methanol

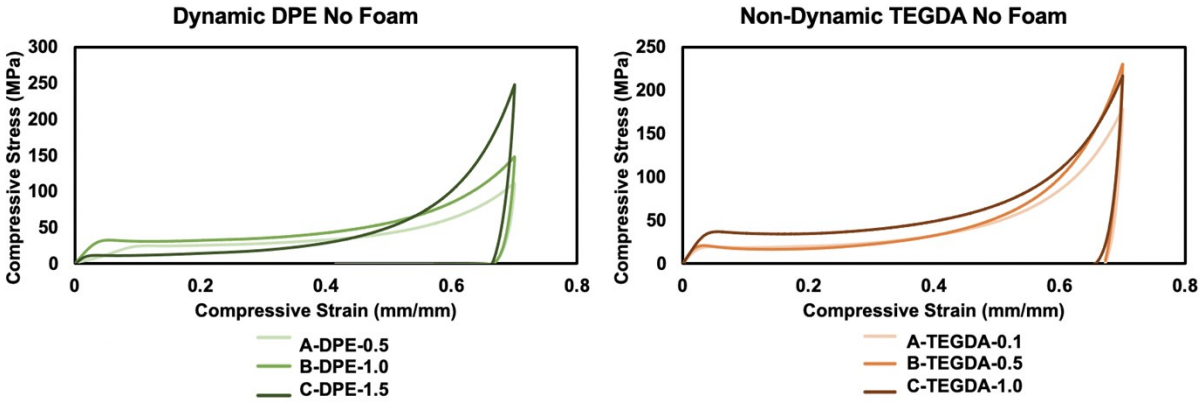

Figure S13. Example compression curves for no foam cylinders

Table S4. Compressive mechanical values for no foam cylinders

Formulation	**Energy Dissipation (mJ/mm^3)**	**Compressive Yield Stress (Mpa)**	**Max Stress (Mpa)**	**Young's Modulus**
A-DPE-0.5	24.89 ± 2.78	23.34 ± 1.29	117.87 ± 4.67	292.57 ± 28.38
B-DPE-1.0	33.62 ± 0.88	30.69 ± 1.42	150.36 ± 3.56	958.70 ± 22.69
C-DPE-1.5	32.88 ± 2.46	14.80 ± 2.86	260 ± 21.18	598.19 ± 87.76
A-TEGDA-0.1	29.81 ± 0.57	20.34 ± 0.85	174.93 ± 5.92	760.16 ± 50.43
B-TEGDA-0.5	32.57 ± 1.14	22.12 ± 2.73	231.53 ± 9.80	900.76 ± 73.43
C-TEGDA-1.0	39.11 ± 2.99	33.09 ± 3.63	222.96 ± 22.02	1012.95 ± 101.97

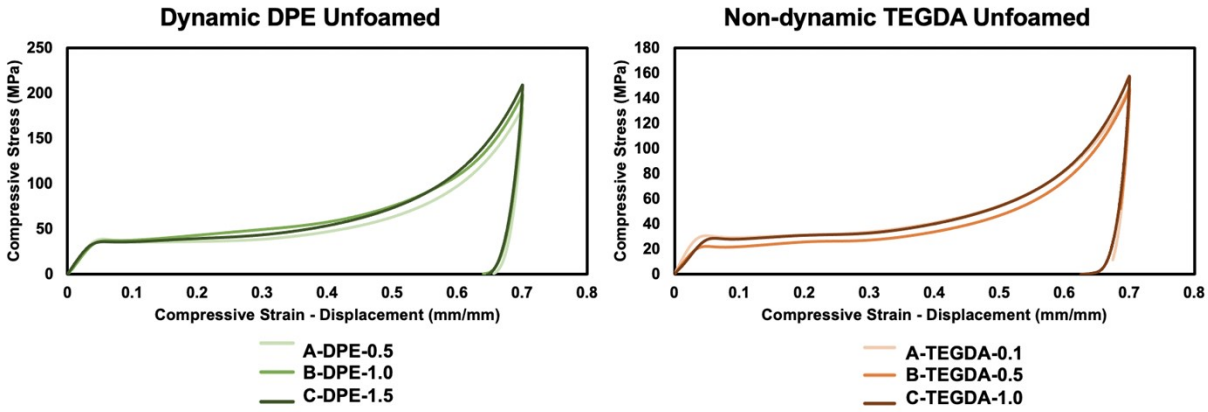

Figure S14. Example compression curves for unfoamed cylinders

Table S5. Compressive mechanical values for unfoamed cylinders

Formulation	**Energy Dissipation (mJ/mm^3)**	**Compressive Yield Stress (Mpa)**	**Max Stress (Mpa)**	**Young's Modulus**
A-DPE-0.5	37.81 ± 0.85	37.59 ± 0.95	183.11 ± 5.83	982.53 ± 21.34
B-DPE-1.0	44.19 ± 0.63	37.76 ± 1.96	209.00 ± 9.45	1011.98 ± 82.08
C-DPE-1.5	43.68 ± 0.67	36.71 ± 1.05	216.41 ± 11.29	980.98 ± 27.43
A-TEGDA-0.1	25.36 ± 4.58	31.79 ± 1.20	150.71 ± 5.14	1125.81 ± 74.47
B-TEGDA-0.5	23.92 ± 1.77	27.61 ± 1.01	134.65 ± 11.32	635.67 ± 194.46
C-TEGDA-1.0	28.53 ± 0.76	32.11 ± 0.20	155.28 ± 4.34	646.40 ± 18.91

