



Bio-inspired processing

Esther Amstad

Materials in nature



<http://news.berkeley.edu/2016/06/15/>



Y. Gu, et al., *e-Polymers* **2020**, 20 (1), 443–457

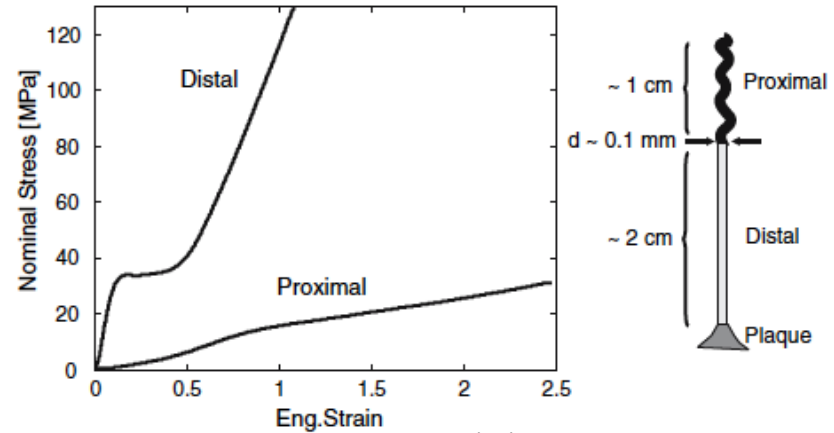


<http://www.followtheyin.com/>

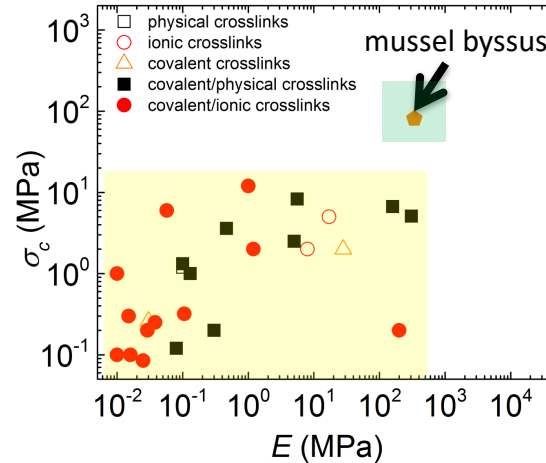


<https://www.newscientist.com/article/dn26994>

The mussel byssus thread



K. Bertoldi, et al., *J. Mater. Sci.* **2007**, 42 (21), 8943–8956



<https://www.rampartsofcivilization.com/?p=5210>

Natural vs. synthetic hydrogels

Mussel byssus



<https://labs.mcdb.ucsb.edu/waite/herbert/research/wet-wonder-glue>

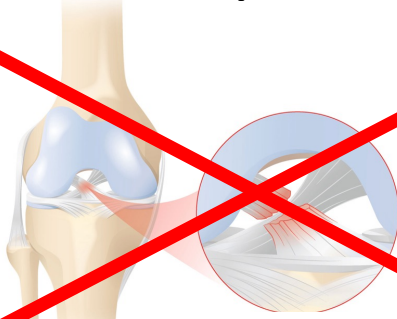
Applications

Soft robotics



<https://www.engineersgarage.com/egblog/soft-robotics-robots-featuring-biological-movements/>

Soft tissue replacements



<https://pyramide.ch/en/joint-and-sport-surgery/knee-surgery/cruciate-ligament/>

Food



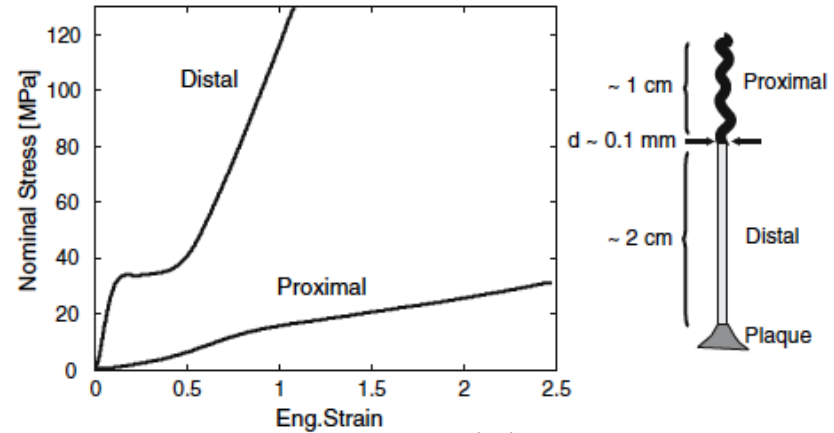
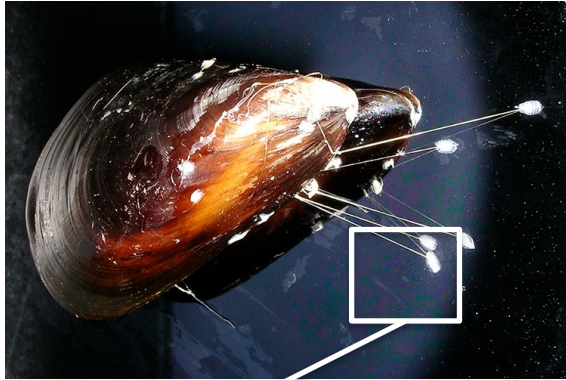
<https://www.organicauthority.com>

Contact lenses

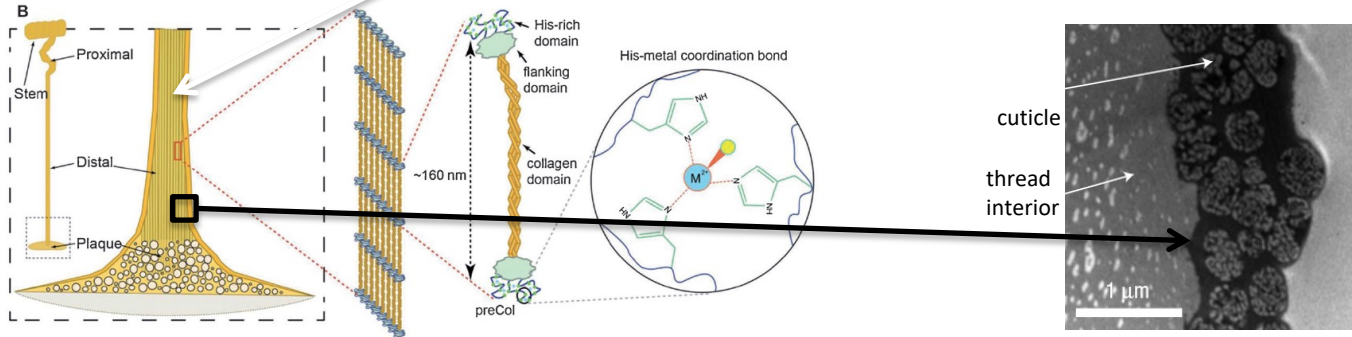


<https://www.freepik.com>

The mussel byssus thread



K. Bertoldi, et al., *J. Mater. Sci.* **2007**, 42 (21), 8943–8956



E. Degtyar, et al., *Angew. Chem. Int. Ed.* **2014**, **53**, 12026-12044

N. Holten-Andersen, et al., *Nat. Mat.* **2007**, **6**, 669-672

Materials in nature



<http://news.berkeley.edu/2016/06/30/>



Y. Gu, et al., *e-Polymers* **2020**, 20 (1), 443–457

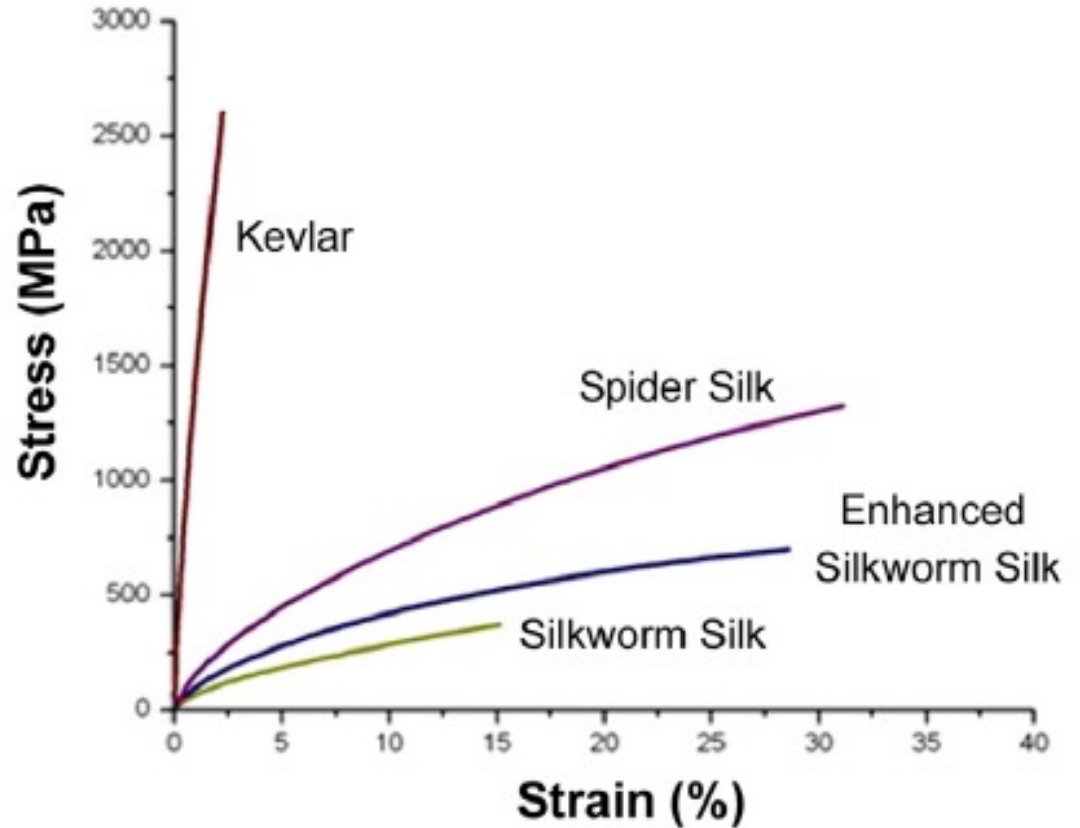
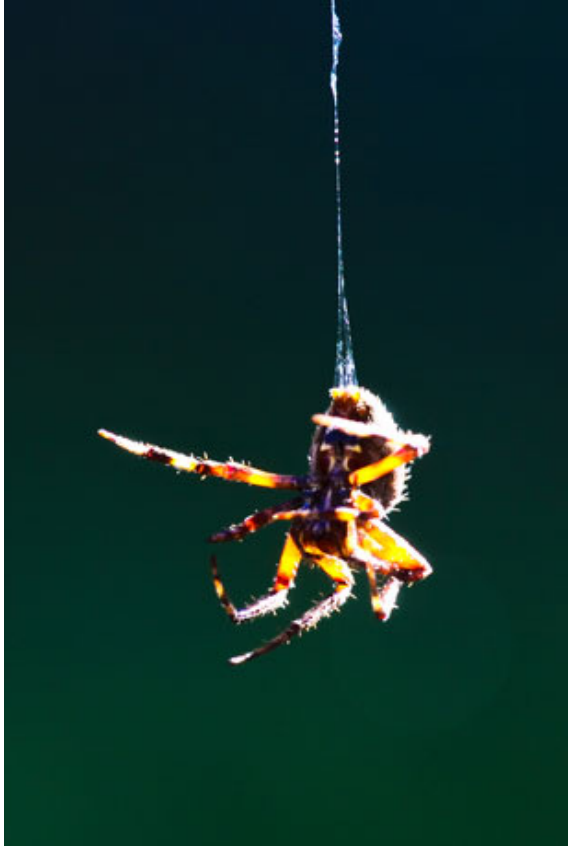


<http://www.followtheyin.com/>

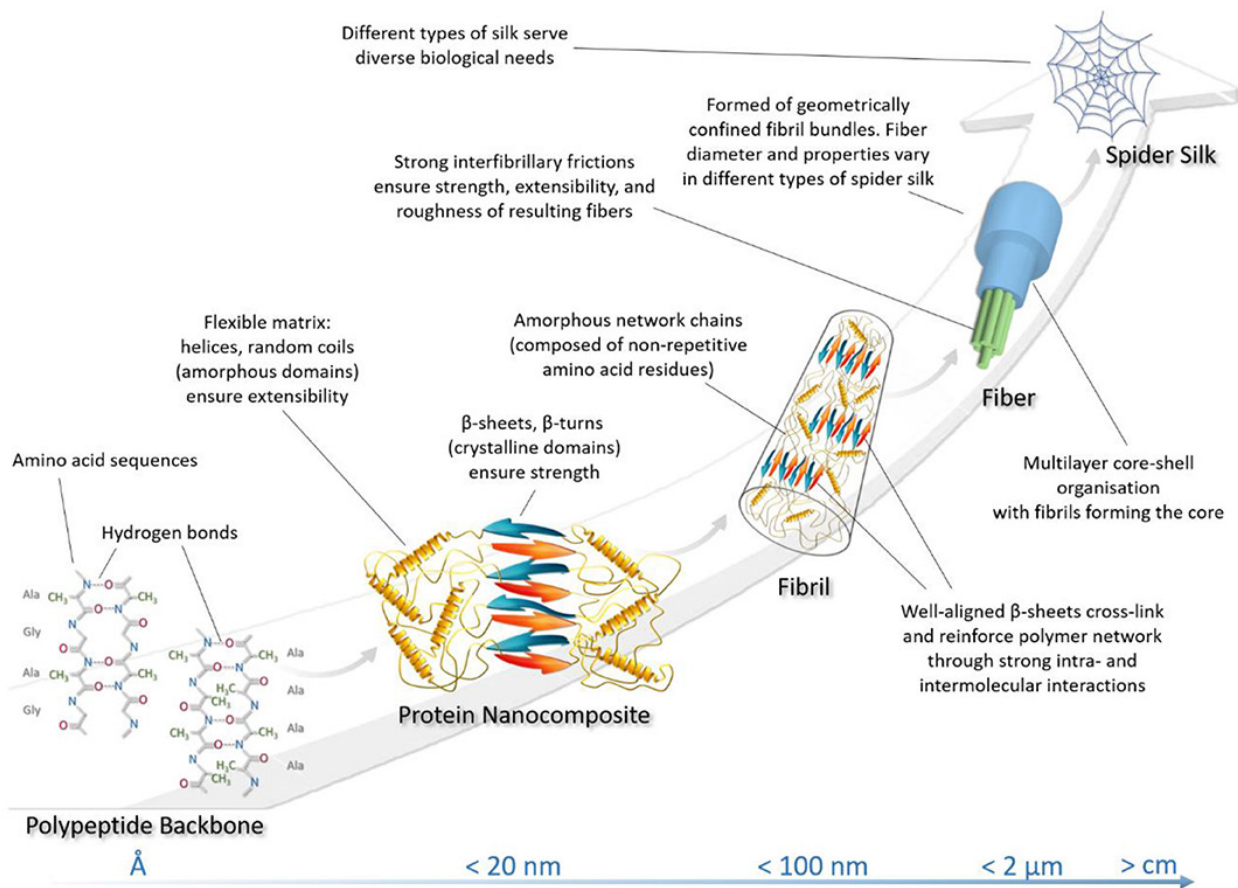


<https://www.newscientist.com/article/dn26994>

Mechanical properties of spider silk

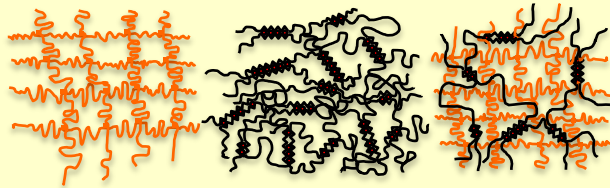
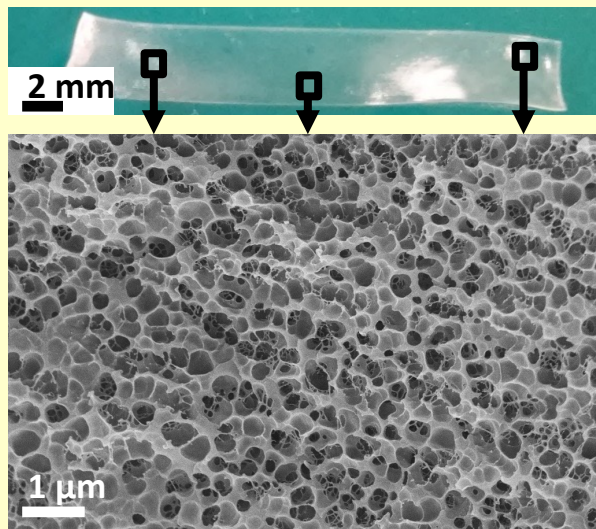


