Superelastic and flexible 3D printed waterborne polyurethane/cellulose nanofibrils structures

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OUTLINE

I Introduction

1.1 Waterborne polyurethane (WPU)

WPU fully reacted urethane polymers dispersed in water, in addition to offering the high performance modern applications need, they contain no residual free isocyanate and a low odor, making them safer and easier to use than the alternative.

- **Advantages of WPU**
  - Solvent free polymers available
  - Tunable chemical structure
  - High tensile strength and elongation
  - Chemical/UV/water resistance
  - Low VOC
  - Biodegradablity
  - Biocompatibility

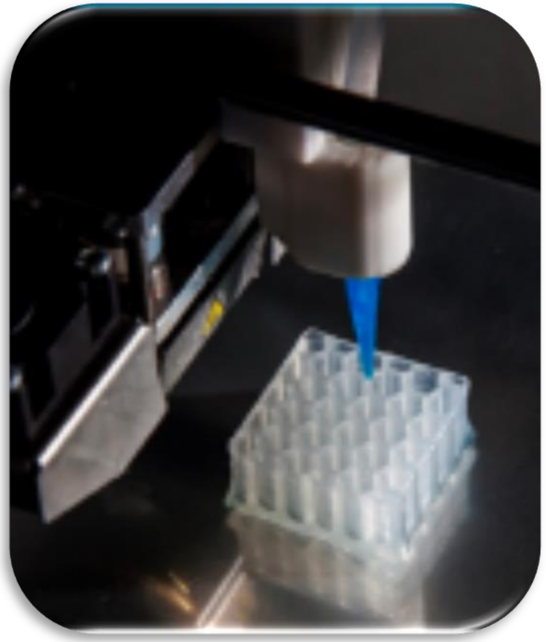
- **Applications**
  - Coatings
  - Graphic arts
  - Adhesives
  - Miscellaneous

1.1 Waterborne polyurethane (WPU)

Drawback of WPU for 3D printing: Low viscosity

Why is 3D printing?

3D printing, or additive manufacturing, rapidly develops to become a promising material fabrication method by layer-by-layer additive manufacturing aimed by a computer design system.



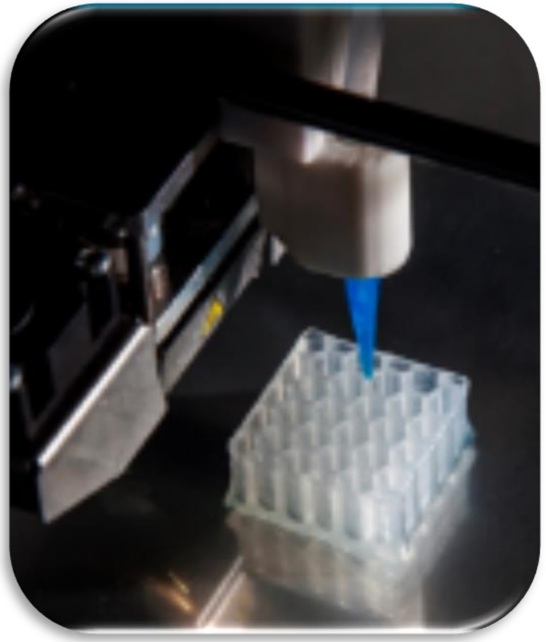
Numerous raw materials: ceramic, nanocellulose, graphene, carbon nanotubes, and polymer…

I Introduction

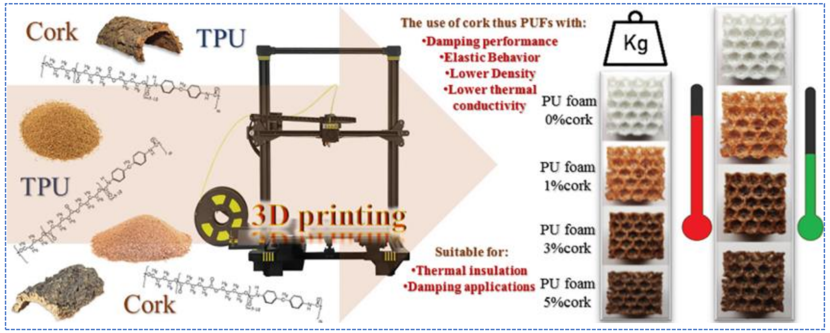
1.1 Waterborne polyurethane (WPU)

