Supporting Information

Solvent triggered shape morphism of 4D printed hydrogels

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1. Rheological characterization

In rheological testing, flow behaviour, shear thinning behaviour and angular frequency sweep of the hydrogels were investigated by varying the percentage of chitosan from 1-8%. Fig. S1a) revealed the flow behaviours of different hydrogels, in which sol-like 1-5% chitosan hydrogels exhibited a good gravity-induced flow.The 6% and 7% hydrogels remained stable after inverting the hydrogel-containing tubes for 5 min after which it flowed due to gravity.The 8% chitosan hydrogel exhibited a good gel-like behaviour and didn't flow even at 10 min, indicating that it can form stable structures post-printing.In the shear thinning test, as shown in fig. S1b), it was found that the viscosity of all the hydrogel samples was decreased with the increased shear rate, demonstrating a shear thinning behaviour. Besides, 1-5% exhibited the lowest viscosity among the entire shear rate, suggesting that they had a poor printability. Interestingly, the viscosity of 6-8% were higher, showing that chitosan acts a viscosity modifier to enhance printability.The viscosity of 8% was highest at low shear rate among all and did not flow after 10 min due to gravity, therefore the ink with 8% chitosan was the most suitable composition to form stable 3D structures.

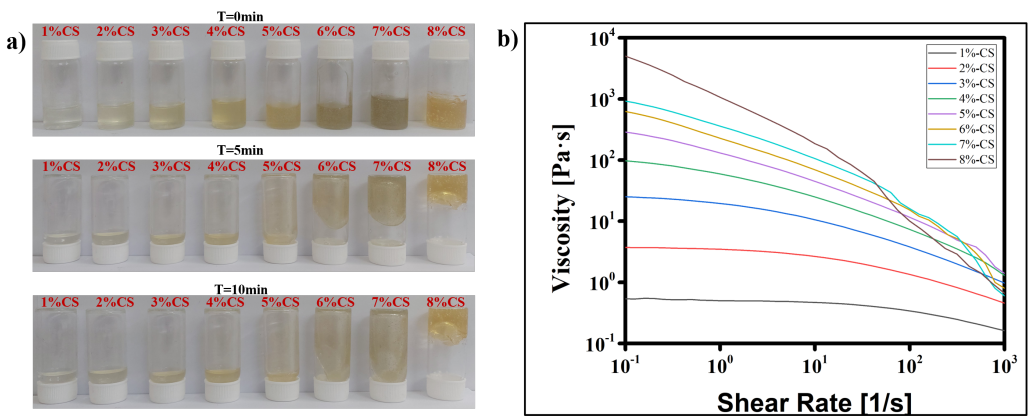


Figure S1: Printability of 1-8% chitosan hydrogel: a) flow behaviour of each hydrogel, b) viscosity as a function of shear rate at room temperature

2. Crosslinking procedure and mechanism

The samples were 3D printed using chitosan ink (the ink contains citric acid, but it's not yet cross-linked).All the samples were treated at 50°C in a vaccum oven for 24 hours and the samples obtained were termed an un-crosslinked printed samples.To obtain cross-linked samples, the dried uncross linked samples containing citric acid were treated at 150°C for 10 min in an oven for the crosslinking reaction to take place as shown in fig. S2 [1].

