

## Influence of Post-Processing on the Properties of 3D-Printed Poly(propylene fumarate) Star Polymer Hydroxyapatite Nanocomposites

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Supplemental Information:

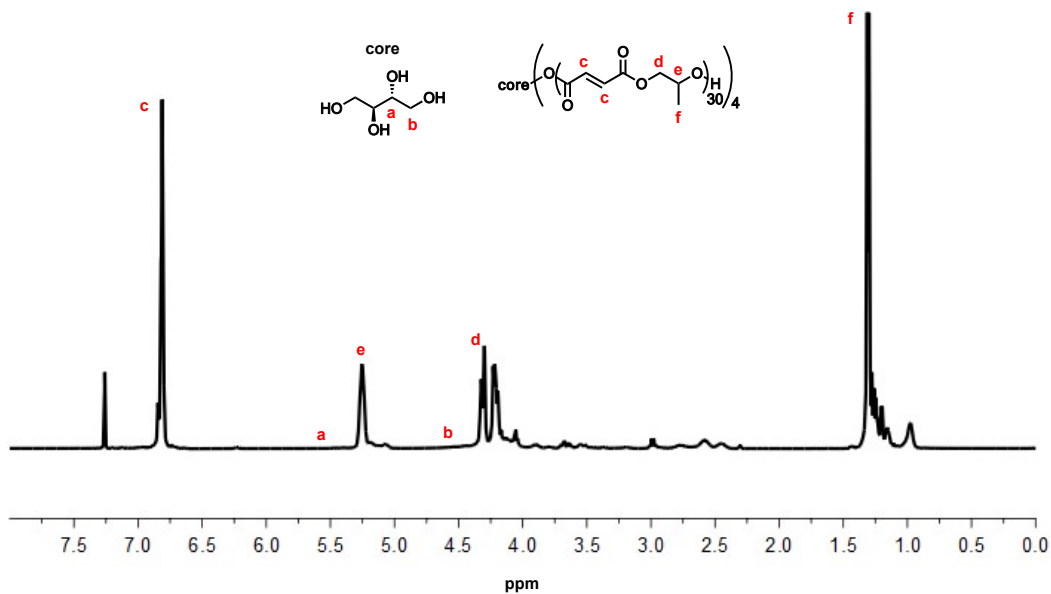


Figure S1: <sup>1</sup>H NMR spectra of PPM Stars with DP 120.

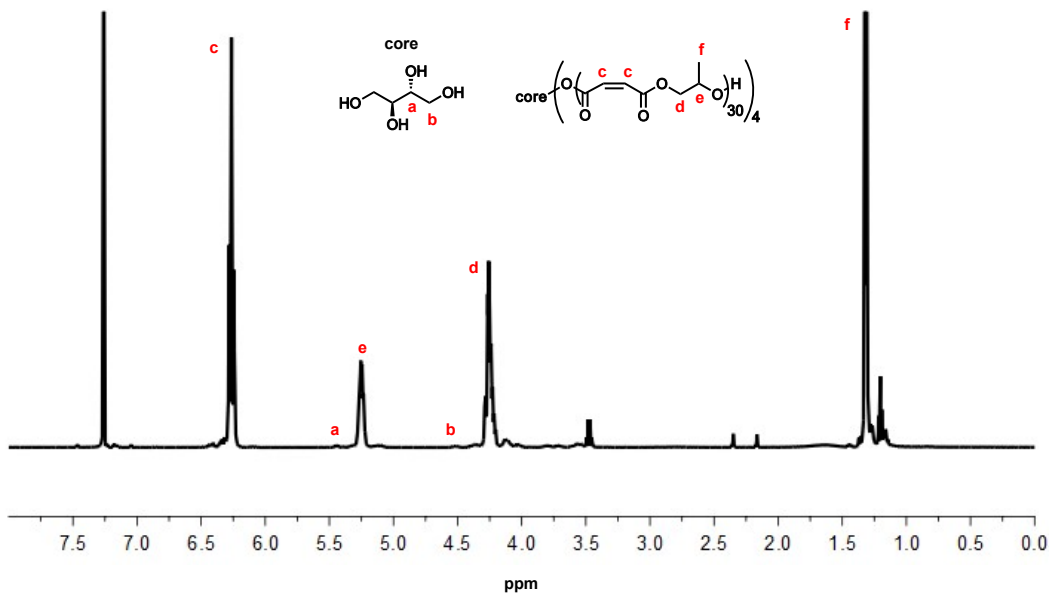


Figure S2: <sup>1</sup>H NMR spectra of PPF Stars with DP 120.

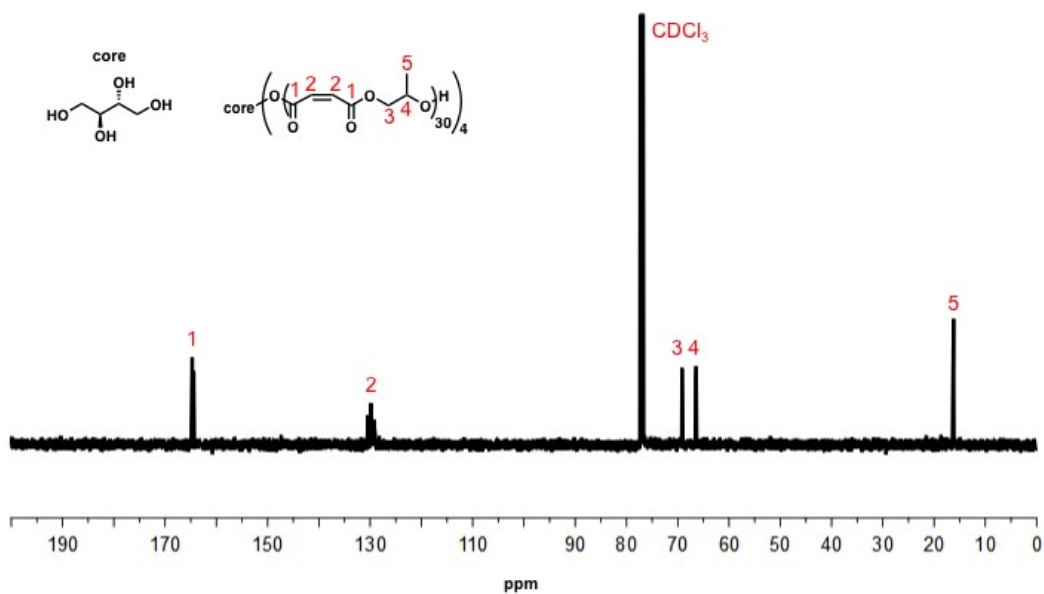


Figure S3:  $^{13}\text{C}$  NMR spectra of PPM Stars with DP 120.

