Facilely prepared starch-based ionic conductive hydrogel, batteries, and self-powered sensors with strain-sensitivity

David Fengwei Xie

EPSRC Fellow

School of Engineering, Newcastle University, UK

david.xie@newcastle.ac.uk

@FengweiXie

www.fwxie.com

Renewably sourced

Renewable and non-biodegradable

- Bio-PE, Bio-PP, Bio-PET, Bio-PAs, Bio-PUs, PEF
- PC

Renewably sourced and biodegradable

- Natural biopolymers (e.g. cellulose, starch)
- PHA
- PLA

Non-biodegradable

Biodegradable

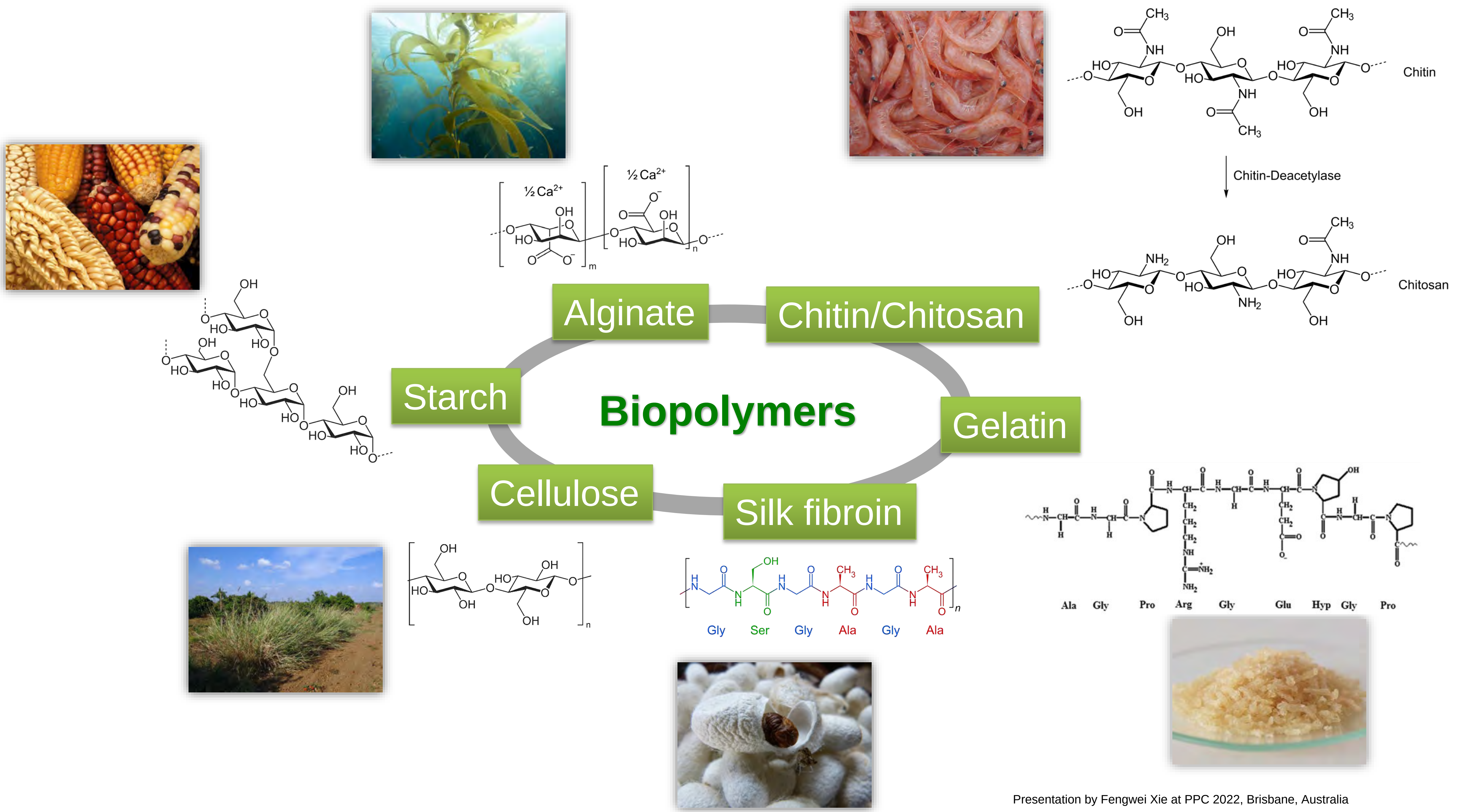
Fossil-based and non-biodegradable

- PE, PP, PET, …

Fossil-based and biodegradable

- PCL, PBAT, PBS
- PVA

Fossil-based

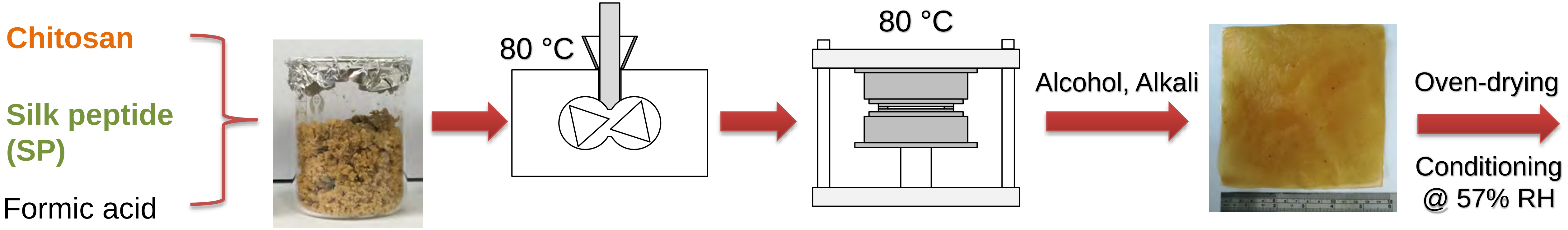


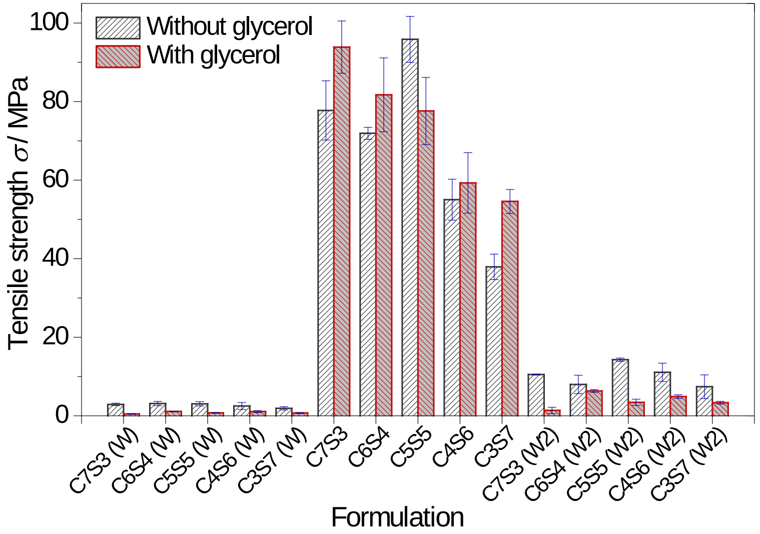
Presentation by Fengwei Xie at PPC 2022, Brisbane, Australia

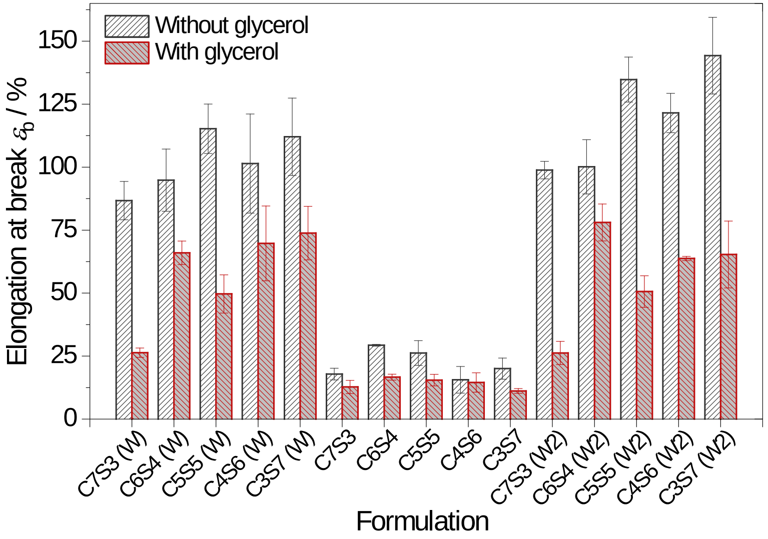
Our research

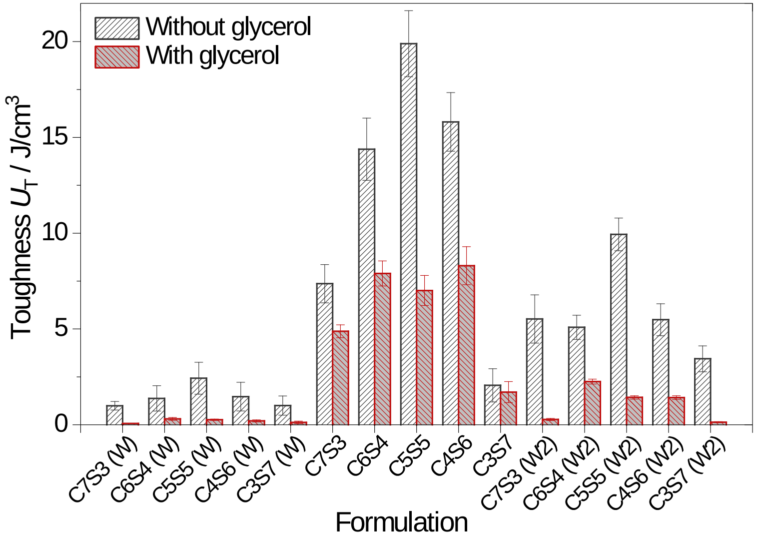
Fundamental Materials Science	Advanced polymer engineering	Smart materials design
• Structural characterisation • Interactions between components • Structure–property/function relationships	• Cost-effective processing • Innovative engineering processes • Processing–structure relationships	• Physical and chemical modification • Materials hybridisation • Polymer (nano)composites

Chitosan/silk peptide composites









Mechanical properties

C5S5 after drying & conditioning @57%RH for 3 wks:
Tensile strength: 95.9 MPa (32 times)
Y's modulus: 1855 MPa (580 times)
Toughness: 19.9 J/cm^{-3} (8.3 times)