- **Features**

✓ Precise control
✓ Digital control
✓ Layer-by-layer



Polyurethane 3D printing material
（Sculpteo Corp.）

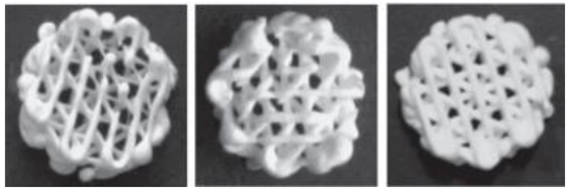


Materials & Design, 2019,179,107905

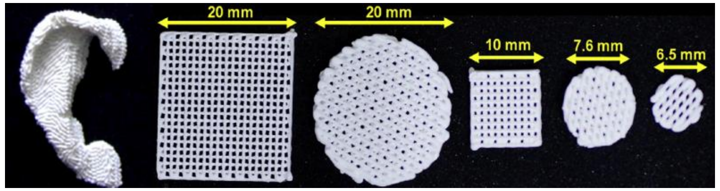
I Introduction

1.1 Waterborne polyurethane (WPU)

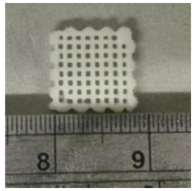
WPU-BASED 3D PRINTING- REFERENCES



WPU-polyethylene oxide



WPU-hyaluronan



WPU-CNF

Drawback of WPU-based 3D printing

- Creep recoverability
- Complex compounding processes
- Rigorous printing demands (-40 ℃~5 ℃)
- Small dimension of printed limited to a lower height (about 2.5 mm)
- Lower printing accuracy

Carbohydrate Polymers 2019, 212, 75–88; Adv. Healthcare Mater. 2014, 3, 1578–1587; Biomaterials 2016, 83 , 156-168.

I Introduction

1.2 Cellulose nanofibrils (CNF)

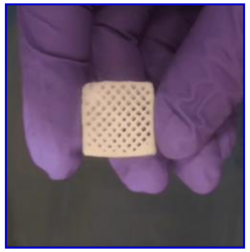
Cellulose Nanofibril (CNF)

