Supplementary Information to support the publication of

Influence of Rheology on 3D Printing with Reactive Polyurethane Reagents

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Table S1. Mass composition of ink formulations required to produce the three mixing modes (MM1, MM2 and MM3).

	Chemicals	Functionality	Units	MM1	MM2	MM3
Isocyanate (NCO) Feed	PMDI	-NCO	Functionality in feed (mol%)	53	53	53
	FS	rheology modifier	Quantity in feed (wt%)	5	2.5	1
Polyol (OH) Feed	PEG-PPG-PEG	-OH	Functionality in feed (mol%)	30	30	30
	1,4 BD	-OH	Functionality in feed (mol%)	16	16	16
	FS	rheology modifier	Quantity in feed (wt%)	5	5	5
	DBTDL	catalyst	Quantity in feed (wt%)	1	1	1

Note: Mass composition of fumed silica (FS) in the isocyanate and polyol feeds was determined with respect to the isocyanate (PMDI) mass and total mass of polyol (PMDI+1,4 BD) respectively.

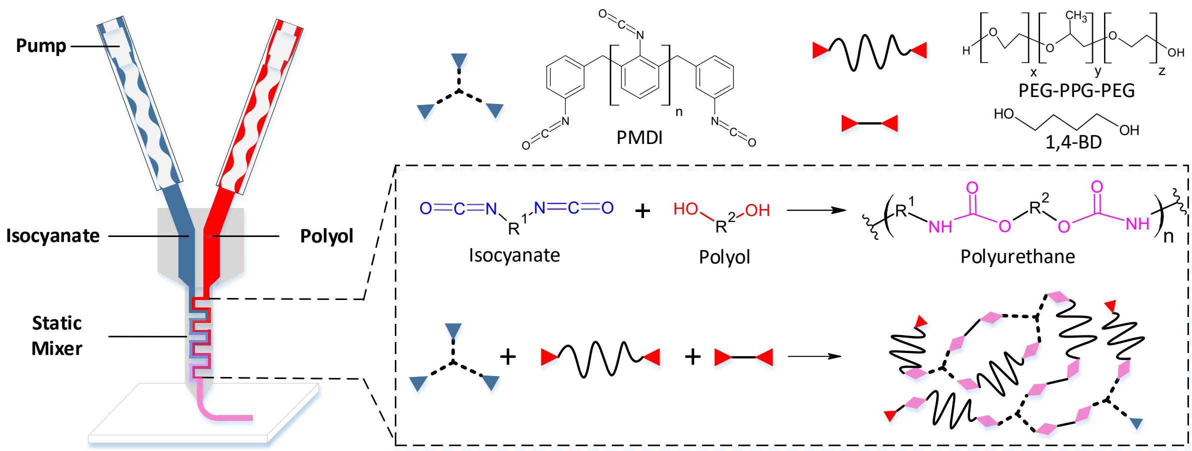

Figure S1. A schematic diagram of how isocyanate and polyol were processed using REX 3D printing to form PU. The chemical structure of isocyanates and polyol used in the study and general PU reaction scheme are presented.