Mechanical properties of spider silk



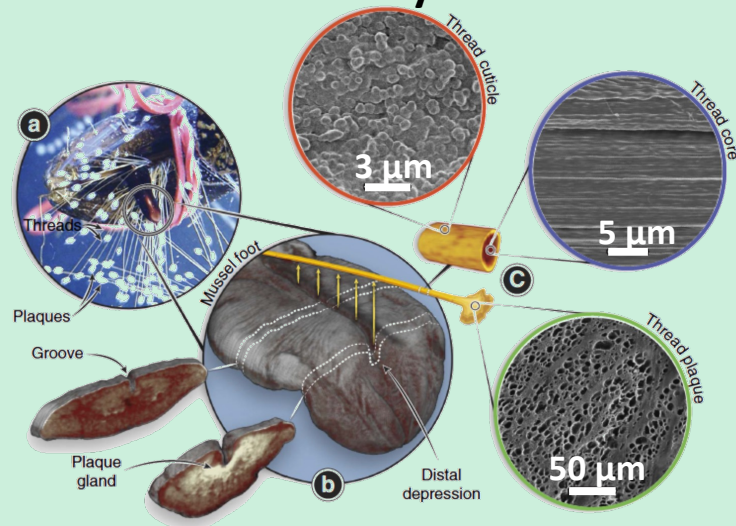
Synthetic vs. natural hydrogels

Synthetic hydrogels

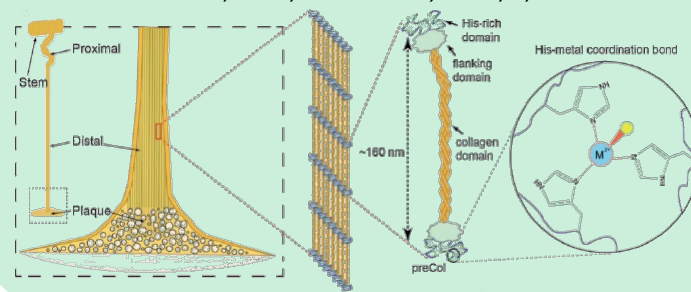


H. Du, under review

Mussel byssus

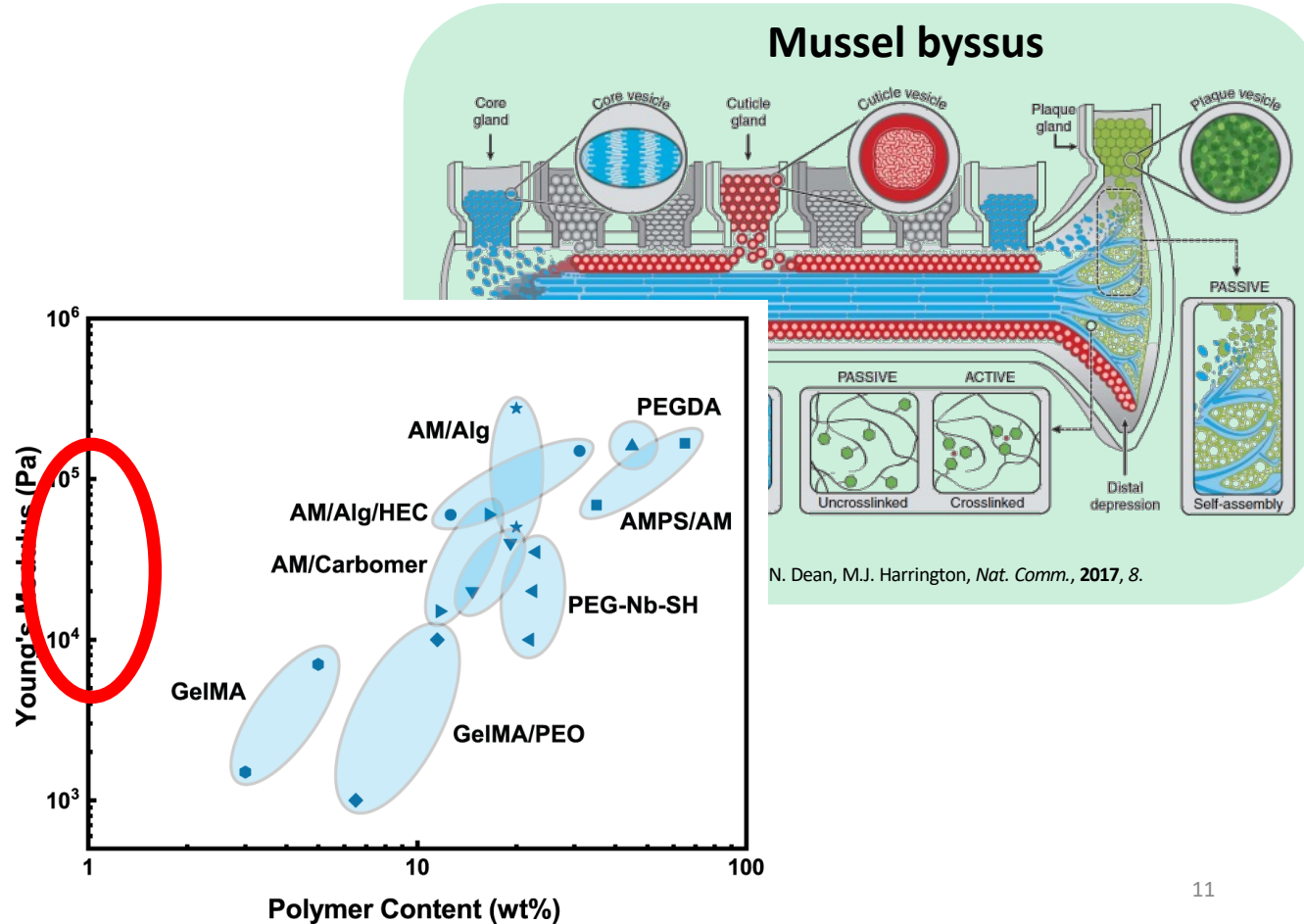


T. Priemel, et al., *Nat. Comm.*, **2017**, 8, 14539

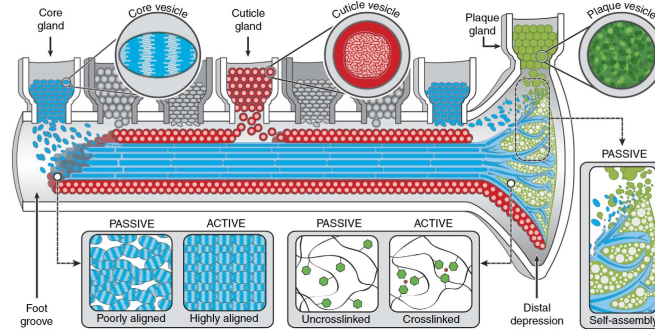


E. Degtyar, et al., *Angew. Chem. Int. Ed.*, **2014**, 53, 12026-12044

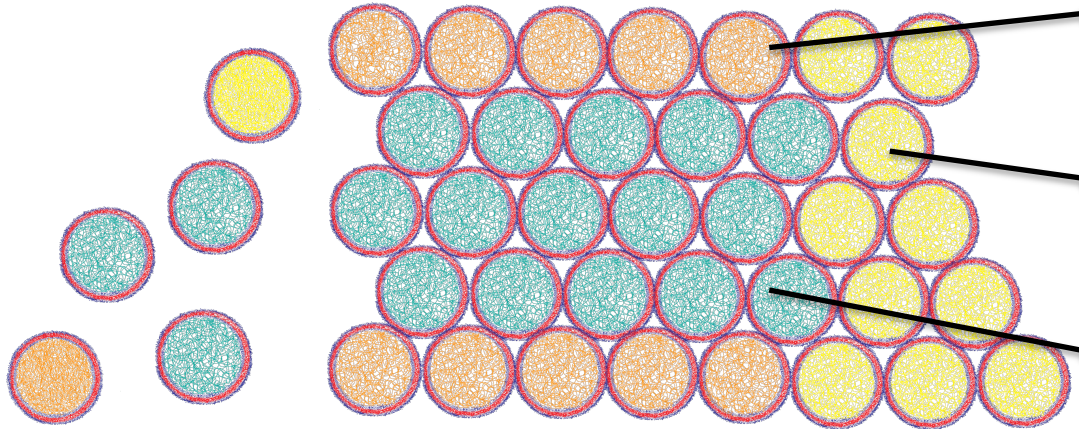
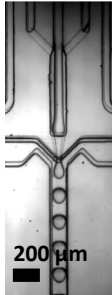
Fabrication of soft materials



Bio-inspired processing

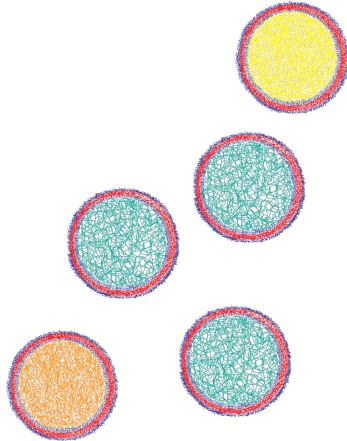
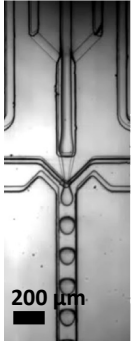


T. Priemel, E. Degtyar, M.N. Dean, M.J. Harrington, *Nat. Comm.* **2017**, 8

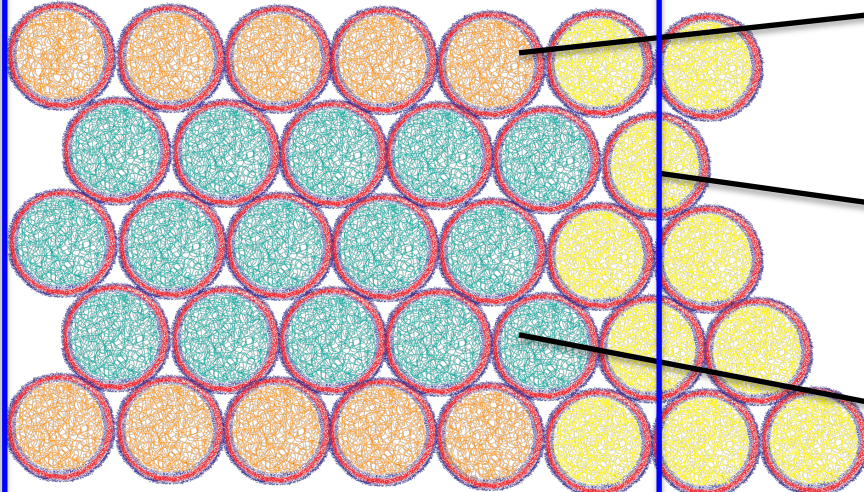


Bio-inspired processing

Selectively permeable capsules



3D printing of granular hydrogels

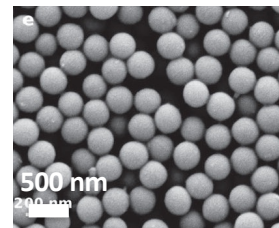
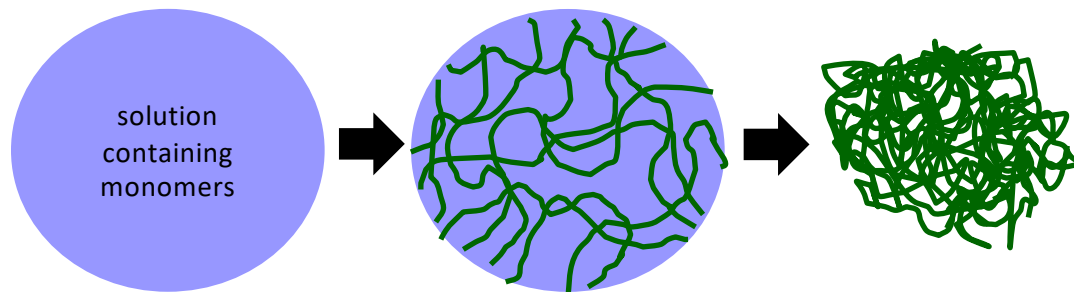


Functionalization

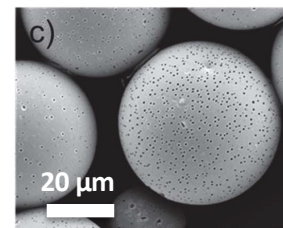


How can capsules be made?

Templates for microparticle production



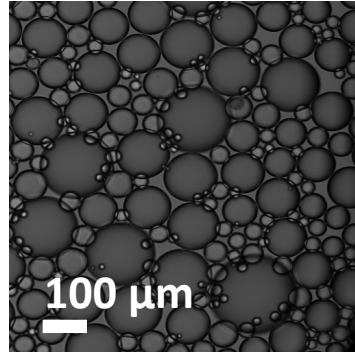
Kuehne, A. J. C. *et al.*, 2011, ChemComm, 47 (45)



Duncanson, W. J., *et al.*, 2012, Soft Matter, 8 (41)

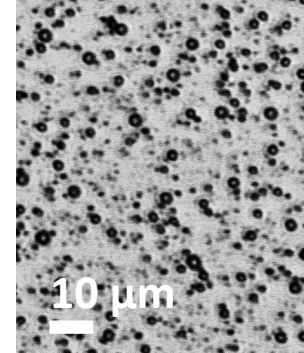
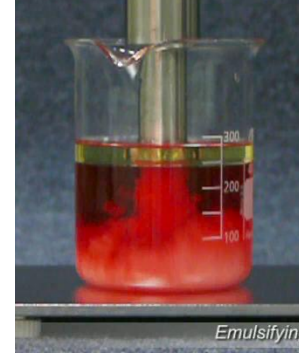
How can emulsions be made?

mechanical mixing



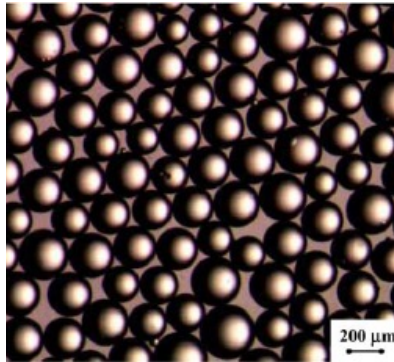
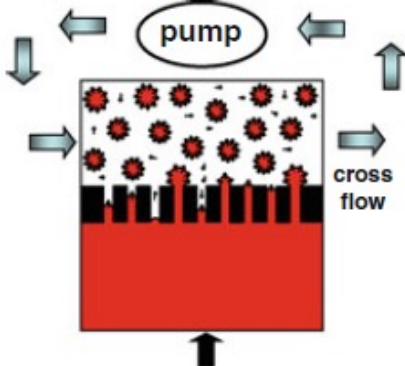
<http://www.csiro.au>

sonication



<http://www.hielscher.com>

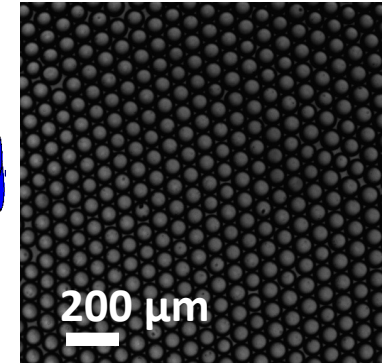
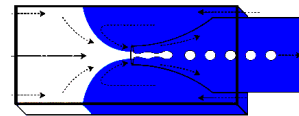
membrane emulsification



Vladislavljec, G.T., et al., *Microfluidics and Nanofluidics*, 2012. **13**(1)

Vladislavljec, G. T. et al., 2006, *Journal of Colloid and Interface Science* **299**(1)

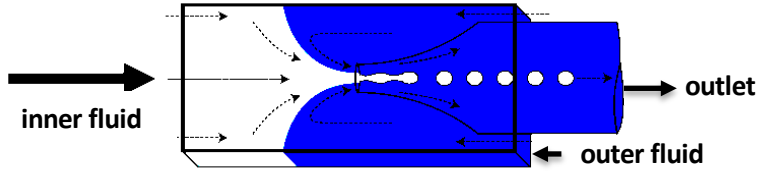
microfluidics



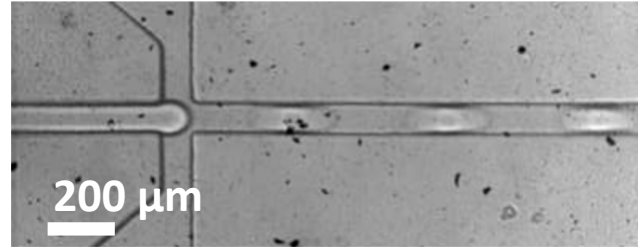
Utada, A.S., et al., *Mrs Bulletin*, 2007. **32**(9):

Microfluidics: Production of single emulsion drops

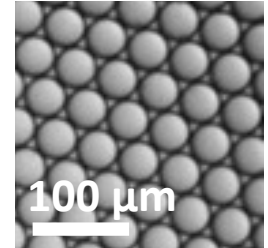
Production of single emulsions



Adapted from: Utada, A.S., et al., Mrs Bulletin, 2007. 32(9): p. 702-708

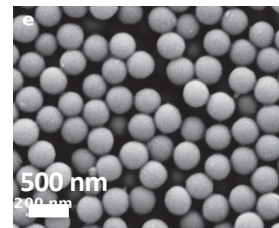
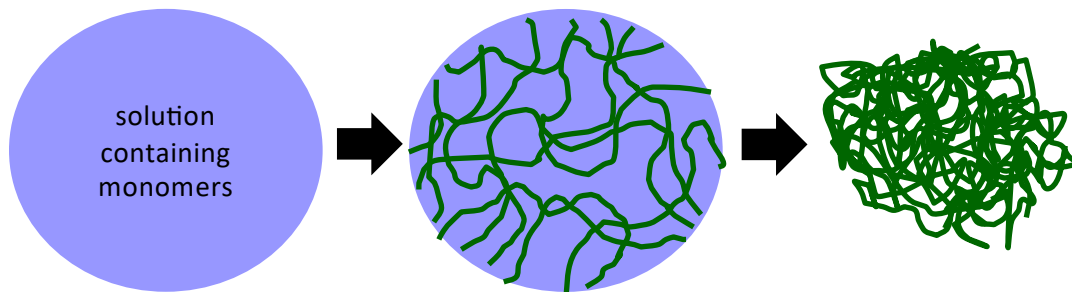


movie 100 $\times$ slowed down

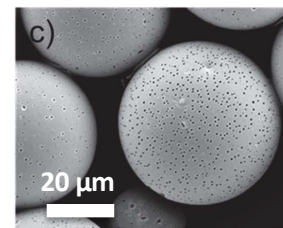


How can capsules be made?

Templates for microparticle production

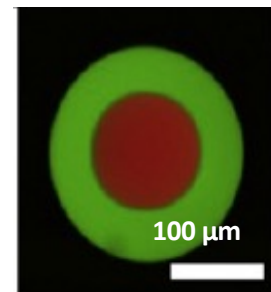
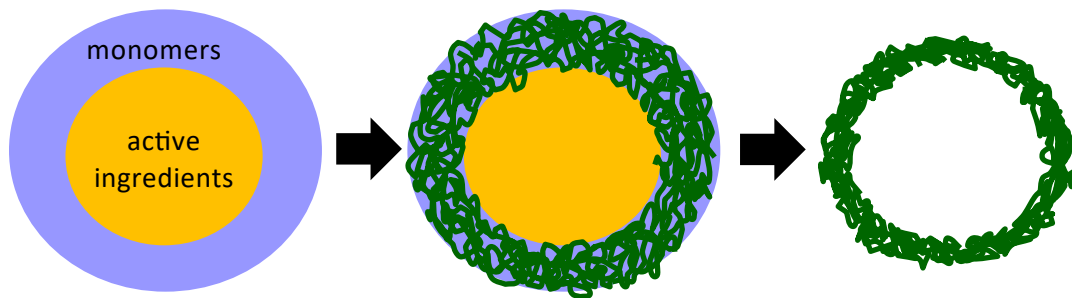


Kuehne, A. J. C. *et al.*, 2011, ChemComm, 47 (45)

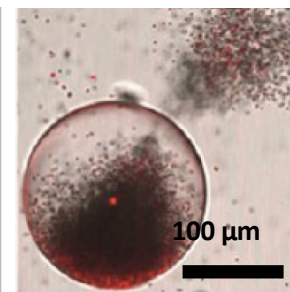


Duncanson, W. J., *et al.*, 2012, Soft Matter, 8 (41)

Templates for microcapsule production



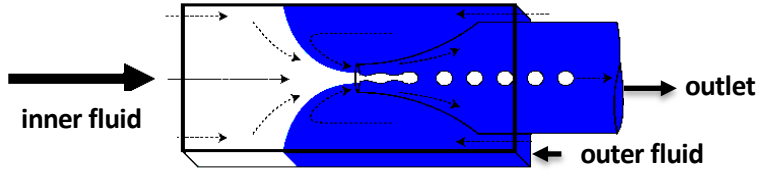
S. Seiffert, *et al.* JACS **132**, 6606, (2010)



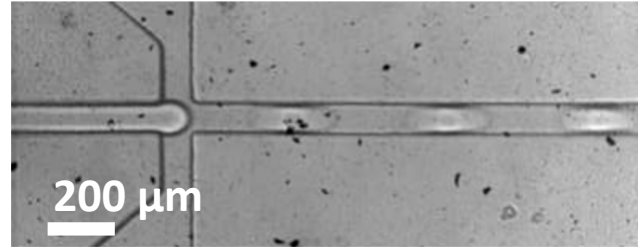
Abbaspourrad, A., *et al.*, 2011, JACS, 135 (20)

Microfluidics: Production of double emulsion drops

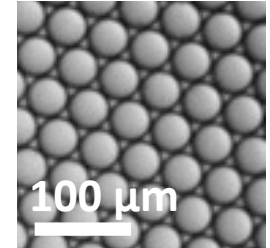
Production of single emulsions



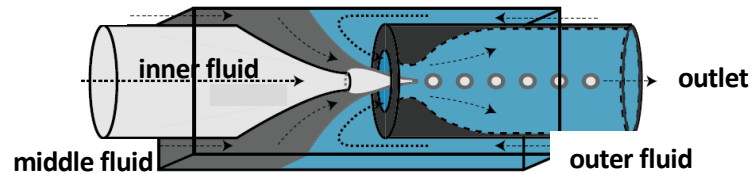
Adapted from: Utada, A.S., et al., Mrs Bulletin, 2007. **32**(9): p. 702-708



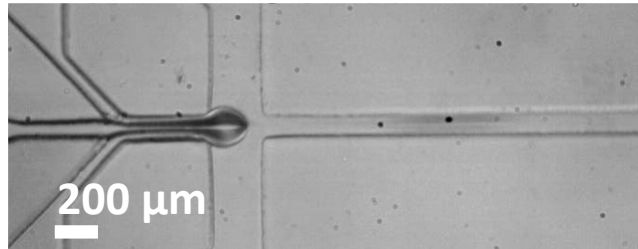
movie 100 $\times$ slowed down



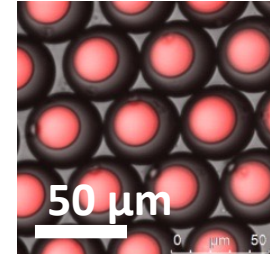
Production of double emulsions



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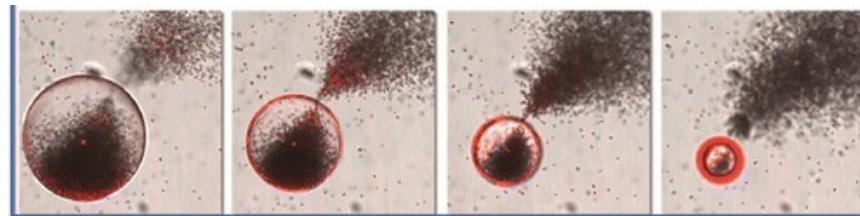


