Supporting Information

Solvent-assisted rapid manufacturing of free-form soft polymer structures with hierarchical pores

Smruti Parimita[a], Umamaheshwari Ravikumar[b], Hariharan Krishnaswamy[a,e], Pijush Ghosh[c,d,*]

[a]*Manufacturing Engineering Section, Department of Mechanical Engineering, IIT Madras, Chennai-600036, India*
[b]*National Centre for Nanoscience and Nanotechnology, University of Madras, Chennai, India - 600025*
[c]*Department of Applied Mechanics and Biomedical Engineering, Indian Institute of Technology Madras, Chennai-600036, India*
[d]*Centre for Soft and Biological Matter, Indian Institute of Technology Madras, Chennai-600036, India*
[e]*Additive Manufacturing Research Group, Indian Institute of Technology Madras, Chennai-600036, India*

*Corresponding author
Email address: pijush@iitm.ac.in (Pijush Ghosh)

S1. Characterization of suspension bath

In order to characterize the suspension bath, the linear viscoelastic region was studied by varying the strain sweeps from 0.1% to 1000% at a frequency of 1 Hz. The results showed that the suspension bath containing CMC1.0, CMC2.0, and CMC3.0 exhibited liquid-like behavior whereas CMC4.0, CMC5.0, and CMC6.0 showed a gel-like behavior. It can be concluded that the latter compositions were in a solid state at rest and transformed into a fluid state upon shearing the bath (when the nozzle translates shearing the media). The yield stress of the CMC6.0 is 50 Pa (figure S1), which is in agreement with the literature[1].

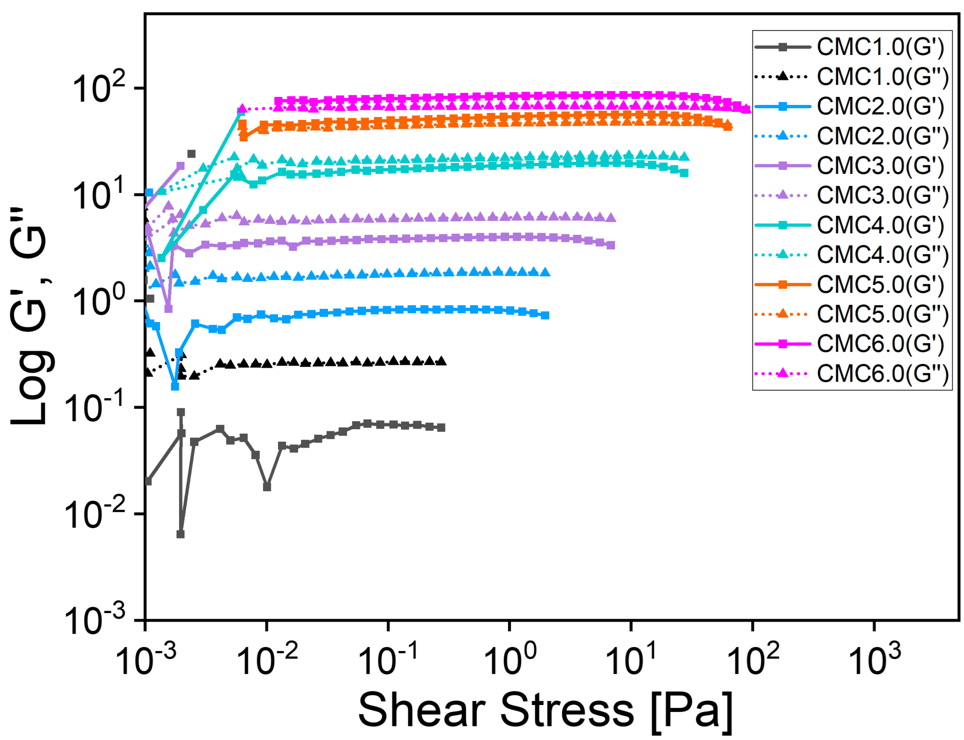

Figure S1: Strain sweeps from 0.1% to 1000% at a frequency of 1 Hz denoting the storage and loss moduli of the suspension bath with different concentrations of CMC