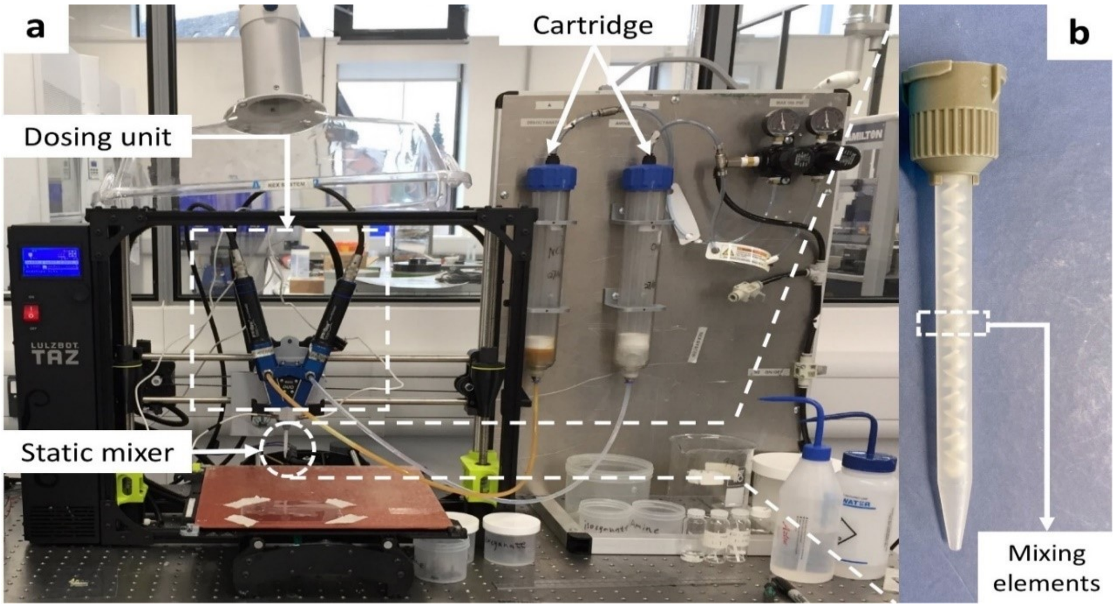

Figure S2. a) REX system apparatus. b) Blow up of Static mixer section.

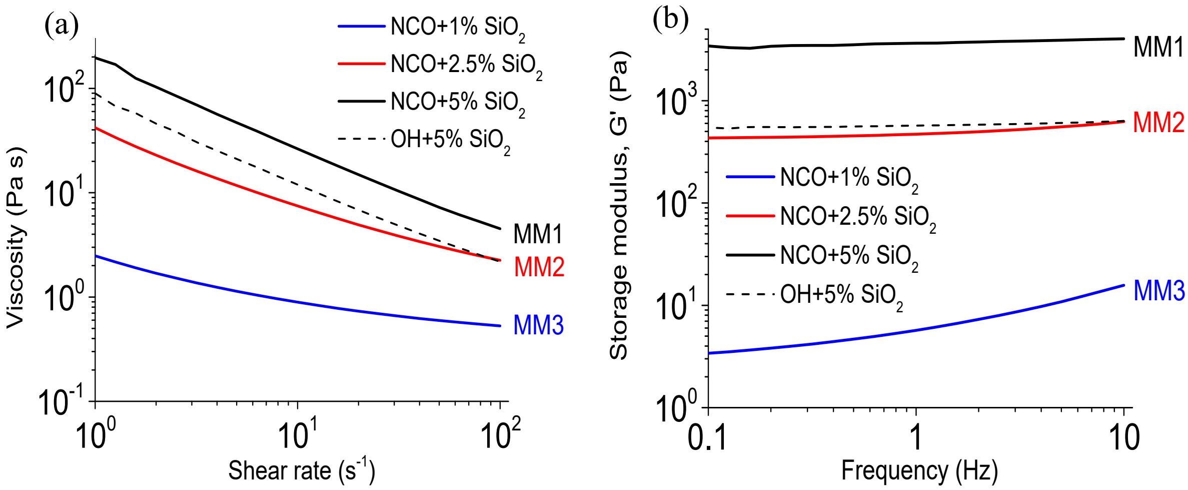

Figure S3. The rheological property comparisons between the feed mixtures designed to produce MM1, MM2 and MM3 mixing mode behaviour. **a)** A plot of viscosity as a function of shear rate for all the mixing modes. **b)** A plot of the storage module against frequency for the different particle content loadings that result in the three mixing modes.