Meng, L. et al. *ACS Sustainable Chem. Eng.* 2019, 7 (2), 2792-2802

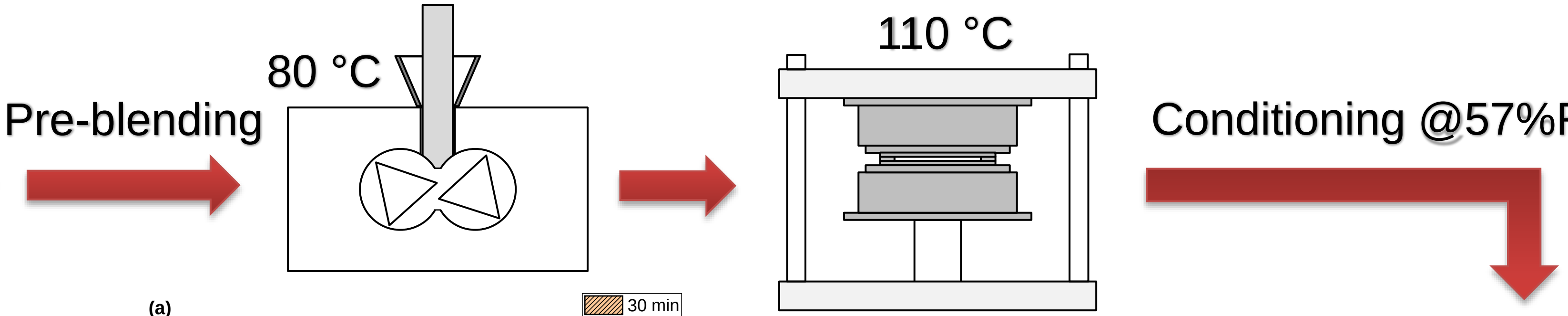
Chitosan/carboxymethyl cellulose/clay

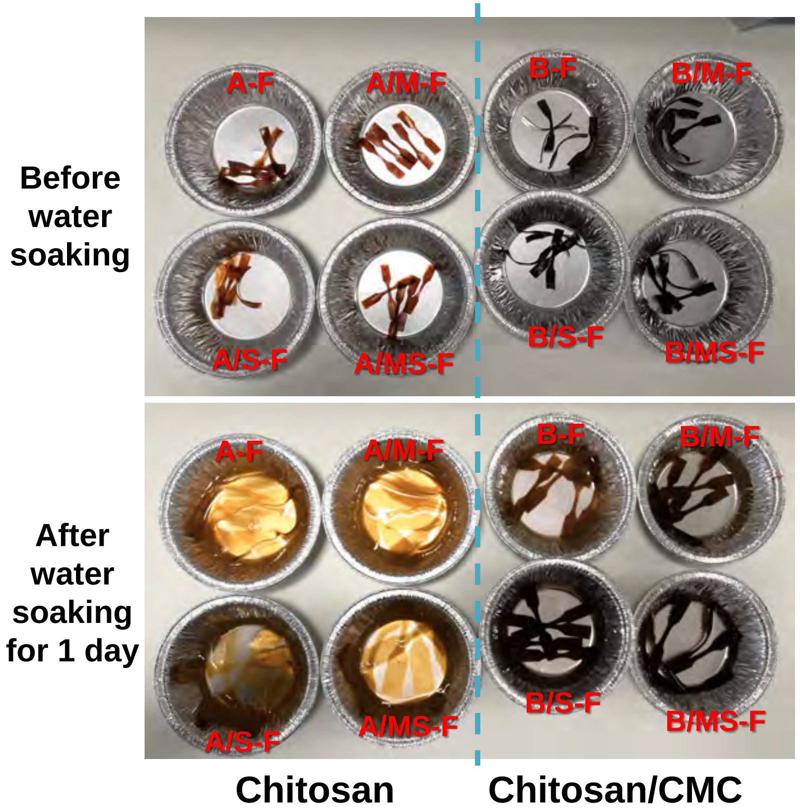
Chitosan

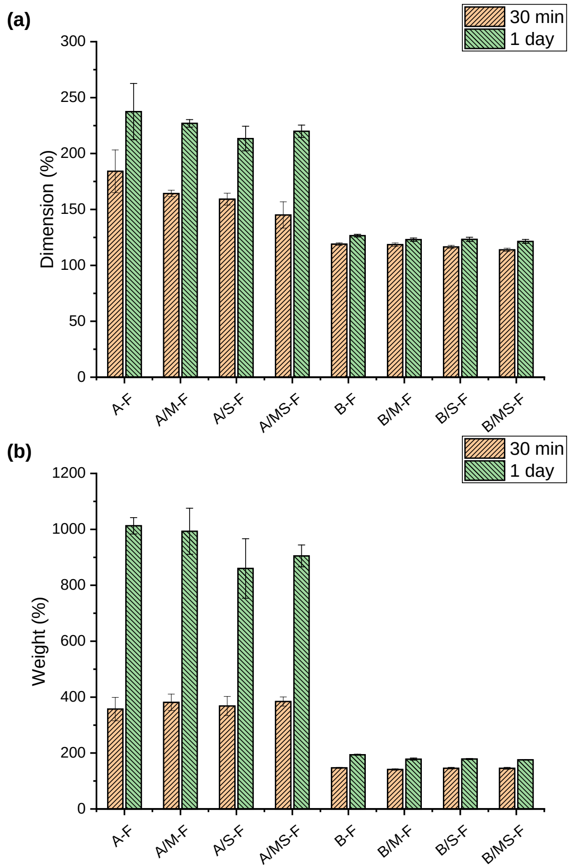
Carboxymethyl cellulose (CMC)

Montmorillonite (MMT) or Sepiolite (SPT)

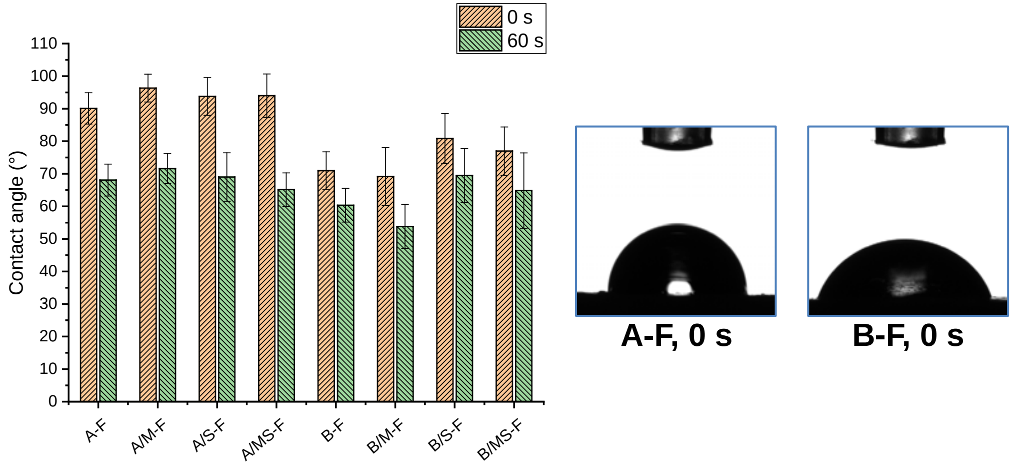
Formic acid solution







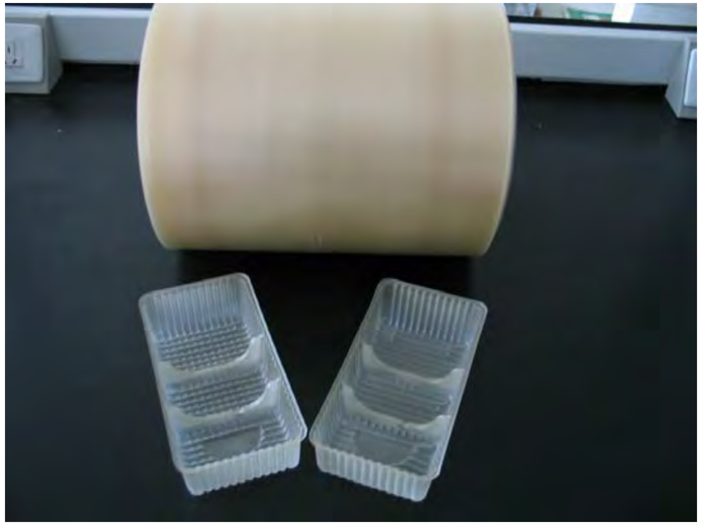
Dimensional and weight changes

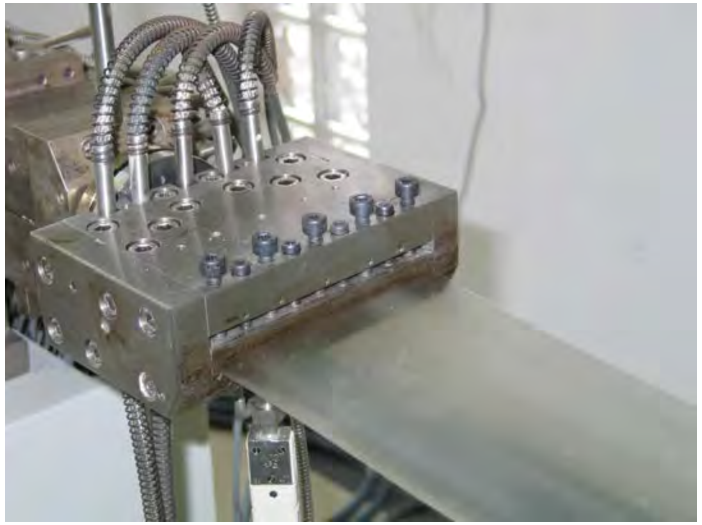


Contact angle

✓ **Chitosan/CMC films had better hydrolytic stability despite higher hydrophilicity than chitosan films**

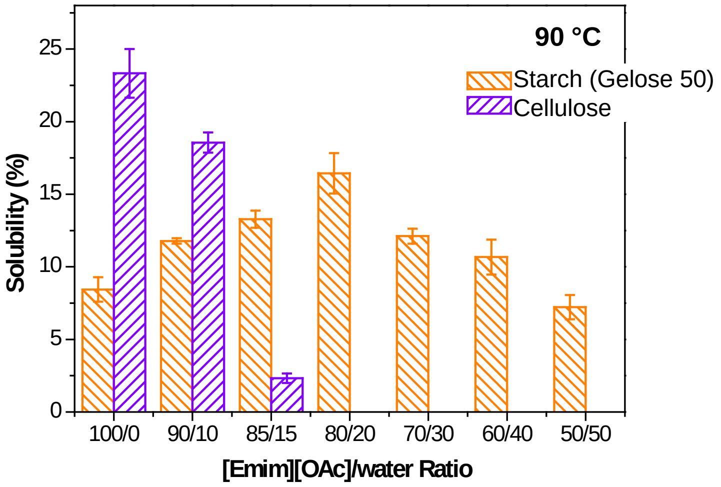
Chen, P. et al. *Compos. Sci. Technol.* 2020, 189, 108031