The fidelity of printed structures is ensured by the faster recovery of the supporting bath (media). This property (of the bath) was quantified by simulating a three-interval thixotropy test, as illustrated in fig.S2. During the first step, a shear rate of 0.1 s^{-1} was applied to the CMC hydrogels for 60 s. The second step involves the instantaneous application of a high shear rate, 500 s^{-1}, that was held for 10 s. In the final step, the shear rate was reduced to its initial 0.1 s^{-1} and retained for 120 s. The above three steps correspond to the pre-printing, printing and post-printing stages. The results showed that the CMC6.0 had good thixotropy behavior when applied as a suspension medium.

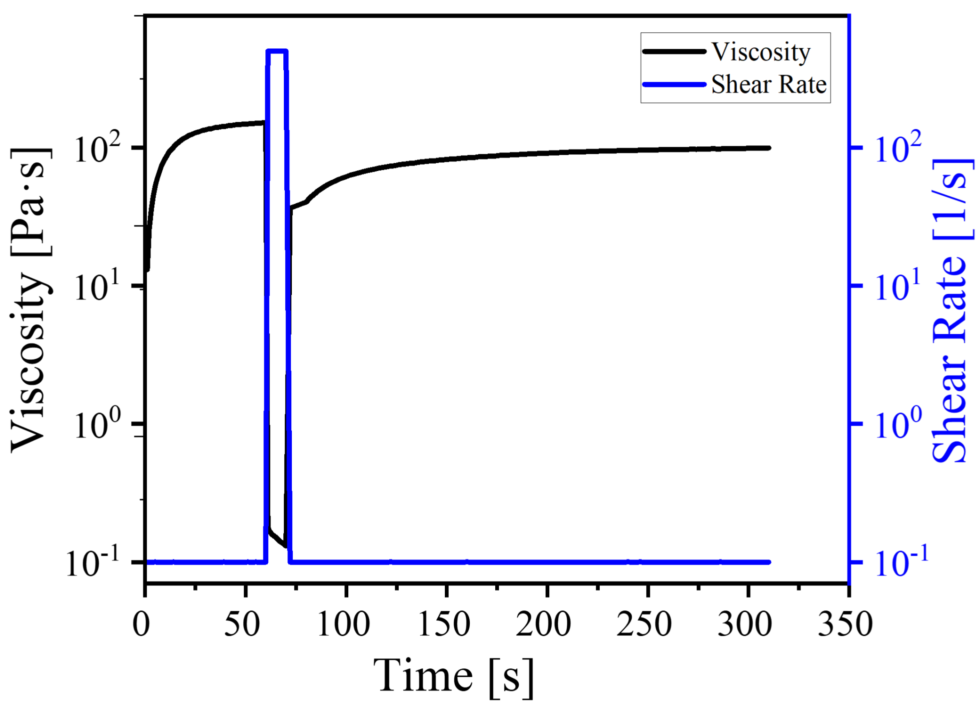

Figure S2: A three-interval thixotropy test of the CMC6.0 suspension bath

S2. Thermogravimetric Analyis

Pyrolysis tests were conducted to ensure the complete removal of residual solvent and non-solvent in the printed structures after the complete phase separation process. The tests were performed in a differential thermogravimetric analyzer (Make: Q500 Hi-Res Thermogravimetric analyser) with a precision of temperature measurement of ± 0.1°C and weight measurement of $\pm 0.01\%$. The sample weight loss and the rate of weight loss were recorded continuously as a function of temperature for 30-300 °C. The experiments were performed at atmospheric pressure, under a nitrogen atmosphere, with a flow rate of 30mL/min at heating rate of 10°C/min. Fig.S3 shows that characteristics plot of the weight loss of the constituents with an increase in temperature. It can concluded from the plot that there was a complete extraction of the solvents in the printed structure.