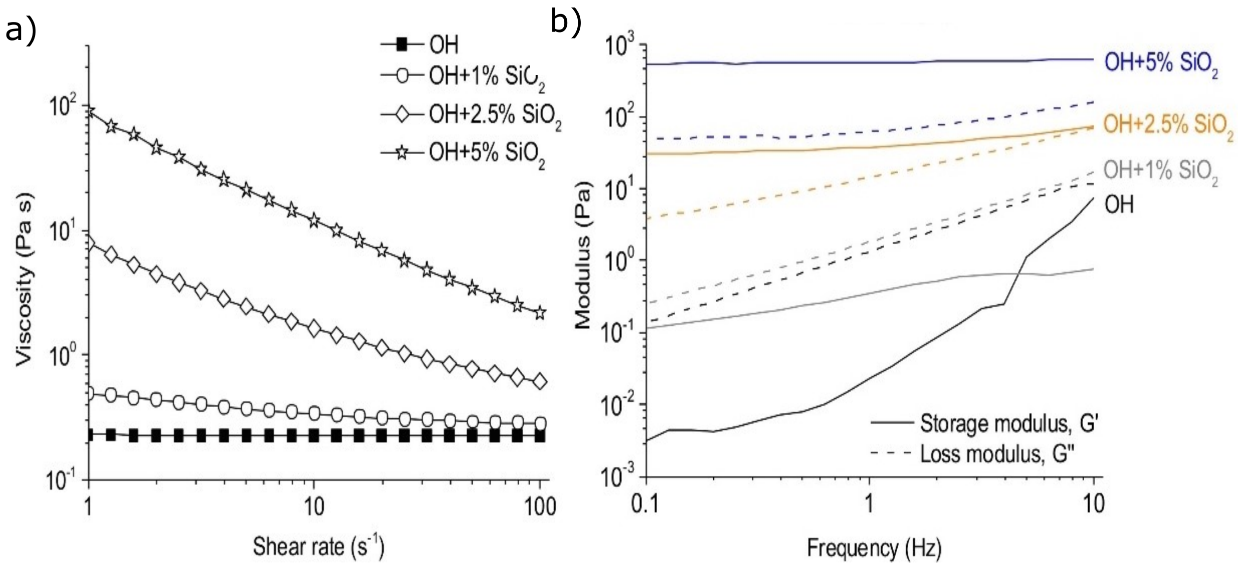

Figure S4. Plots of viscosity as a function of shear rate and both storage and loss moduli as a function of frequency for NCO feeds.

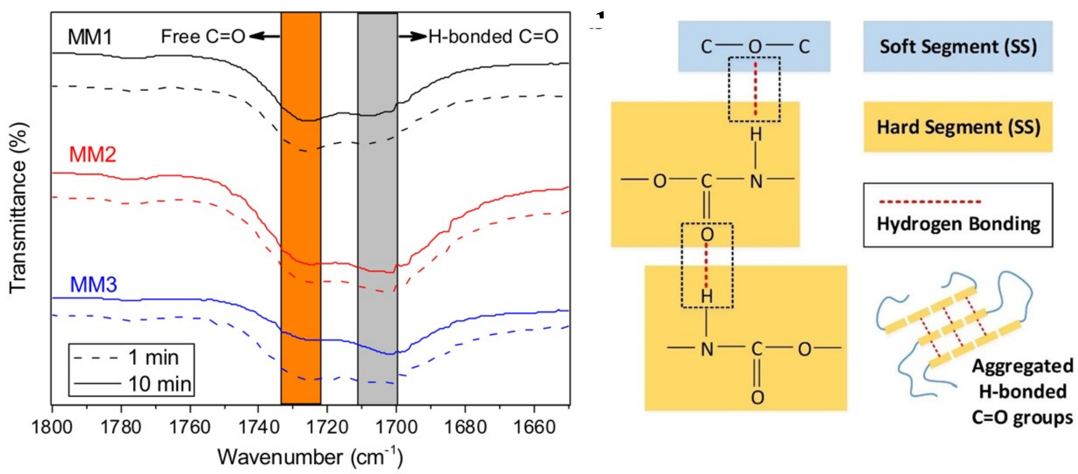

Figure S5. FTIR spectra of PU samples synthesis after printing at 1 minute (dash line) and 10 minutes (solid line) from the 3 mixing modes. (a**)** The amplified spectra of free and hydrogen bonded carbonyl absorbance bands (C=O) in the spectra. and (b**)** Schematic of hard segment, soft segment and hydrogen bond within the printed PU structure and aggregated hydrogen bonded urethane carbonyl group.