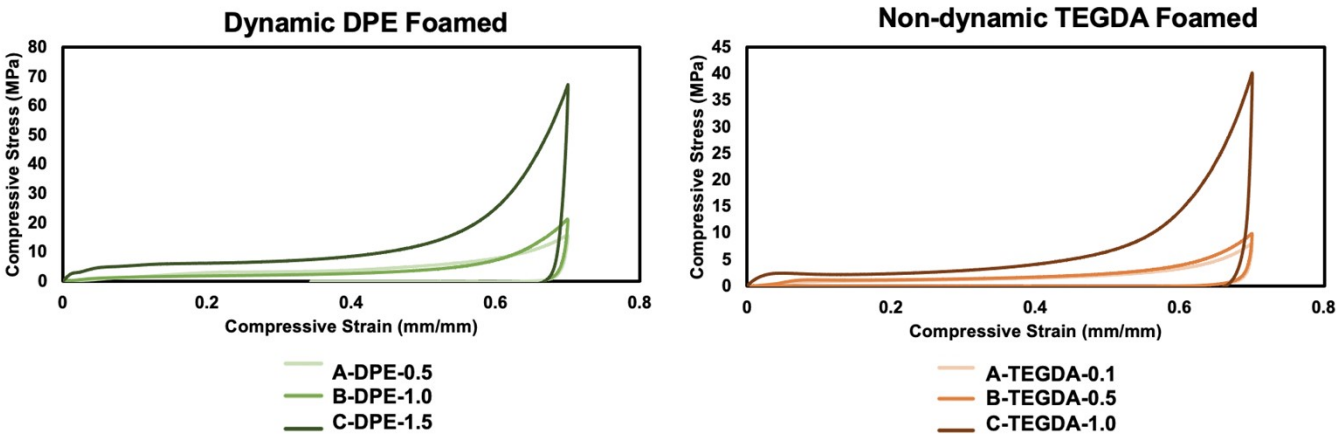

Figure S15. Example compression curves for foam cylinders

Table S6. Compressive mechanical values for foam cylinders

Formulation	Energy Dissipation (mJ/mm^3)	Plateau Stress (Mpa)	Max Stress (Mpa)	Young's Modulus
A-DPE-0.5	3.21 ± 0.28	3.34 ± 0.23	16.65 ± 1.31	17.84 ± 1.95
B-DPE-1.0	2.48 ± 0.26	1.54 ± 0.19	17.01 ± 3.85	33.77 ± 10.97
C-DPE-1.5	8.85 ± 0.77	5.01 ± 0.34	63.66 ± 8.50	195.10 ± 13.55
A-TEGDA-0.1	1.22 ± 0.29	0.92 ± 0.18	7.86 ± 1.68	14.42 ± 3.88
B-TEGDA-0.5	1.57 ± 0.15	1.08 ± 0.06	11.32 ± 1.75	20.60 ± 0.57
C-TEGDA-1.0	4.84 ± 0.20	2.47 ± 0.08	42.02 ± 2.59	110.35 ± 3.66

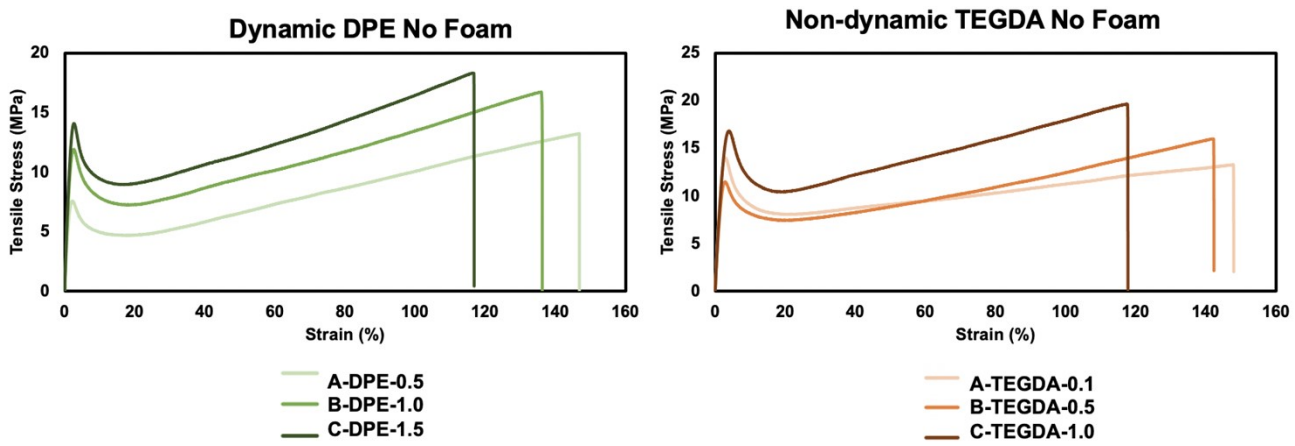

Figure S16. Example stress-strain tension curves for no foam dogbones

Table S7. Tension mechanical values for no foam dogbones

Formulation	Ultimate Tensile Strength (Mpa)	Strain at break (%)	Young's Modulus	Yield Strength (Mpa)
A-DPE-0.5	13.73 ± 1.14	140.64 ± 14.60	6.88 ± 1.38	10.09 ± 3.09
B-DPE-1.0	17.94 ± 3.17	146.19 ± 11.35	6.56 ± 0.75	12.17 ± 3.32
C-DPE-1.5	17.81 ± 1.26	112.42 ± 8.03	8.12 ± 0.62	14.83 ± 1.60
A-TEGDA-0.1	12.32 ± 1.82	151.02 ± 20.13	6.84 ± 1.51	13.39 ± 3.25
B-TEGDA-0.5	16.33 ± 0.31	145.51 ± 6.85	6.25 ± 0.48	10.56 ± 1.01