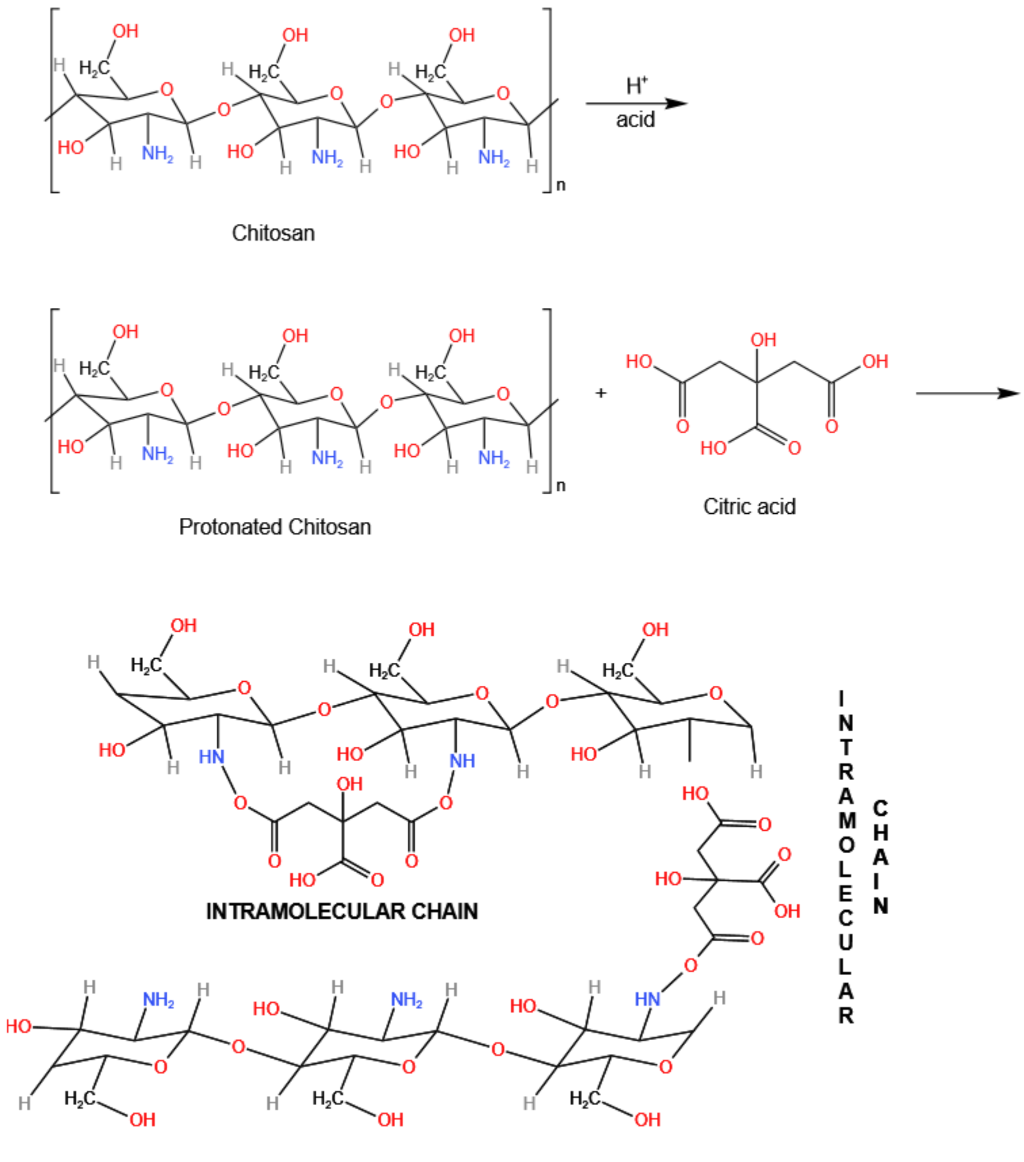


Figure S2: Crosslinking mechanism of chitosan with citric acid

To study the effect of crosslinking and mechanism of crosslinking, swelling measurements and FTIR analysis were conducted.

- **Swelling measurements**

  Samples of diameter 20 mm were 3D printed for the swelling measurements.The swelling degree of the uncrosslinked, and cross-linked printed samples were measured by gravimetric method.Samples of each system were immersed into 100ml of distilled water.Weight of each sample was measured before (W_1) and after immersion (W_2) for 24 hours at room temperature.Swelling degree was calculated by the following equation:

  $$S\% = (W_2 - W_1)/W_1 * 100 \tag{1}$$

  Measurements were taken in triplicate for each system. The results showed that the uncrosslinked samples and cross-linked samples had swelling degree of 1550% and 250% respectively.The decreasing in the swelling values in the citric acid cross-linked structures could be explained by a higher crosslinking degree, which reduced the free volume and chain mobility, thus, hindering the water entry in the networks[2, 3].