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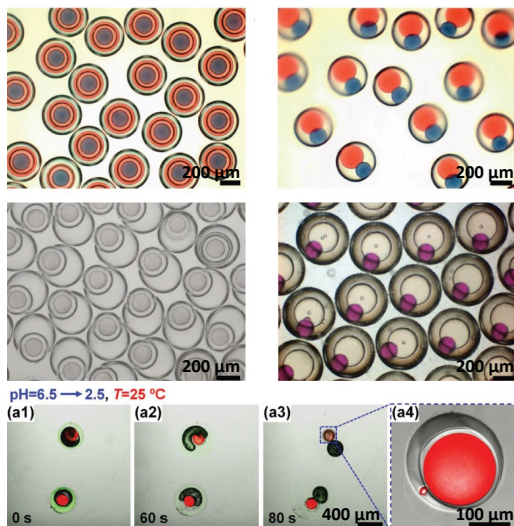
Synthetic compartments

Controlled release



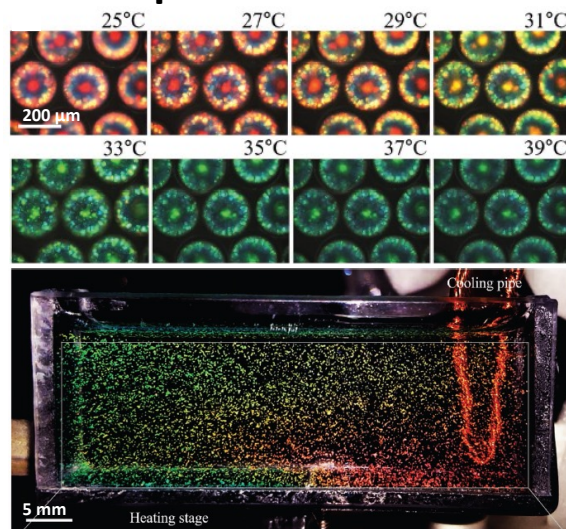
A. Abbaspourrad, *et al.*, *JACS*, **2013**, 135, 7744–7750

Containers for reactions



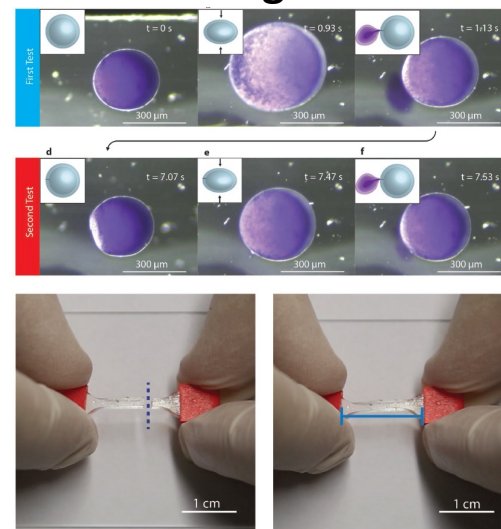
C.-L. Mou, *et al.*, *Adv. Sci.*, **2018**, 5 (6), 1700960

Temperature sensors



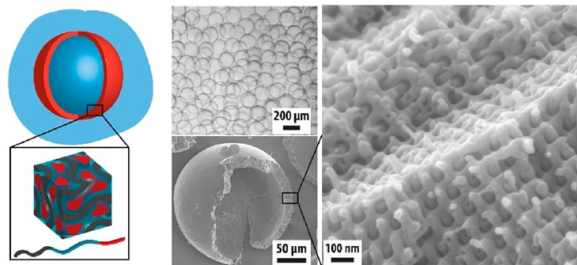
T.M. Choi, *et al.*, *Adv. Mat.*, **2018**, 30 (43), 1803387

Self-healing materials

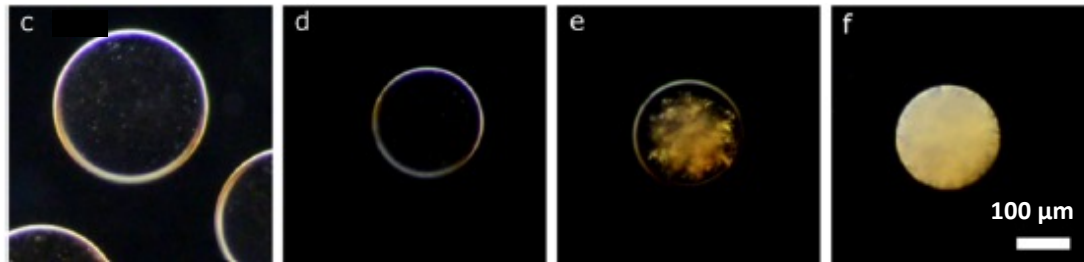


D.G. Moore, *et al.*, *Adv Mat Interfaces*, **2018**, 5 (18), 1800813

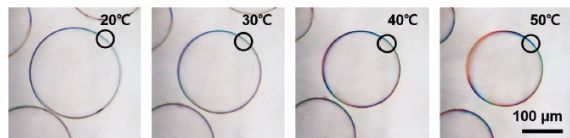
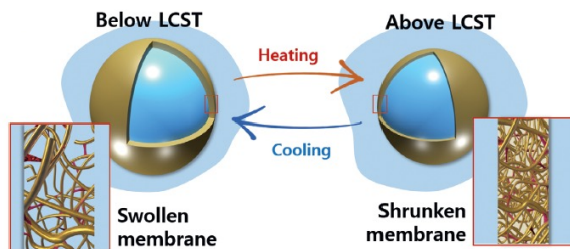
Controlling the structure of shells



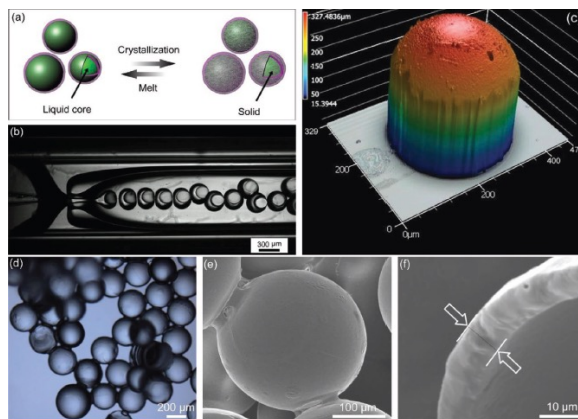
Werner, J. G., *et al.*, *ACS Nano* **2021**, 15 (2), 3490–3499.



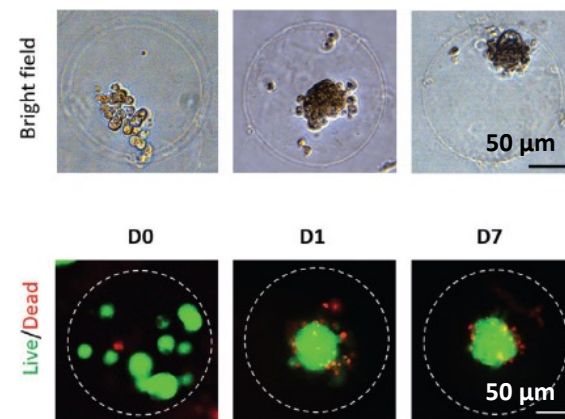
Wilson-Whitford, S. R., *et al.*, *ACS Appl. Mater. Interfaces* **2021**, 13 (4), 5887–5894.



Choi, Y. H., *et al.*, *Adv. Funct. Mater.* **2021**, 31 (24), 2100782



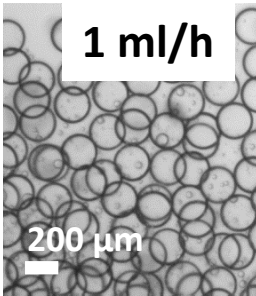
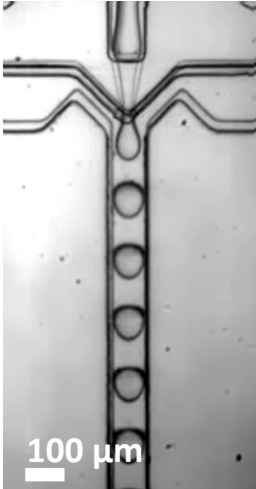
Liu, J., *et al.*, *Adv. Mater. Technol.* **2020**, 5 (10), 2000286



Liu, H., *et al.*, *Adv. Sci.* **2020**, 7 (11), 1903739

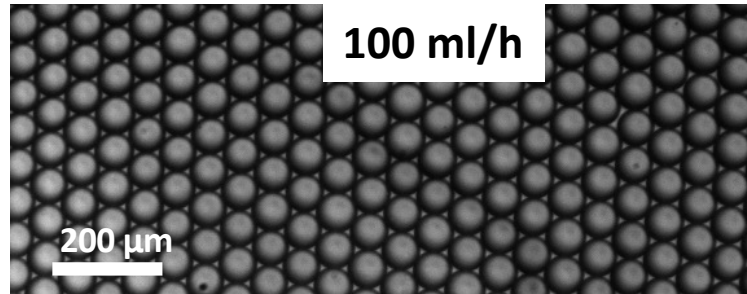
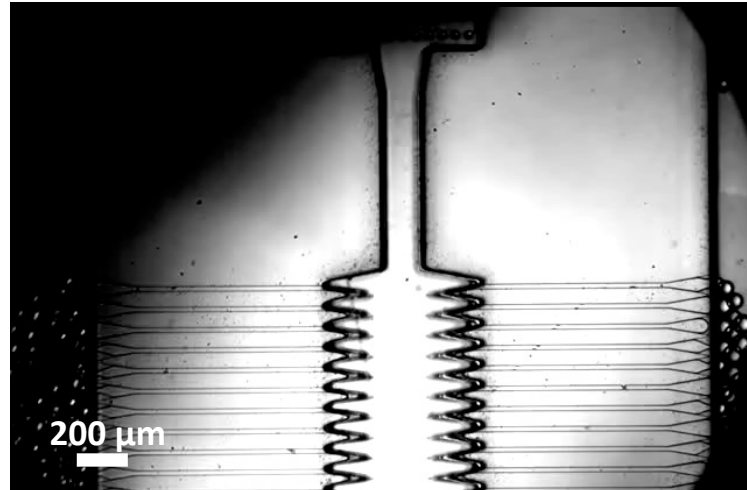
High throughput production of drops

Microfluidics: Double emulsions

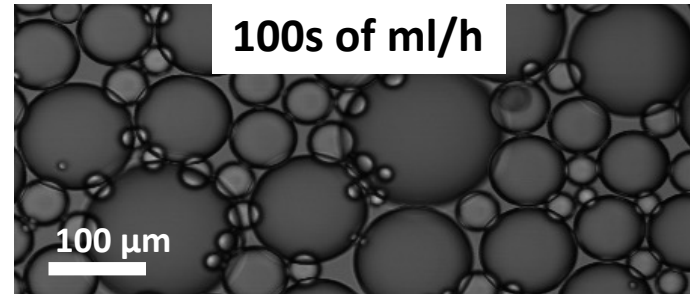


Production of emulsions in the lab

Parallelized microfluidic device

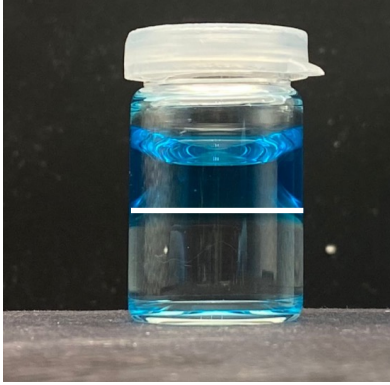


Bulk emulsification

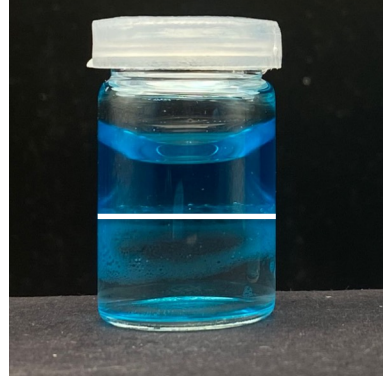


Stabilization of emulsions

Before emulsification



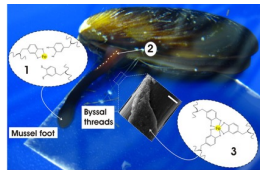
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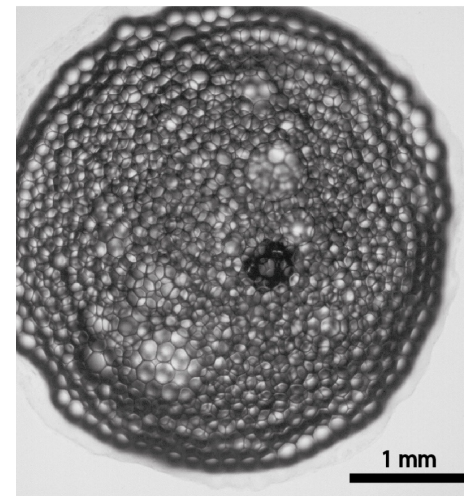
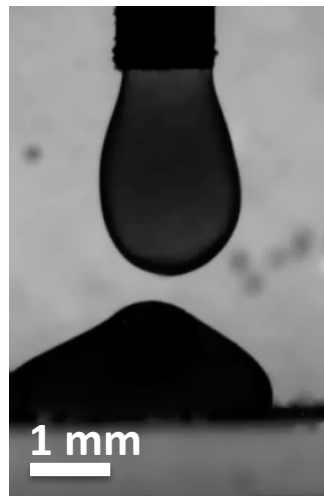
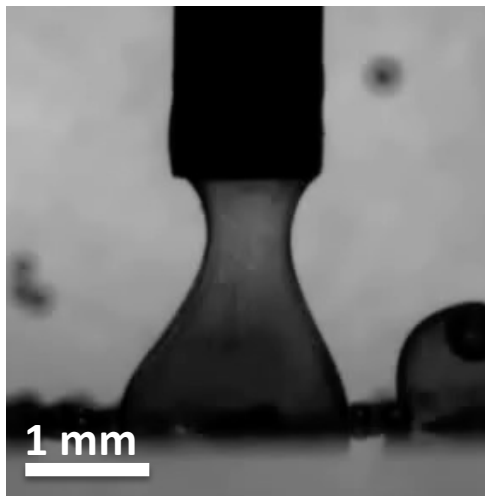
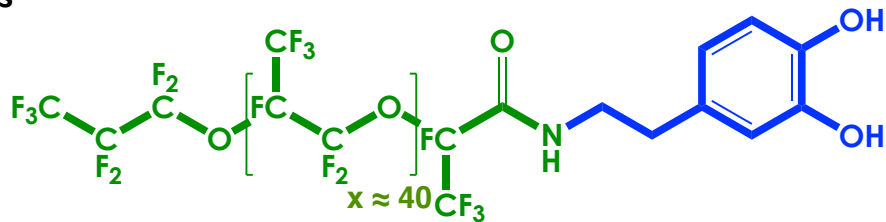
Gaia
DeAngelis

Ionic crosslinking of surfactants

Adhesion of the mussel byssus



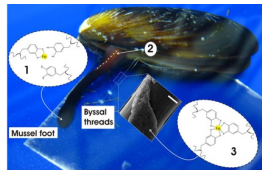
Holten-Andersen, N.; et al.,
PNAS, **2011**, *108*, 2651–2655



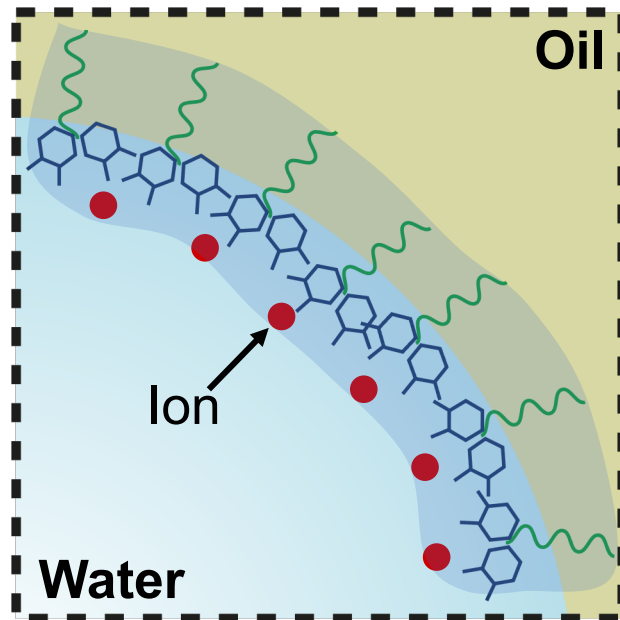
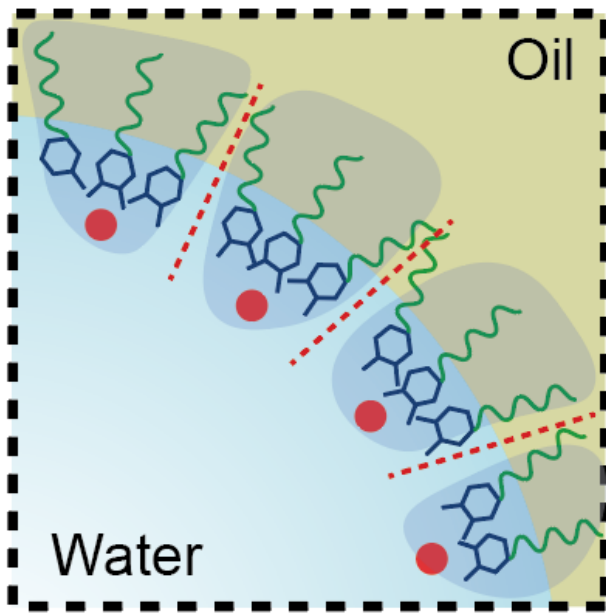
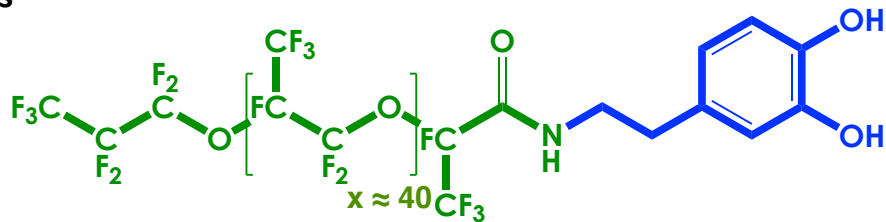
Gianluca
Etienne

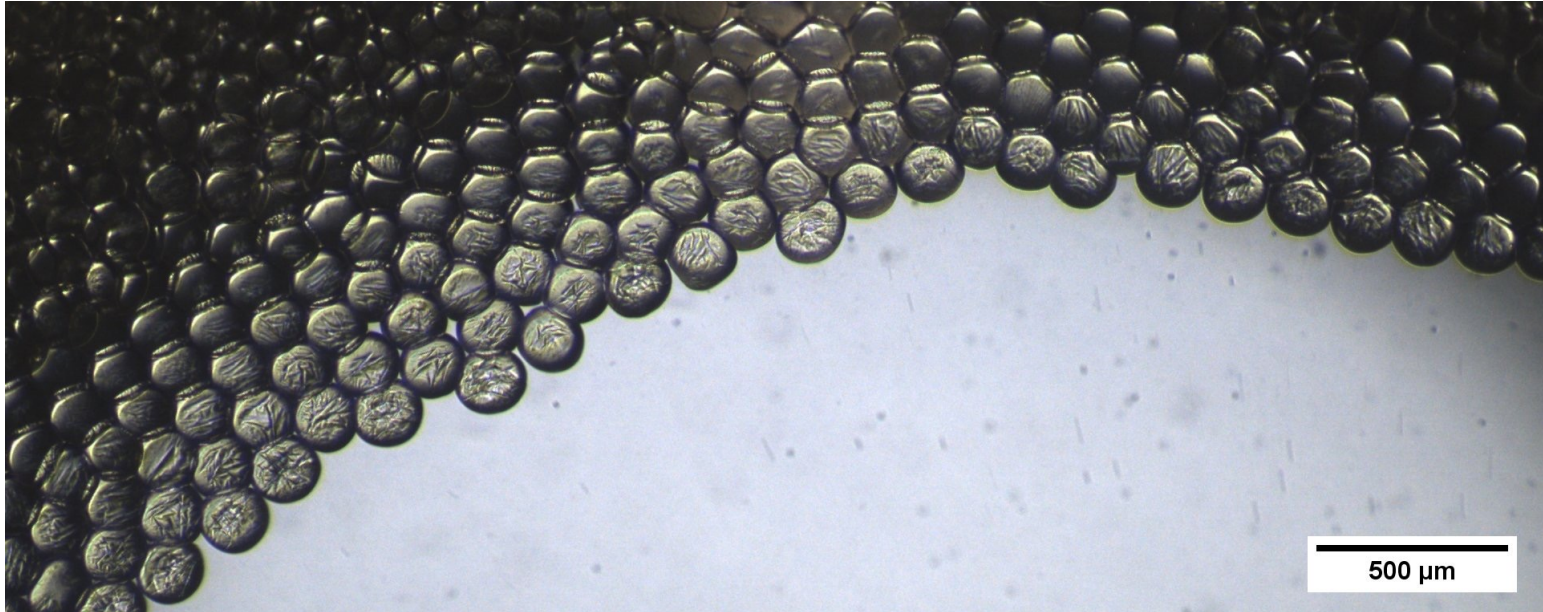
Ionic crosslinking of surfactants

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Holten-Andersen, N.; et al.,
PNAS, **2011**, *108*, 2651–2655