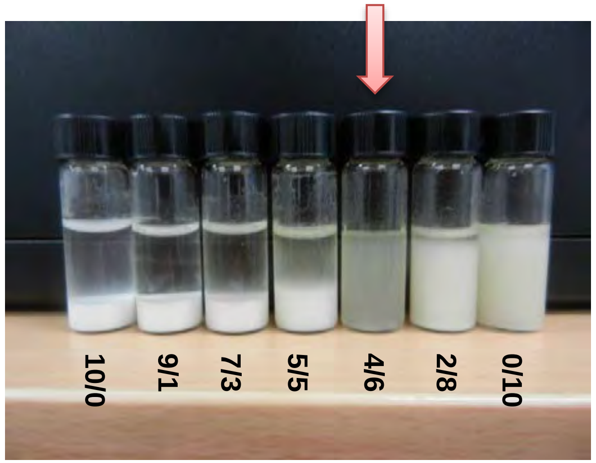


Starch processing

Aqueous ionic liquid–assisted starch processing at moderate conditions

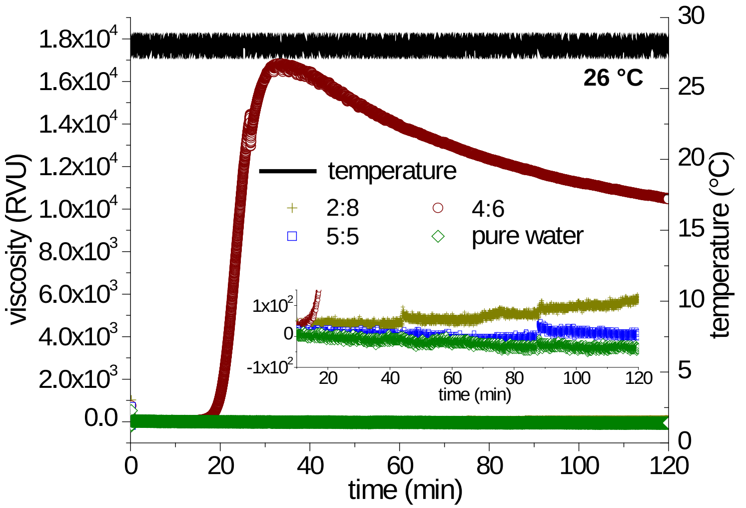


Solubility

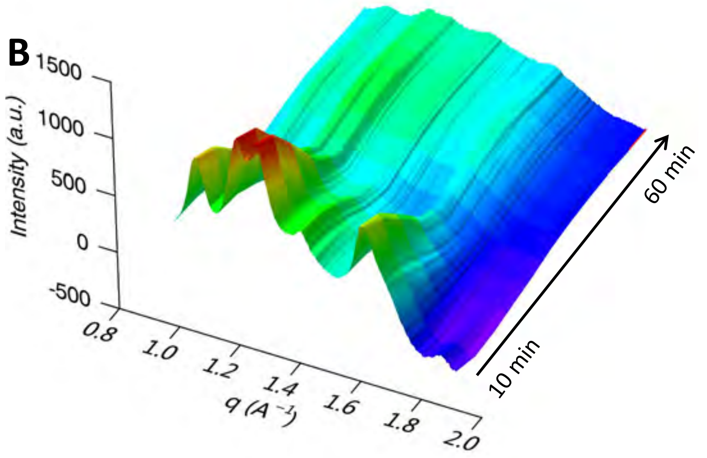


Maize starch 1 h after mixing with water:[C_2mim][OAc] mixtures

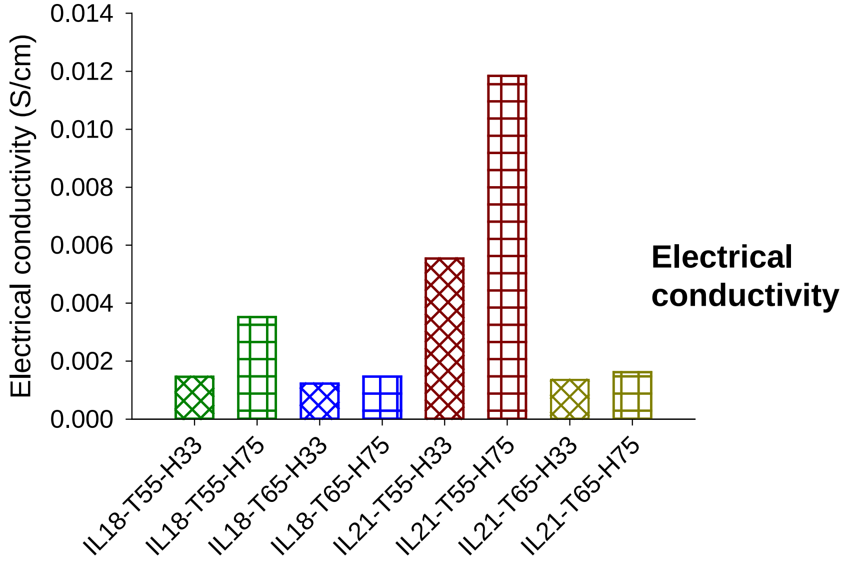
Starch films plasticised by water:[C_2min][OAc] prepared by hot-processing at 55–65 °C



Rapid visco-analyser (RVA): Maize starch in water:[C_2min][OAc] mixtures

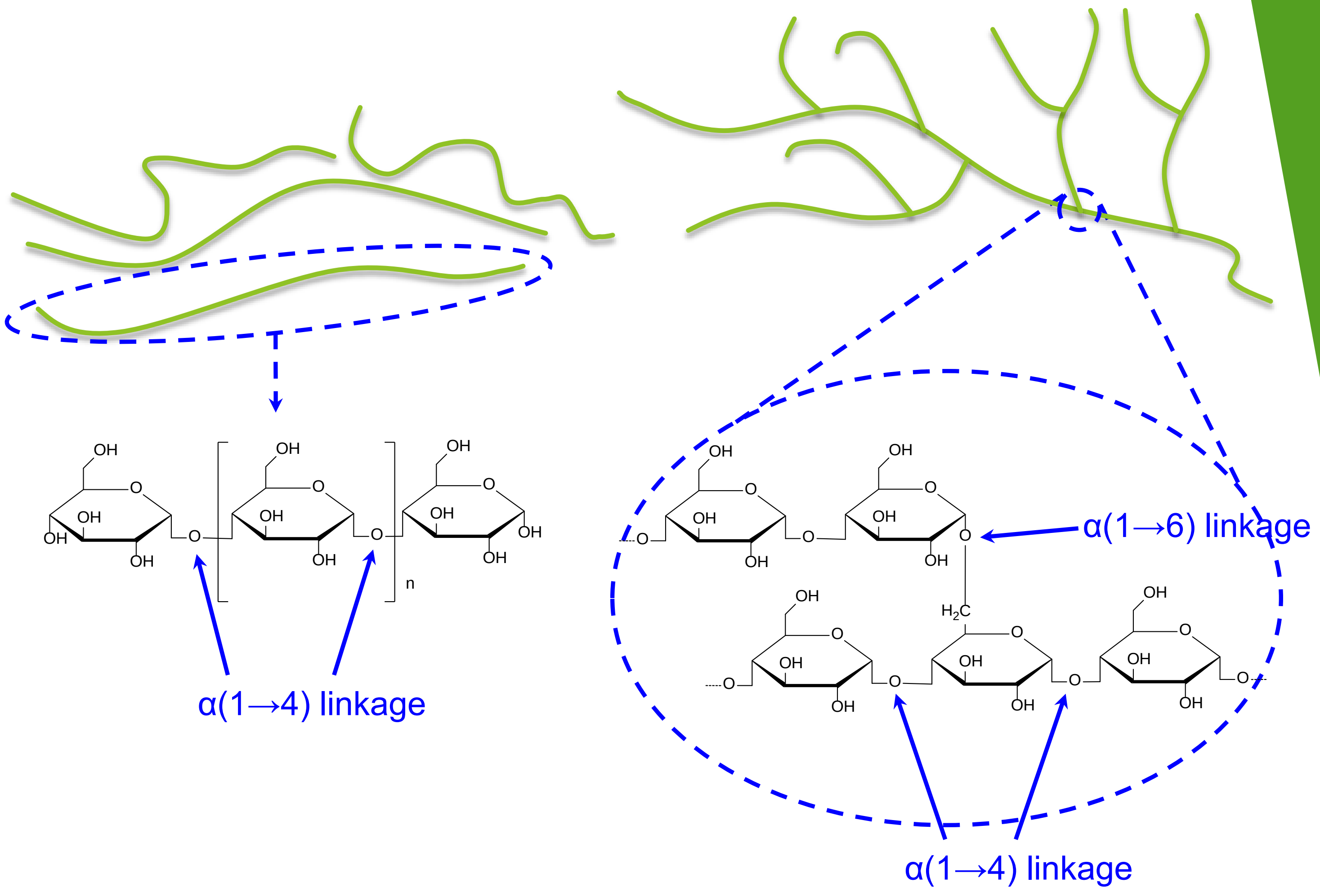


Synchrotron WAXS: Maize starch in 4:6 wt/wt (6.7:1 mol/mol) water:[C_2mim][OAc]



Tan, X. et al. *Phys. Chem. Chem. Phys.* 2016, 18 (39), *27584-27593*; Mateyawa, S. et al. *Carbohydr. Polym.* 2013, 94 (1), 520-530; Zhang, B. et al. *ACS Sustainable Chem. Eng.* 2017, 5 (5), 3737-3741; Zhang, B. et al. *ACS Sustainable Chem. Eng.* 2017, 5 (6), 5457-5467

Starch



Amylose

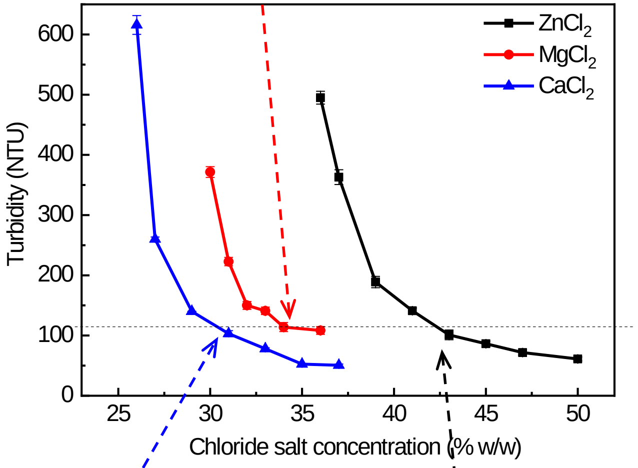
M_w: 10^5–10^6

Amylopectin

M_w: 10^7–10^9

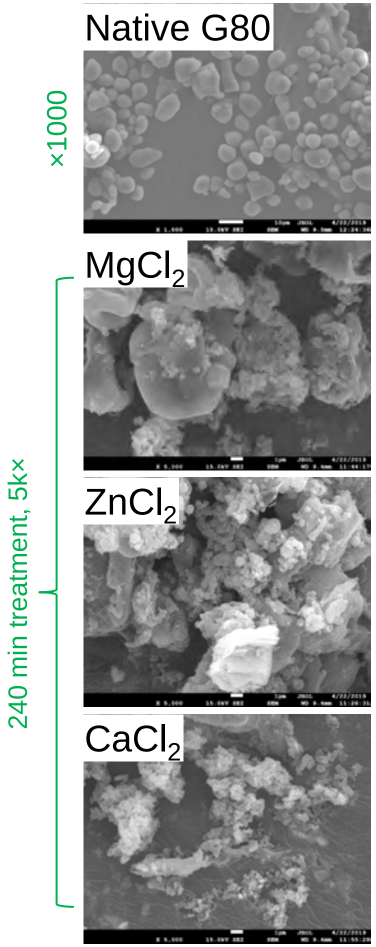
Aqueous metal chloride salt–assisted starch processing at moderate conditions

- G80: a high-amylose starch
- 50 °C for 4 h; 2% starch conc.