Properties

Abundant	Renewable	Biodegradable

3D printing

Strength Rigidity

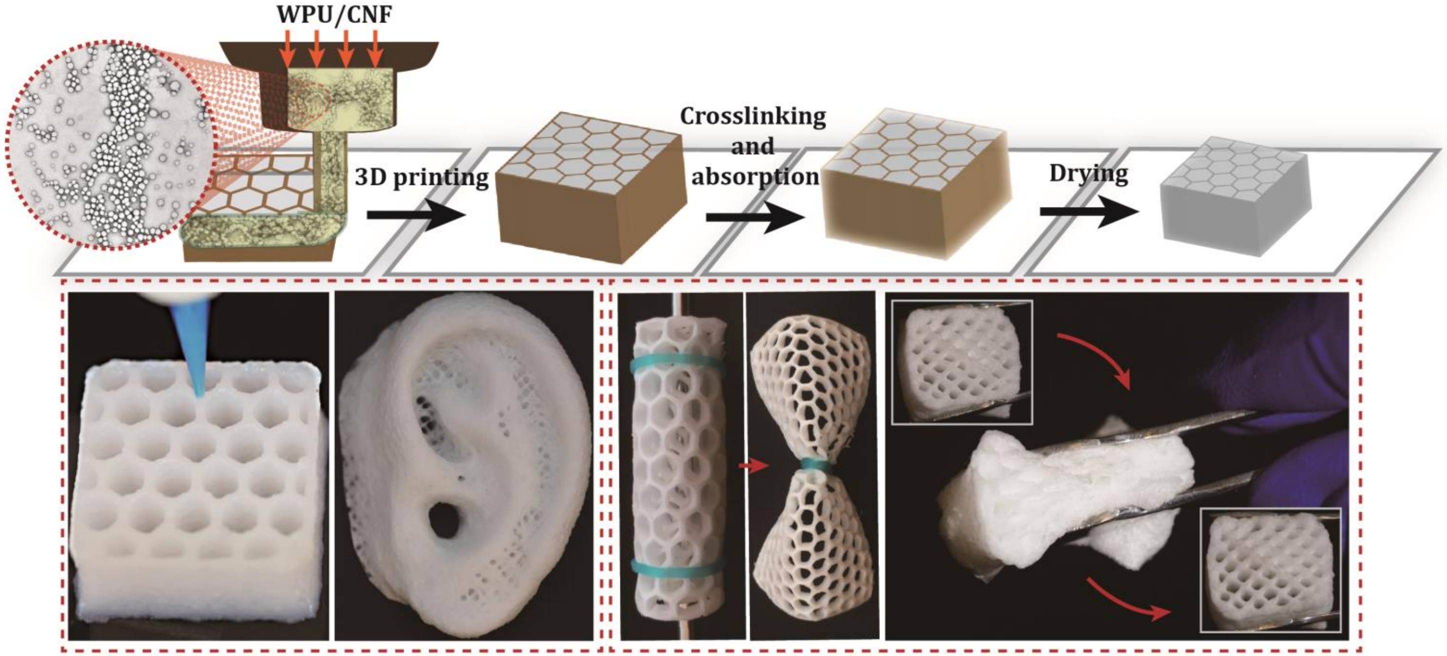


Superelasticity

Ⅱ Targets and Methods

2.1 Targets

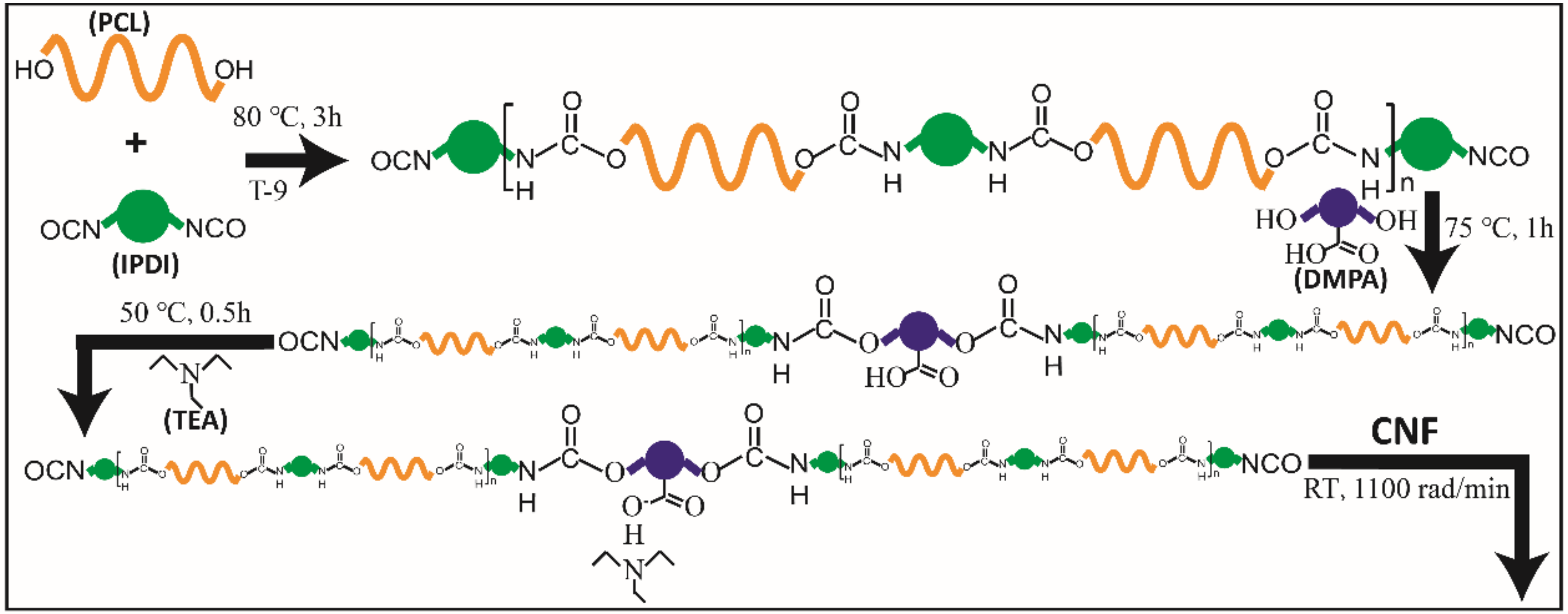
Cellulose nanofibrils (CNF) can enhance the printability of waterborne polyurethane (WPU) and WPU/CNF ink to fabricate flexible 3D printing scaffolds.



Enhanced Printability **High Flexibility**

2.2 Methods

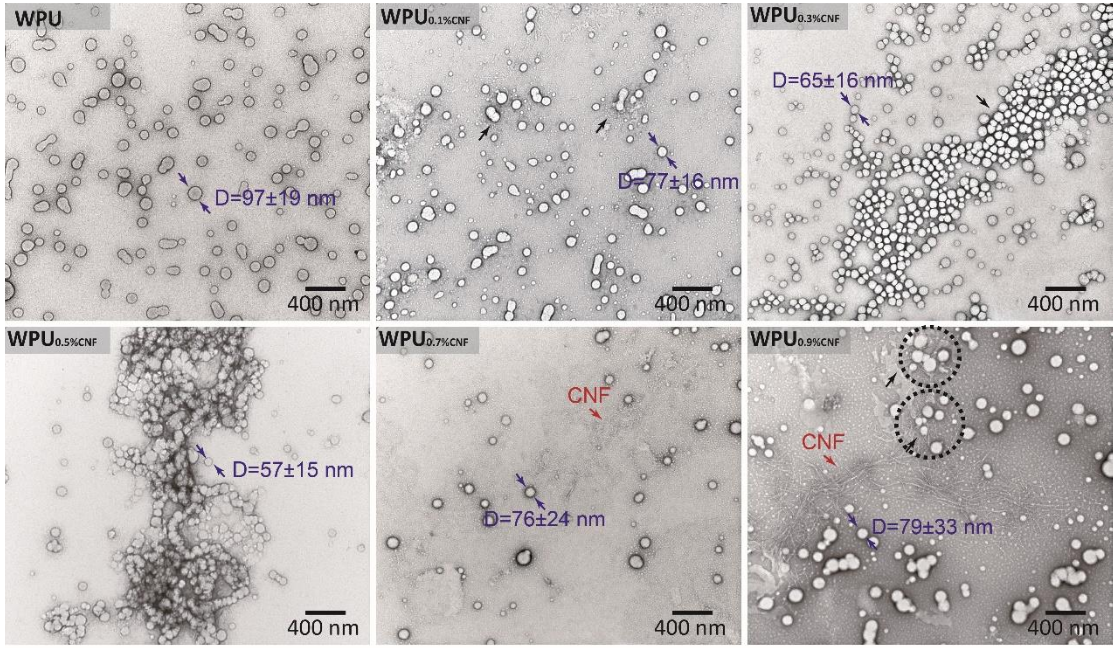
In-situ synthesis of WPU/CNF suspension.