C-TEGDA-1.0	20.47 ± 2.45	104.39 ± 14.40	8.64 ± 1.48	20.14 ± 3.41

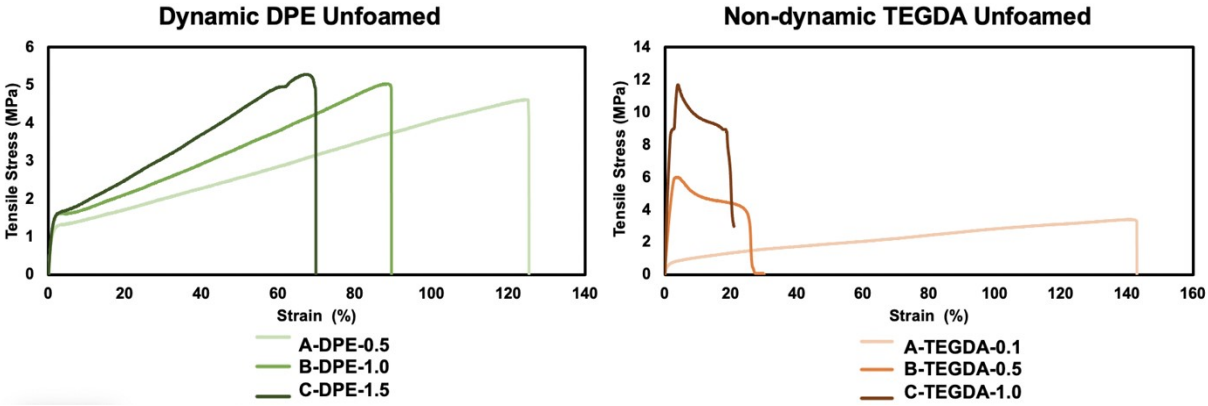

Figure S17. Example stress-strain tension curves for unfoamed dogbones

Table S8. Tension mechanical values for unfoamed dogbones

Formulation	**Ultimate Tensile Strength (Mpa)**	**Strain at break (%)**	**Young's Modulus**	**Yield Strength (MPa)**
A-DPE-0.5	4.77 ± 0.13	128.71 ± 2.35	0.97 ± 0.35	0.84 ± 0.38
B-DPE-1.0	5.02 ± 0.37	87.55 ± 8.14	1.35 ± 0.30	1.94 ± 0.70
C-DPE-1.5	5.54 ± 0.35	74.29 ± 8.20	2.24 ± 0.47	1.88 ± 0.47
A-TEGDA-0.1	3.41 ± 0.34	135.89 ± 18.02	1.24 ± 0.43	1.11 ± 0.34
B-TEGDA-0.5	5.04 ± 0.32	33.40 ± 11.55	3.30 ± 0.50	5.61 ± 0.33
C-TEGDA-1.0	7.80 ± 1.84	20.97 ± 3.51	6.10 ± 0.86	10.65 ± 1.81

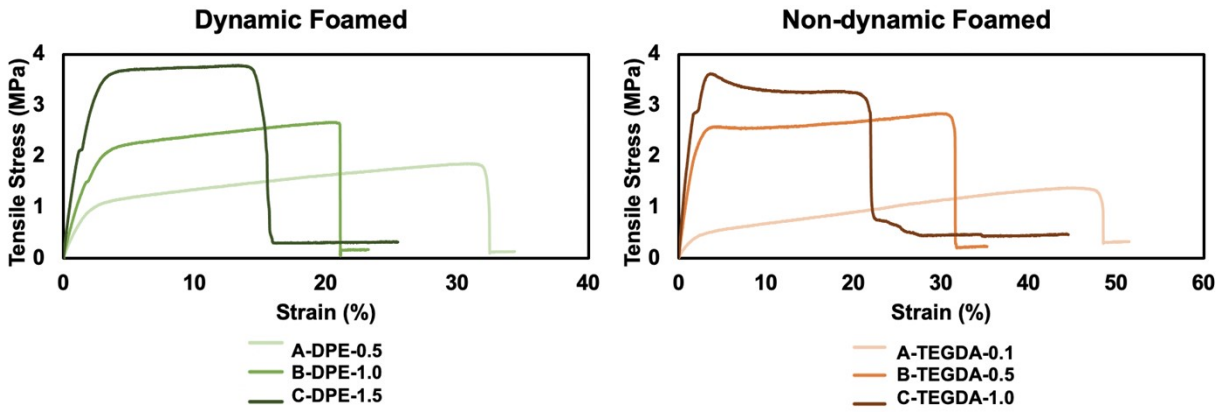

Figure S18. Example stress-strain tension curves for foam dogbones

Table S9. Tension mechanical values for foam dogbones

Formulation	Ultimate Tensile Strength (Mpa)	Strain at break (%)	Young's Modulus
A-DPE-0.5	1.96 ± 0.24	29.75 ± 3.75	0.67 ± 0.19
B-DPE-1.0	2.58 ± 0.1	20.85 ± 0.89	0.92 ± 0.04
C-DPE-1.5	3.67 ± 0.42	15.13 ± 2.0	1.53 ± 0.22
A-TEGDA-0.1	1.36 ± 0.05	43.49 ± 1.53	0.29 ± 0.04
B-TEGDA-0.5	2.82 ± 0.41	27.33 ± 2.40	1.18 ± 0.19
C-TEGDA-1.0	3.12 ± 0.23	21.74 ± 2.35	1.30 ± 0.08

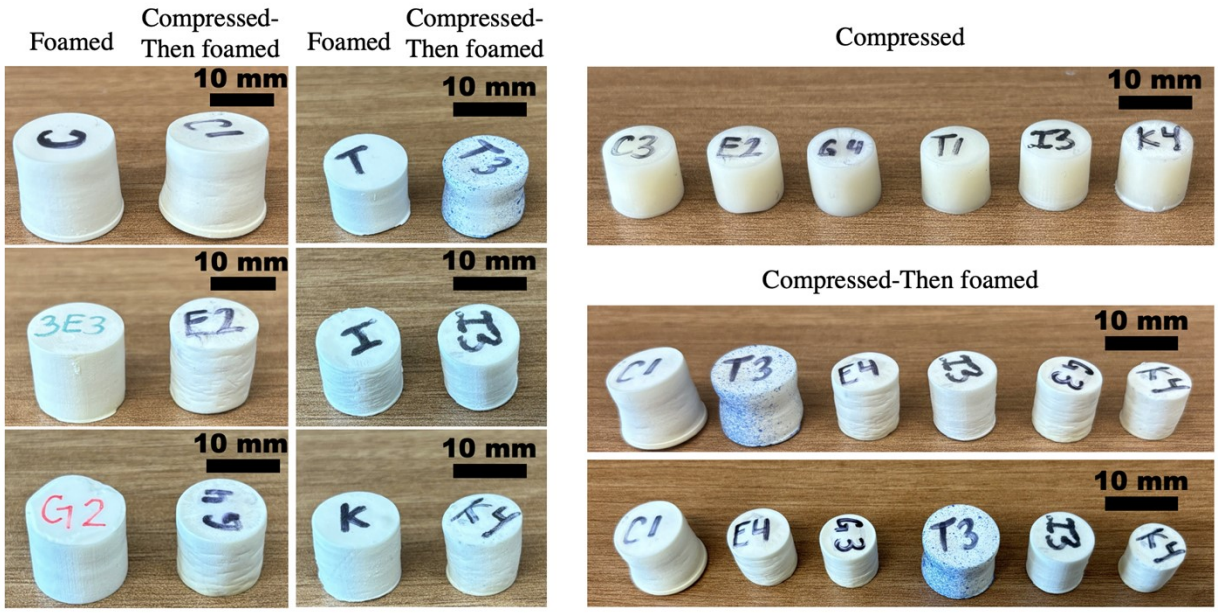

Figure S19. Samples of 3D printed as foamed cylinders compared to 3D printed compressed then foamed cylinders (left) and 3D printed cylinders left out several days after initial compression and then after foaming (right)