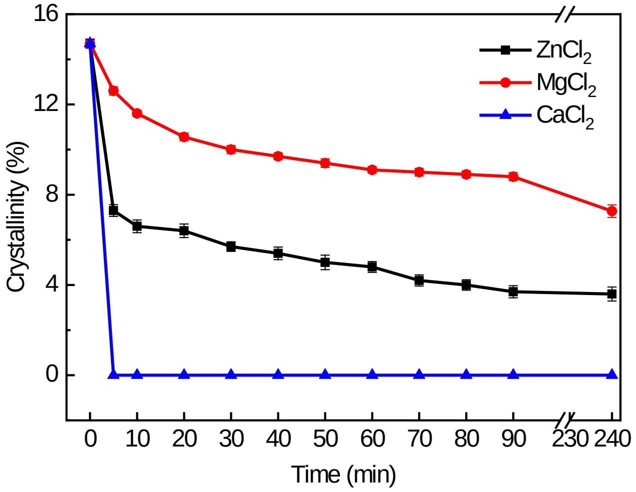


Turbidity

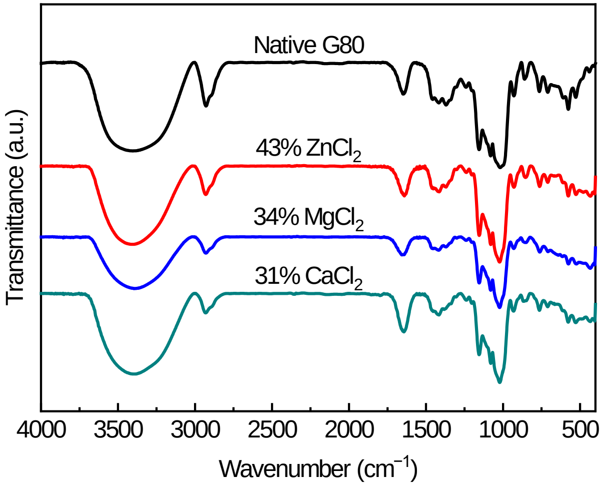
Salt conc. for granule disappearance: 43% $ZnCl_2$, 34% $MgCl_2$, 31% $CaCl_2$



Regenerated starch showing nanoparticles



Crystallinity from XRD



FTIR

- ✓ **Structural disorganisation ability: $CaCl_2$ > $ZnCl_2$ > $MgCl_2$**
- ✓ **Metal chloride salt solutions have no derivatising effect on starch**

Li, Y. et al. *ACS Sustainable Chem. Eng.* 2020, 8 (12), 4838-4847

Aqueous metal chloride salt–assisted starch processing at moderate conditions

G80 high-amylose starch

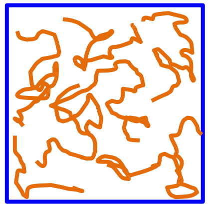
$CaCl_2$ solution (38.5% conc.)

Mixing

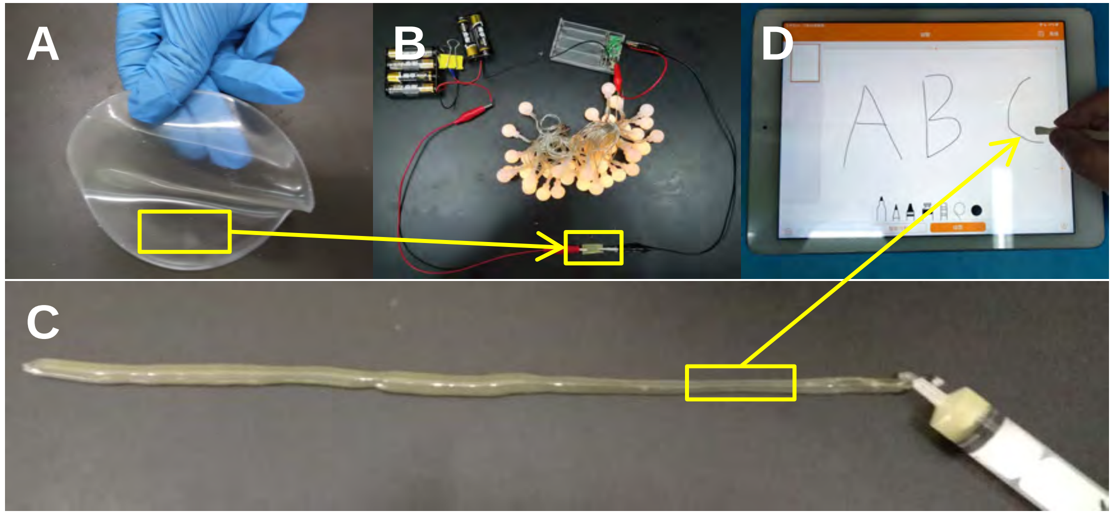
Starch/$CaCl_2$ mass ratio: 2.5:2.0, 2.5:2.2, 2.5/2.5, 2.5:2.8, 2.5:3.1

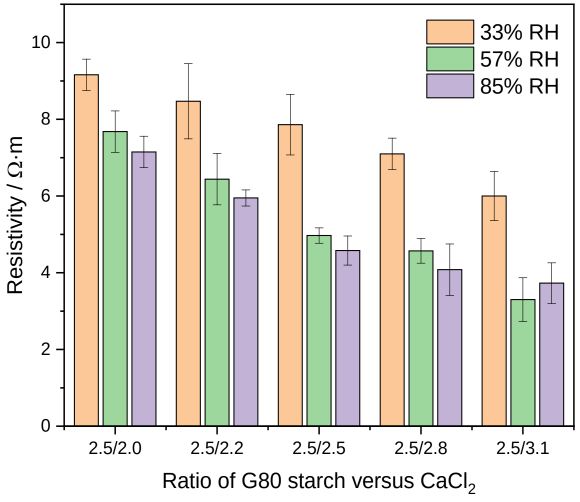
80 °C, 5 min

Conditioning at fixed RH (33%, 57%, 85%)

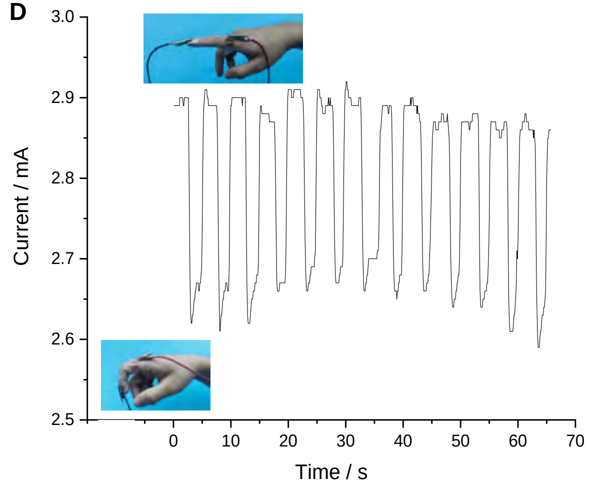


Starch-based film MC: ~36%, 42%, 55%





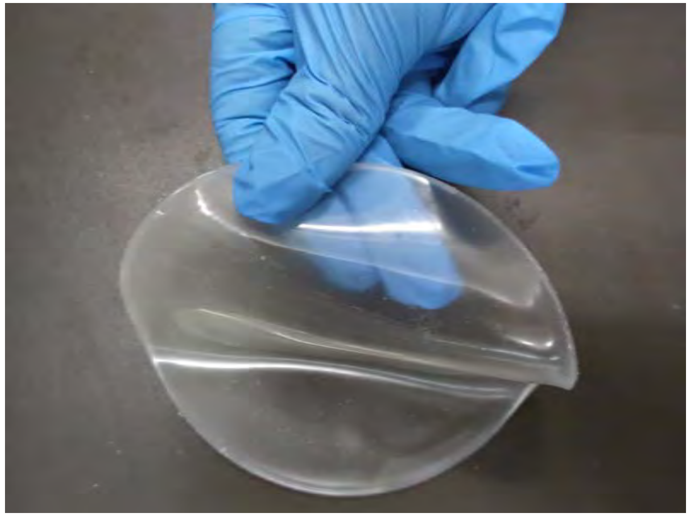
Electrical resistivity



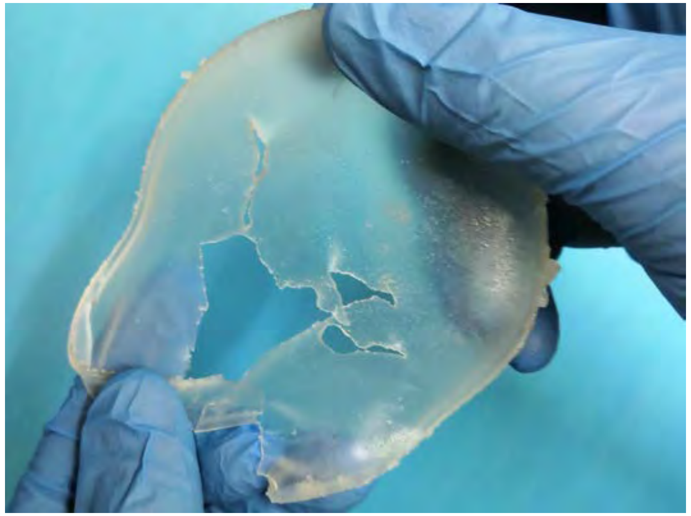
Finger bending

Starch/$CaCl_2$ film with ionic conductivity and strain-responsiveness

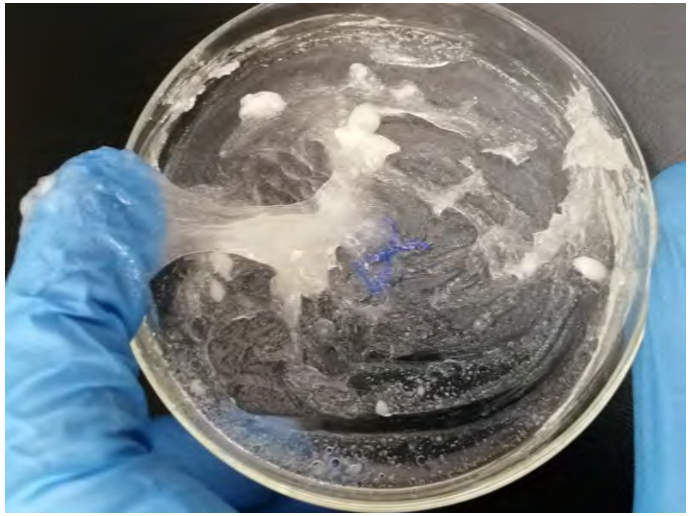
Liu, P. et al. *ACS Sustainable Chem. Eng.* 2020, 8 (51), 19117-19128