3.1 Synthesis and rheological characterization of WPU_{CNF}

WPU was synthesized with in-situ emulsification by CNF, showing

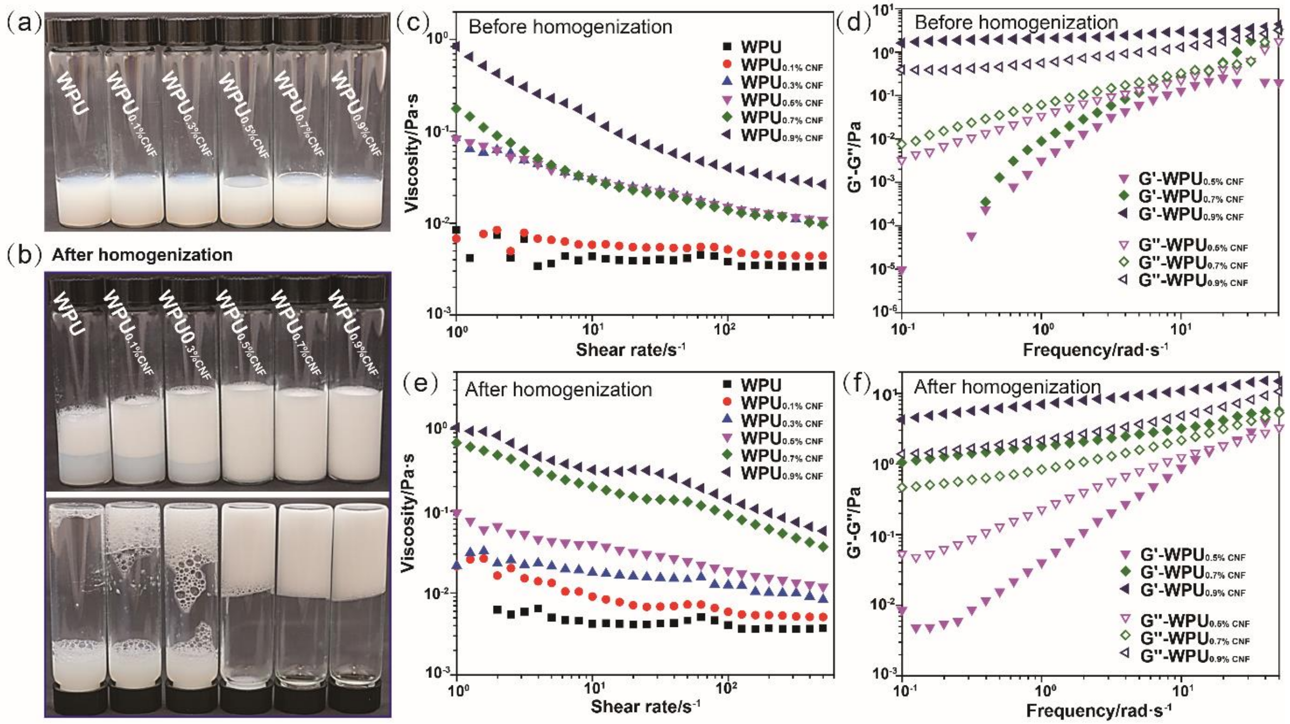
- Reduced WPU particle sizes
- Bead-on-String structure