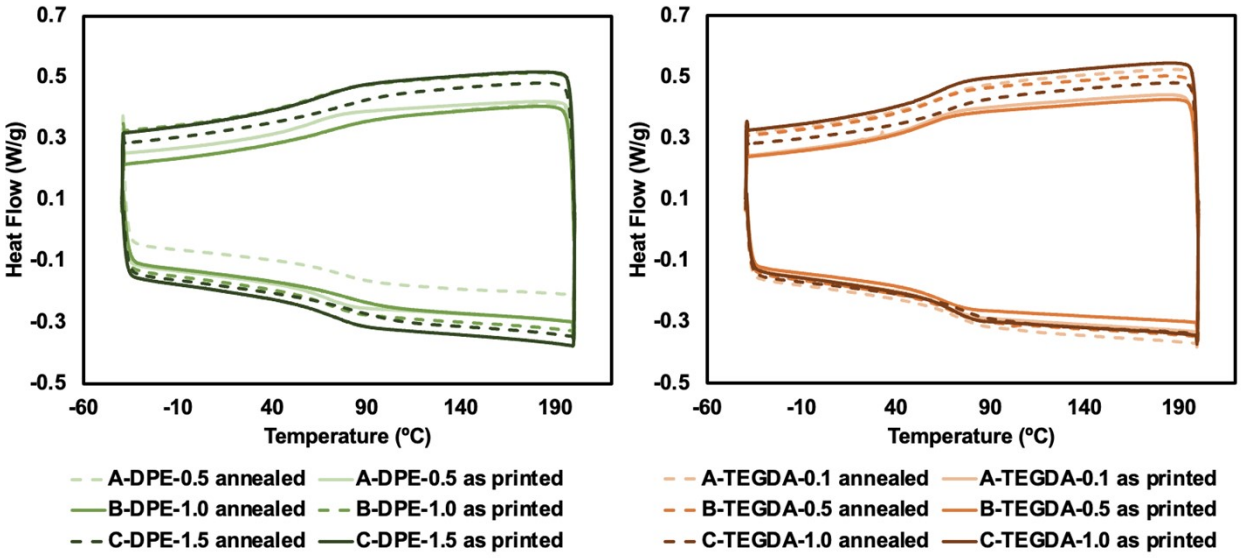

Figure S20. DSC curves for all dynamic and non-dynamic formulations, with the full second cycles plotted.

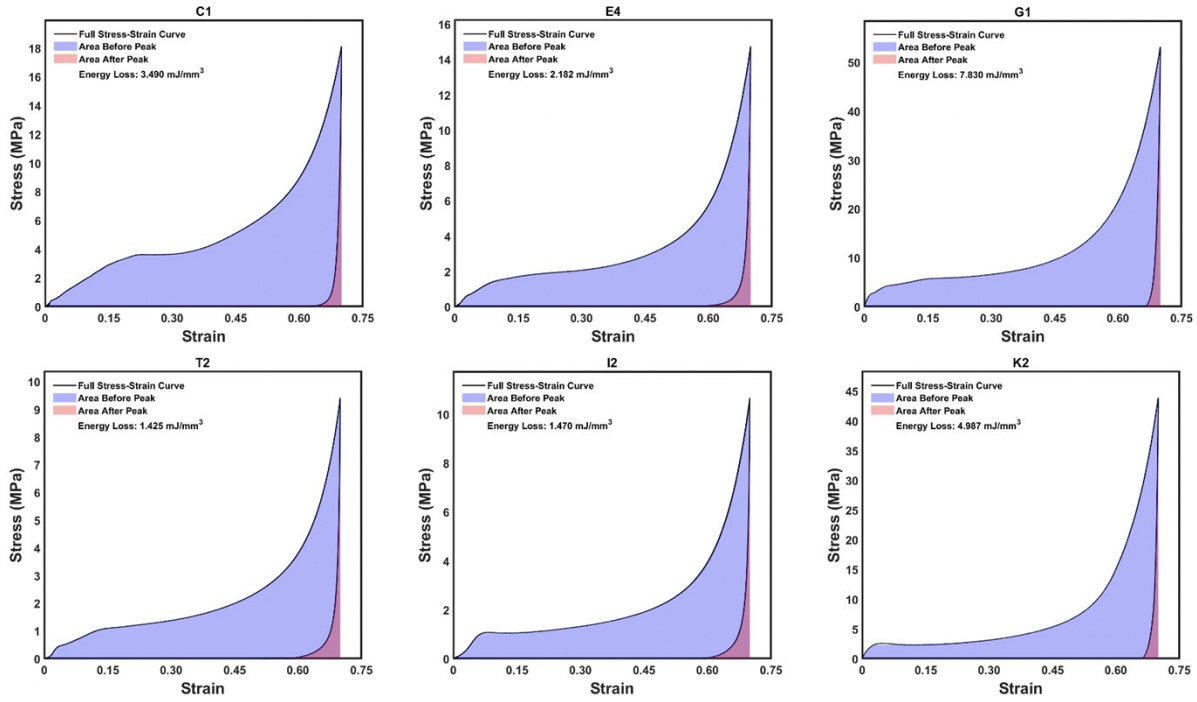

Figure S21. Example curves of area used for energy dissipation calculations through the hysteresis during the loading and unloading phases of the compression test. The energy dissipation is represented by the bigger area (light purple).