Starch/$CaCl_2$



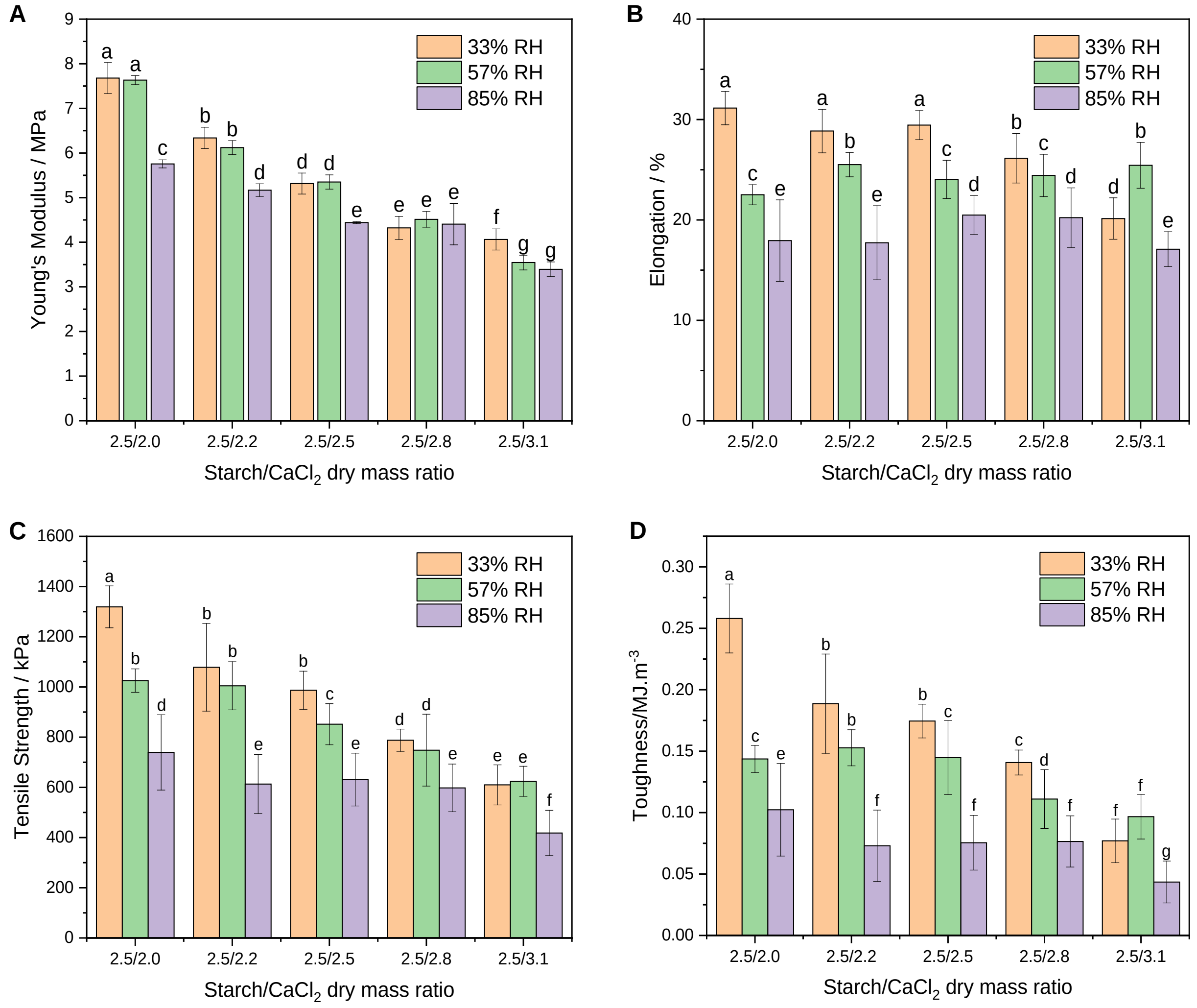
Starch/$MgCl_2$



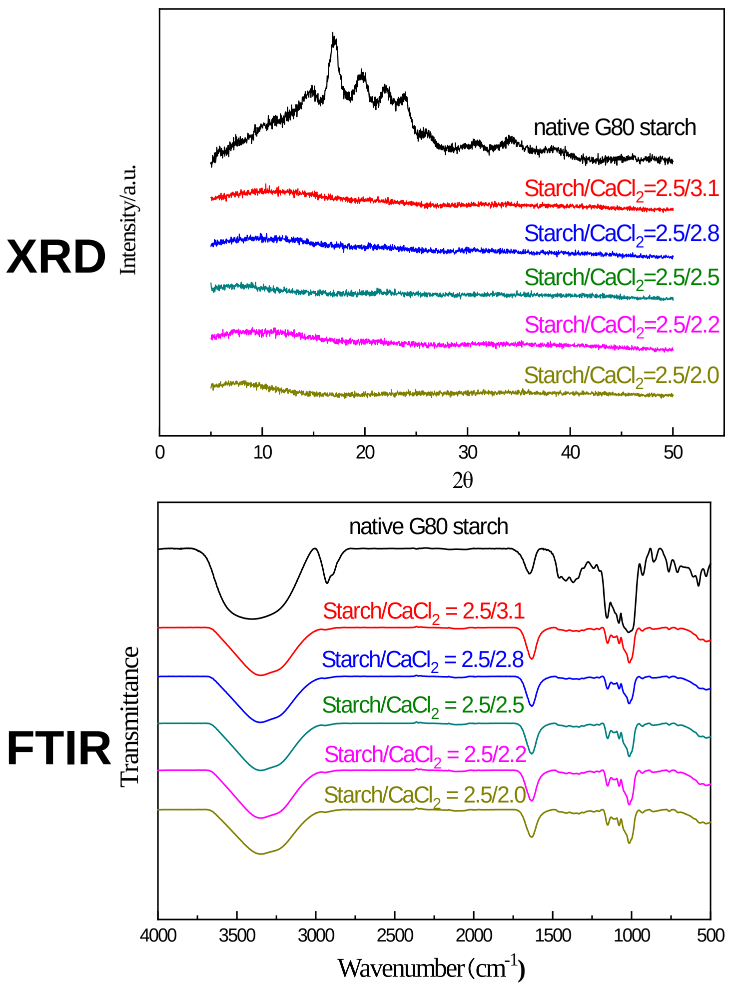
Starch/$ZnCl_2$

Liu, P. et al. *ACS Sustainable Chem. Eng.* 2020, 8 (51), 19117-19128

Starch/$CaCl_2$ films – Structure and properties



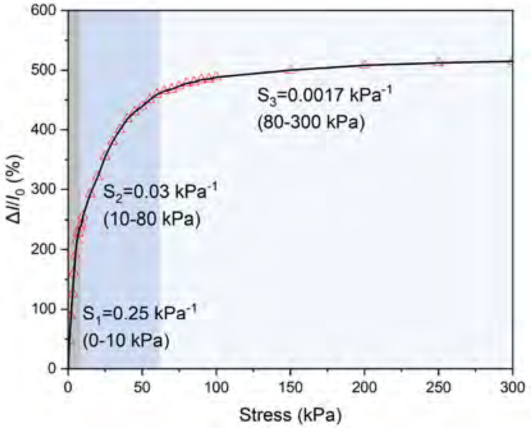
Mechanical properties



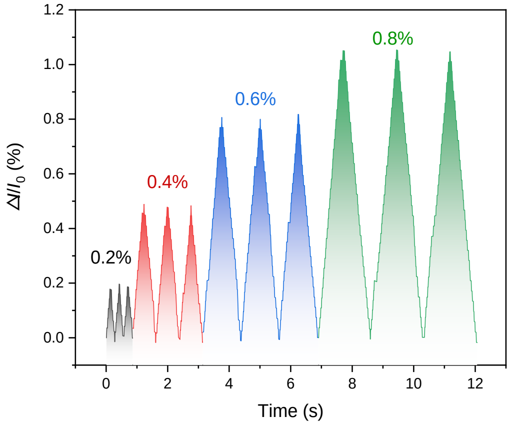
- ✓ **Tuneable properties**
- ✓ **Amorphous structure**
- ✓ **Starch–Ca^{2+} complex with excess free Ca^{2+} ions**

Liu, P. et al. *ACS Sustainable Chem. Eng.* 2020, 8 (51), 19117-19128

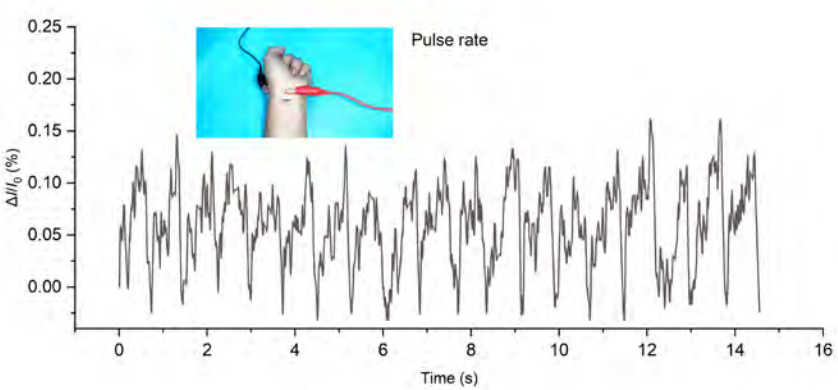
Plasticised starch-based hydrogel as flexible sensor