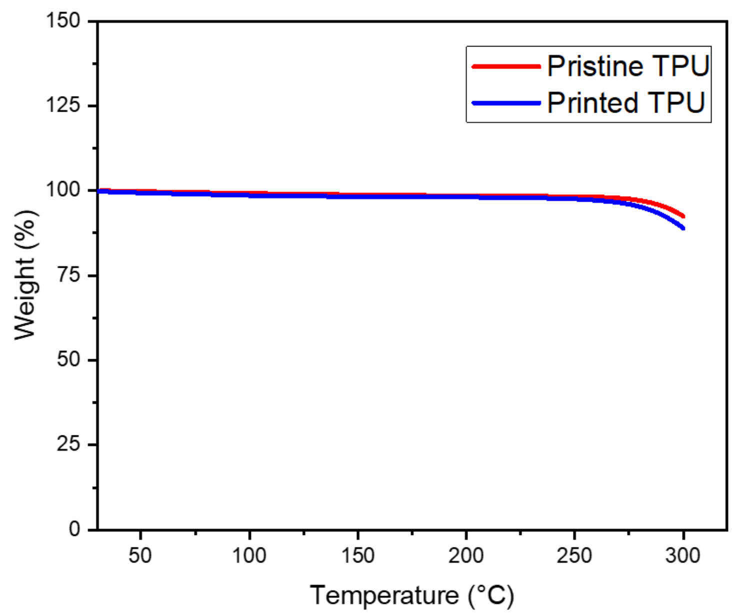

Figure S3: Thermogravimetric analysis (TGA) to investigate presence of a residual solvent or nonsolvent in the fabricated 3D structures by NIPS: weight (%) as a function of the temperature of pristine TPU and 3D printed TPU with a residence time of 30 min in water

S3. Porosity estimation

A liquid displacement method was used to measure the porosity of the samples. The TPU filament (TPU20, TPU40, and TPU60) was cut into equal weight for the test. The initial volume of ethanol was taken in a measuring cylinder, and the volume was recorded as V1. Then, the sample was immersed in ethanol for 10 min until the solution was free of air bubbles, at which time the ethanol completely filled the pores of the samples, and the new volume was recorded as V2. After removing the sample, the remaining volume of ethanol was recorded as V3. The porosity was calculated as

$$Porosity = \frac{V1 - V3}{V2 - V3} X100\% \tag{1}$$

S4. SEM image of outer surface

The outer surface of the 3D printed structure was rough in nature but didn't show significant porosity unlike the inner cross-section images of the structures.

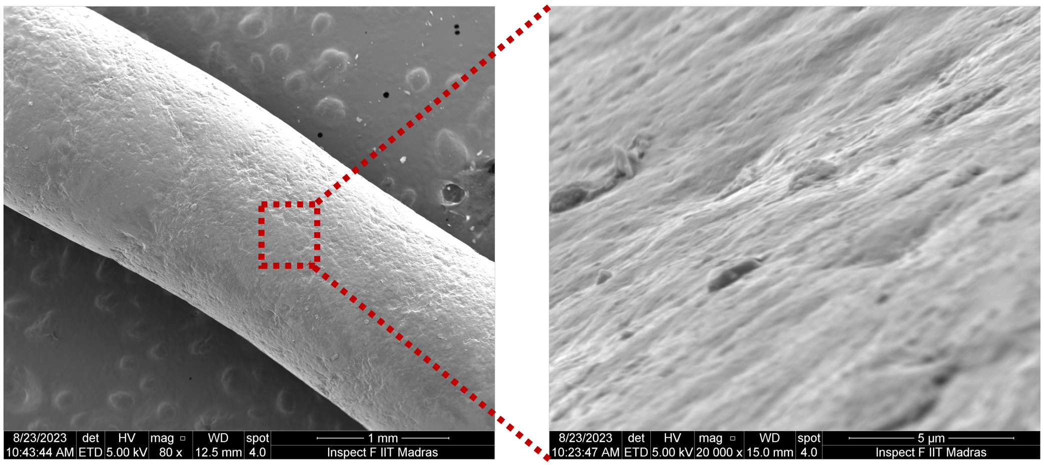

Figure S4: SEM image of the outer surface of the LLPS-3D printed filament

S5. Printing parameter analysis

The printing parameters, such as extrusion pressure and printing speed influencing the rapid-liquid printing in suspension medium were studied. Different compositions were tested using nozzle diameters of 10G, 15G, and 23G. The TPU ink was less viscous (compared to ink printed using DIW in air) and, therefore, was easily extrudable using the three nozzles. However, a 10G nozzle cannot be utilized to print small structures due to lower resolution, and 23G resulted in filaments that coiled upon further air-drying. Therefore, all our studies were carried out using a 15G nozzle. The nozzle-to-substrate distance was adjusted to achieve good print fidelity.