- **Fourier Transform Infrared Spectrophotometer**

  The FTIR spectra of chitosan samples were obtained by using Bruker's fourier transform infrared spectrophotometer.64 scans were collected in the range 800-4000 cm^{-1} with a resolution of 8 cm^{-1}. The IR spectra were analysed using lab solutions series software.

  Fig.S3 shows the ATR-FTIR spectrum of the chitosan(CS) and chitosan-citric acid(CS-CA) cross-linked films.The main characteristic bands associated with chitosan molecular were detected from the spectra.The amide I band is associated with stretching vibrations of C-O and appears at 1642 cm^{-1}.While,the amide II associated with C-N stretching and N-H vibration, has a band at 1577 cm1.The ATR-FTIR result implies that citric acid has been cross-linked with the chitosan molecules at 150°C for 10 min successfully.

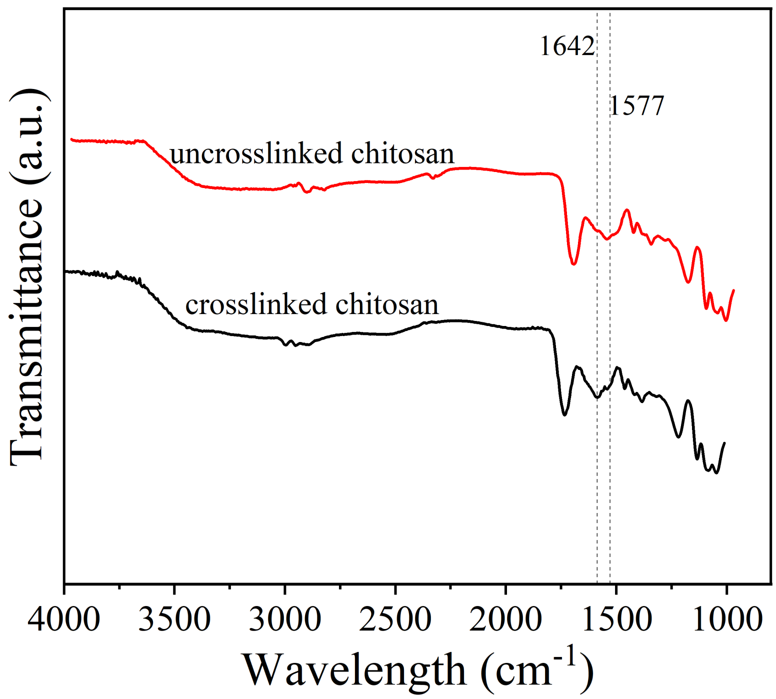


Figure S3: FTIR spectra of 3D printed chitosan films before and after the crosslinking with citric acid

3. Printability and shape fidelity

- Study of extrusion pressure (see figureS4)
- Study of printing speed (see figure S5)
- Analysis of shape fidelity (see figure S6)

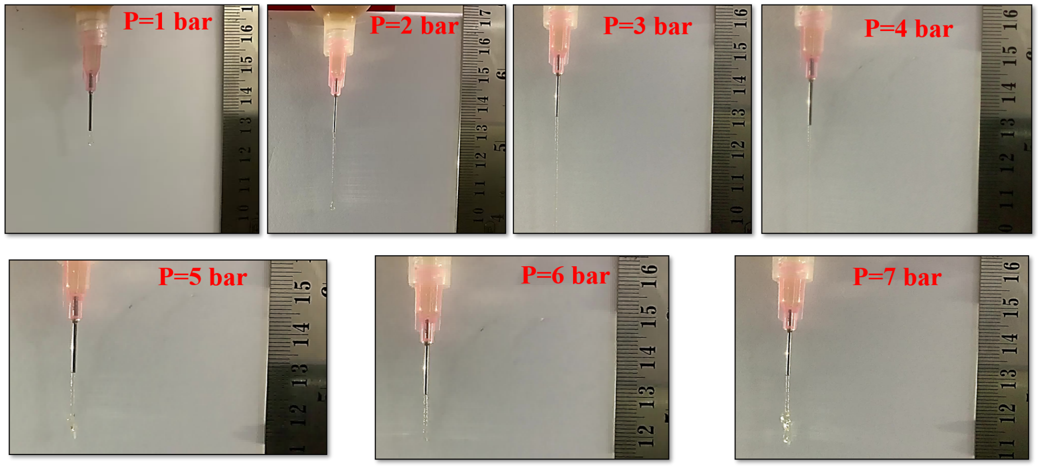


Figure S4: Study of extrusion pressure at different pressure(1-7 bar)