3.1 Synthesis and rheological characterization of WPU_{CNF}

WPU was synthesized with in-situ emulsification by CNF, showing

- Enhanced viscosity
- Stabilized emulsion

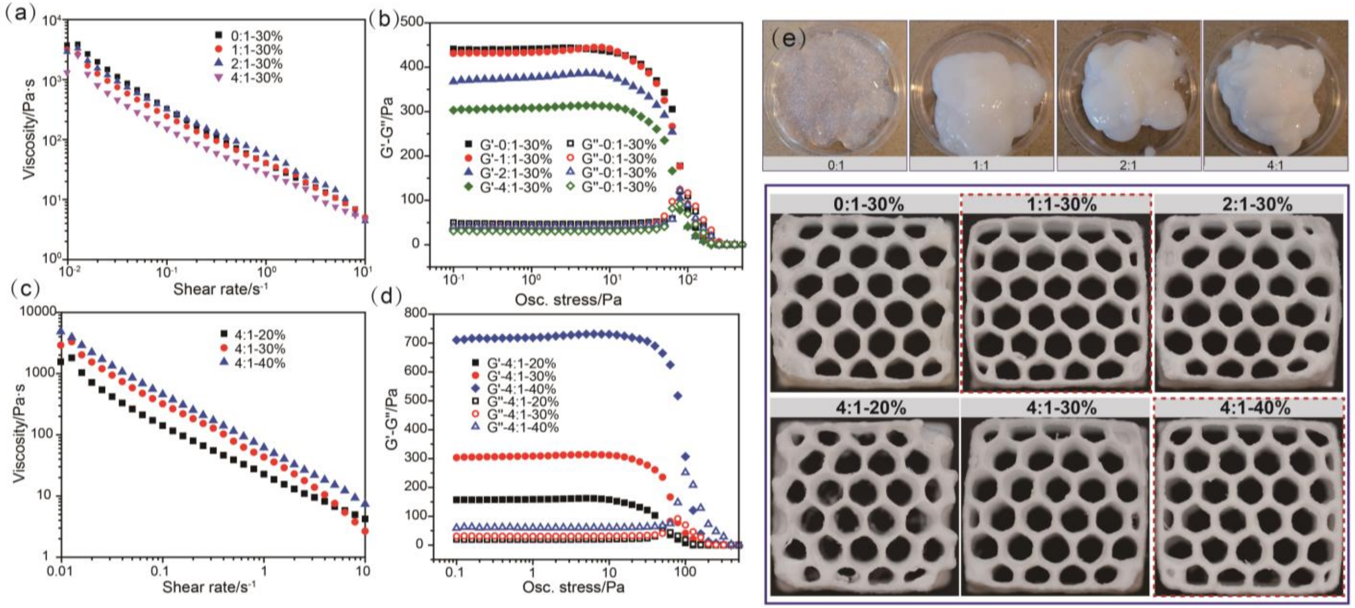


Ⅲ Results and Discussion

3.2 3D printing of WPU$_{CNF}$/CNF composite ink

Enhanced Printability

Printing inks are composed of WPU-0.9%CNF and 1% CNF with different ratios after dewatering.



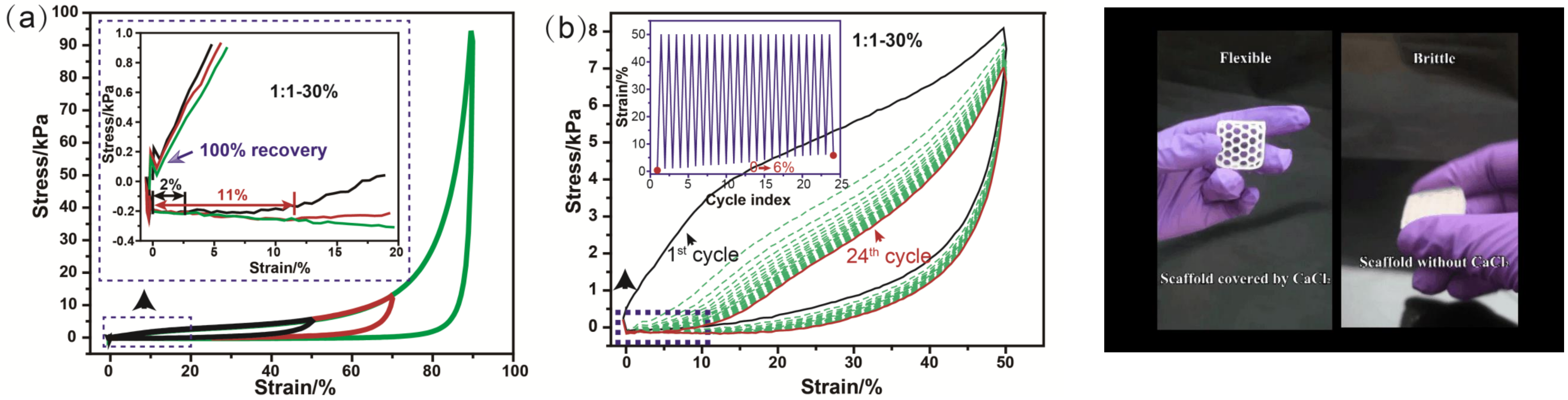
- ➢Ink designation - WPU:CNF-dewater%
- ➢All inks show high zero-shear viscosity and shear-thinning properties, ideal for 3D printing and shape fidelity
- ➢Inks of 1:1-30% and 4:1-40% show the best printing performance, with approximate 1.4% CNF concentration