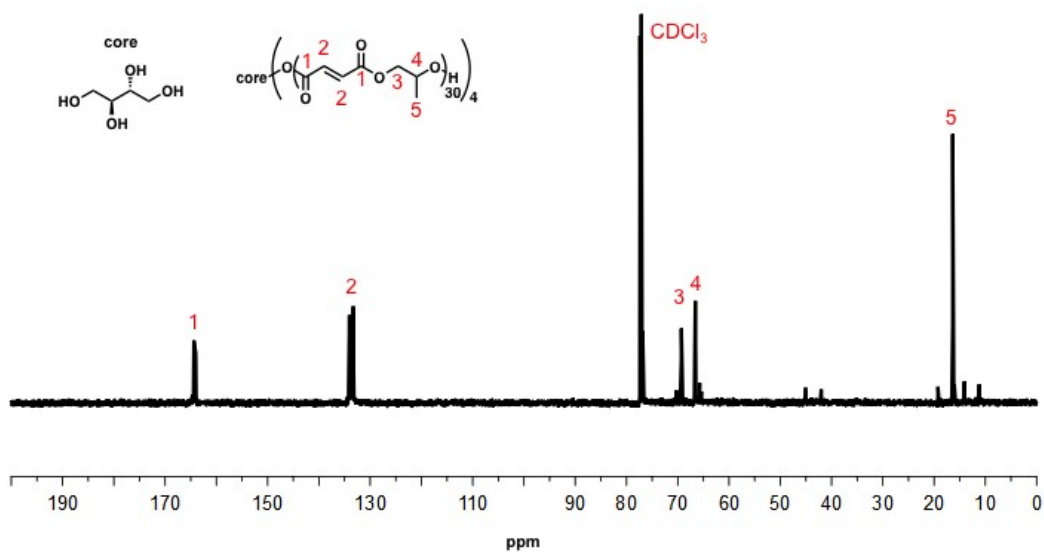


Figure S4:  $^{13}\text{C}$  NMR spectra of PPF Stars with DP 120.

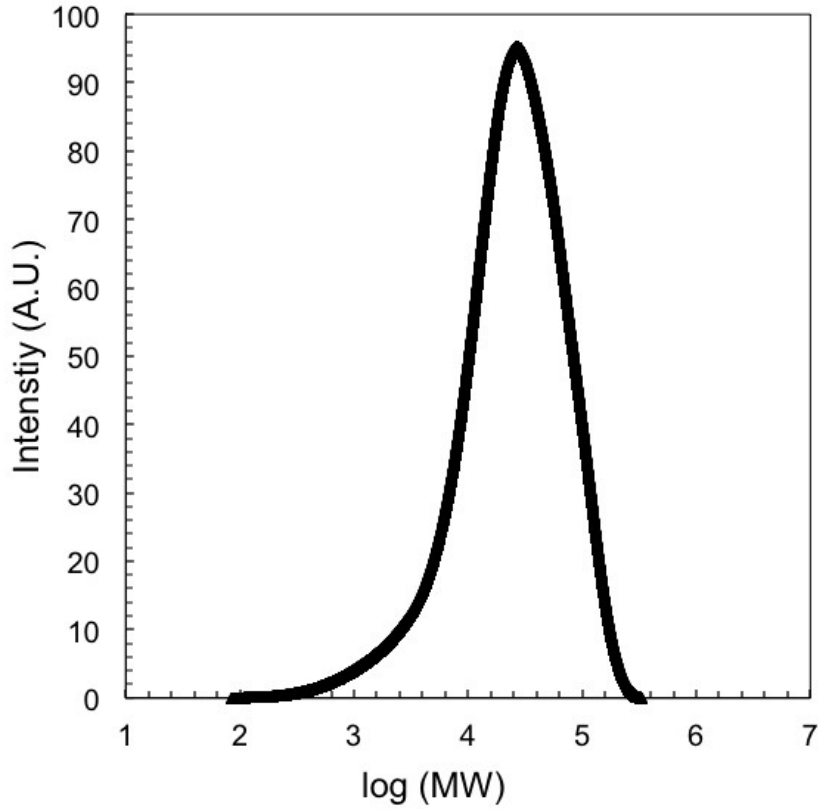


Figure S5: Size-exclusion chromatography of PPF Stars.

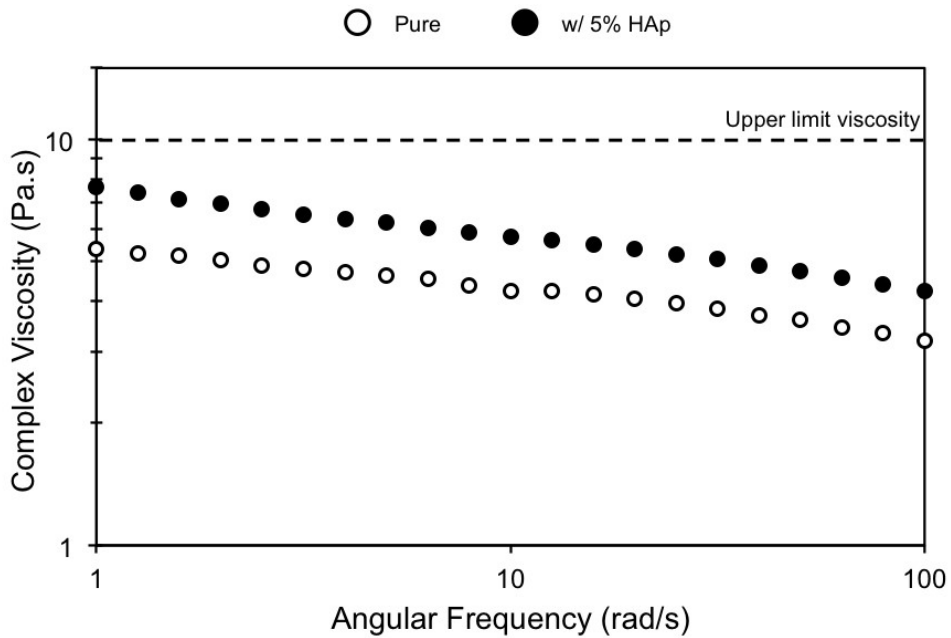


Figure S6: Viscosity of unfilled and composite (5%, wt) resin was determined to fall below the printable region of 10 Pa.s and thus was deemed capable of being printed. The composite raised the overall viscosity by roughly 1.5 Pa.s.