Table S2. FTIR spectroscopic data for isocyanate and C-H reference absorbances at different reaction times. Estimated process induced deviation between individual experiments is less than ± 3

	Time (min)	$A_{NCO(t)}$	$A_{CH(t)}$
PMDI	0	78.55	12.98
MM1	1	12.89	10.66
	10	9.42	9.78
MM2	1	10.28	10.56
	10	5.67	7.32
MM3	1	10.50	10.18
	10	2.72	5.65

$$Reaction\ conversion\ = 1 - \frac{A_{NCO(t)}/A_{CH(t)}}{A_{NCO(t_0)}/A_{CH(t_0)}} \tag{S1}$$

The reaction conversion is determined using the equation S1, by applying the absorbance band data in Table S2. $A_{NCO(t_0)}$ and $A_{NCO(t)}$ denotes the peak area of isocyanate group at the beginning of reaction and at the reaction time t, respectively. $A_{CH(t_0)}$ and $A_{CH(t)}$ denotes the peak area of reference peak C-H stretching at the beginning of reaction and at the reaction time t, respectively.

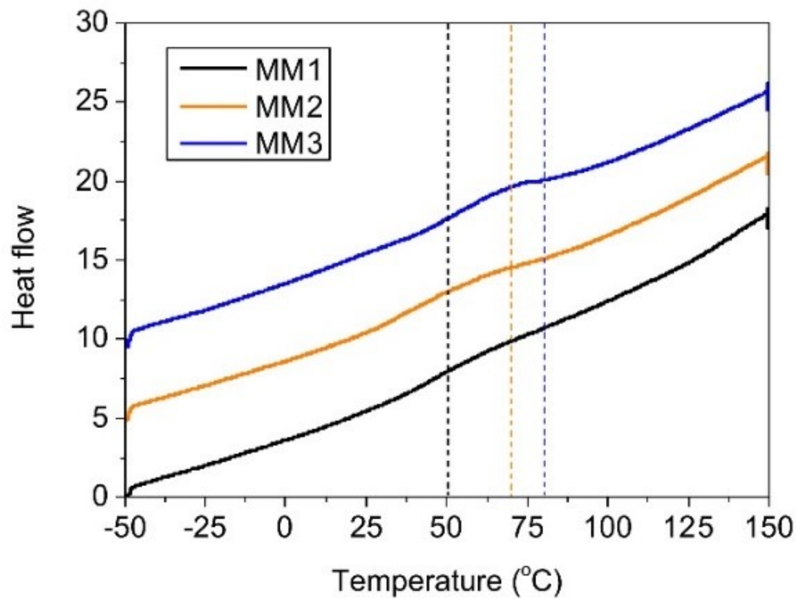

Figure S6. DSC data for the PU samples printed from three mixing modes.