Ⅲ Results and Discussion

3.3 Superelastic behavior of 3D printed structures

High Flexibility

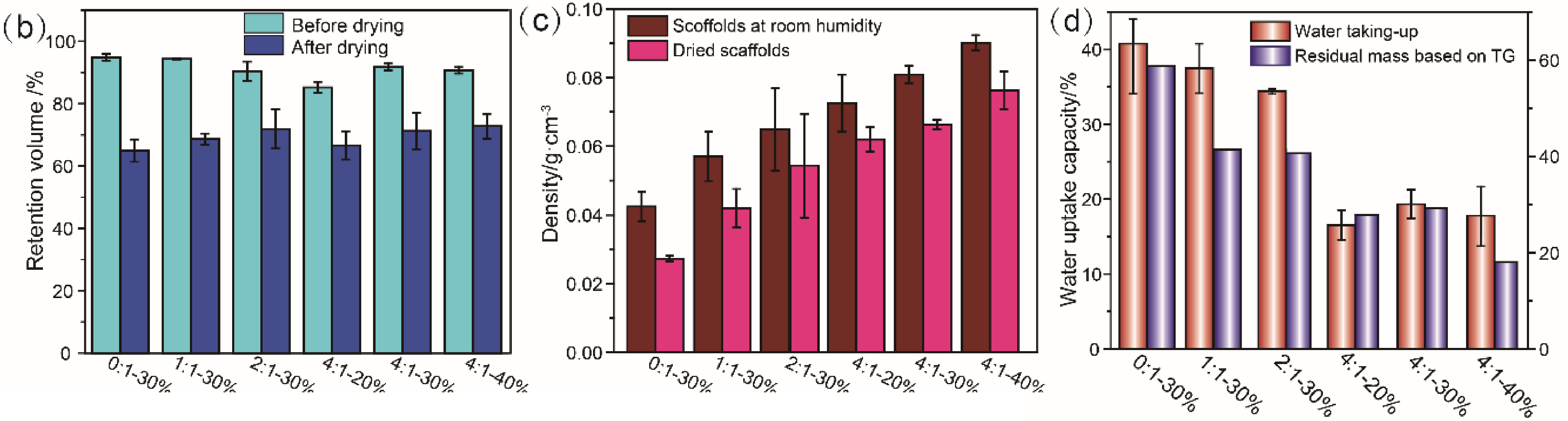
Mechanism of $CaCl_2$ crosslinking and water absorption on cellulose nanofibrils and apparent flexibility .



The compressive stress-strain curves of 3D printed scaffolds showed excellent compressibility and shape recovery performance.

Ⅲ Results and Discussion

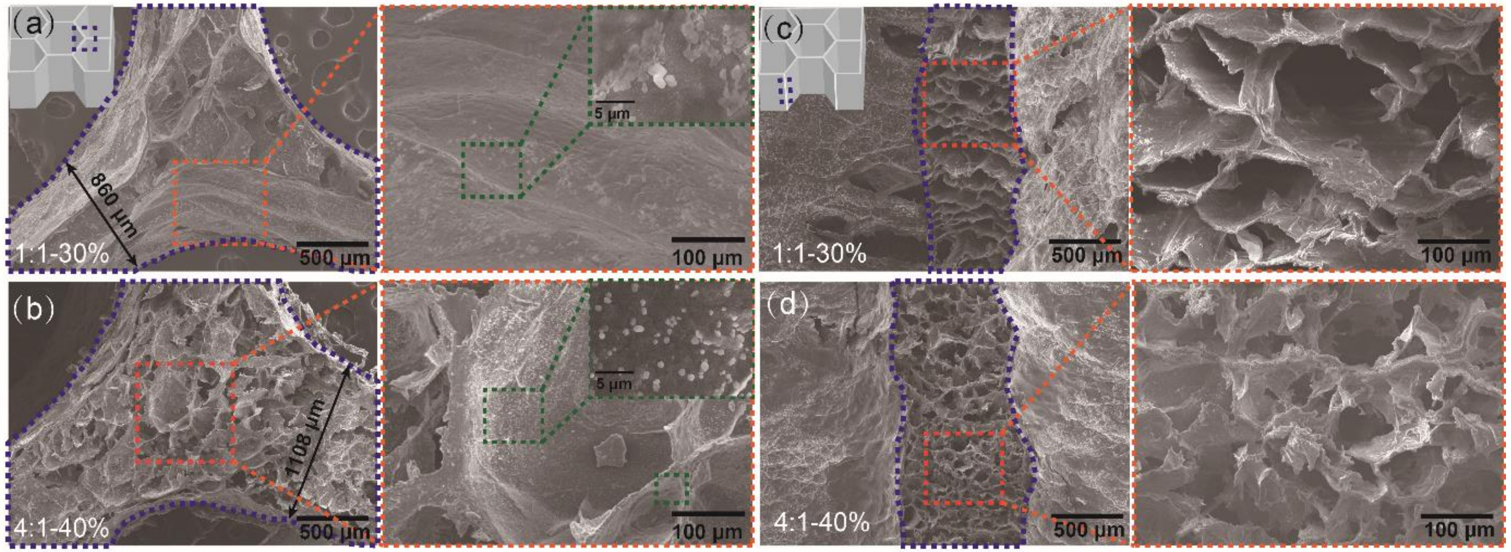
3.4 Chemical characterization of 3D printed structure