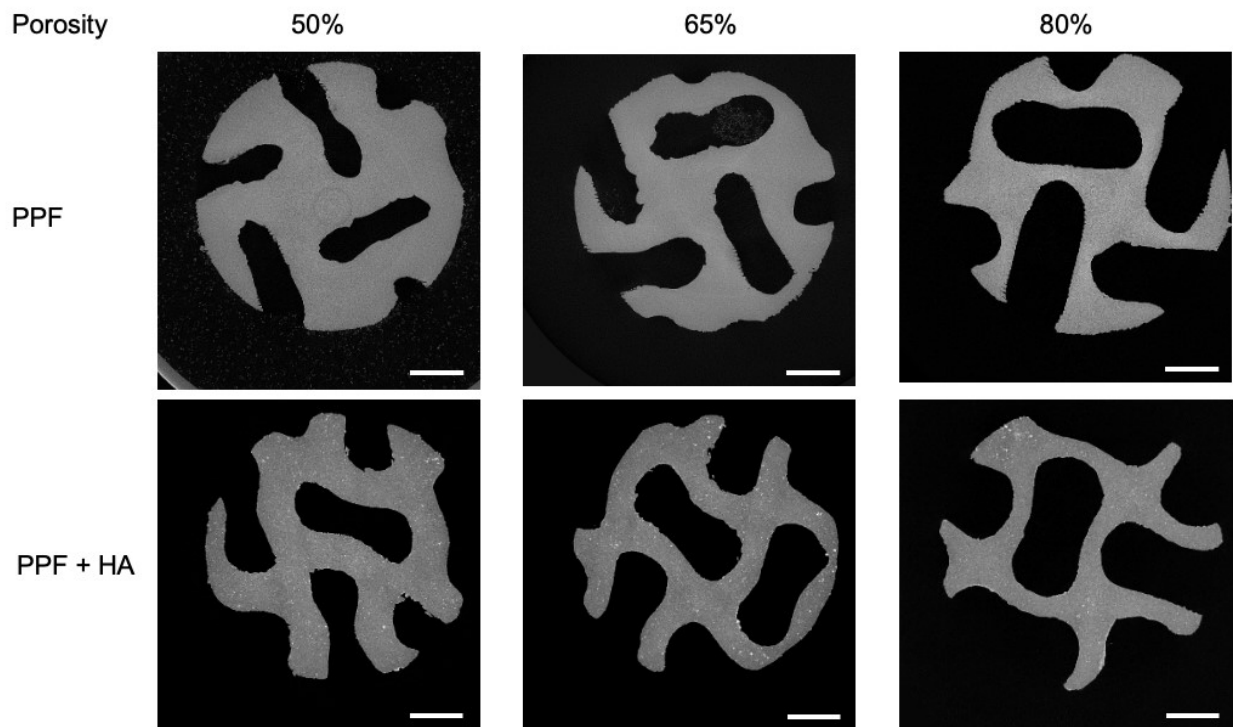


Figure S7:  $\mu$ CT cross-sections of varying porosities of scaffolds with and without hydroxyapatite nanoparticles. Nanoparticles can be seen dispersed through the polymer matrix as white clusters. Scale bars: 2 mm.

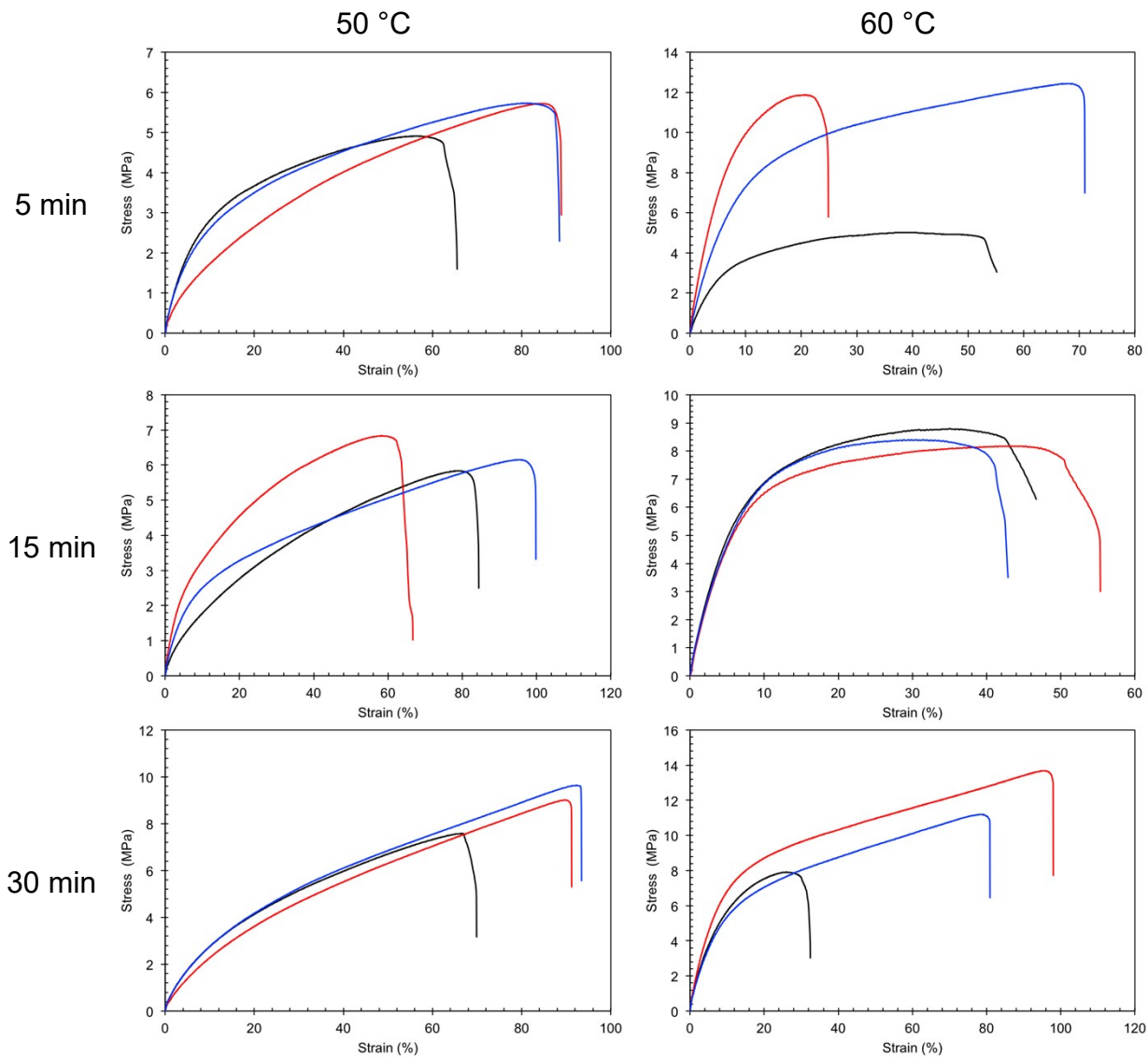


Figure S8: Raw tensile curves for 2 days in unfilled printed samples (n=3) for each condition. Colors indicate different sample runs.