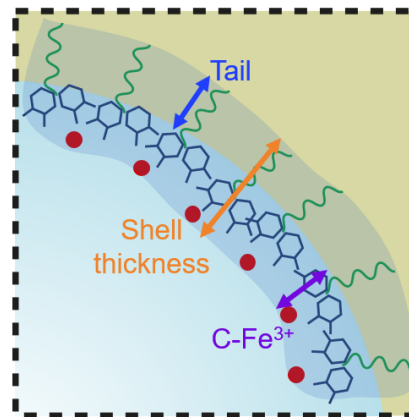
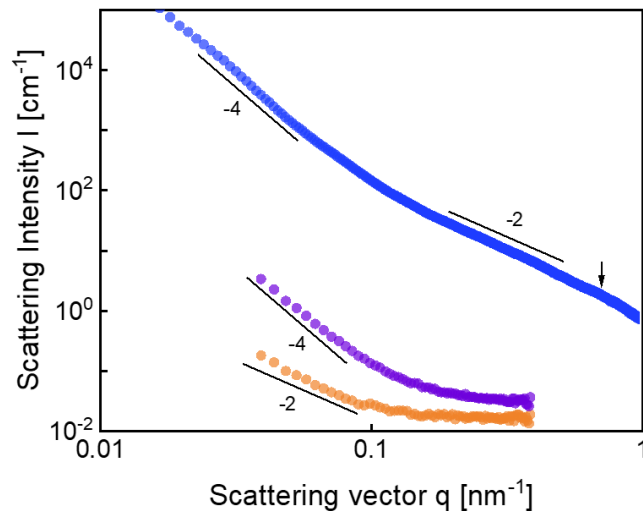
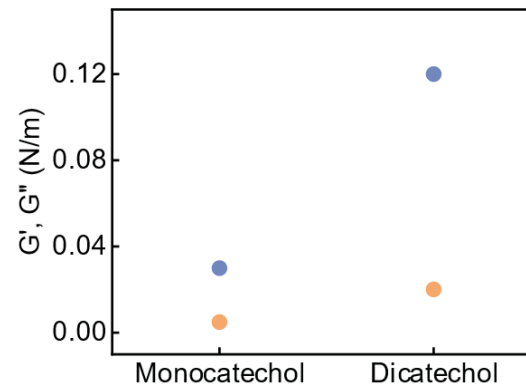
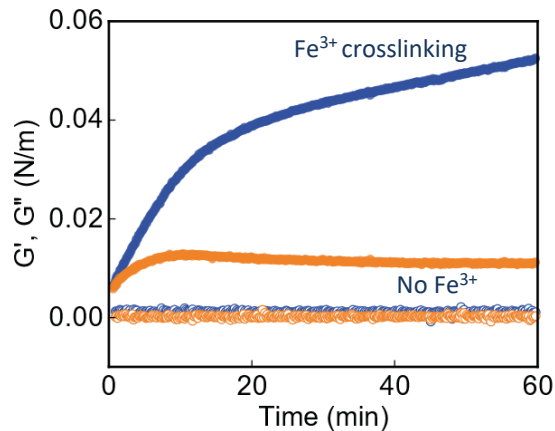


FC(F)(F)C(F)(F)OC(C)(F)C(F)(F)OC(F)(F)(F)C(=O)N(C)CCOC(=O)CCOC(=O)CC(C)COC(=O)CC(C)CNC(C)CCNC(=O)CCc1ccc(O)c(O)c1

Mechanical properties of viscoelastic films



Gaia
De Angelis



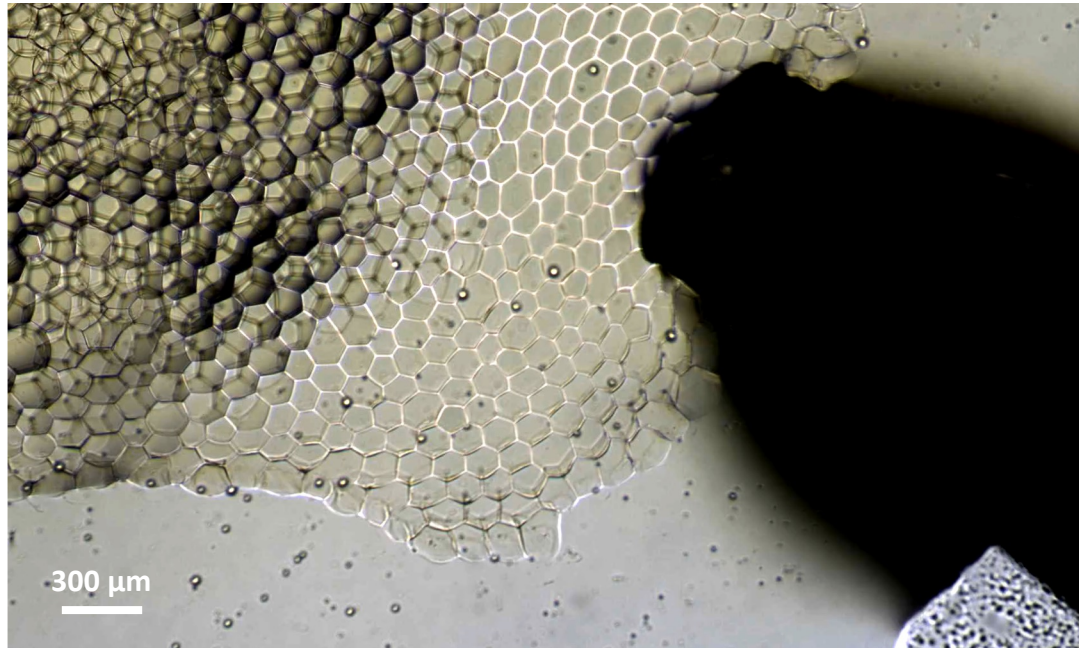
Shell thickness: 11 nm
Tail: 9 nm
C- Fe^{3+} : 2 nm

Self-healing of pyrogallol-ion crosslinked scaffolds

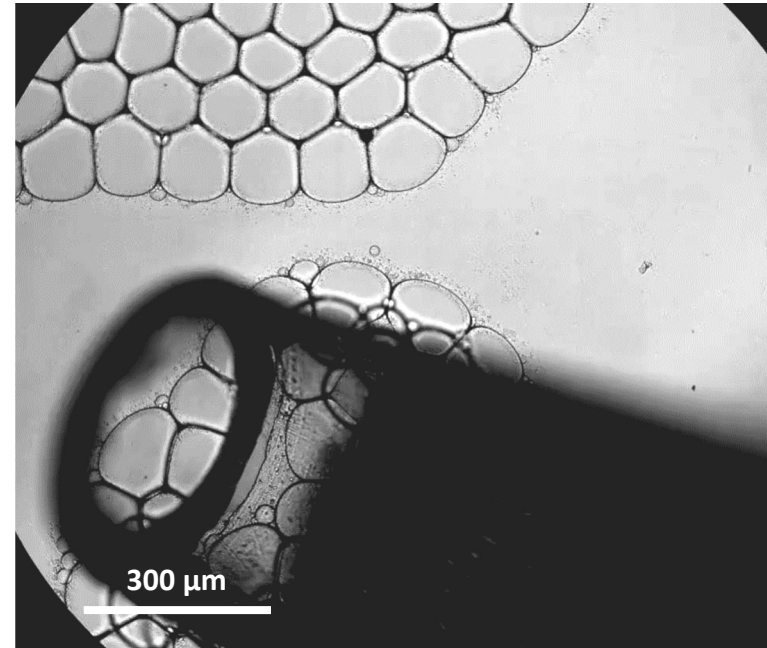


Gaia
DeAngelis

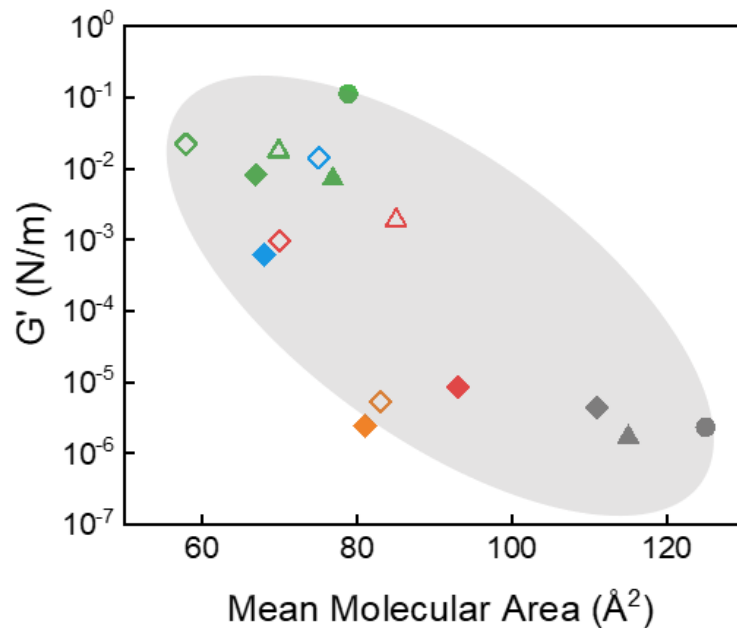
crosslinking with Fe^{3+}



crosslinking with Co^{2+}



Gaia
DeAngelis



○ DC
△ DNC
◇ DG

Fe 3+
Cu 2+
Co 2+
Ca 2+

Interior - pH

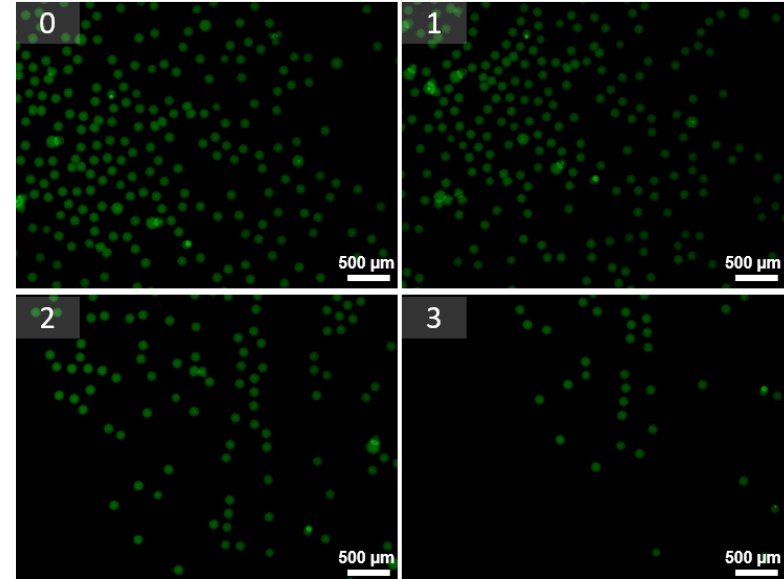
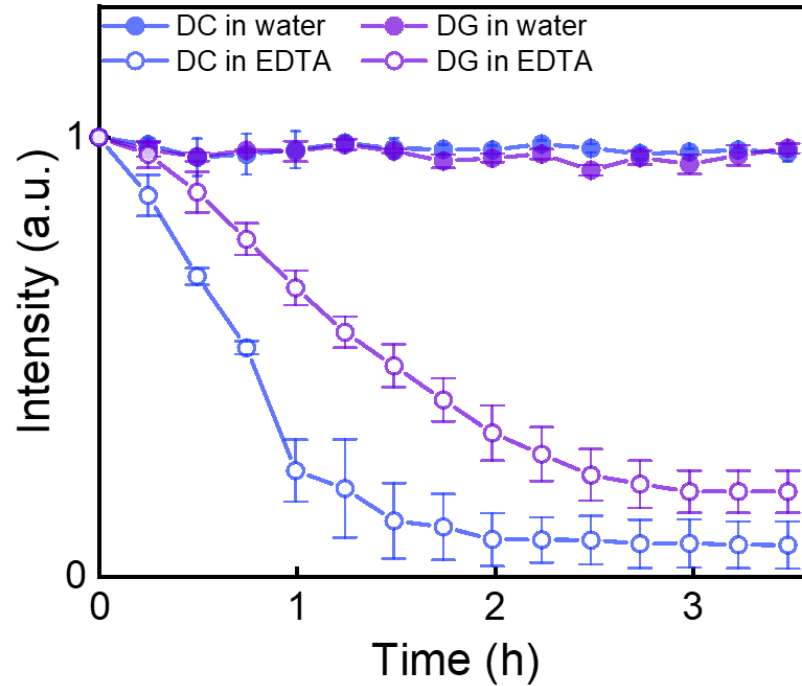
☐ pH 9

☒ pH 7

Capsule permeability

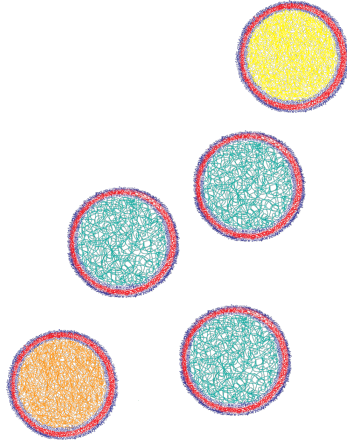
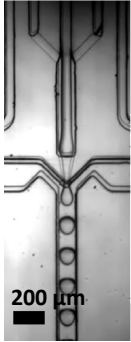