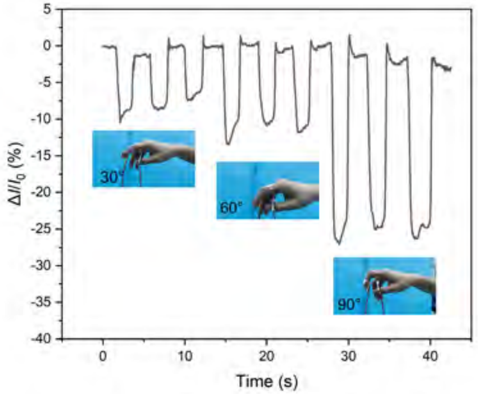
Compression sensitivity



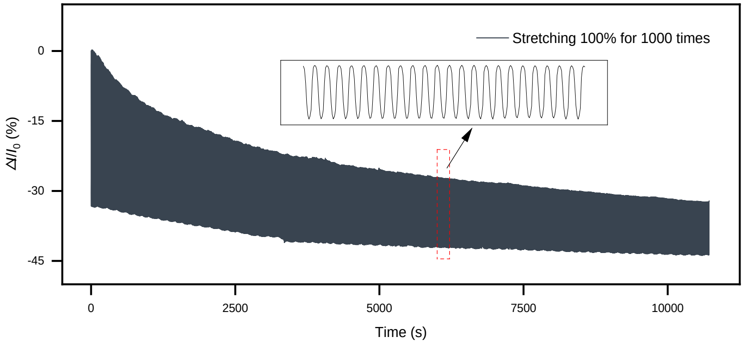
Stretching sensitivity



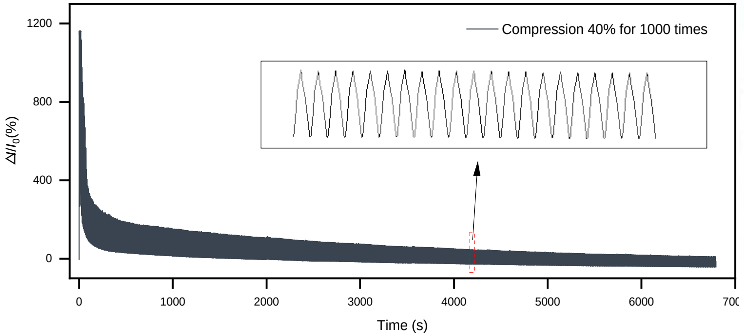
Pulse



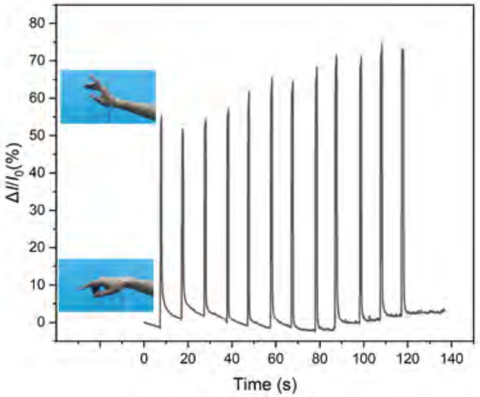
Finger bending



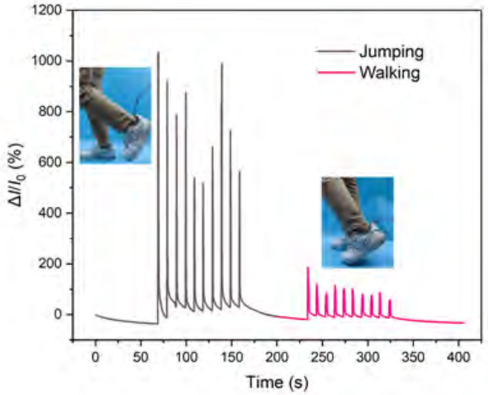
Repeated stretching



Repeated compression



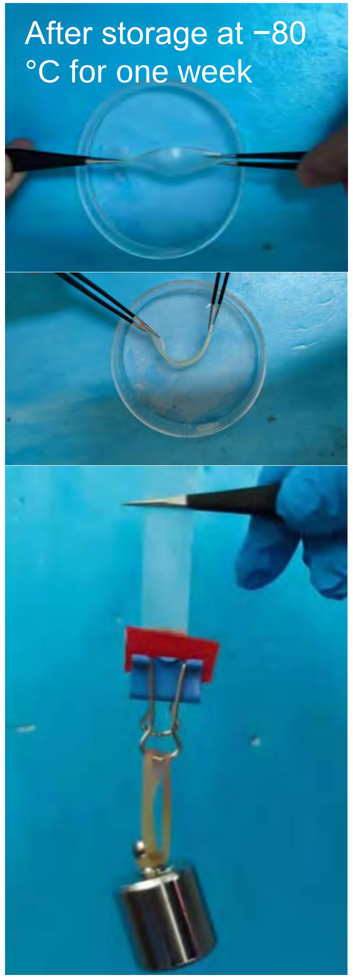
Wrist rotation



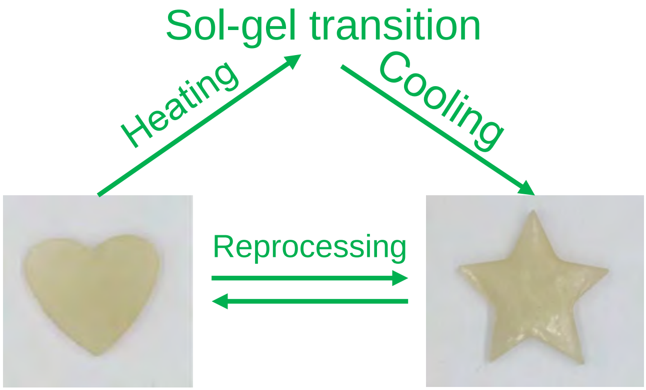
Foot stepping

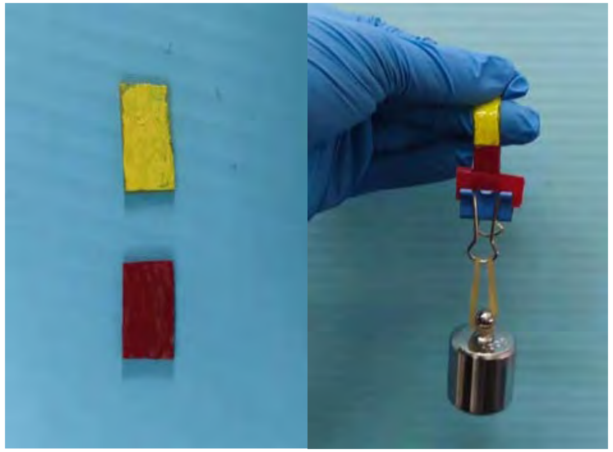
[Ma, C. et al. *ACS Sustainable Chem. Eng.* 2022, 10 (20), 6724-6735]

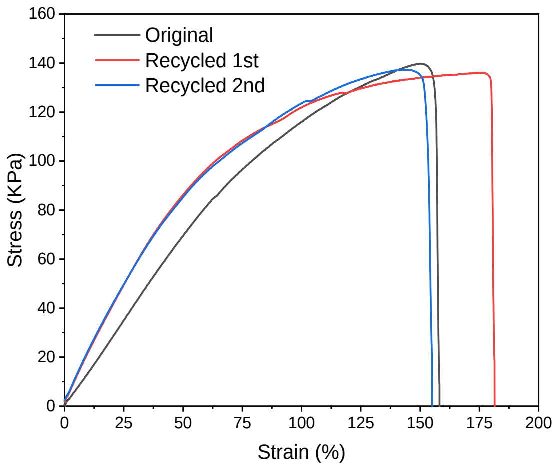
Plasticised starch-based hydrogel

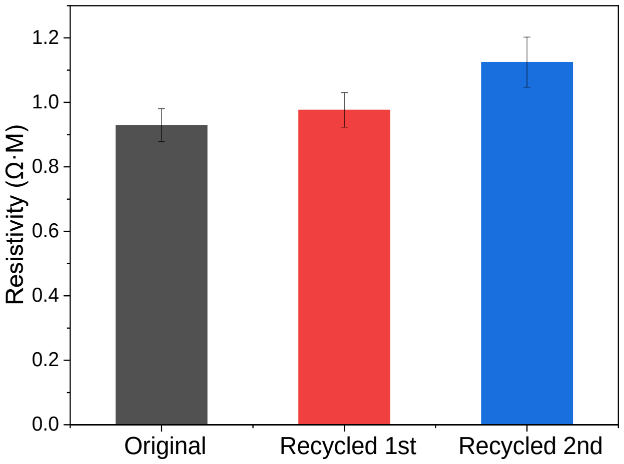


Anti-freezing

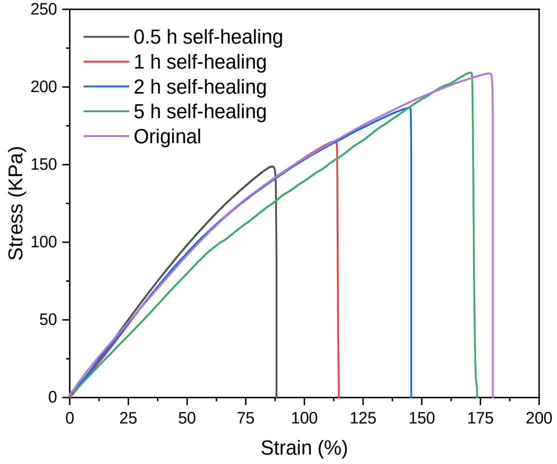


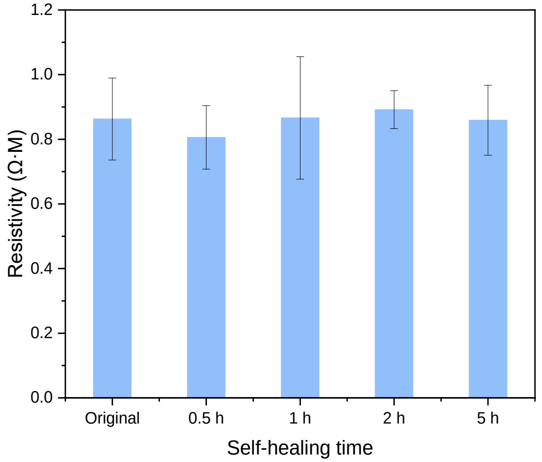






Reprocessing at 70 °C



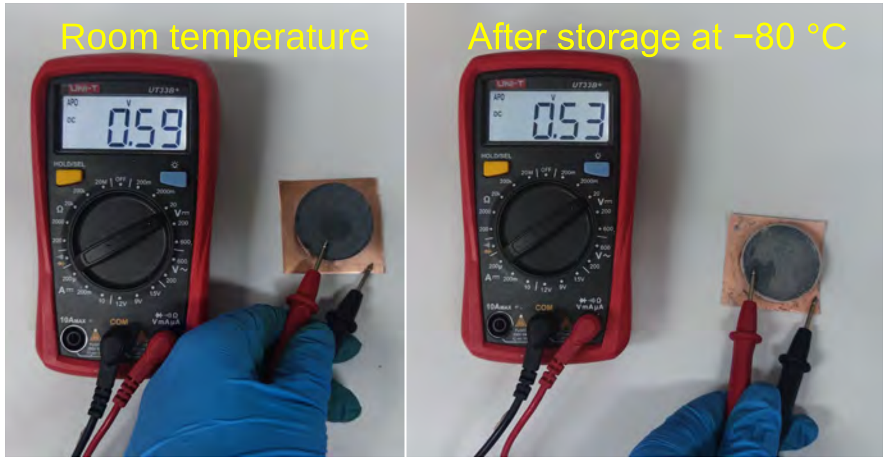


Self-healing at 55 °C

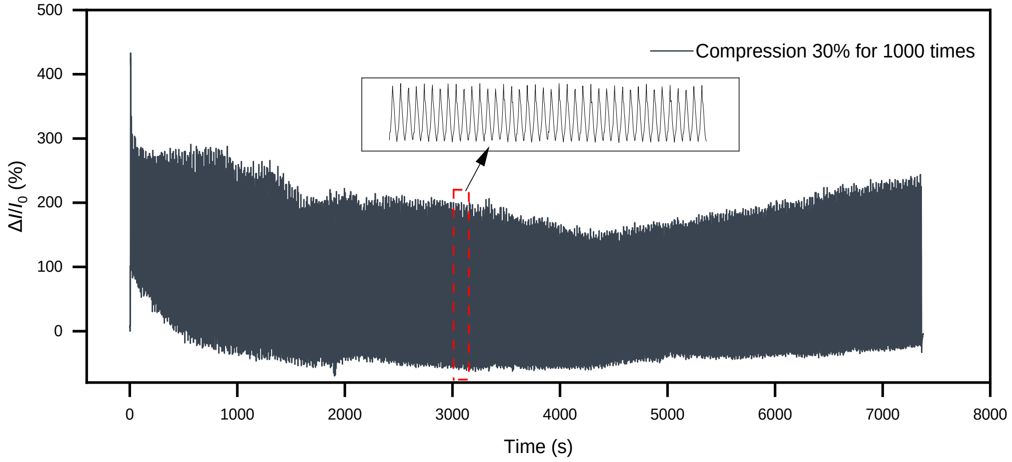
Ma, C. et al. *ACS Sustainable Chem. Eng.* 2022, 10 (20), 6724-6735