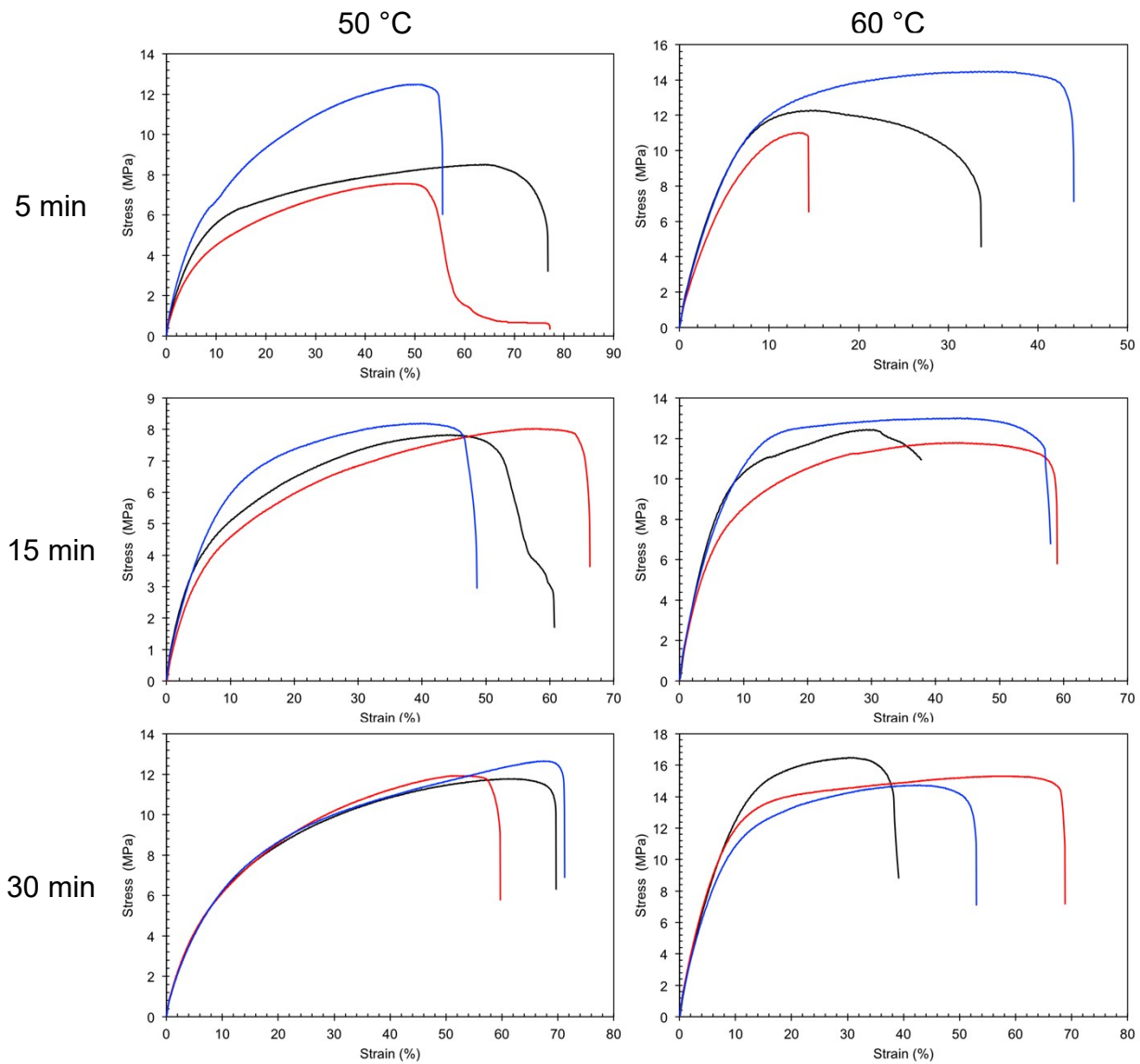


Figure S9: Raw tensile curves for 4 days in unfilled printed samples (n=3) for each condition. Colors indicate different sample runs.

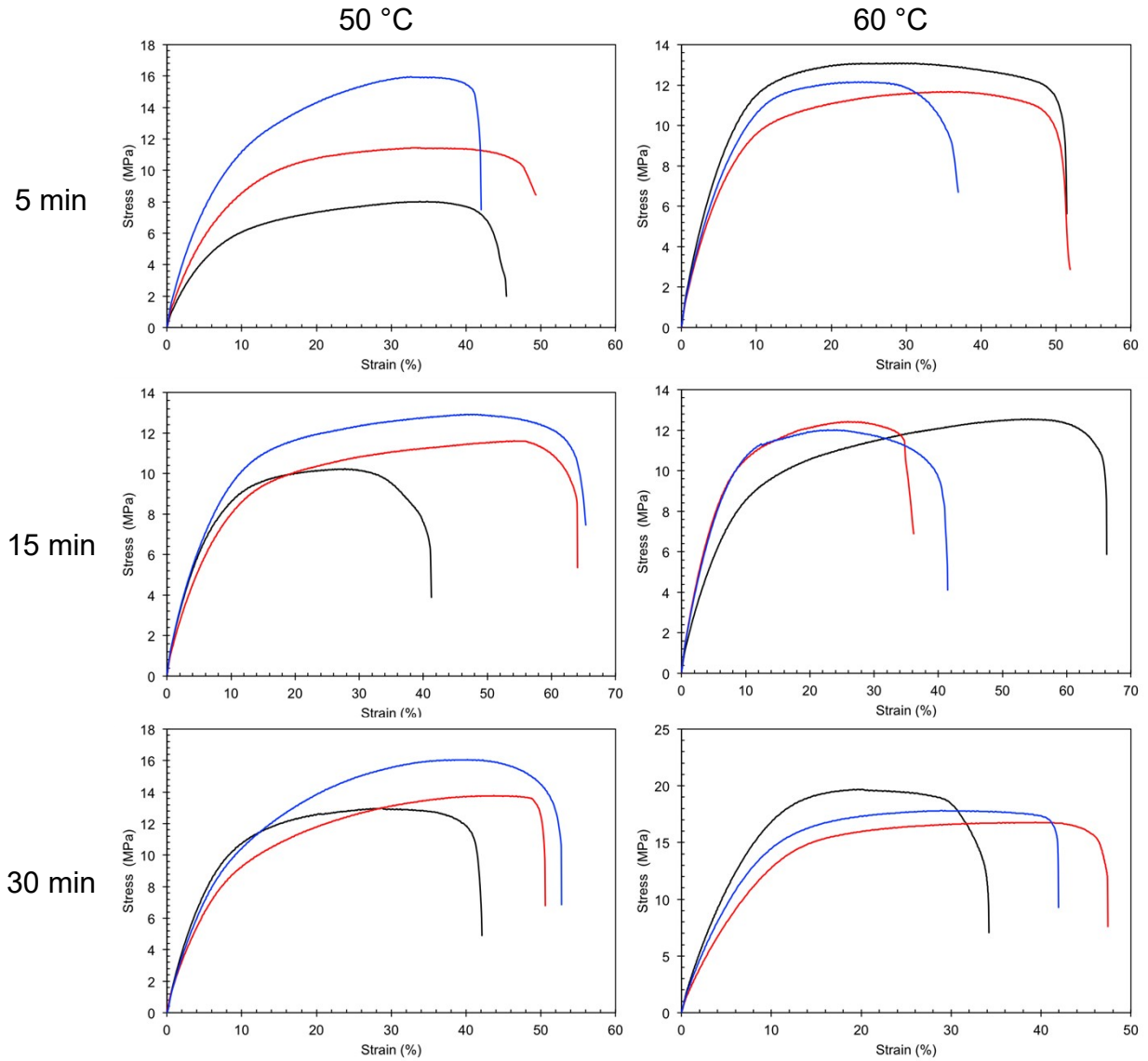


Figure S10: Raw tensile curves for 6 days in unfilled printed samples (n=3) for each condition. Colors indicate different sample runs.