The influence of the extrusion pressure was studied by extruding the TPU ink in a water (non-solvent) bath using a 15G nozzle. At 0.5 bar, the extrusion was inconsistent irrespective of the compositions. Upon increasing the extrusion pressure, continuous filaments were formed. However, high pressure resulted in a die-swelling effect in the filament. A pressure range of 1 to 5 bar was found to extrude the tested inks without die swelling defects.

The influence of printing speed (S) was studied by printing a 20mm straight line in the suspension medium. The printing speed was varied from 1-5mm/sec. The diameter of the filament was measured at different printing speeds and is plotted in figure S5. It was observed that an increase in printing speed resulted in progressive fiber thinning and lack of ink deposition in the suspension media, as the 3D printer does not have enough time to deposit the ink. However, slower speed resulted in a larger variation of the diameter of filament in comparison to nozzle diameter of 1.5 mm. Table S1 lists the experimental details carried out. This study provides insights into corresponding input parameters such as printing speed, printing pressure, nozzle diameter, and layer thickness during the slicing of the 3D model. Based on the study, a set of printing parameters was chosen to print complex structures. The quantified error in filament diameter, layer thickness, and line width (obtained using image analysis) were added and given as input parameters in the slicing software.

Table S1: Optimised printing parameters for printing TPU structures

Concentration of TPU, TPU_n(%(w/v)	TPU20	TPU30	TPU40	TPU50	TPU60
Extrusion pressure, P (bar)	5	4	3	2	1
Printing speed,S (mm/sec)	1	2	3	4	5