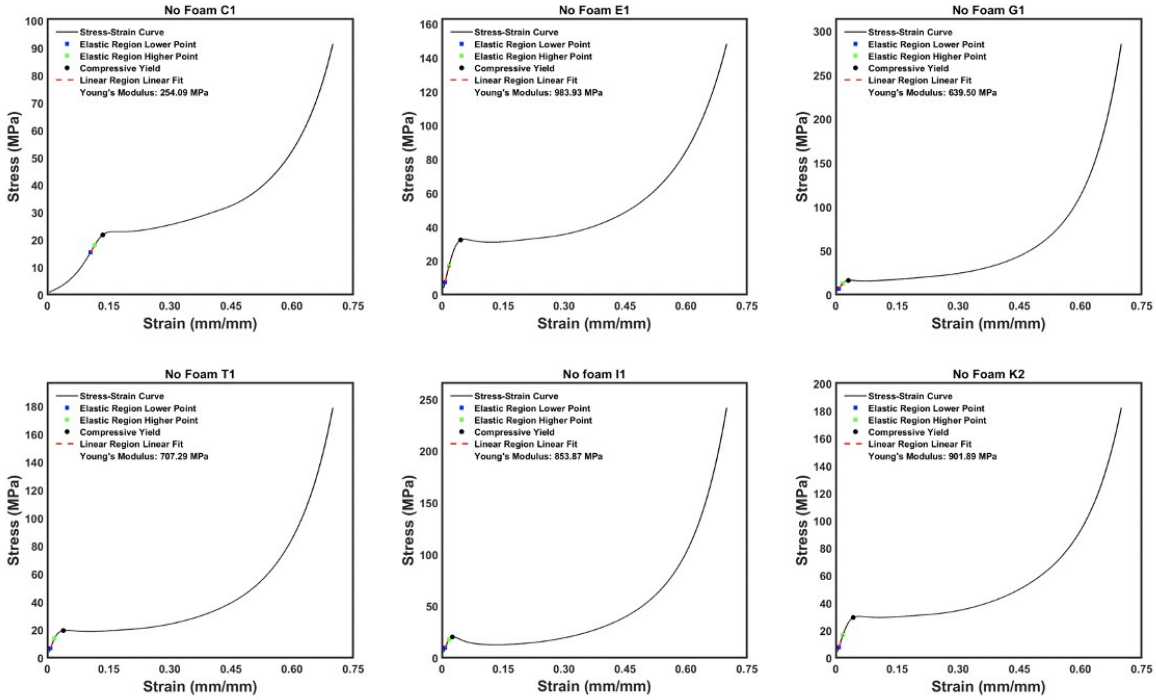

Figure S22. No foam example curves with highlighted elastic regions and compressive yields.

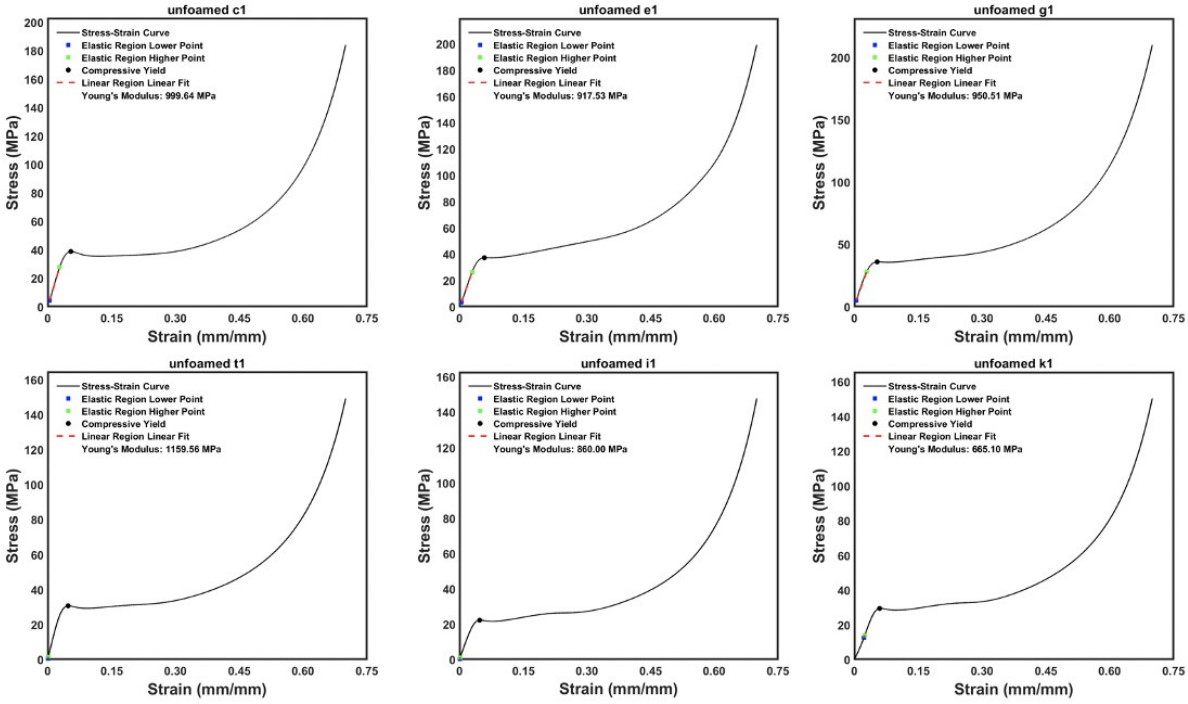

Figure S23. Unfoamed example curves with highlighted elastic regions and compressive yields.

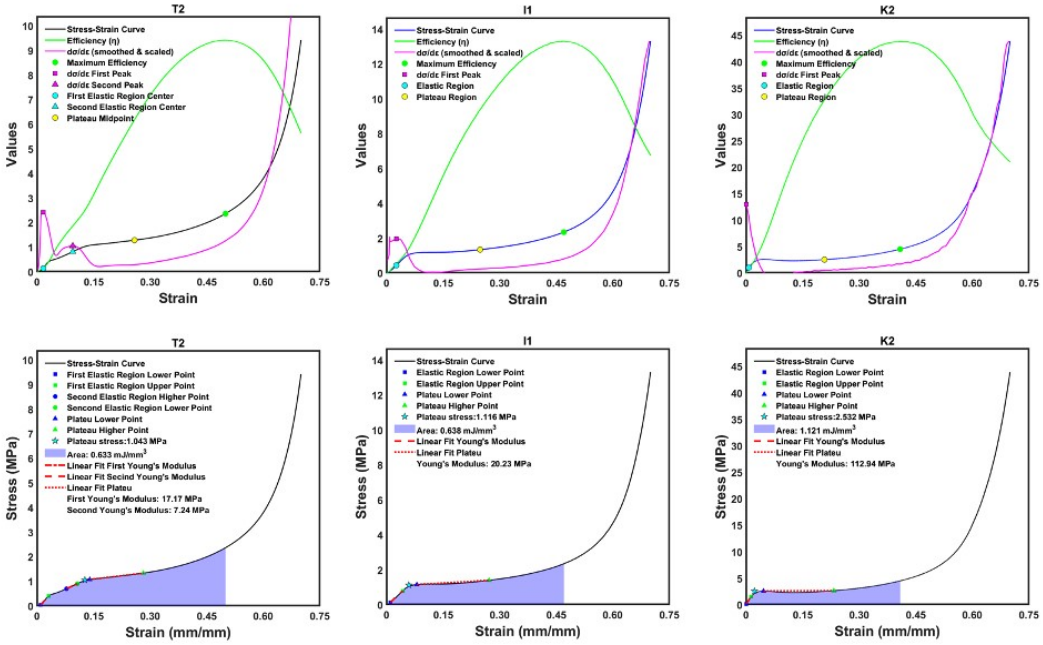

Figure S24. Sample mechanical analysis of the compressive behavior of the foamed polymers for dynamic DPE polymers. Top figures show stress-strain curve (black) along with the energy efficiency curve (green) and the derivative curve (pink). Bottom figures show stress-strain curve

with the linear fittings for the modulus of elasticity and for the plateau region. The star points to the plateau stress.