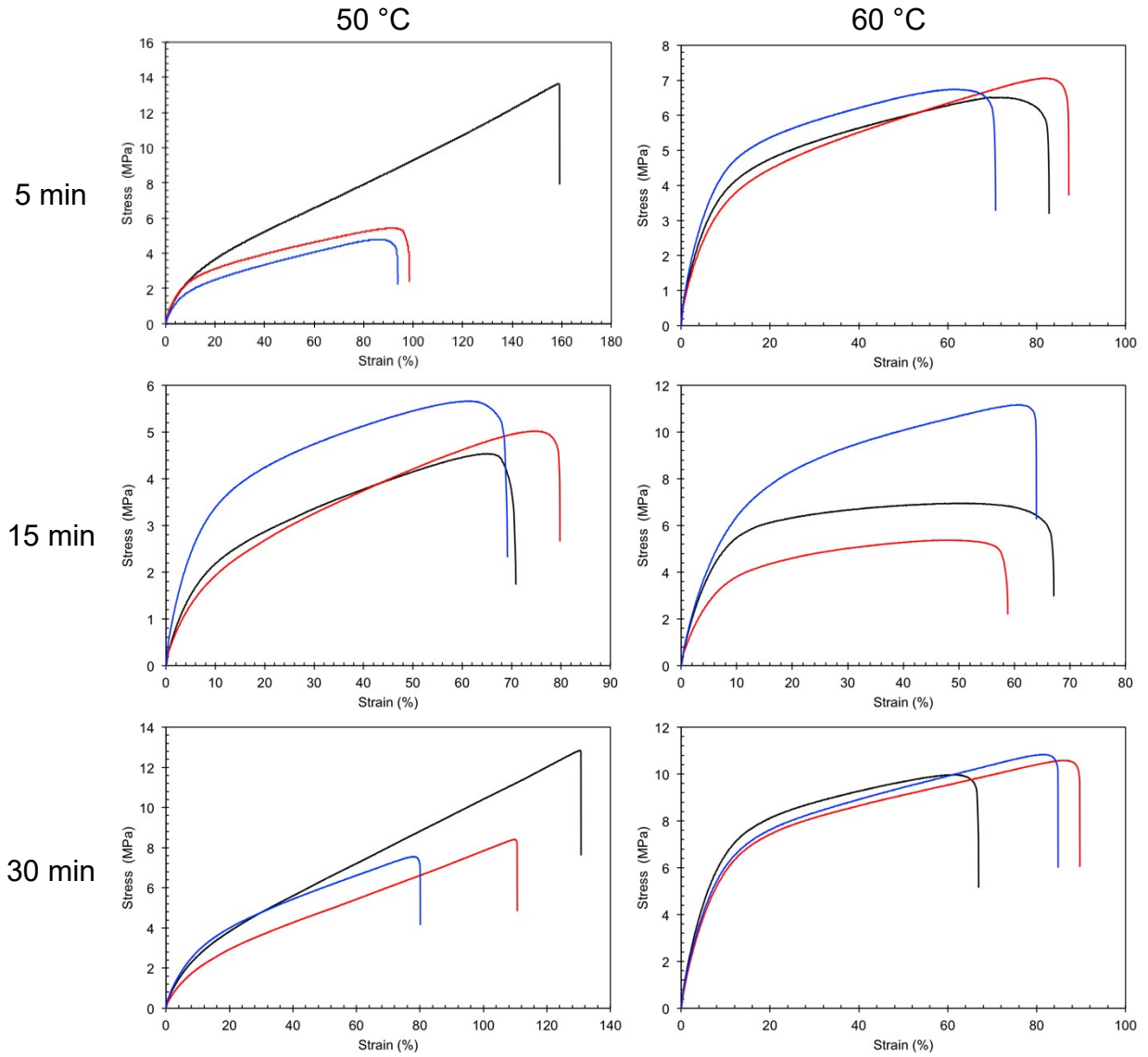


Figure S11: Raw tensile curves for 2 days in composite printed samples (n=3) for each condition. Colors indicate different sample runs.