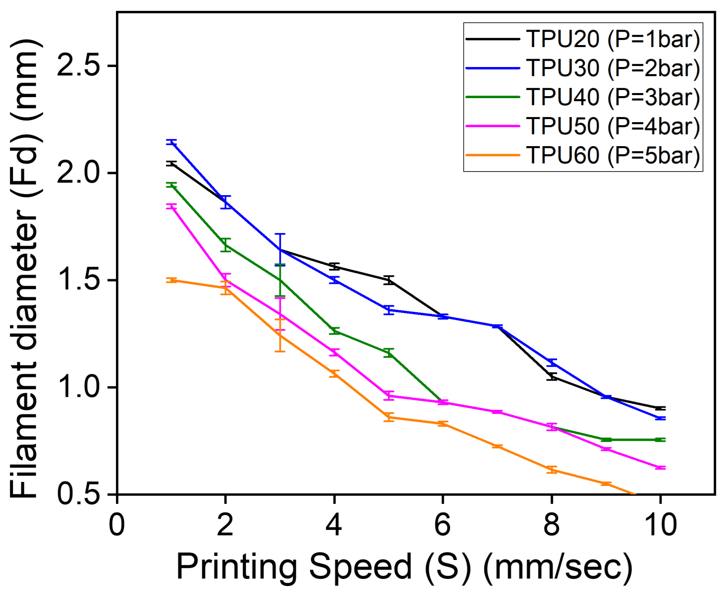

Figure S5: Study of printing parameters with varying TPU compositions

S6. 3D printing of free-form structures

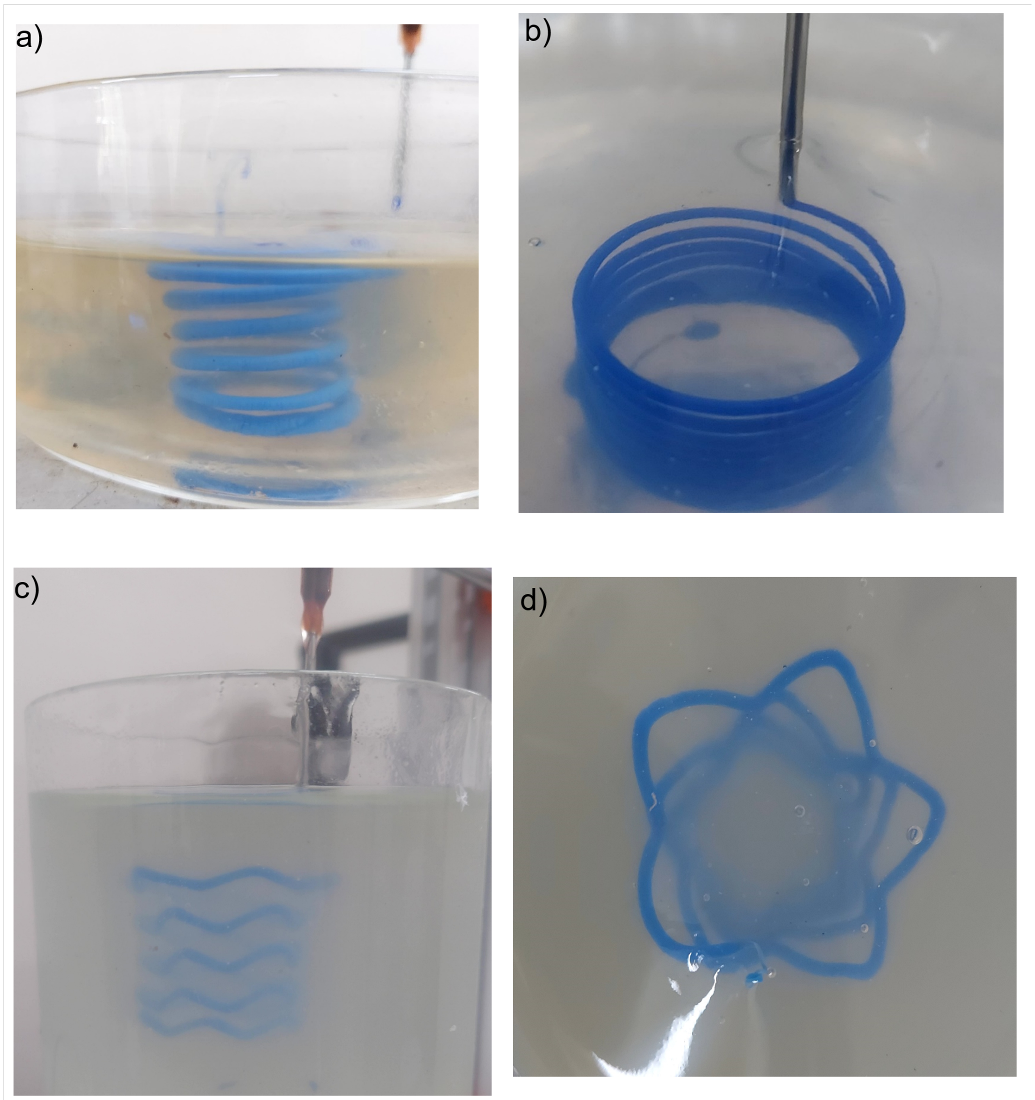

Figure S6: Real-time image of a spring-like free-form structure printed inside a suspension medium without any physical support a) and c)-Side view and b) and d)-top view),

S7. Supplementary videos

SV1: LLPS-3D printing of polymer in water, demonstrating phase separation of polymer ink in nonsolvent
SV2: Printing a grid/scaffold-like structure in water
SV3: Printing a star-shaped structure in water
SV4: Printing inside a 0% CMC gel (water) suspension medium
SV5: Printing inside a 3% CMC gel suspension medium
SV6: Printing inside a 6% CMC gel suspension medium
SV7: Printing a freeform circular spring in a CMC gel suspension medium
SV8: Printing a freeform square spring in a CMC gel suspension medium
SV9: Printing a freeform flower spring in a CMC gel suspension medium

References

[1] R. Karyappa, T. Ching, M. Hashimoto, Embedded ink writing (eiw) of polysiloxane inks, ACS applied materials & interfaces 12 (20) (2020) 23565–23575.