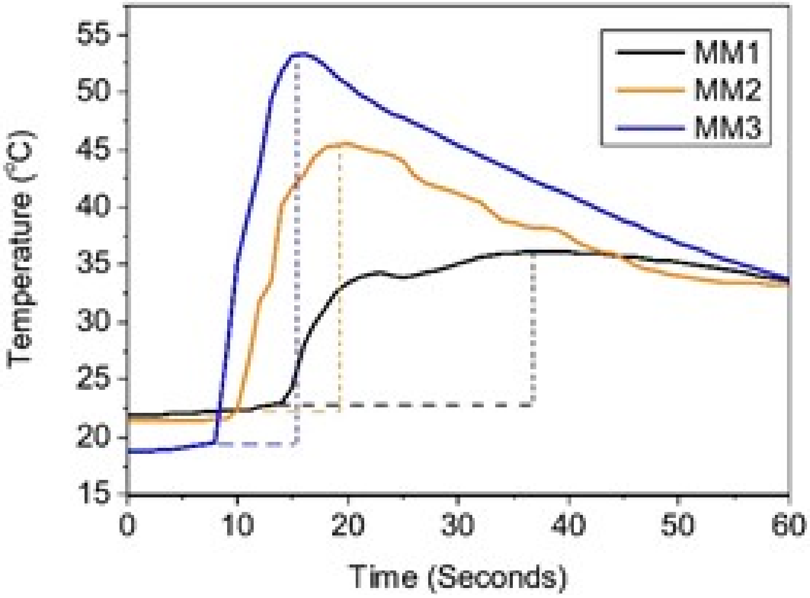

Figure S7. Reaction exotherm profiles for the PU samples printed from MMs.

Table S3. Example reaction exotherm data of PU samples printed from MM1, MM2 and MM3 at first 60 seconds for a single experiment.

Time (s)	**Temperature (^{o}C)**		
	MM1	MM2	MM3
0	21.91	21.45	18.74
1	21.9	21.45	18.73
2	21.9	21.48	18.79
3	21.93	21.52	18.88
4	21.99	21.47	18.97
5	22.09	21.46	19.08
6	22.13	21.47	19.21
7	22.18	21.48	19.35
8	22.28	21.55	19.47
9	22.32	21.67	27.49
10	22.34	22.41	35.22
11	22.32	26.85	39.77
12	22.64	31.74	43.45
13	22.86	33.58	49.48
14	22.99	40.14	51.78
15	24.26	41.67	53.15
16	28.03	42.85	53.38
17	29.8	44.39	52.98
18	31.32	45.29	52.26
19	32.64	45.37	51.34
20	33.41	45.52	50.57
21	33.85	45.28	49.85
22	34.19	44.93	49.24
23	34.28	44.73	48.63
24	34.08	44.47	48.06

25	33.85	44	47.77
26	34.07	42.84	47.37
27	34.33	42.14	46.84
28	34.51	41.73	46.36
29	34.74	41.47	45.87
30	35.11	41.15	45.37
31	35.37	40.76	44.92
32	35.63	40.38	44.5
33	35.84	39.61	44.06
34	35.96	38.88	43.59
35	36.02	38.6	43.13
36	36.05	38.37	42.7
37	36.07	38.18	42.28
38	36.07	38.14	41.85
39	36.06	38.02	41.42
40	36.04	37.46	40.97
41	36	36.93	40.55
42	35.95	36.48	40.12
43	35.9	36.16	39.7
44	35.81	35.91	39.28
45	35.71	35.59	38.85
46	35.62	34.99	38.44
47	35.48	34.64	38.02
48	35.38	34.41	37.64
49	35.32	34.18	37.26
50	35.18	34.01	36.9
51	35.01	33.87	36.55
52	34.87	33.76	36.19
53	34.74	33.63	35.84
54	34.57	33.41	35.52
55	34.42	33.41	35.2
56	34.26	33.37	34.87
57	34.06	33.35	34.55
58	33.88	33.32	34.26
59	33.76	33.28	33.96
60	33.61	33.26	33.68

The rate of reaction exotherm is calculated according to equation S2. T_1 and T_2 are the sample temperature at t_1 and t_2, respectively, whereas t_1 and t_2 are the starting point when the temperature increased and the time when peak temperature was reached, respectively.