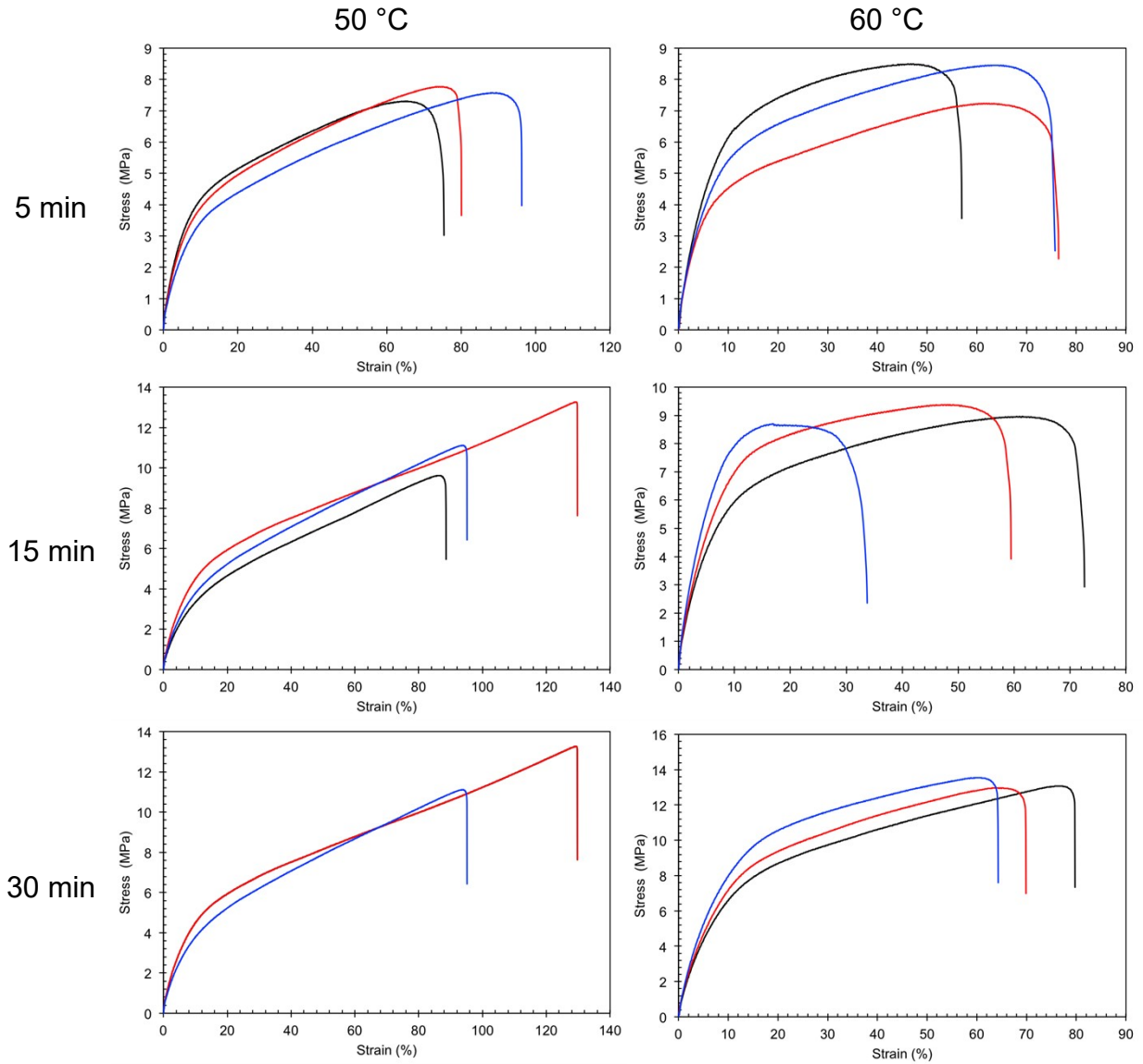


Figure S12: Raw tensile curves for 4 days in composite printed samples (n=3) for each condition. Colors indicate different sample runs.

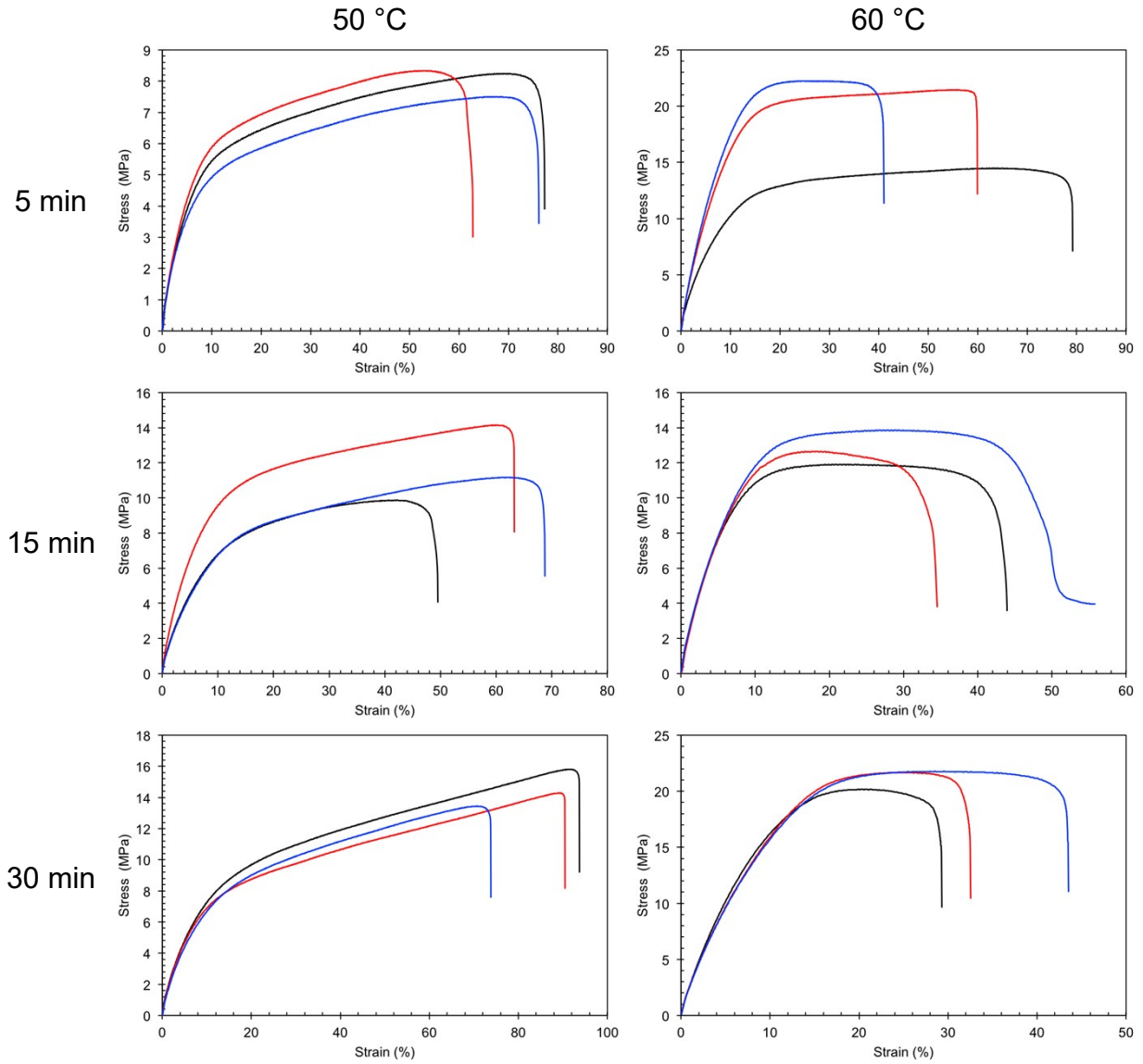


Figure S13: Raw tensile curves for 6 days in composite printed samples (n=3) for each condition. Colors indicate different sample runs.