Gaia
DeAngelis

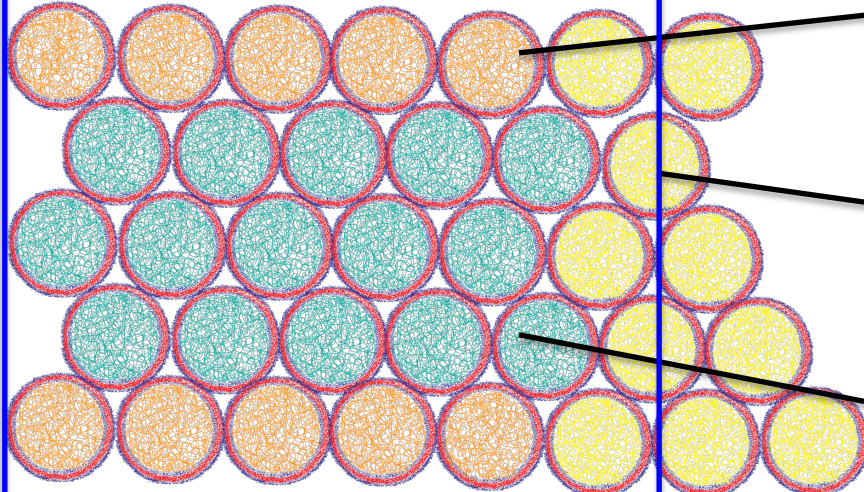


Bio-inspired processing

Selectively permeable capsules



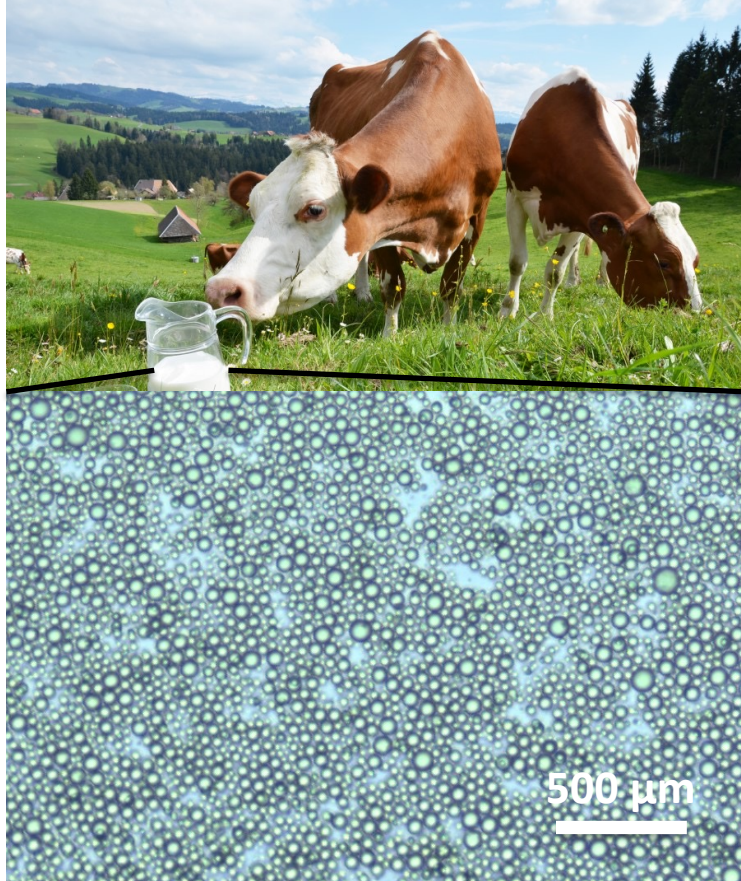
3D printing of granular hydrogels



Functionalization

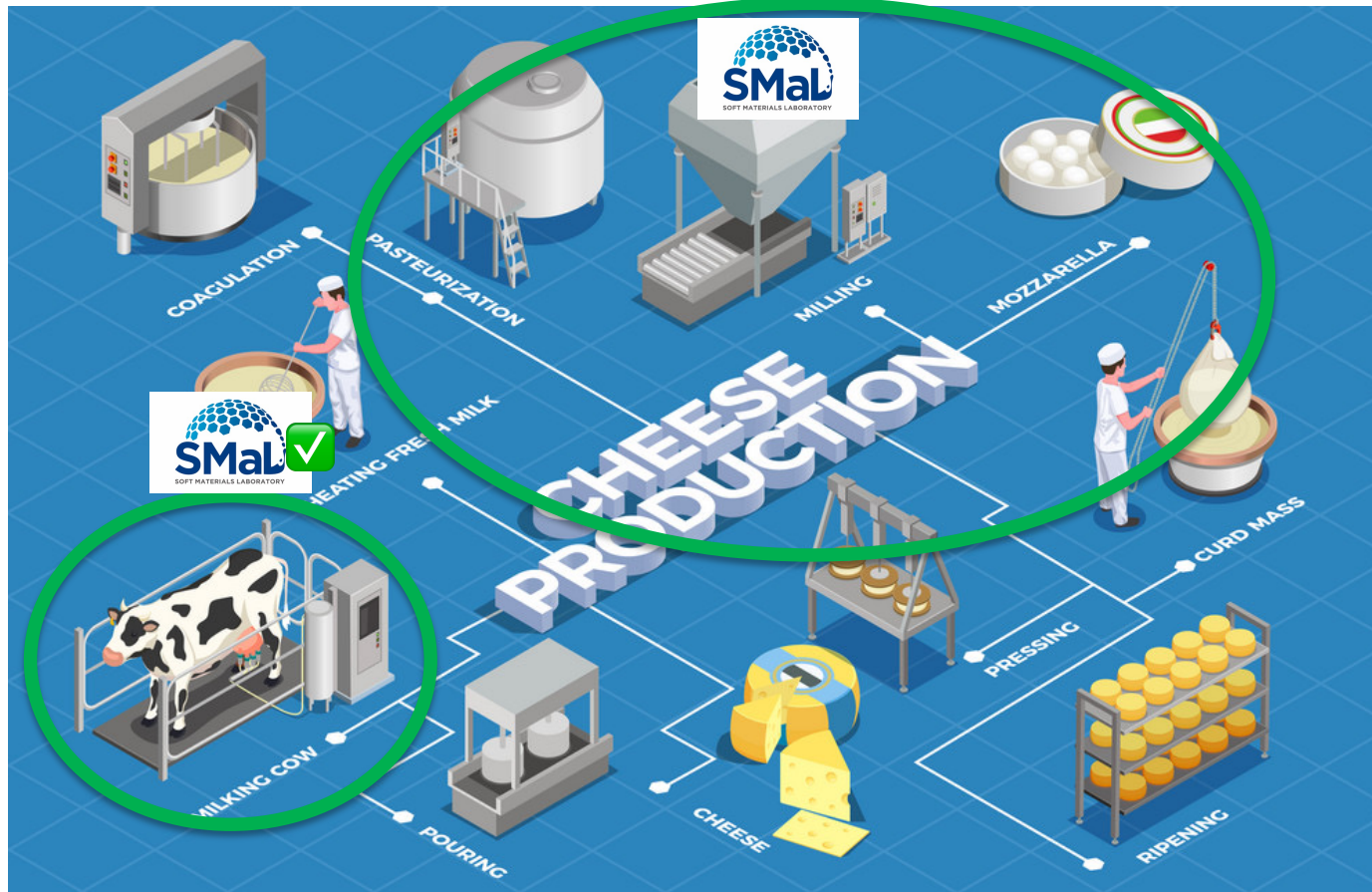


Emulsion drops

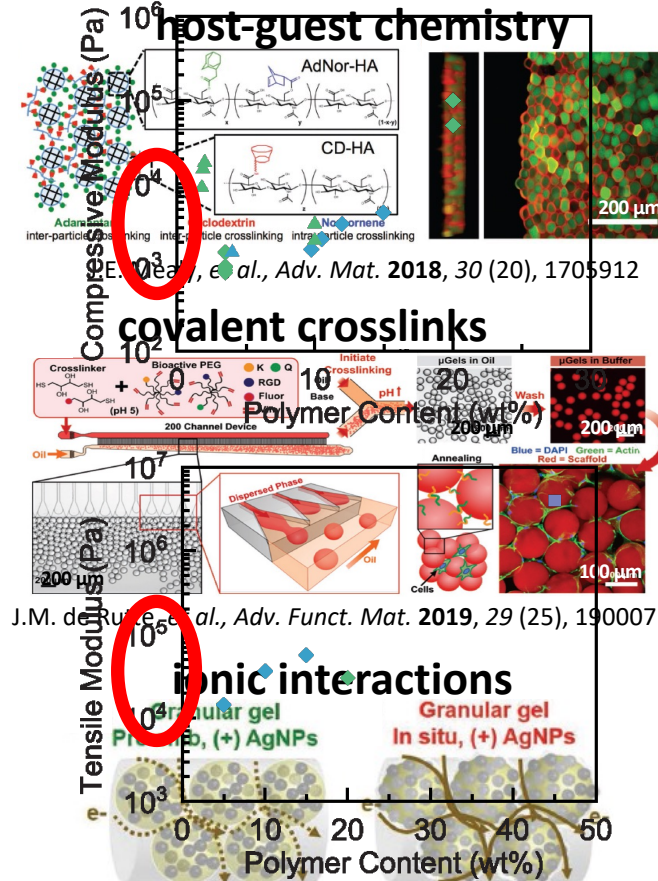
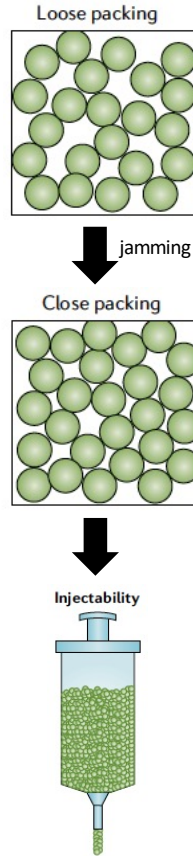


https://www.clipartmax.com/middle/m2H7K9b1b1A0G6K9_9lef-kla4-140927-girl-thinking-cartoon/

Emulsions



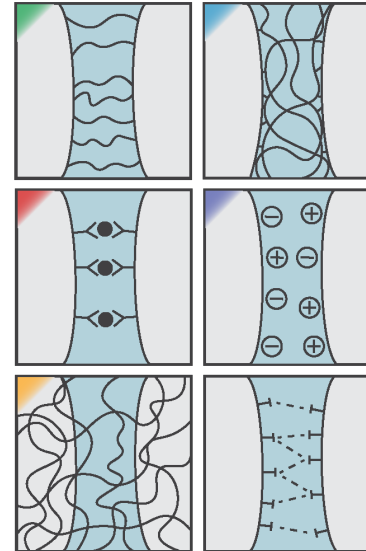
Granular hydrogels



J.M. de Groot et al., *Adv. Funct. Mat.* **2019**, 29 (25), 1900071

M. Shin, A. Charlet, et al., *Chem. Sci.* **2022**, 13, 11229
<https://doi.org/10.1039/D1SC06231J>

Interparticle interaction	Microgel composition
● Covalent	◆ Biopolymer
● Binder / additive	▲ PEG
● Coordination	■ Monomer
● Electrostatic	
● Interpenetrating percolating network	



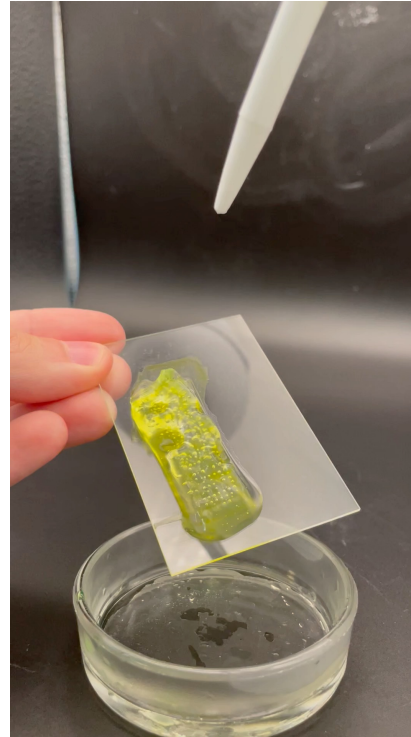
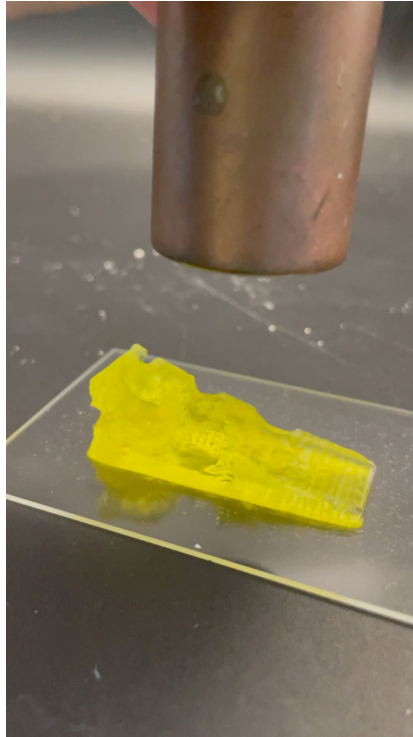
A. Charlet, et al., *Chem. Sci.* **2022**,
<https://doi.org/10.1039/D1SC06231J>

Adapted from A.C. Daly,
 et al., *Nat. Rev. Mat.*
2020, 5 (1), 20–43

Mechanics of soft granular materials



Matteo
Hirsch



From cheese to materials



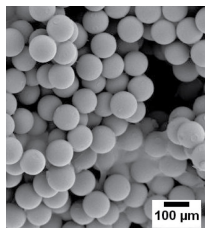
<https://recipes.timesofindia.com/articles/features/know-your-cheese-a-complete-guide-to-types-of-cheese/articleshow/82065716.cms>



https://www.clipartmax.com/middle/m2H7K9b1b1A0G6K9_9lef-kla4-140927-girl-thinking-cartoon/



Alvaro
Charlet

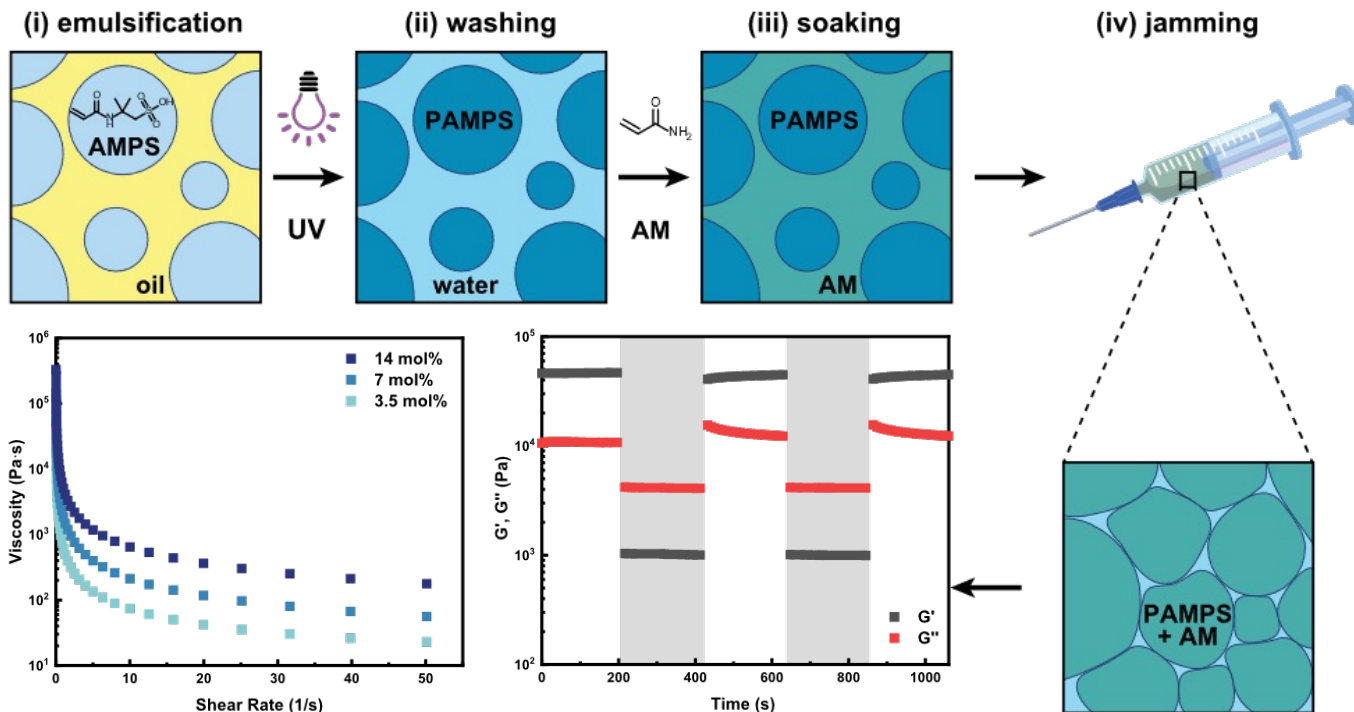


3D printing of load-bearing hydrogels



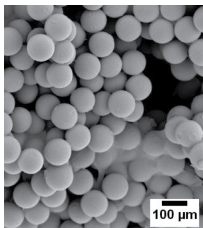
Matteo
Hirsch

Microgel ink preparation





Alvaro
Charlet

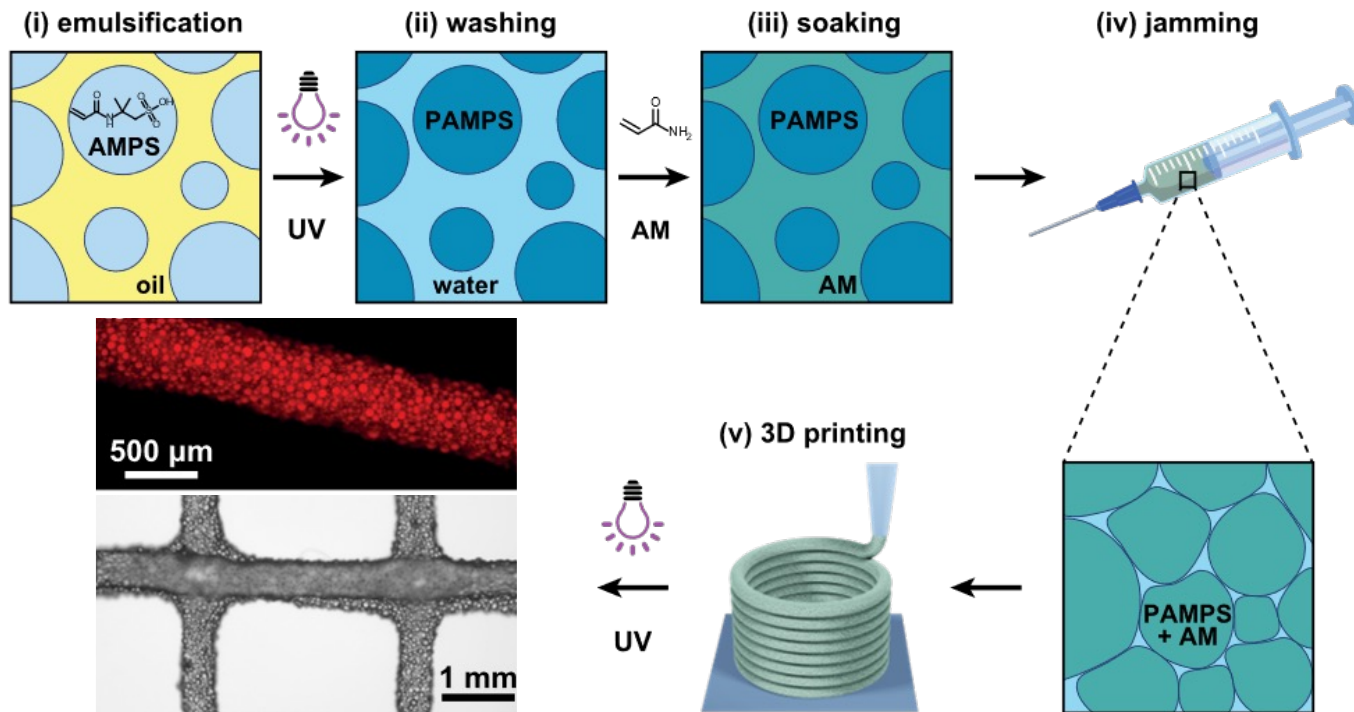


3D printing of strong and tough hydrogels



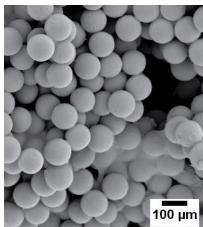
Matteo
Hirsch

Microgel ink preparation





Alvaro
Charlet

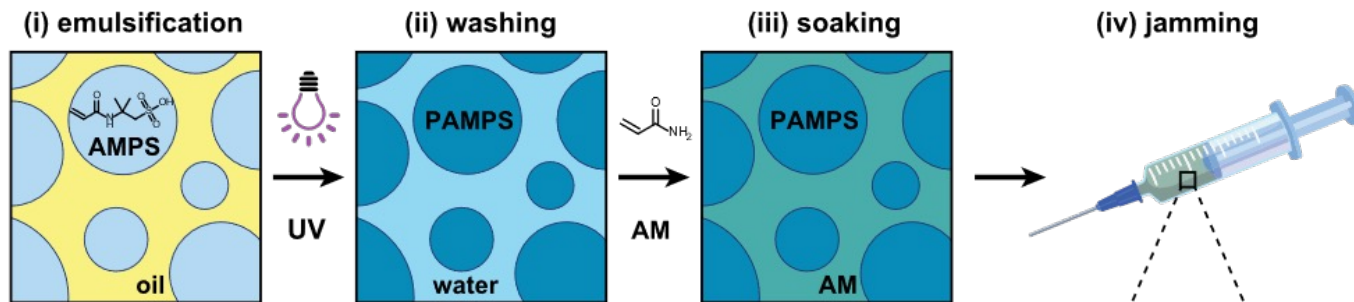


3D printing of strong and tough hydrogels

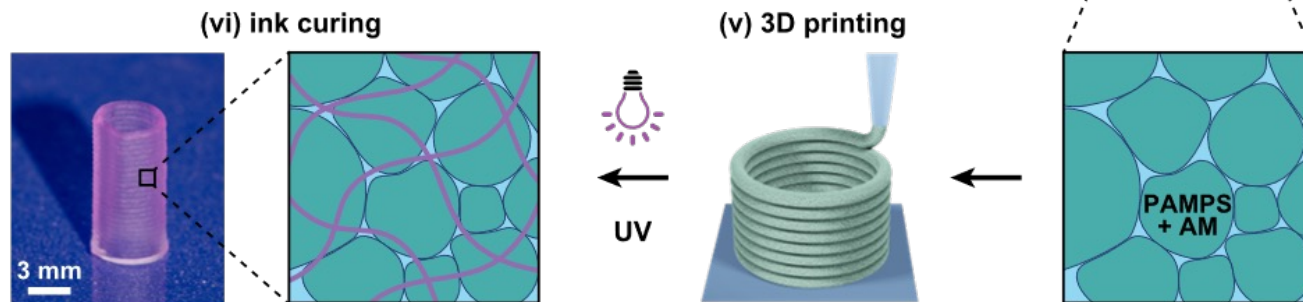


Matteo
Hirsch

Microgel ink preparation



DNGH 3D printing and post-curing



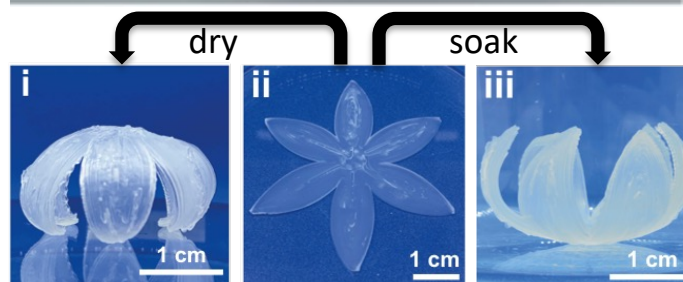
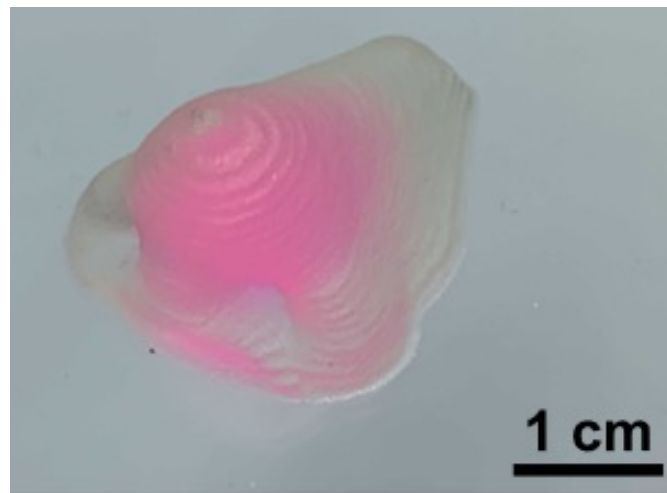
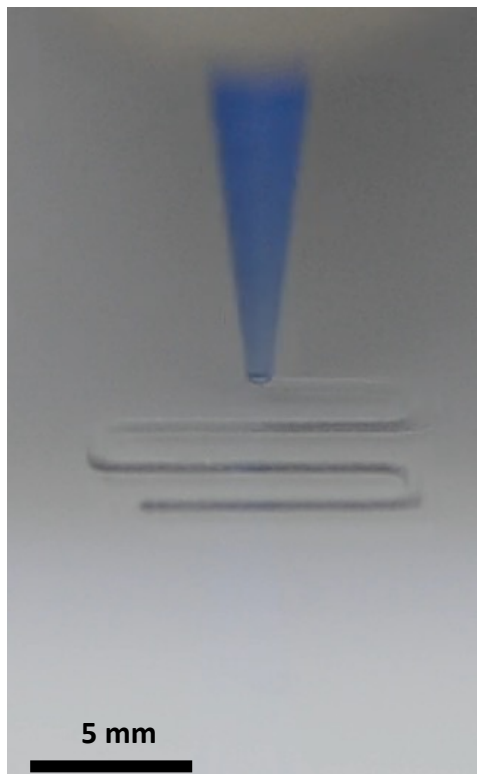