$$\Delta T/\Delta t = \frac{T_2 - T_1}{t_2 - t_1} \qquad \text{(S2)}$$

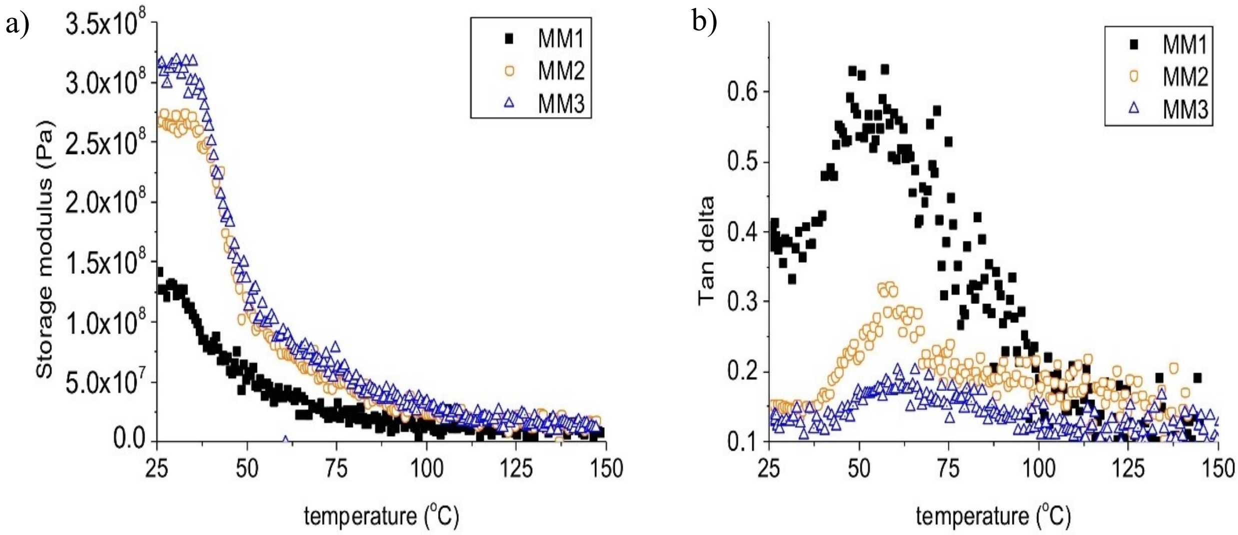

Figure S8. DMA temperature scans of PU samples from three mixing modes, (a) storage modulus and (b) tan delta.

Table S4. Standardised printing parameters adopted for woodpile feature block structures for the MM3 formulation**.**

Parameters	Values (units)
Temperature[i]	Ambient condition
Extrusion flow rate	2 ml/min
Print speed	28mm/s
Layer height	1mm
Infill distance (D_{I_set})	3mm
Infill direction	[0,90]
Infill type	Zig-zag

i. The system temperature and the print bed temperature were all kept at ambient condition throughout all the printing.