- Over 90% originally designed volume could be retained after 3D printing, and 65-73% after freeze-drying.
- The densities of all monoliths under 43±3% relative humidity are higher than the dried state.
- WPU_{CNF}/CNF scaffolds present high water uptake capacity of 17%~37%.
- The ash yield indicates that the water absorption by the 3D printed CNF monoliths is mainly due to the hygroscopic salt.

Ⅲ Results and Discussion

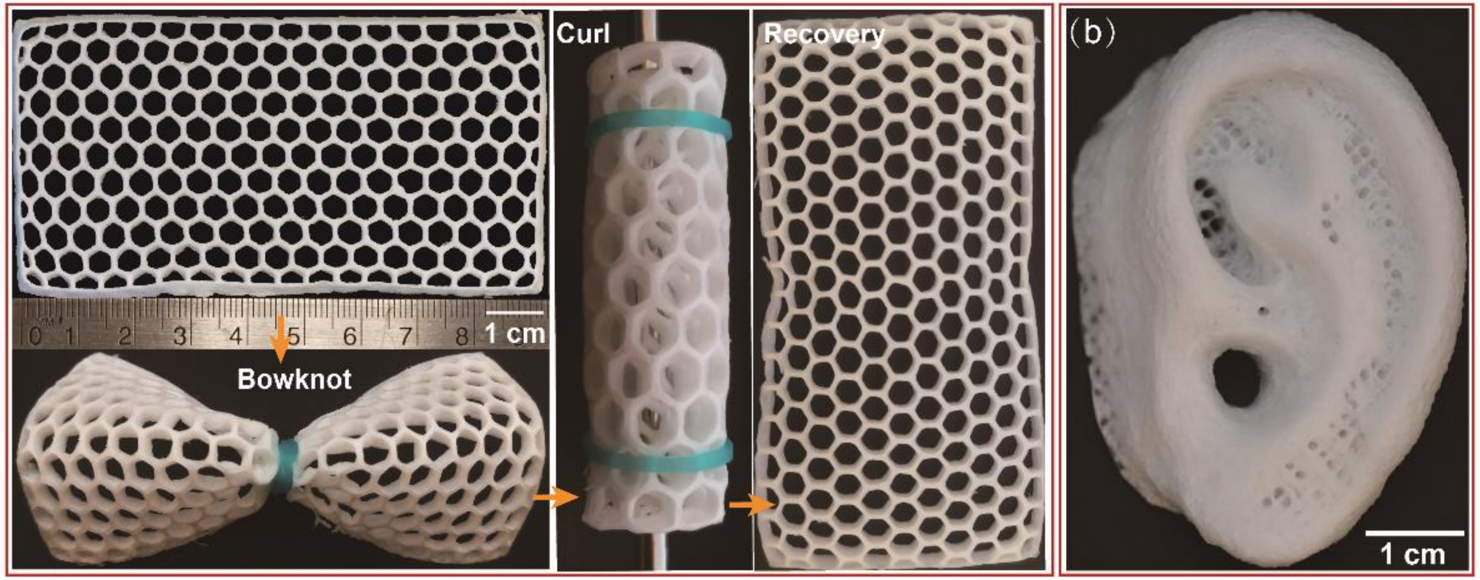
3.5 Morphological characterization of 3D printed structure



- The cross-section of 3D printing scaffolds of at optimized printing parameters of 1:1-30% and 4:1-40%.
- The high magnification with green frame showed the morphology and coverage density of $CaCl_2$ covering on 1:1-30% and 4:1-40% cell walls.
- The longitudinal direction of all scaffolds exhibit the similar porous layered stacking structure formed by layer-by-layer printing.