Alvaro
Charlet

3D printing of strong and tough granular hydrogels



Matteo
Hirsch

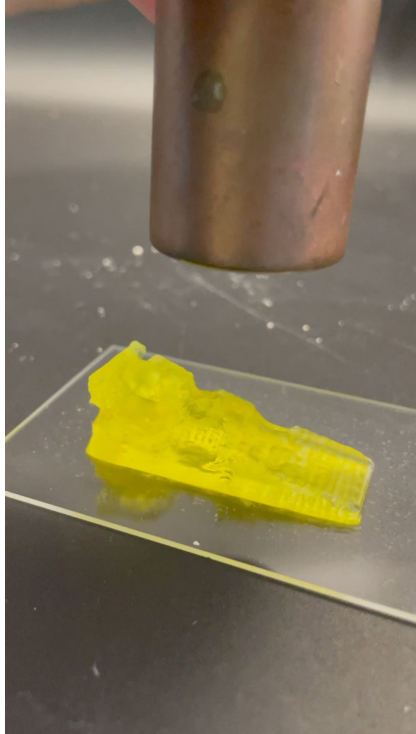


Mechanics of soft granular materials

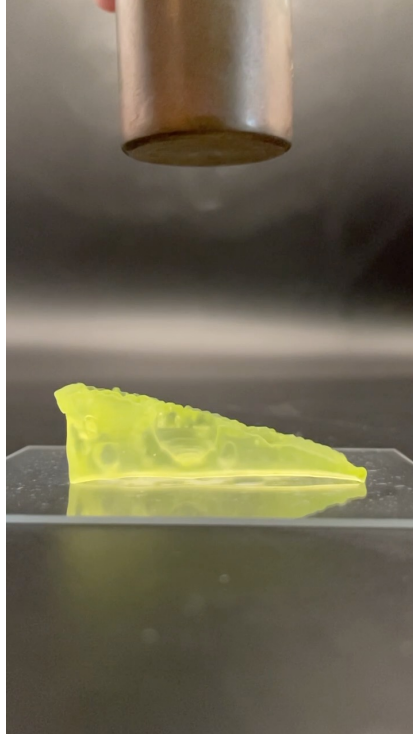


Matteo
Hirsch

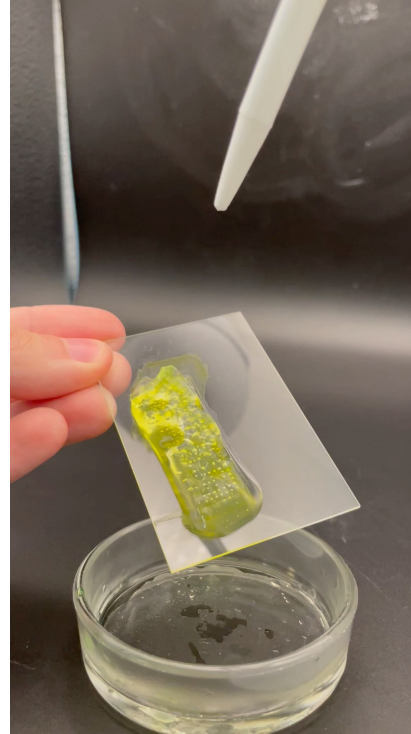
without 2nd network



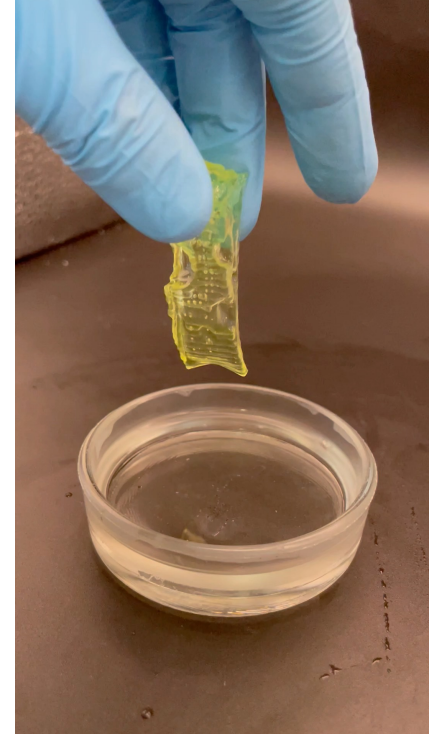
with 2nd network



without 2nd network



with 2nd network



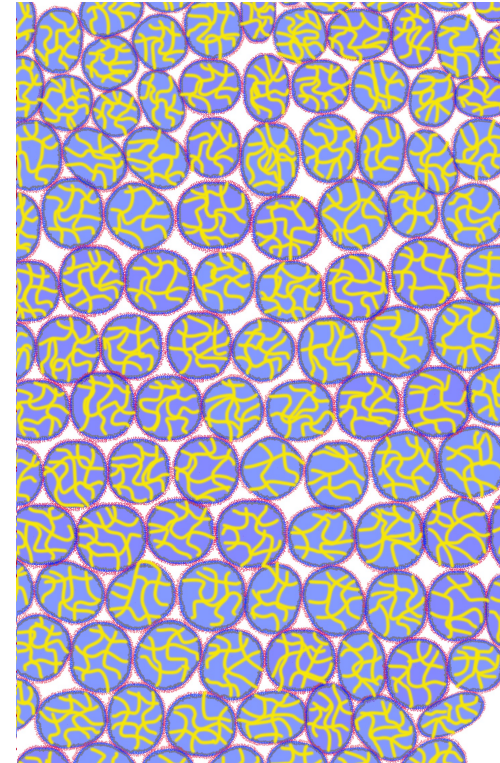
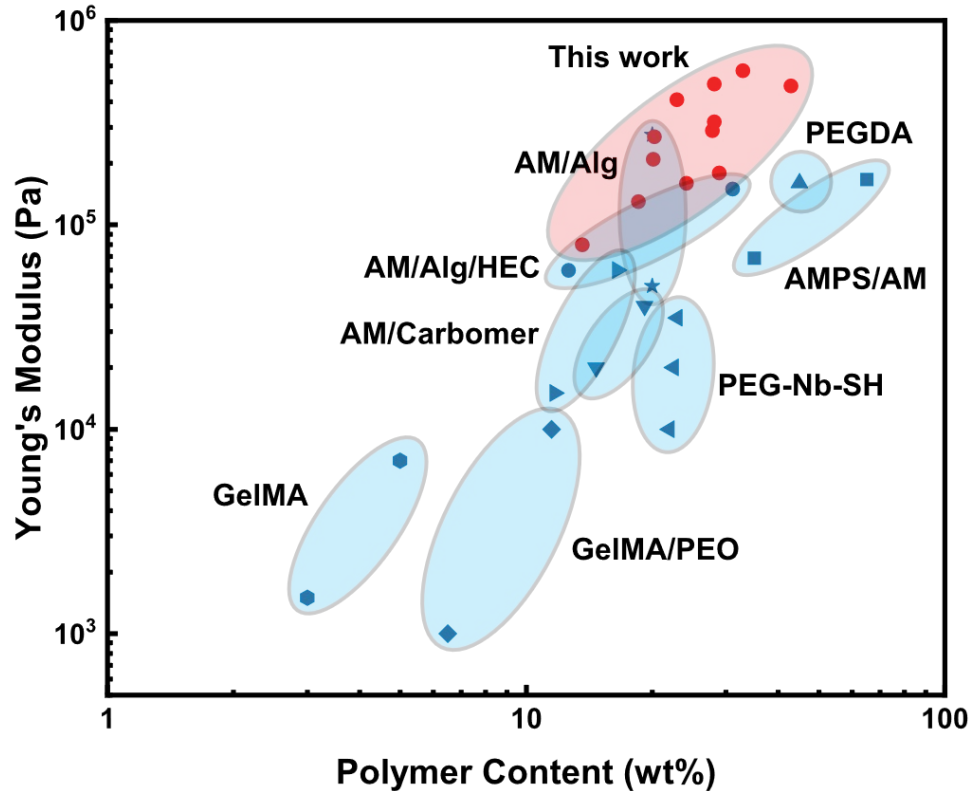


Alvaro
Charlet

Mechanical properties of 3D printed granular hydrogels



Matteo
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3D printing direction

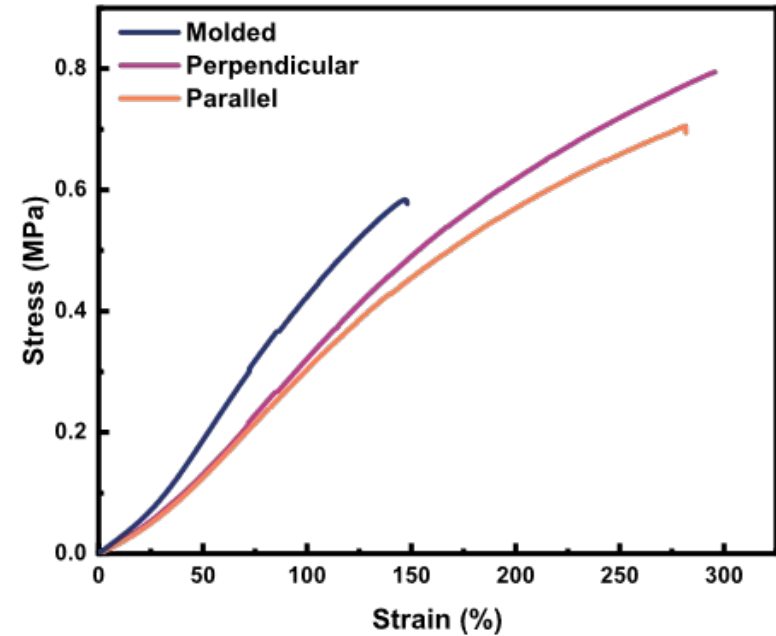


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Hirsch

Perpendicular



Parallel



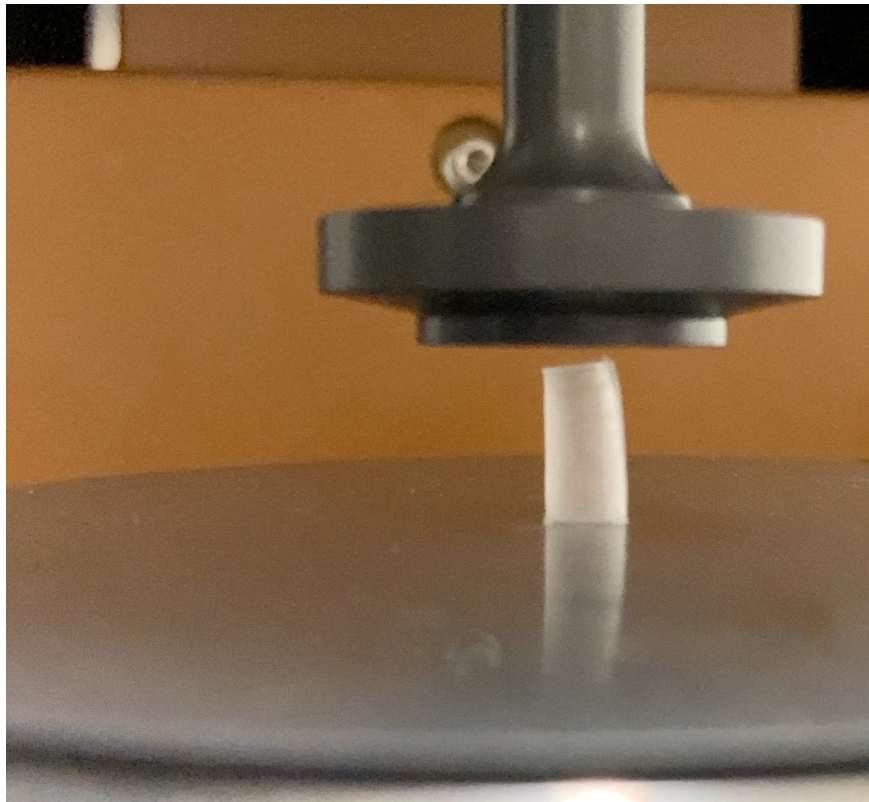


Alvaro
Charlet

3D printing of strong and tough granular hydrogels



Matteo
Hirsch



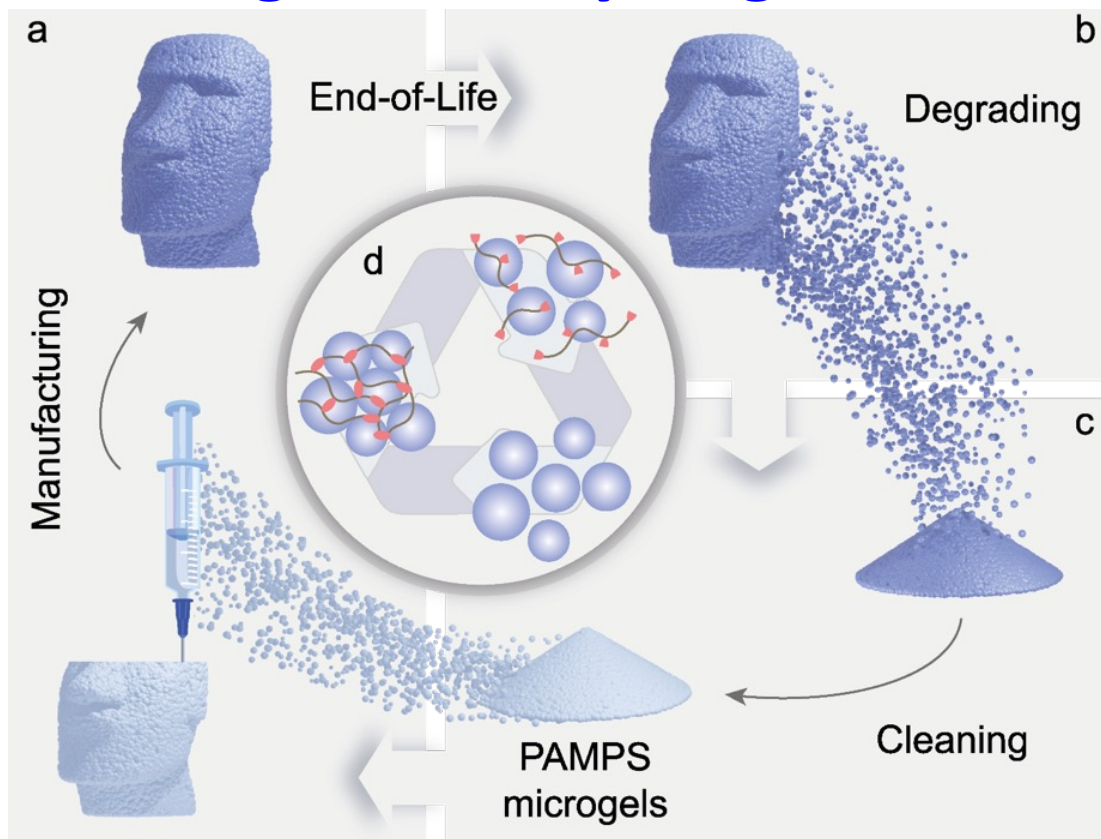


Alvaro
Charlet

Recyclable double network granular hydrogels



Matteo
Hirsch



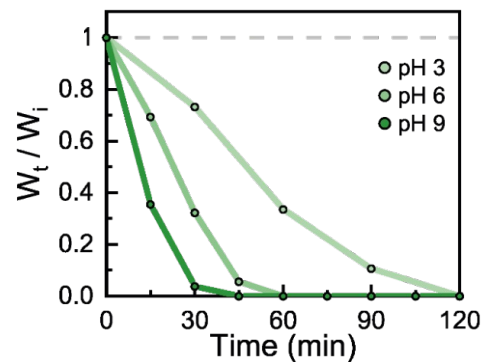
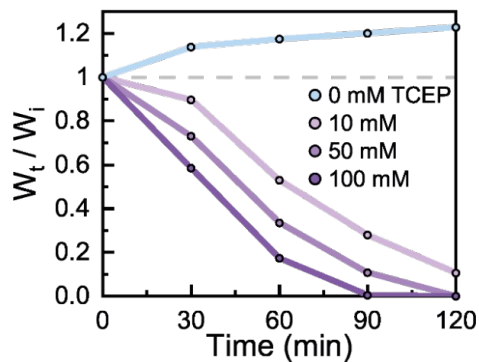
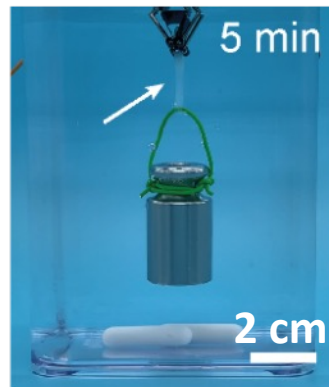
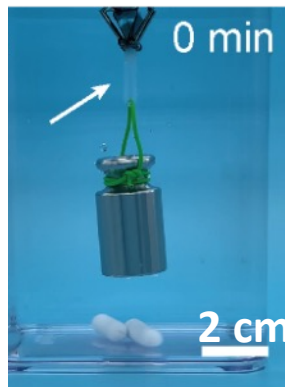
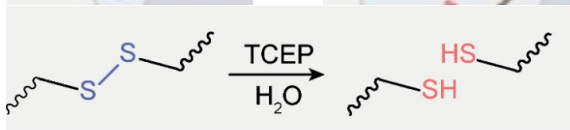
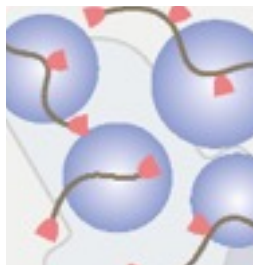
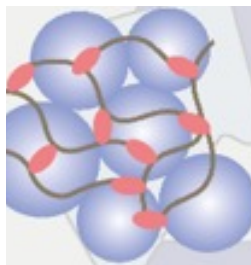


Alvaro Charlet

Degradation kinetics



Matteo Hirsch



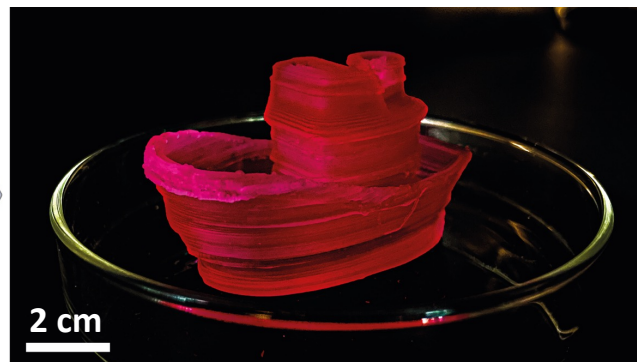
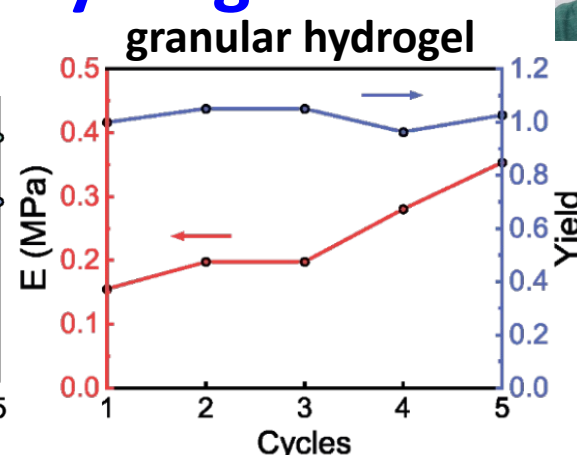
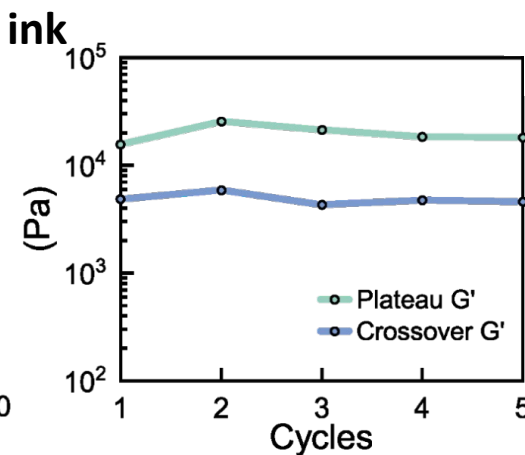
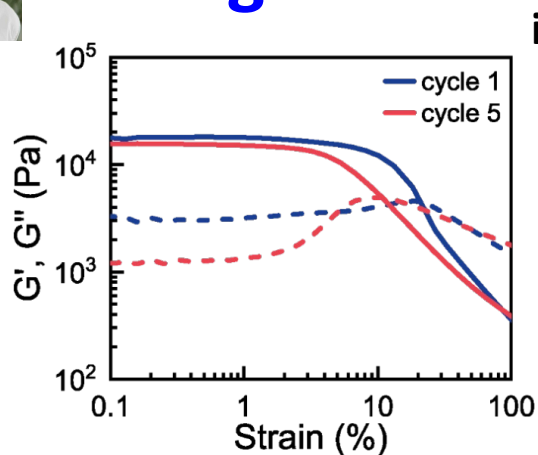