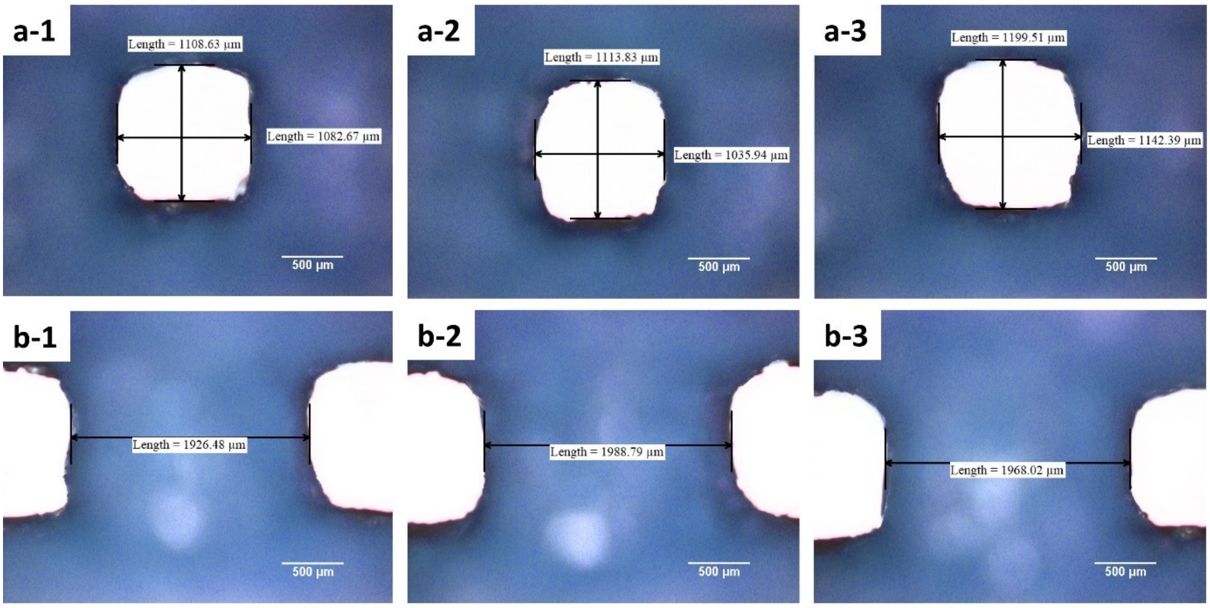

Figure S9. Woodpile feature block size measurements. a-1, a-2, a-3: three separate measurements of W_{b1} and W_{b2}. b-1, b-2 and b-3: three separate measurements of W_L. (W_{b1} and W_{b2}: the width of the block; W_L: Line width; D_I: Infill distance).

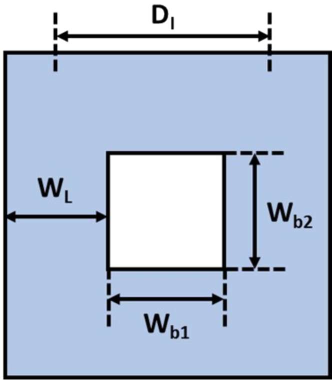

Figure S10. Schematic of block feature (W_{b1} and W_{b2} = the width of the block; W_L - Line width; D_I = Infill distance, i.e. the travel distance between in-plane adjacent beads).

A B C D

Figure S11. Side view of the woodpile prints of MM1 being printed using different layer heights: (A) 0.5, (B) 0.75 and (C) 1 mm respectively. (D) is the MM3 print that is included in the main manuscript as Figure 6 to enable direct comparison The white "bar" has been added to differentiate the new data from the data in the manuscript

Table S5. Block feature size measurements.

Feature block size	1st Measurement (mm)	2nd Measurement (mm)	3rd Measurement (mm)	Average (mm)
D_I	3.034	3.101	3.167	3.101±0.054
W_L	1.926	1.988	1.968	1.961±0.026
W_{b1}	1.108	1.113	1.199	1.140±0.042
W_{b2}	1.082	1.035	1.142	1.086±0.044

Table S6. The calculated percentage deviation of the block woodpile feature

Feature block size	1st Measurement Deviation (%)	2nd Measurement Deviation (%)	3rd Measurement Deviation (%)	Average Deviation (%)
D_I Deviation [i]	1.13%	3.37%	5.57%	3.4
W_L Deviation [ii]	-1.77%	1.39%	0.37%	1.2
W_{b1} Deviation [iii]	-2.81%	-2.37%	5.18%	3.4
W_{b2} Deviation [iv]	-0.40%	-4.73%	5.12%	1.7

i. D_I Deviation=100 x $(D_I-D_{I\_set})/D_{I\_set}$ (Note: D_{I_set} from Table S5)
ii. W_L Deviation=100 x $(W_L- W_{L\_average})/ W_{L\_average}$
iii. W_{b1} Deviation=100 x $(W_{b1}- W_{b1\_average})/ W_{b1\_average}$
iv. W_{b2} Deviation=100 x $(W_{b2}- W_{b2\_average})/ W_{b2\_average}$