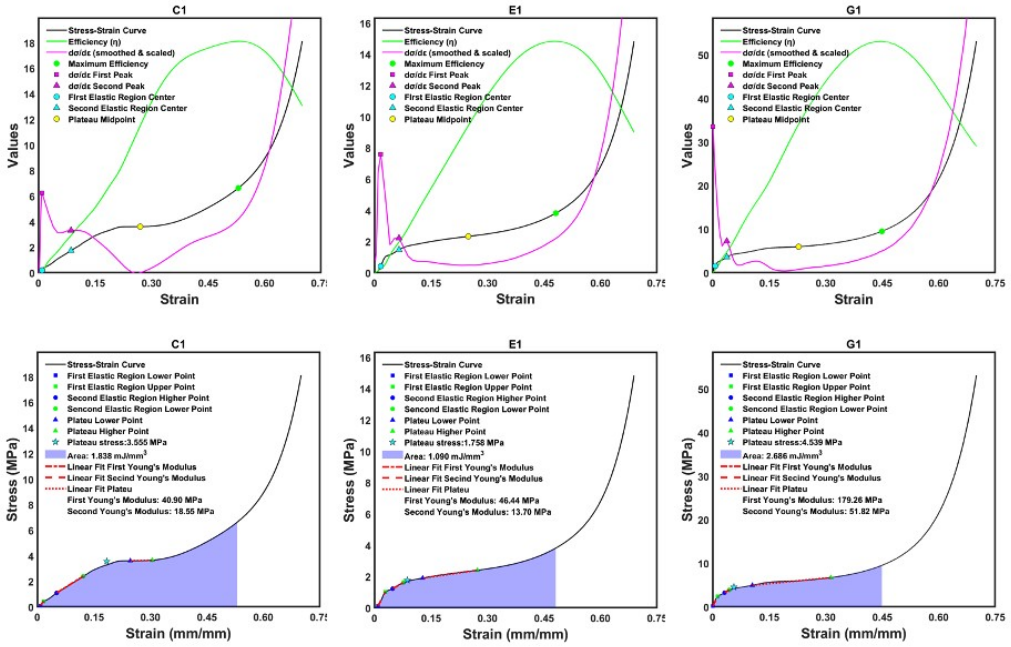

Figure S25. Sample mechanical analysis of the compressive behavior of the foamed polymers for non-dynamic TEGDA polymers. Top figures show stress-strain curve (black) along with the energy efficiency curve (green) and the derivative curve (pink). Bottom figures show stress-strain curve with the linear fittings for the modulus of elasticity and for the plateau region. The star points to the plateau stress.

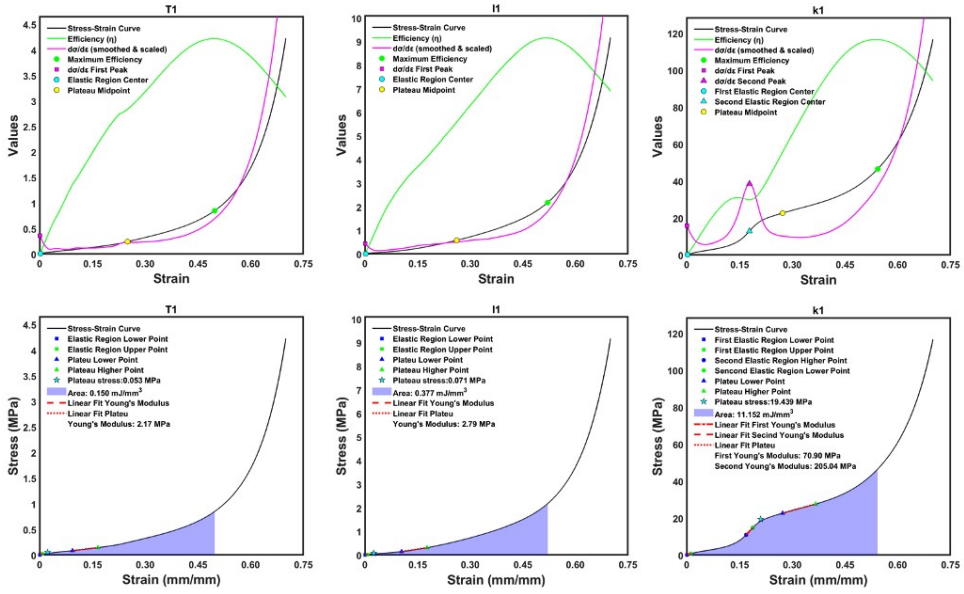

Figure S26. Sample mechanical analysis of the compressive behavior of the foamed polymers for dynamic DPE PC polymers. Top figures show stress-strain curve (black) along with the energy efficiency curve (green) and the derivative curve (pink). Bottom figures show stress-

strain curve with the linear fittings for the modulus of elasticity and for the plateau region. The star points to the plateau stress.

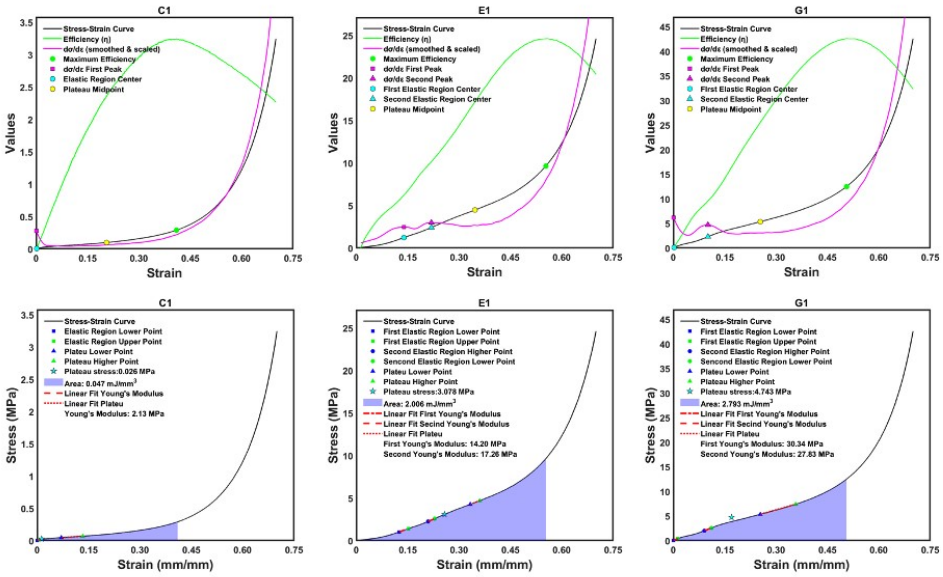

Figure S27. Sample mechanical analysis of the compressive behavior of the foamed polymers for non-dynamic TEGDA PC polymers. Top figures show stress-strain curve (black) along with the energy efficiency curve (green) and the derivative curve (pink). Bottom figures show stress-strain curve with the linear fittings for the modulus of elasticity and for the plateau region. The star points to the plateau stress.