Starch-based hydrogel as battery (Zn-H_2)

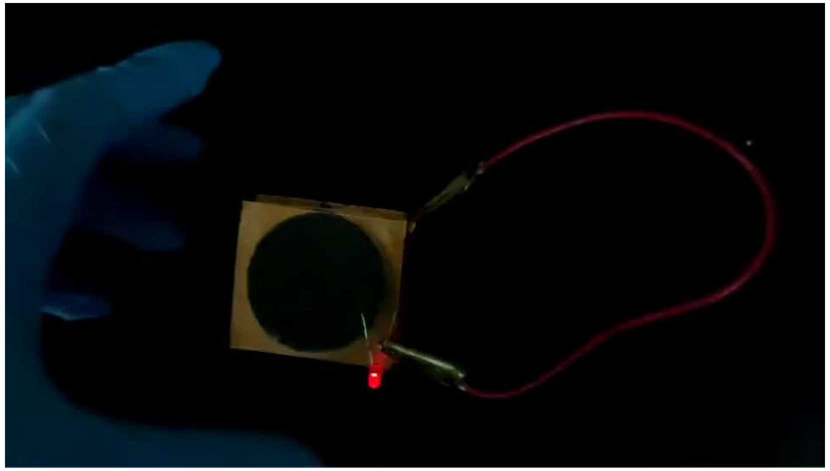
Flexibility



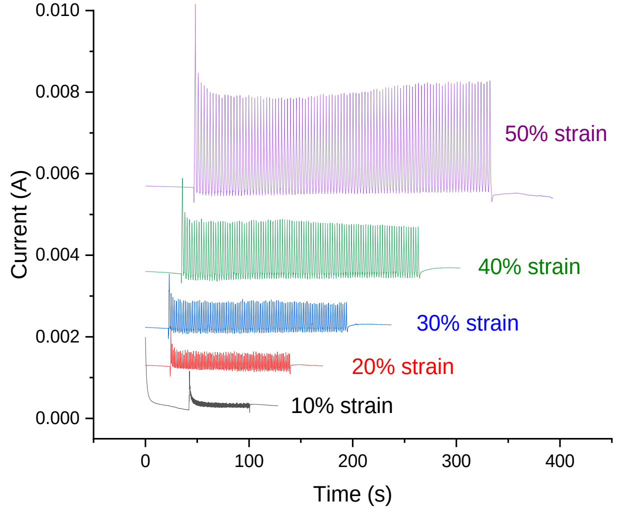
Starch/$CaCl_2$/Zn + copper sheet



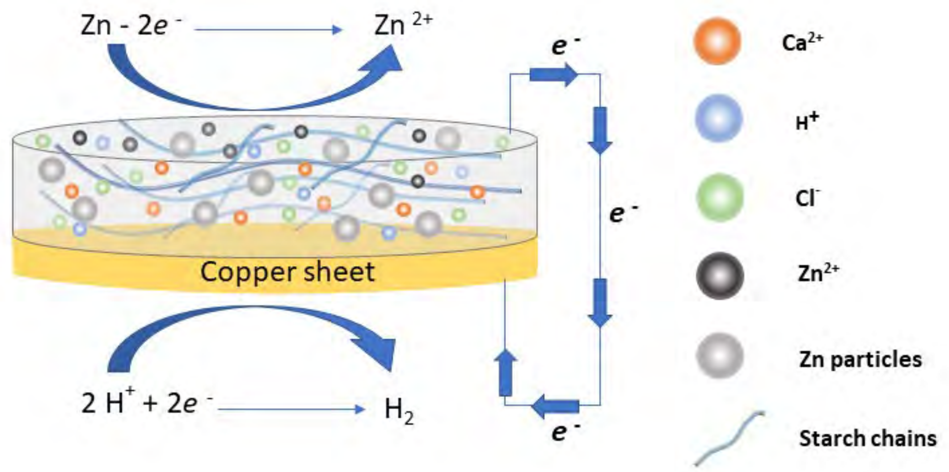
Repeated compression



Strain-sensitivity



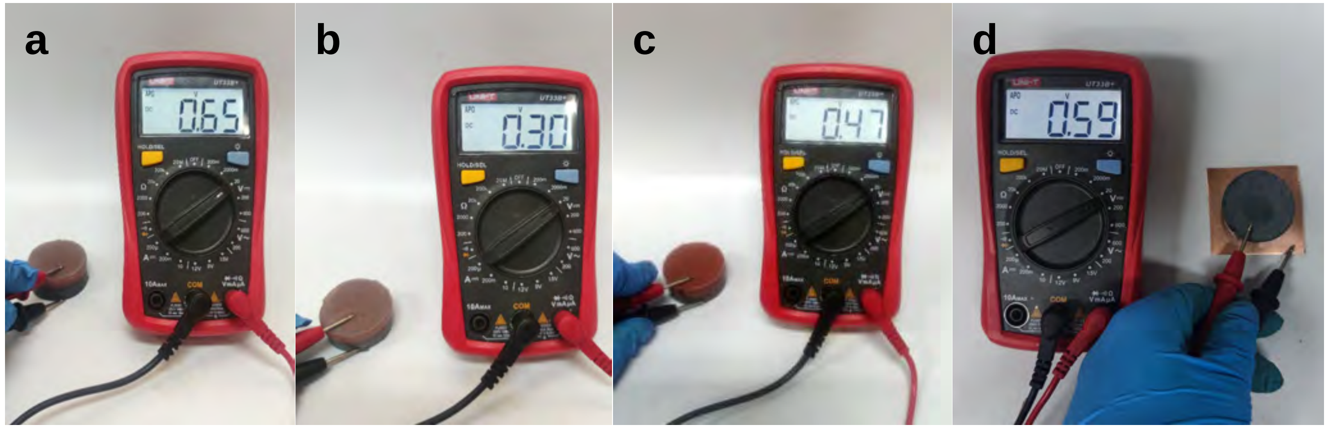
Different strains of compression



Proposed mechanism

Ma, C. et al. *ACS Sustainable Chem. Eng.* 2022, 10 (20), 6724-6735

Starch-based hydrogel as battery

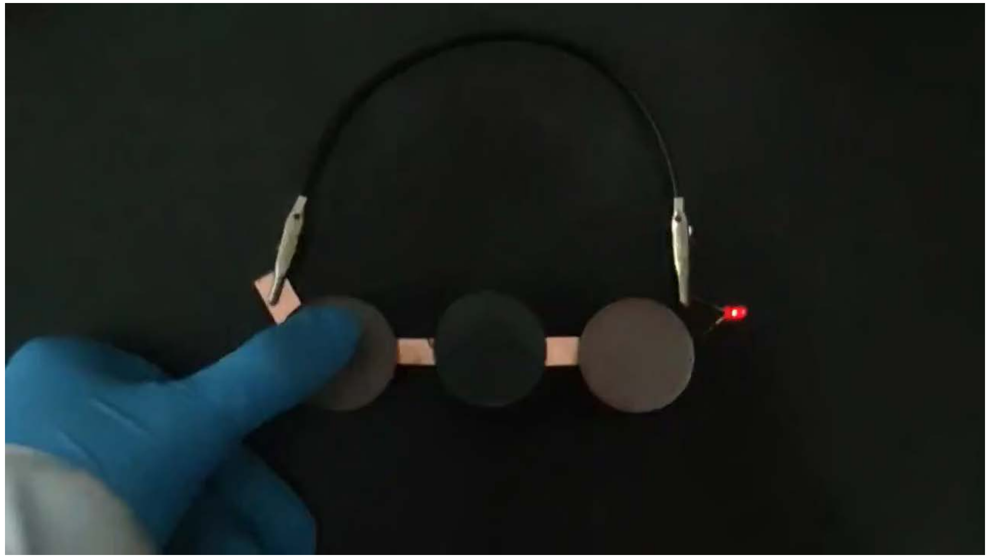


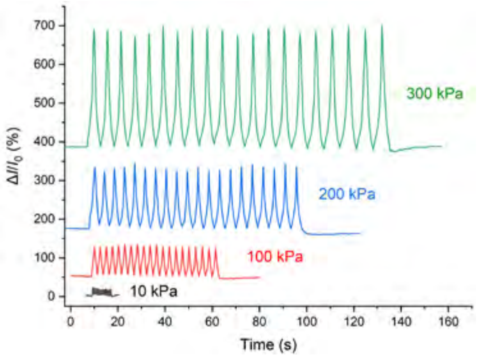
			Voltage (V)
a)	Fe-Cu	Starch/$CaCl_2$/Fe + Starch/$CaCl_2$/CuCl_2/Cu	0.65
b)	Sn-Cu	Starch/$CaCl_2$/Sn + Starch/$CaCl_2$/CuCl_2/Cu	0.30
c)	Zn-H_2	Starch/$CaCl_2$/Zn + Starch/$CaCl_2$/Cu	0.47
d)	Zn-H_2	Starch/$CaCl_2$/Zn + copper sheet	0.59

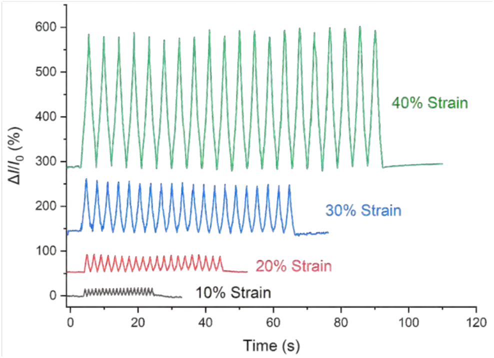
Ma, C. et al. *ACS Sustainable Chem. Eng.* 2022, 10 (20), 6724-6735