Alvaro
Charlet

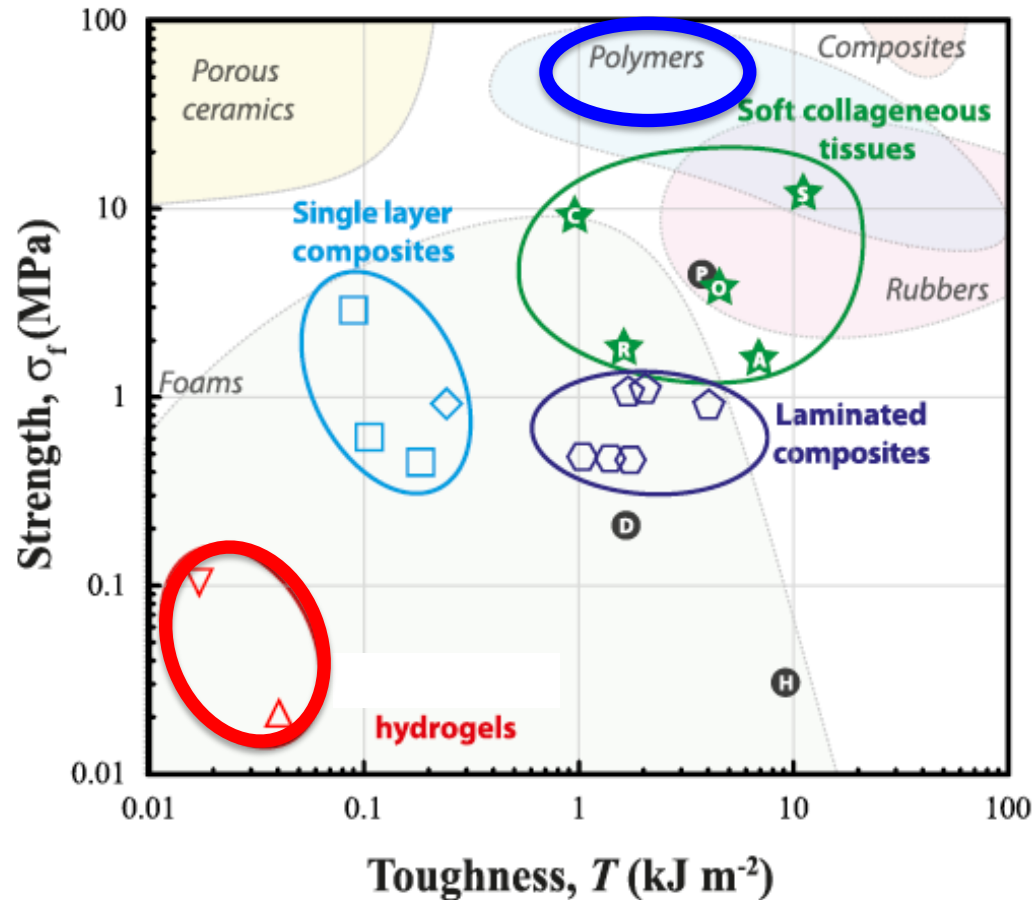
Mechanical properties of recyclable granular double network hydrogels



Matteo
Hirsch



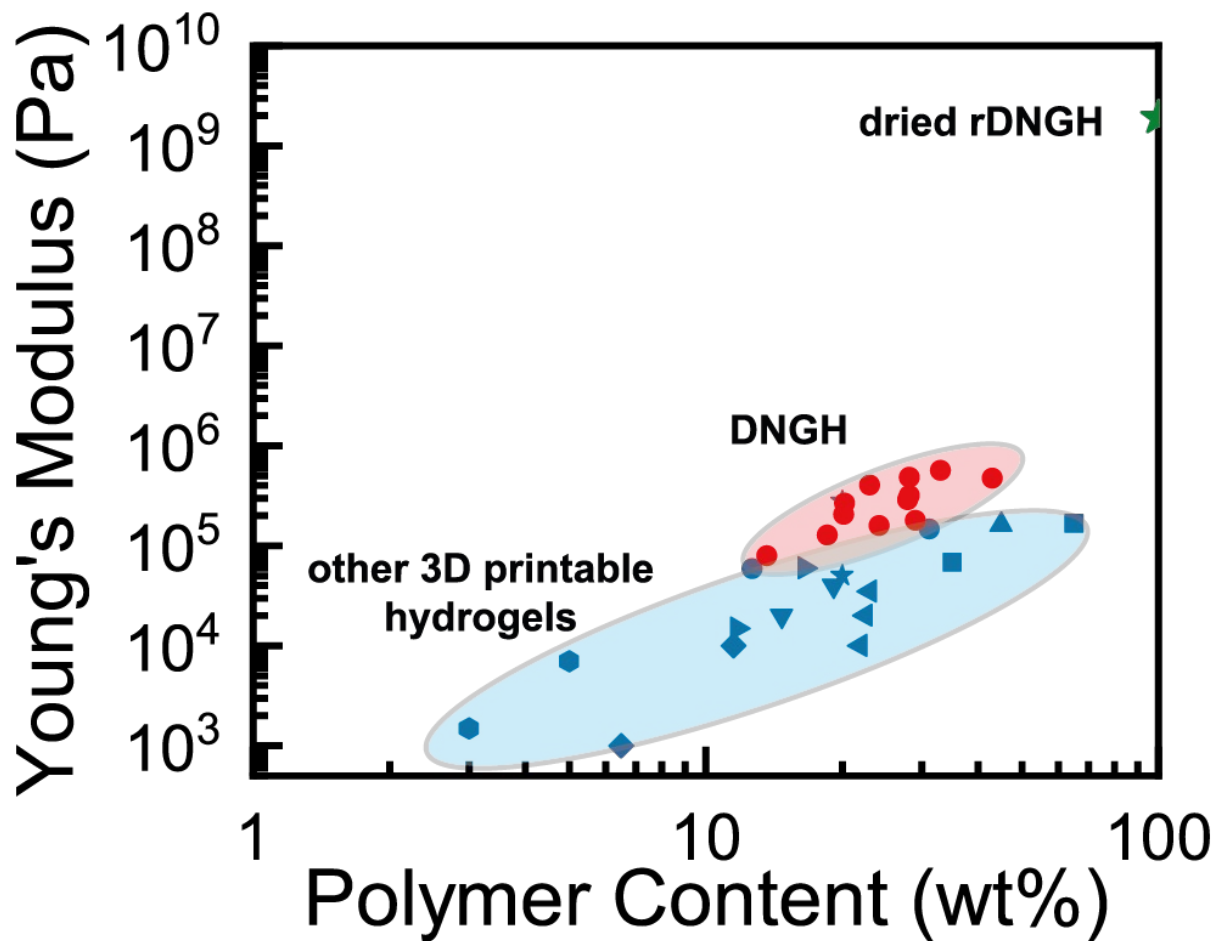
Mechanical properties of polymers





Alvaro
Charlet

Stiffness of dried hydrogels



Matteo
Hirsch

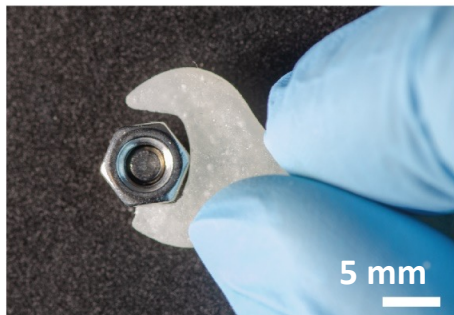
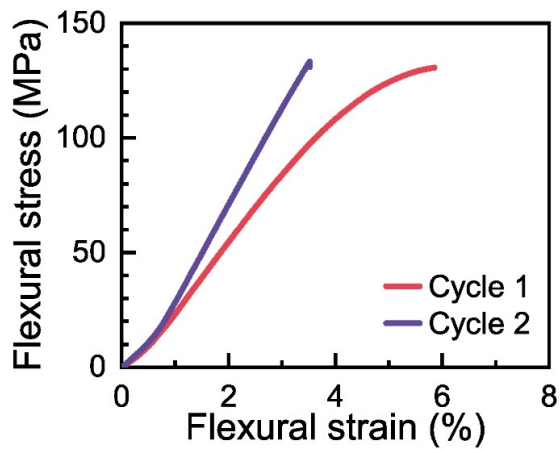
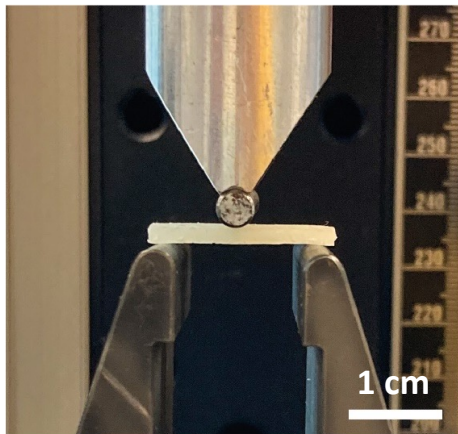


Alvaro
Charlet

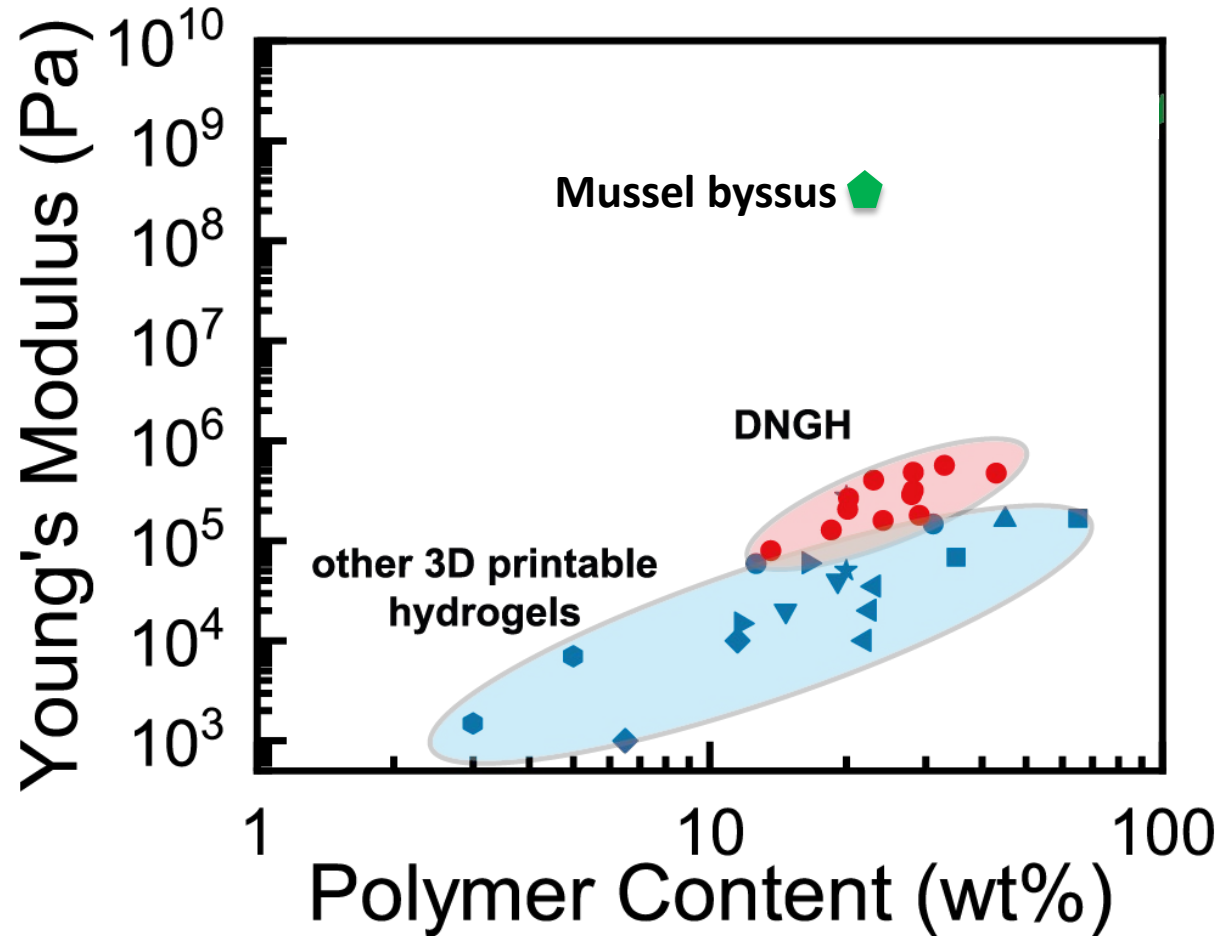
Dried hydrogels



Matteo
Hirsch



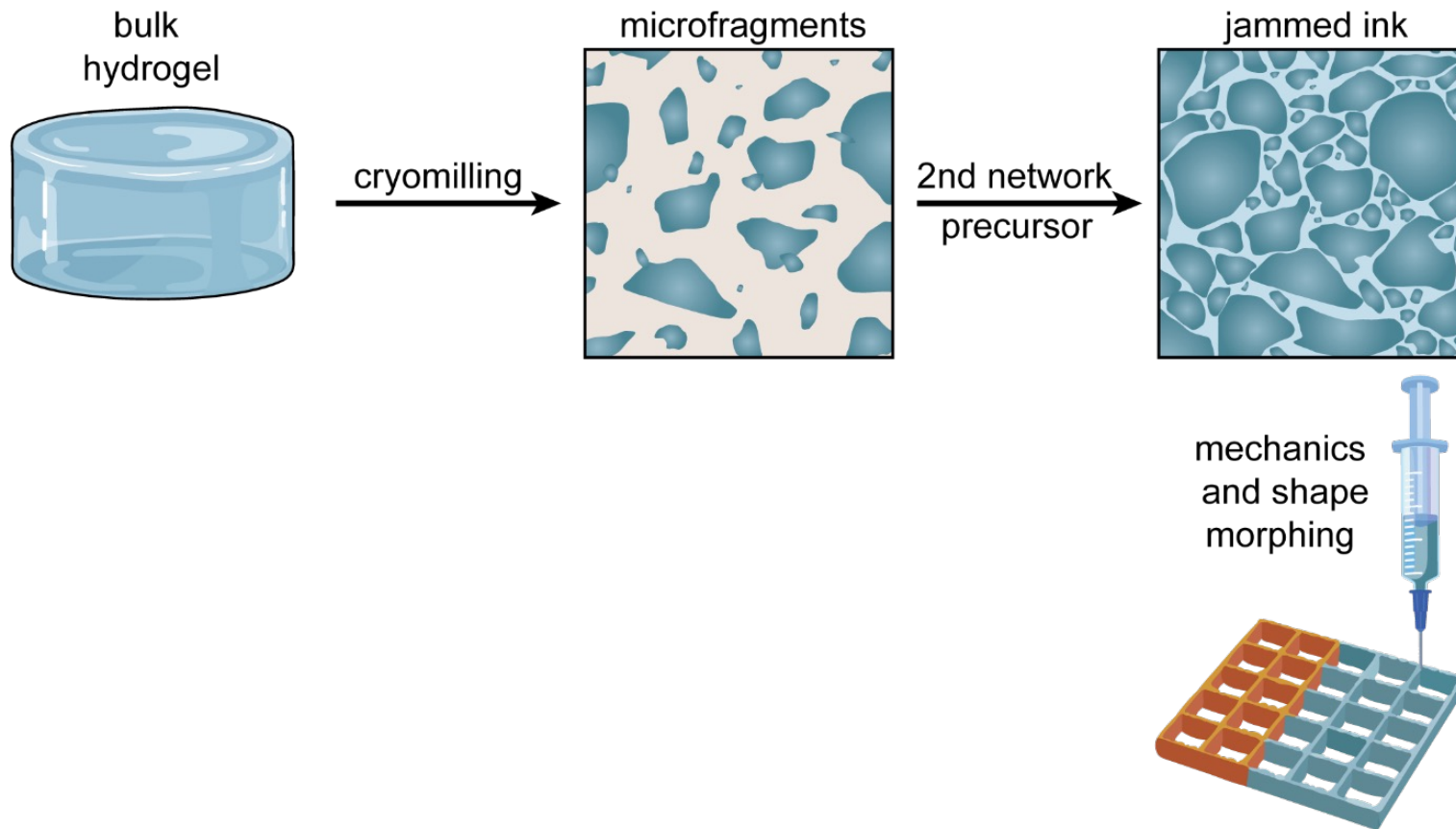
Mechanical properties of hydrogels





Lorenzo
Lucherini

Metal reinforced DNGHs



Matteo
Hirsch

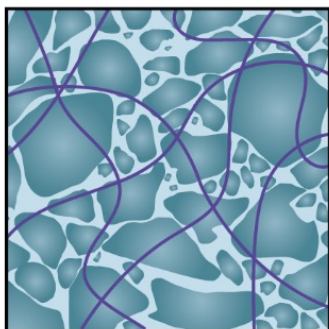


Lorenzo
Lucherini

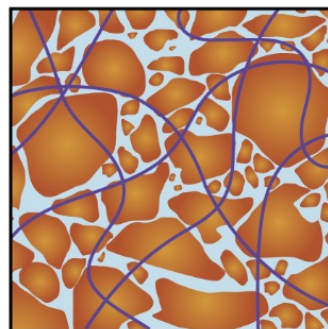
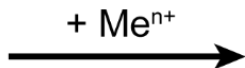
Microfragment reinforced granular hydrogels



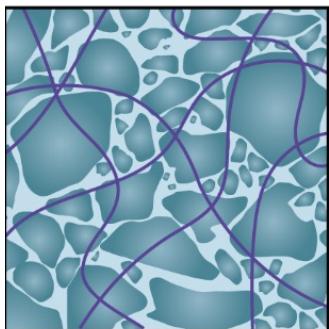
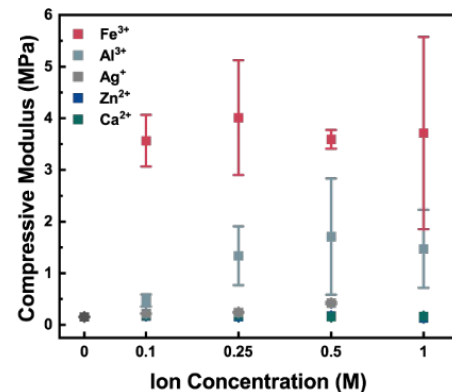
Matteo
Hirsch



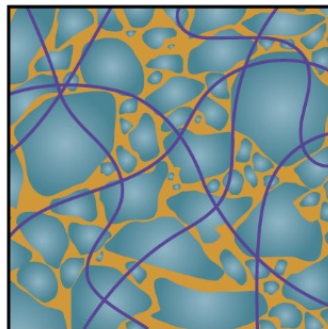
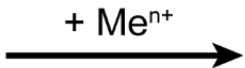
PAA mfs PAM mx