Table S10. Compressive data values for as foamed and PC foams, with the percent change from as foamed to a PC foam listed as either percent increase (I) or decrease (D).

Formulation	Energy Dissipation ($mJ/mm^{3)}$	Percent Change (%)	Plateau Stress (Mpa)	Percent Change (%)	Max Stress (Mpa)	Percent Change (%)	Young's Modulus	Percent Change (%)
A-DPE-0.5	3.21 ± 0.28	153 % D	3.34 ± 0.23	197 % D	16.65 ± 1.31	72 % D	17.84 ± 1.95	166 % D
A-DPE- 0.5 PC	0.42 ± 0.13		0.02 ± 0.01		4.58 ± 1.93		1.63 ± 0.45	
B-DPE-1.0	2.48 ± 0.26	61 % I	1.54 ± 0.19	60 % I	17.01 ± 3.85	65 % I	33.77 ± 10.97	51 % D
B-DPE-1.0 PC	4.65 ± 0.80		2.85 ± 0.75		28.01 ± 2.92		19.96 ± 7.67	
C-DPE-1.5	8.85 ± 0.77	20 % D	5.01 ± 0.34	56 % D	63.66 ± 8.50	27 % D	195.10 ± 13.55	156 % D
C-DPE-1.5 PC	7.22 ± 0.37		2.83 ± 1.20		46.53 ± 3.45		24.34 ± 9.00	
A-TEGDA-0.1	1.22 ± 0.29	90 % D	0.92 ± 0.18	187 % D	7.86 ± 1.68	44 % D	14.42 ± 3.88	151 % D
A-TEGDA-0.1 PC	0.46 ± 0.07		0.03 ± 0.02		4.43 ± 0.25		2.02 ± 0.23	
B-TEGDA-0.5	1.57 ± 0.15	31 % D	1.08 ± 0.06	176 % D	11.32 ± 1.75	1 % D	20.60 ± 0.57	149 % D
B-TEGDA-0.5 PC	1.15 ± 0.04		0.07 ± 0.01		11.39 ± 1.79		3.00 ± 0.23	
C-TEGDA-1.0	4.84 ± 0.20	127 % I	2.47 ± 0.08	152 % I	42.02 ± 2.59	198 % I	110.35 ± 3.66	61 % I
C-TEGDA-1.0 PC	21.61 ± 1.71		18.32 ± 1.40		125.10 ± 13.19		206.22 ± 33.65	

Table S11. Dimensions of as printed unfoamed cylinders, after 70% height compression and after recovery of height after several days for dynamic DPE formulations.

A-DPE-0.5	intial Height	initial diameter	compressed height	compressed diameter	recovered height	recovered diameter	% height recovery	%diameter recovery
1	10.31	11.62	4.10	19.44	9.81	12.38	95.15	106.54
2	10.24	11.68	3.95	19.94	9.71	12.35	94.82	105.74
3	10.23	11.69	3.96	19.69	9.72	12.33	95.01	105.47
						avg	95.00	105.92
						stdev	0.16	0.56
B-DPE-1.0	intial Height	initial diameter	compressed height	compressed diameter	recovered height	recovered diameter	% height recovery	%diameter recovery
1	10.31	11.64	4.17	19.65	9.72	12.40	94.28	106.53
2	10.13	11.69	4.80	17.46	9.96	12.13	98.32	103.76
3	10.19	11.65	3.43	21.00	9.99	12.34	98.04	105.92
						avg	96.88	105.41
						stdev	2.26	1.45
C-DPE-1.5	intial Height	initial diameter	compressed height	compressed diameter	recovered height	recovered diameter	% height recovery	%diameter recovery
1	10.47	11.56	3.46	20.59	10.14	12.52	96.85	108.30
2	10.40	11.60	3.87	19.58	9.99	12.46	96.06	107.41
3	10.55	11.58	4.23	19.35	10.11	12.24	95.83	105.70
						avg	96.25	107.14
						stdev	0.53	1.32

Table S12. Dimensions of as printed unfoamed cylinders, after 70% height compression and after recovery of height after several days for non-dynamic TEGDA formulations.

A-TEGDA-0.1	intial Height	initial diameter	compressed height	compressed diameter	recovered height	recovered diameter	% height recovery	%diameter recovery
1	10.65	11.70	3.79	20.39	10.38	12.24	97.46	104.62
2	10.85	11.74	3.87	19.95	10.36	12.29	95.48	104.68
3	10.58	11.69	3.71	20.15	10.32	12.22	97.54	104.53
						avg	96.83	104.61
						stdev	1.17	0.08
B-TEGDA-0.5	intial Height	initial diameter	compressed height	compressed diameter	recovered height	recovered diameter	% height recovery	%diameter recovery
1	10.45	11.63	3.66	19.94	9.93	12.62	95.02	108.51
2	10.49	11.59	3.97	19.22	10.07	12.30	96.00	106.13
3	10.63	11.61	3.83	19.69	10.09	12.42	94.92	106.98
						avg	95.31	107.21
						stdev	0.59	1.21
C-TEGDA-1.0	intial Height	initial diameter	compressed height	compressed diameter	recovered height	recovered diameter	% height recovery	%diameter recovery
1	10.72	11.52	4.06	19.43	10.08	12.37	94.03	107.38
2	10.74	11.48	3.65	19.74	10.05	12.55	93.58	109.32
3	10.70	11.51	4.04	19.69	10.06	12.39	94.02	107.65
						avg	93.87	108.11
						stdev	0.26	1.05