Starch-based hydrogel as battery (Zn-Cu)

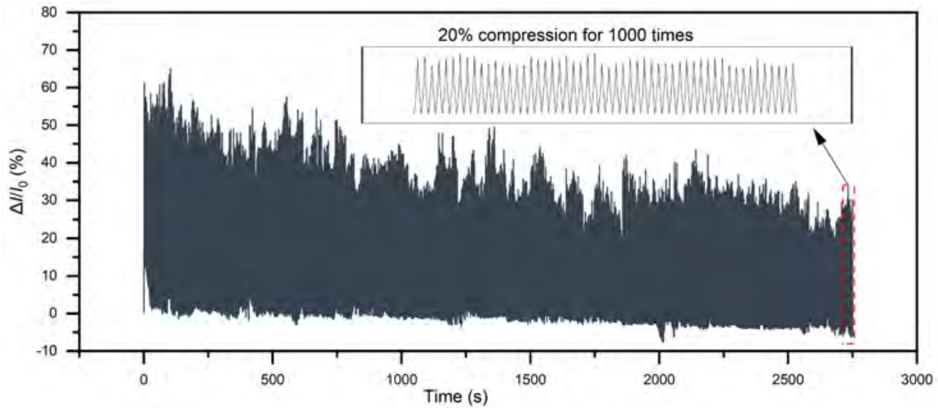
Starch/$CaCl_2$/Zn + Starch/$CaCl_2$/$CuCl_2$/Cu



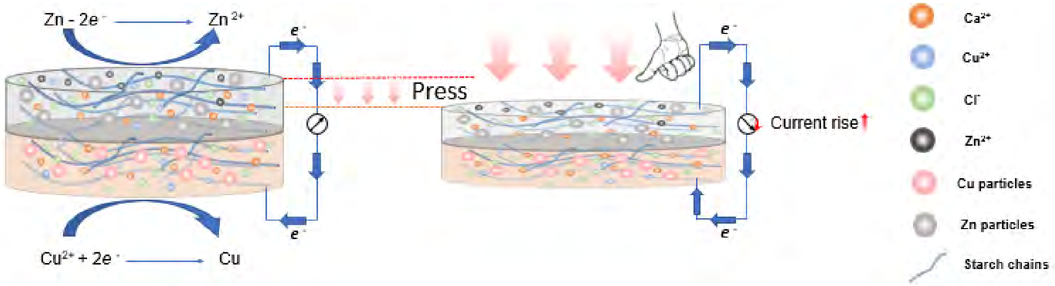




Different strains and stresses of compression



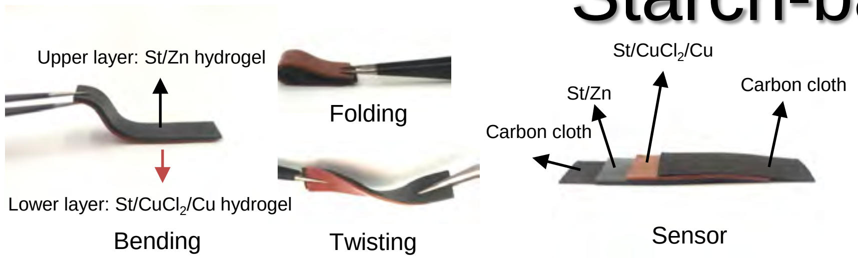
Repeated compression



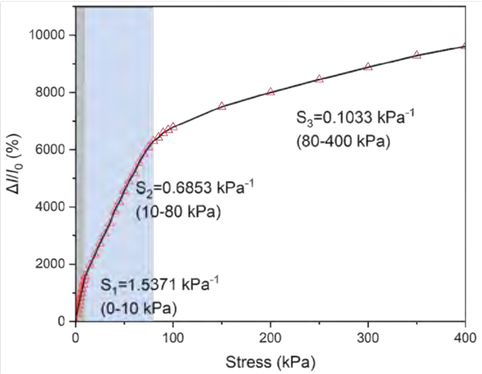
Proposed mechanism

Ma, C. et al. *ACS Sustainable Chem. Eng.* 2022, 10 (20), 6724-6735

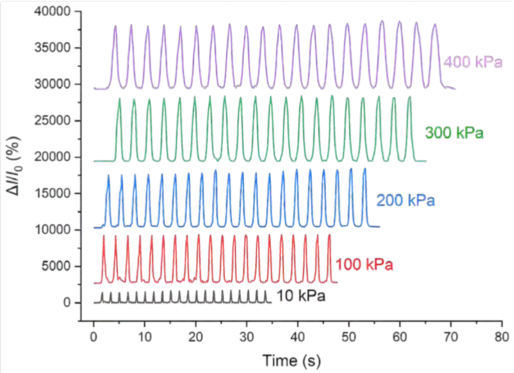
Starch-based self-powered sensor



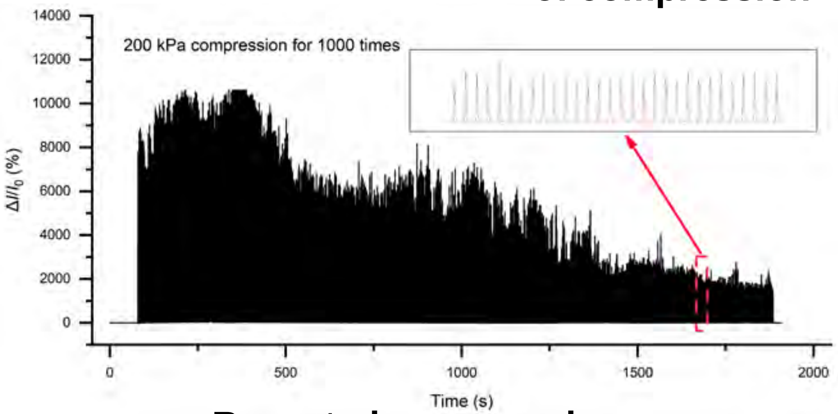
Zn-Cu battery + carbon cloth



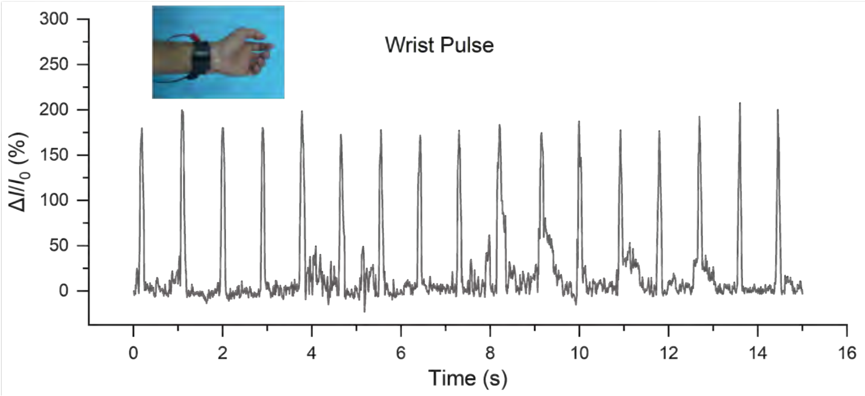
Compression sensitivity

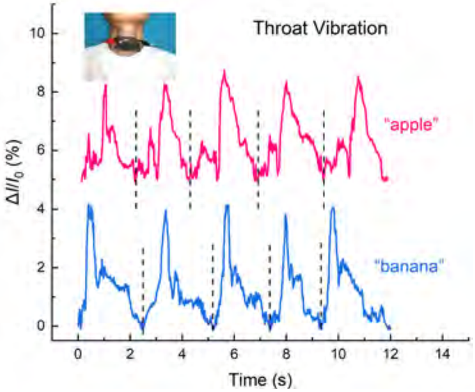


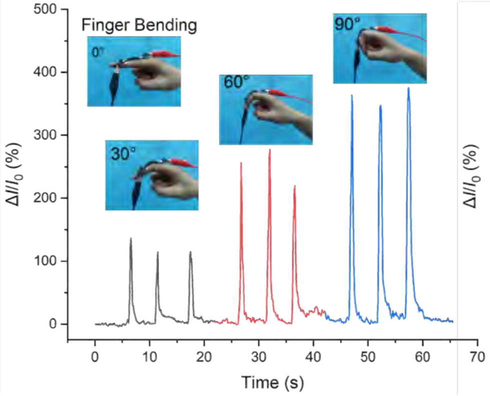
Different stresses of compression

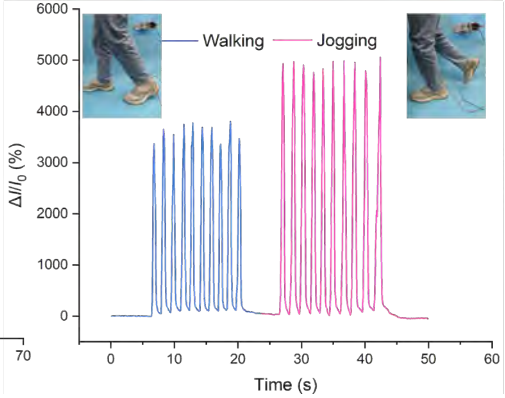


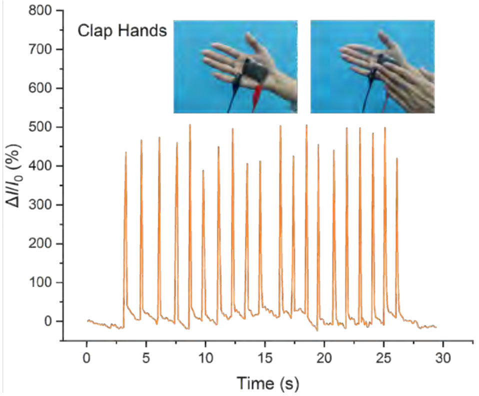
Repeated compression











Sensing performance

Ma, C. et al. *ACS Sustainable Chem. Eng.* 2022, 10 (20), 6724-6735

Summary

- **Starch-based hydrogels and flexible electronics**
  - Metal chloride salt ($ZnCl_2$, $MgCl_2$ and $CaCl_2$) solutions can effectively gelate or dissolve high-amylose starch
  - Facile preparation of flexible, reprocessable, ionically conductive, and strain-responsive starch-based hydrogels, with $CaCl_2$
  - Galvanic cell-type Zn-Cu battery showing flexibility and pressure-sensitivity
  - Self-powered flexible sensor for detecting human activities

Facilely prepared starch-based ionic conductive hydrogel, batteries, and self-powered sensors with strain-sensitivity

David Fengwei Xie

EPSRC Fellow

School of Engineering, Newcastle University, UK

david.xie@newcastle.ac.uk

@FengweiXie

www.fwxie.com