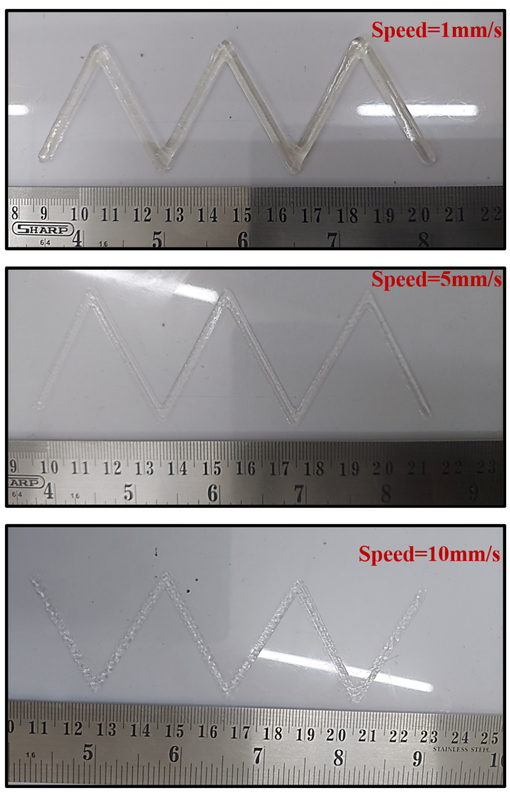
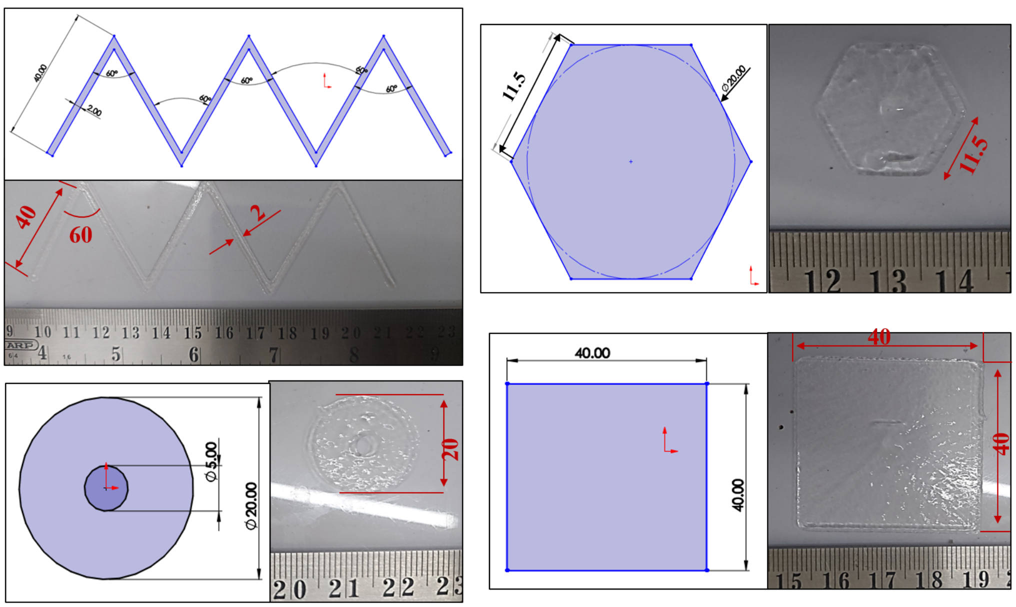


Figure S5: Study of printability at different printing speed(1-10 mm/s)



All dimensions are in mm

Figure S6: Comparison of designed part with printed structures using optimal printing parameters

References

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