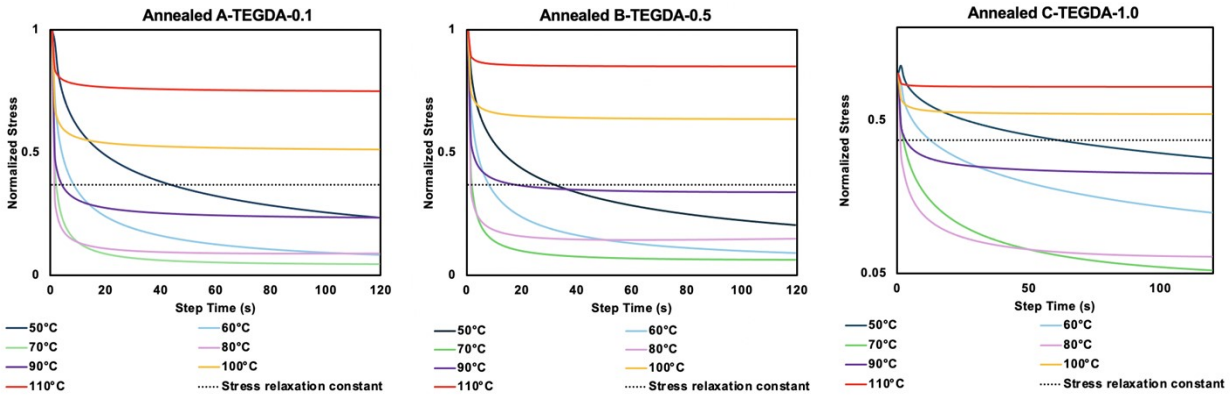

Figure S28. Stress relaxation of annealed non-dynamic TEGDA polymers from 50- 110°C.

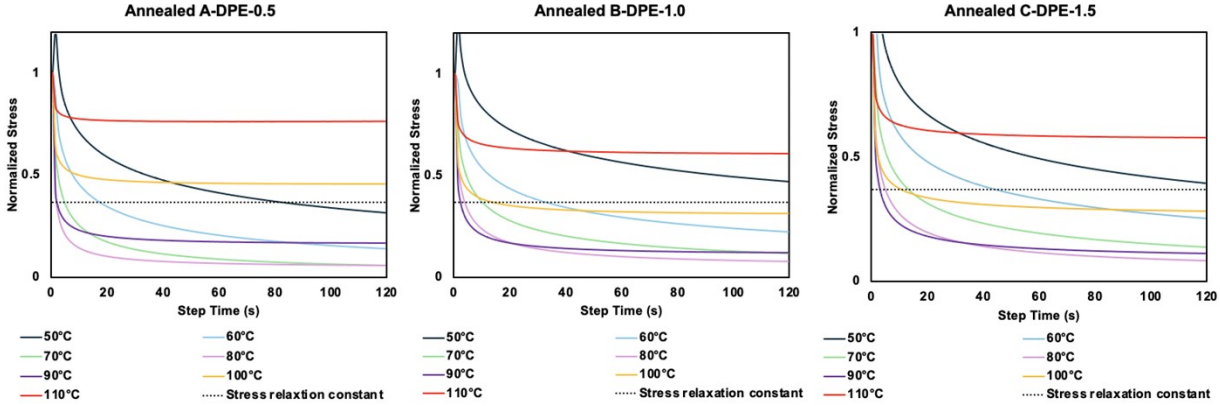

Figure S29. Stress relaxation of annealed dynamic DPE polymers from 50- 110°C.

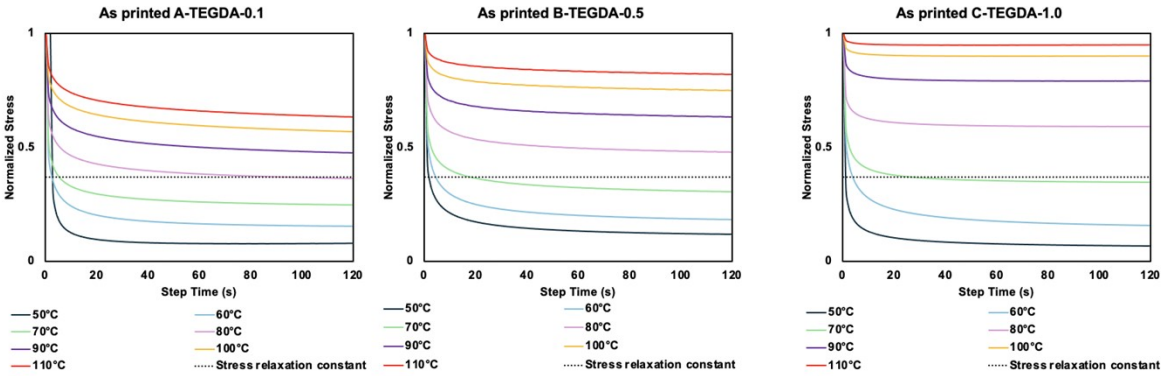

Figure S30. Stress relaxation of as printed non-dynamic TEGDA polymers from 50- 110°C.

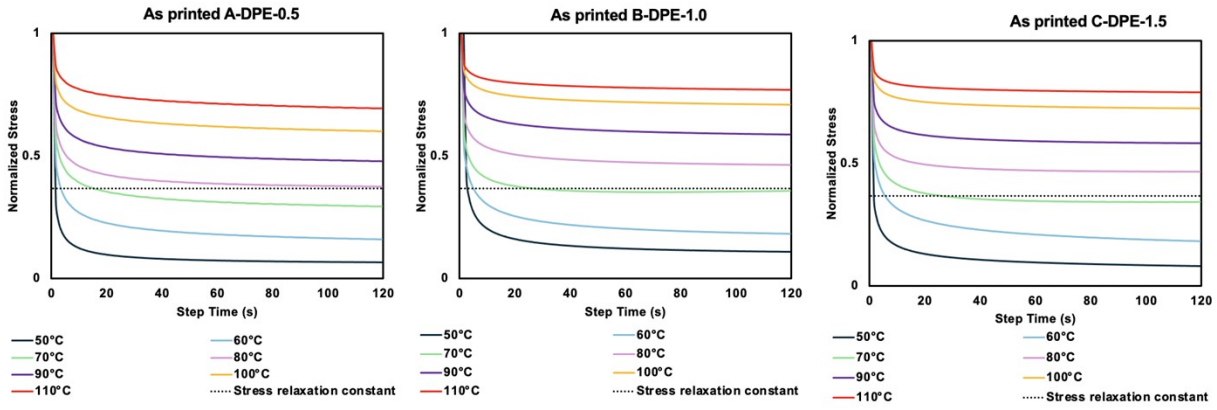

Figure S31. Stress relaxation of as printed dynamic DPE polymers from 50- 110°C.