Ⅲ Results and Discussion

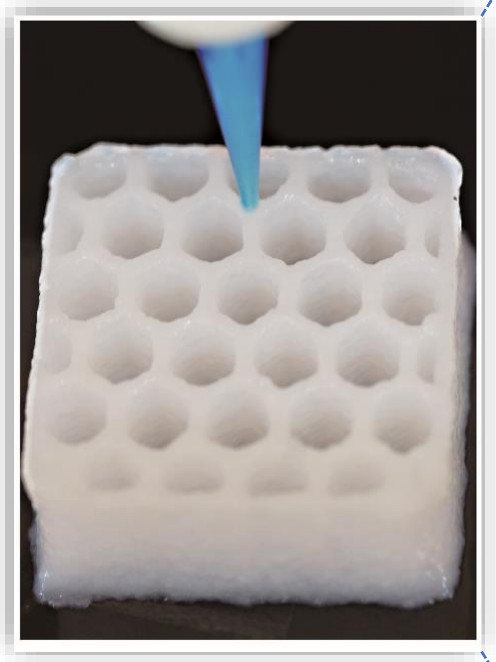
3.6 Complex 3D structure printing

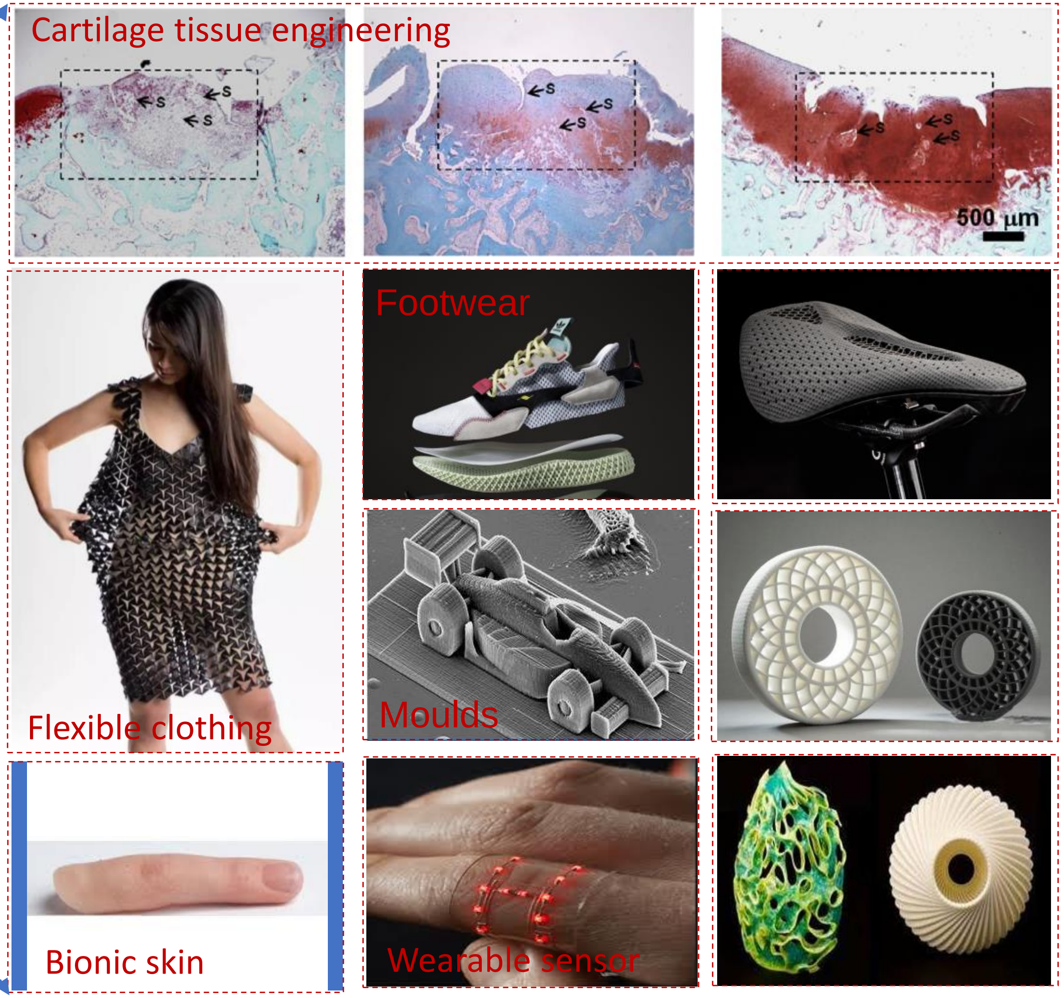


Freeze-dried 3D printed objects with different shapes and dimensions using 4:1-40% WPUCNF/CNF ink:

- **Large scale honeycomb structure (100 × 50 × 5 mm^3) that can be twisted into a bowtie structure and rolled around a stick, as well as recover from the deformation;**
- **A complex human ear shape.**

3.7 Future applications





Biomaterials 2016,83, 156-168

3.8 Conclusions

- In-situ emulsification of waterborne polyurethane with CNF is demonstrated to enhance the suspension viscosity;
- 3D printable WPU/CNF ink is prepared by complexation with additional CNF, post-homogenization, and dewatering, showing improved structural integrity and shape fidelity;
- Divalent hygroscopic salt is used to crosslink CNF and absorb water to enhance the compressibility and flexibility of the 3D printed structure.

Thank you

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