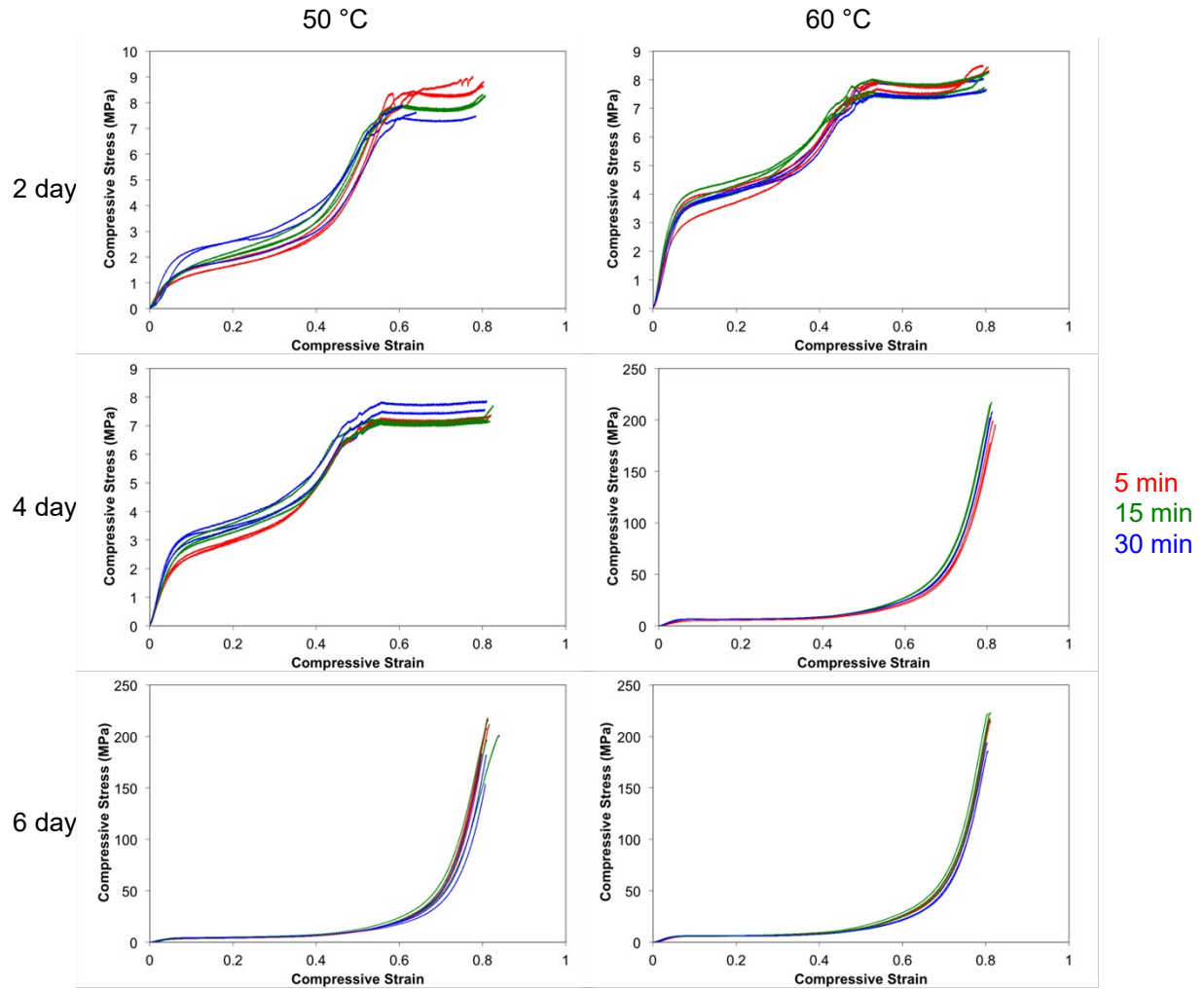


Figure S14: Raw compression curves for pure samples (n=3) for each condition.

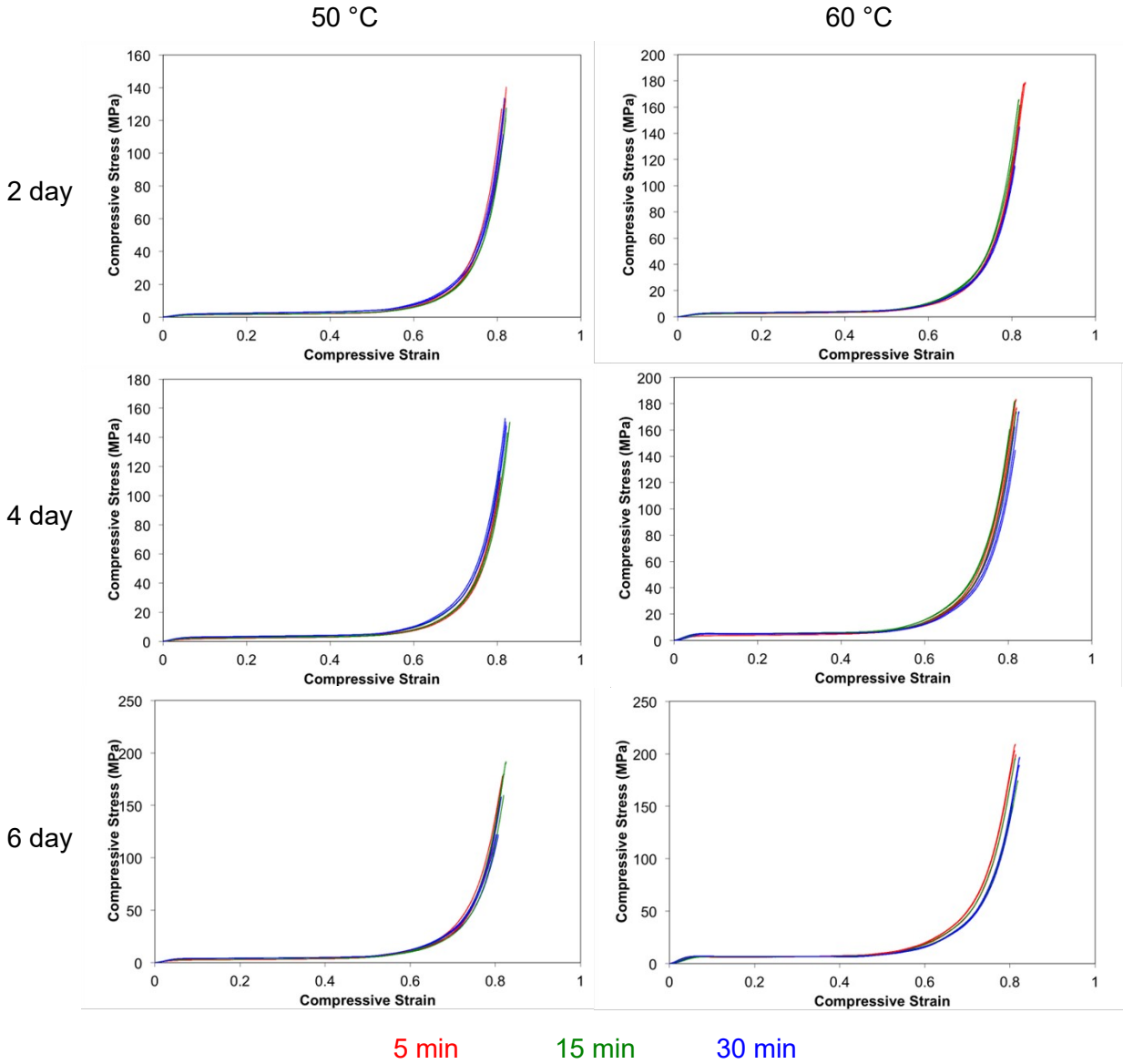


Figure S15: Raw compression curves for composite samples (n=3) for each condition.

System	Temperature (°C)	Drying Time (days)	Post-Cure Time (min)	Modulus (MPa)	Ultimate Tensile Strength (MPa)	Strain at Failure (%)	Compressive Strength (MPa)	Compressive Modulus (MPa)
Unfilled	50	2	5	73 ± 15.7	5 ± 0.5	79.5 ± 16.0	1.8 ± 0.1	24 ± 3
			15	85 ± 28.3	6 ± 0.5	82.6 ± 18.2	2.1 ± 0.1	26 ± 5
			30	80 ± 11.4	9 ± 1.1	84.0 ± 14.4	2.4 ± 0.4	29 ± 17
		4	5	168 ± 15.2	10 ± 2.7	67.4 ± 11.8	3.0 ± 0.1	44 ± 1
			15	159 ± 24.0	8 ± 0.2	60.1 ± 10.0	3.4 ± 0.2	52 ± 8
			30	183 ± 9.5	12 ± 0.5	66.9 ± 6.3	3.5 ± 0.2	61 ± 4
		6	5	232 ± 54.1	12 ± 4.0	44.5 ± 2.9	4.1 ± 0.2	69 ± 11
			15	229 ± 19.7	12 ± 1.3	57.1 ± 13.8	4.6 ± 0.4	85 ± 20
			30	263 ± 17.0	14 ± 1.6	48.5 ± 5.6	4.6 ± 0.2	87 ± 16
Unfilled	60	2	5	165 ± 67.2	10 ± 4.1	49.2 ± 23.2	4.0 ± 0.3	76 ± 14
			15	161 ± 4.1	8 ± 0.3	45.1 ± 5.2	4.3 ± 0.2	86 ± 8
			30	149 ± 15.2	11 ± 2.9	70.5 ± 34.0	4.1 ± 0.0	66 ± 14
		4	5	278 ± 28.6	13 ± 1.9	33.7 ± 19.3	5.4 ± 0.1	90 ± 20
			15	256 ± 11.2	12 ± 0.6	52.1 ± 11.9	6.4 ± 0.1	139 ± 13
			30	264 ± 14.6	16 ± 0.9	53.4 ± 15.2	6.6 ± 0.2	149 ± 22
		6	5	277 ± 17.5	12 ± 0.7	46.1 ± 8.4	6.1 ± 0.1	117 ± 30
			15	259 ± 38.5	12 ± 0.3	47.5 ± 16.5	6.3 ± 0.4	143 ± 12
			30	316 ± 43.3	18 ± 1.5	41.2 ± 6.6	6.2 ± 0.4	113 ± 14
		2	5	69 ± 10.0	8 ± 4.9	117.2 ± 36.4	1.6 ± 0.1	23 ± 2
			15	80 ± 27.9	5 ± 0.6	73.3 ± 5.7	1.7 ± 0.1	25 ± 5
			30	74 ± 14.2	10 ± 2.8	107.2 ± 25.5	2.4 ± 0.1	38 ± 3
		4	5	138 ± 7.1	9 ± 1.9	79.1 ± 14.5	2.3 ± 0.1	34 ± 3

Composite	50	15	130 ± 14.0	9 ± 1.2	77.7 ± 16.1	2.7 ± 0.2	48 ± 3
			144 ± 11.8	13 ± 1.2	118.2 ± 20.0	3.4 ± 0.1	67 ± 1
		6	5	217 ± 50.7	10 ± 3.6	72.2 ± 7.8	3.1 ± 0.2
	15		222 ± 46.0	12 ± 2.3	62.2 ± 12.2	3.4 ± 0.0	71 ± 6
	30		204 ± 12.2	15 ± 1.2	86.0 ± 10.7	4.3 ± 0.1	76 ± 25
	Composite	50	2	139 ± 8.7	7 ± 0.3	80.3 ± 8.5	2.6 ± 0.1
152 ± 26.6				8 ± 3.0	63.3 ± 4.2	2.9 ± 0.1	47 ± 11
6			5	161 ± 15.2	10 ± 0.4	80.5 ± 12.0	3.3 ± 0.1
		15	193 ± 18.9	10 ± 2.7	60.2 ± 3.7	3.9 ± 0.0	83 ± 4
		30	213 ± 18.3	9 ± 0.3	55.3 ± 19.8	5.0 ± 0.2	102 ± 15
Composite		60	4	193 ± 9.7	13 ± 0.3	71.3 ± 7.8	5.1 ± 0.2
	5			298 ± 25.1	16 ± 5.1	51.6 ± 24.1	6.2 ± 0.2
	6		15	299 ± 16.7	15 ± 5.5	40.7 ± 5.3	6.5 ± 0.1
		30	319 ± 8.6	21 ± 0.9	35.1 ± 7.5	6.6 ± 0.2	172 ± 26

Figure S16: Table with tensile and compression data

Source	UTS	Modulus	Strain at Failure	Compressive Modulus	Compressive Strength
System (HAp or Unfilled)	0.6683	0.0001*	<.0001*	0.2063	<.0001*
Days in Oven	<.0001*	<.0001*	<.0001*	<.0001*	<.0001*
Temperature of Oven	<.0001*	<.0001*	<.0001*	<.0001*	<.0001*
Post-Cure	<.0001*	0.1428	0.1703	<.0001*	<.0001*
System*Days in Oven	0.1804	0.9721	0.4202	0.0173*	0.0320*
System*Temperature of Oven	0.9594	0.3598	0.1912	0.9097	0.1456
System*Post-Cure	0.8291	0.7480	0.6057	0.4415	0.5710
Days in Oven*Temperature of Oven	0.0596	0.8155	0.1866	0.0007*	<.0001*
Days in Oven*Post-Cure	0.1954	0.2241	0.3368	0.7041	0.8840
Temperature of Oven*Post-Cure	0.8512	0.7720	0.6530	0.8538	0.3361
System*Days in Oven*Temperature of Oven	0.0039*	0.0145*	0.1237	<.0001*	<.0001*
System*Days in Oven*Post-Cure	0.9011	0.1436	0.5157	0.9123	0.6944
System*Temperature of Oven*Post-Cure	0.7699	0.4760	0.0922	0.7626	0.2051
Days in Oven*Temperature of Oven*Post-Cure	0.9672	0.9019	0.0490*	0.7987	0.3063
System*Days in Oven*Temperature of Oven*Post-Cure	0.0589	0.3509	0.5700	0.4698	0.3495

Figure S17: Table dictating the F-test results of significance for a linear regression model with 4 degrees of freedom related to each property analyzed. Red indicates high significance, whereas blue indicates some significance.