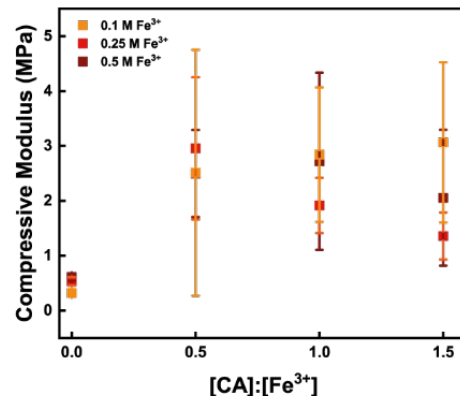
mfDNGH



PAM mfs PAA mx



mxDNGH



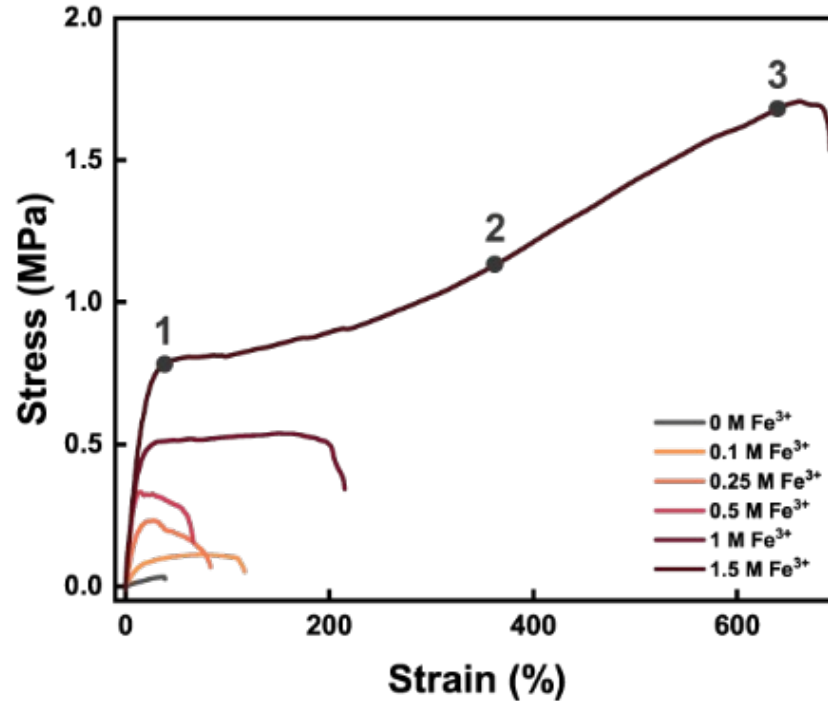


Lorenzo
Lucherini

Yielding of metal reinforced DNGHs



Matteo
Hirsch



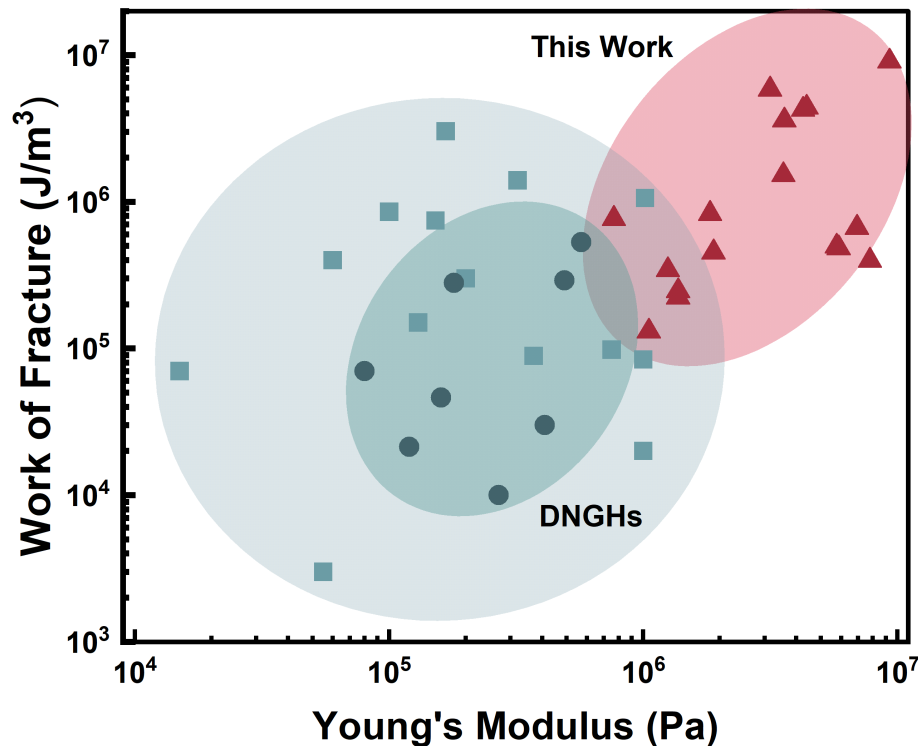


Lorenzo
Lucherini

Mechanical properties of metal reinforced DNGHs



Matteo
Hirsch



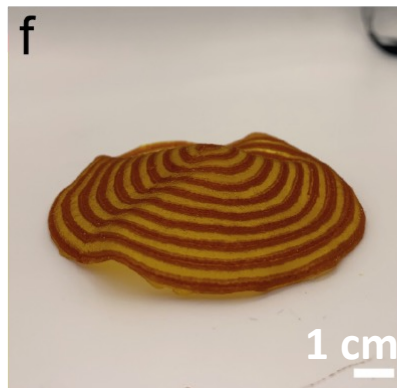
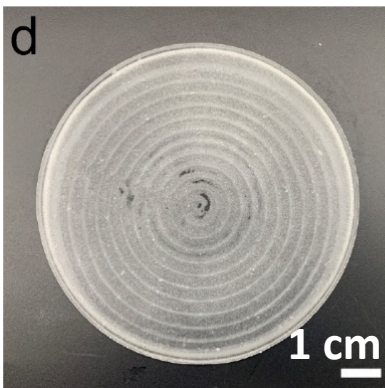
Shape morphing metal reinforced DNGHs



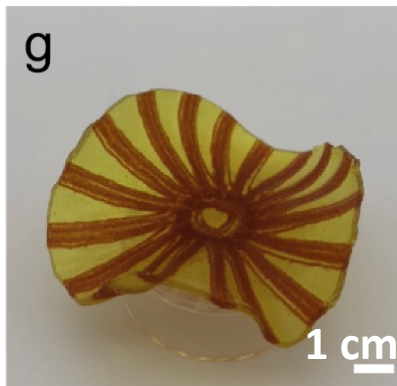
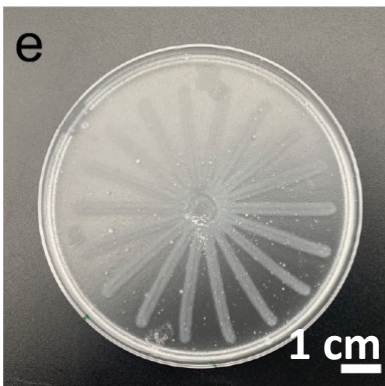
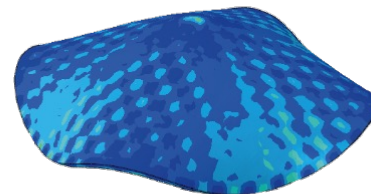
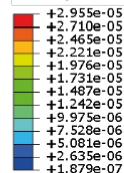
Lorenzo
Lucherini



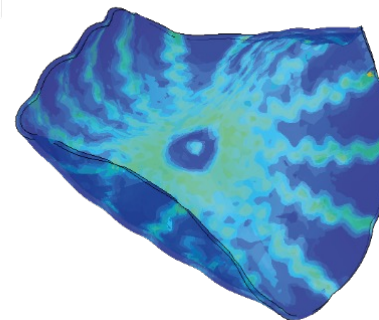
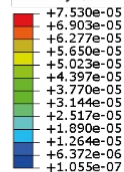
Matteo
Hirsch



Elastic energy
density (MJ/mm³)



Elastic energy
density (MJ/mm³)

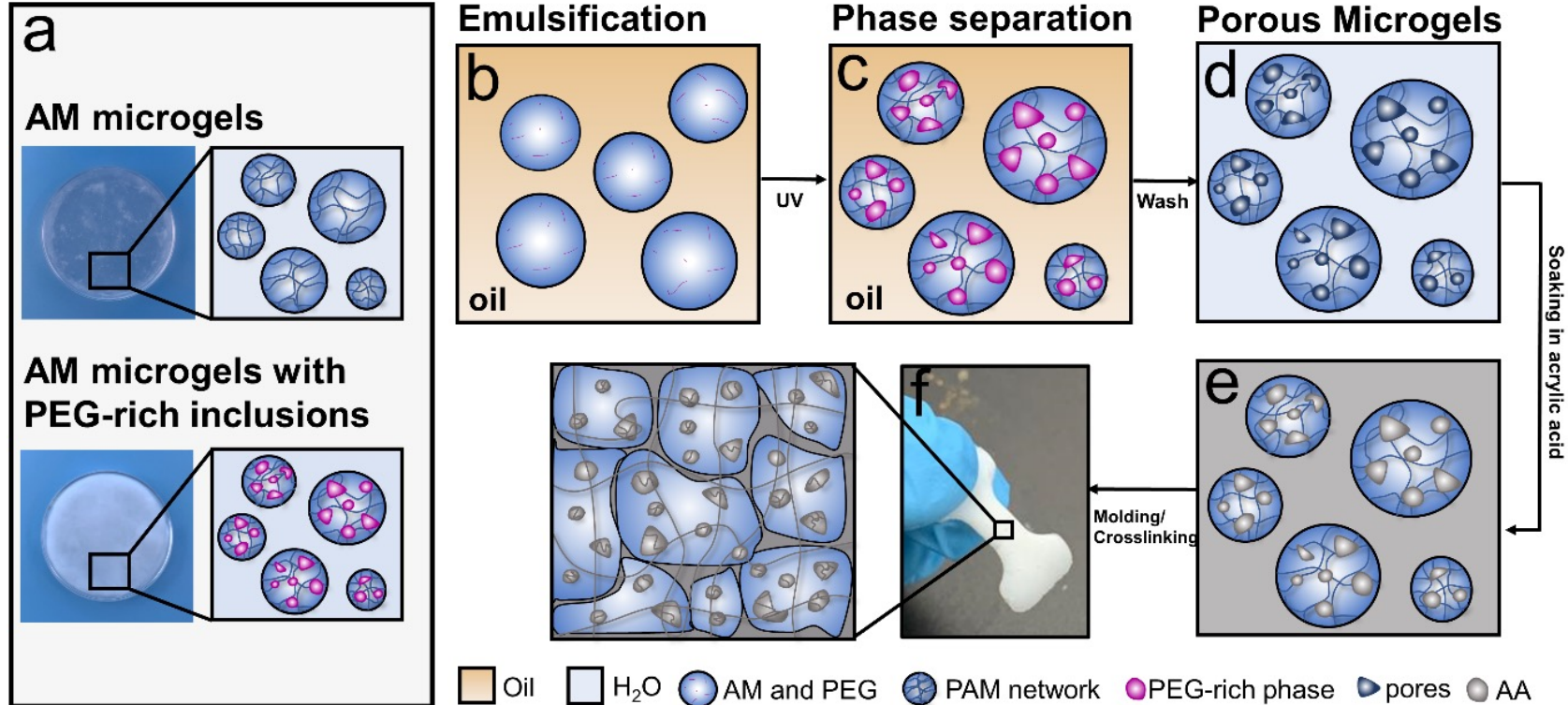


In collaboration with the CREATE lab from Prof. Josie Hughes, EPFL

Ionic reinforcement of nm-sized domains



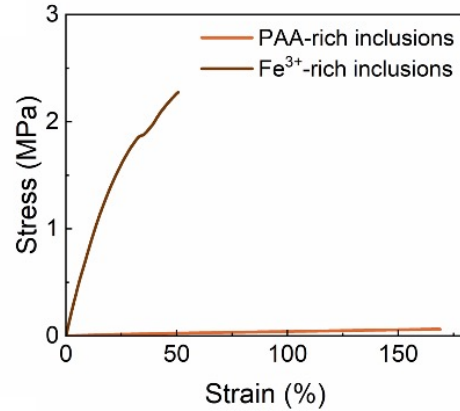
Alexandra Thoma



Influence of ionic reinforcement of nm-sized domains on mechanical properties of DNGHs



Alexandra
Thoma





Ran
Zhao

Turgor pressure: *in situ* stiffening of DNGHs



Alexandra
Thoma



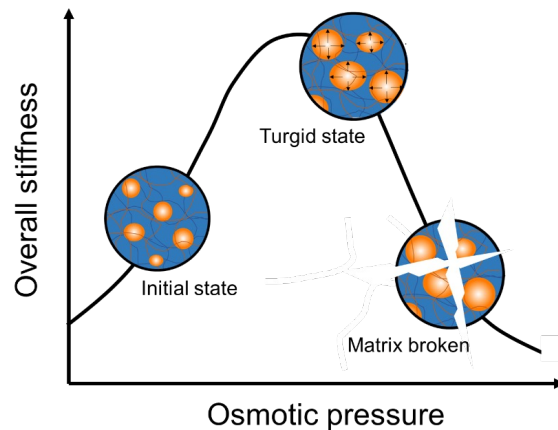
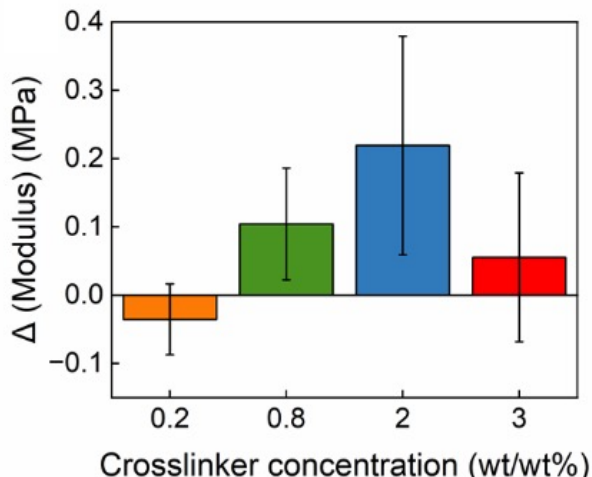
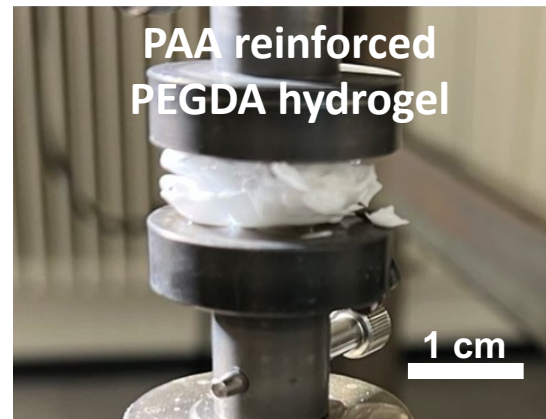
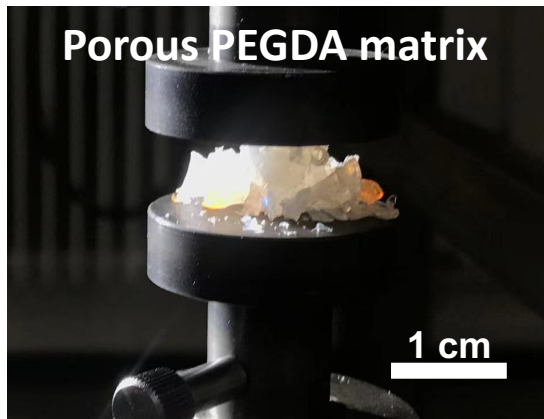
In situ stiffening of DNGHs



Ran
Zhao



Alexandra
Thoma



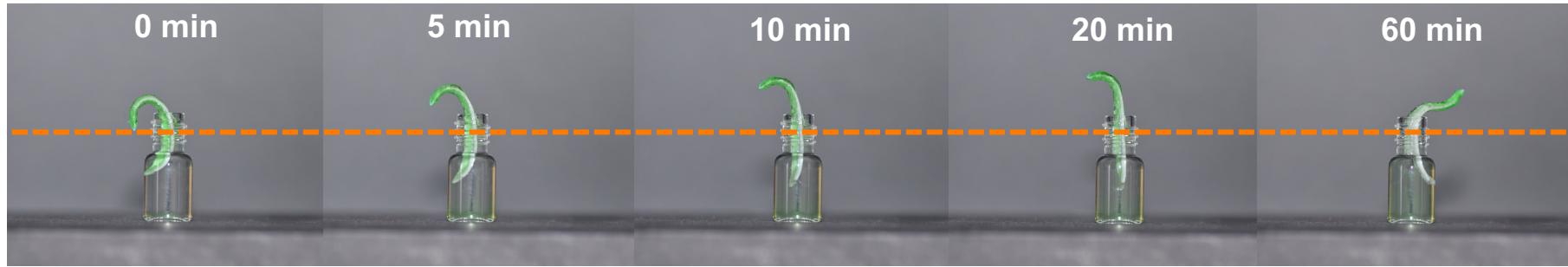
In situ stiffening of DNGHs



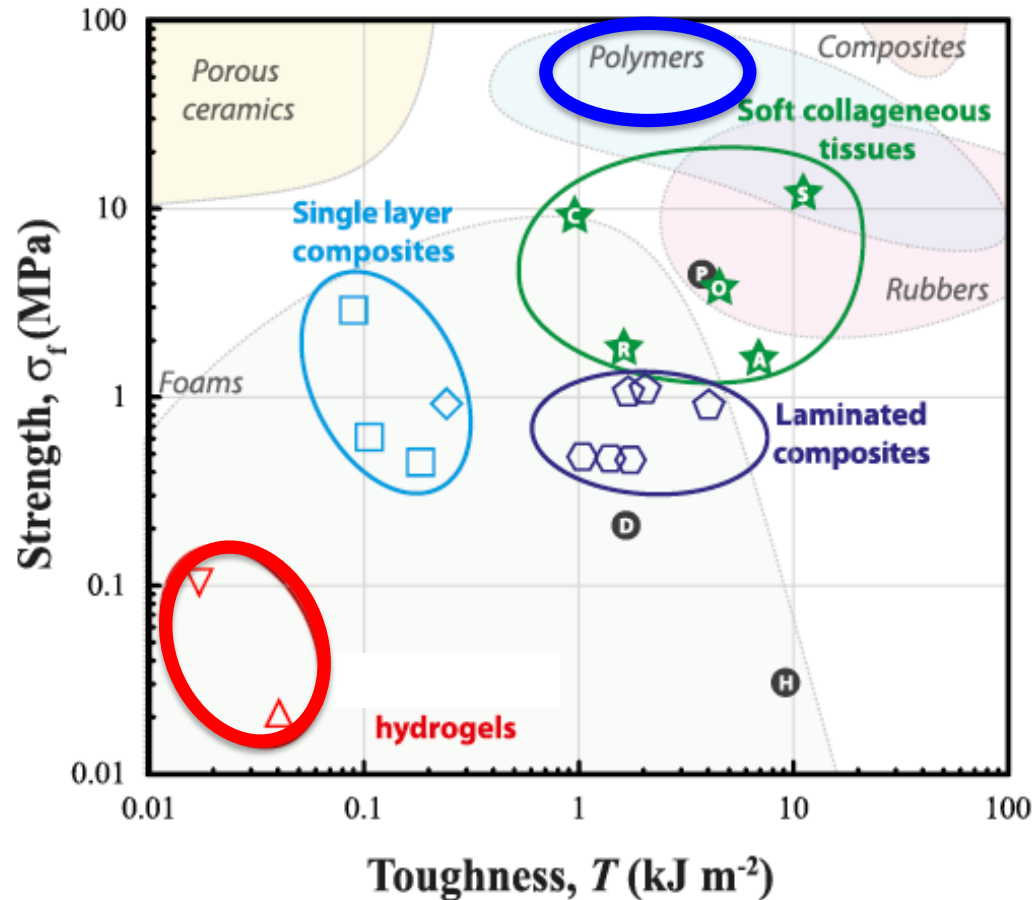
Ran
Zhao



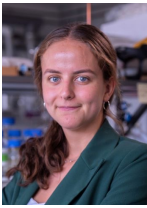
Alexandra
Thoma



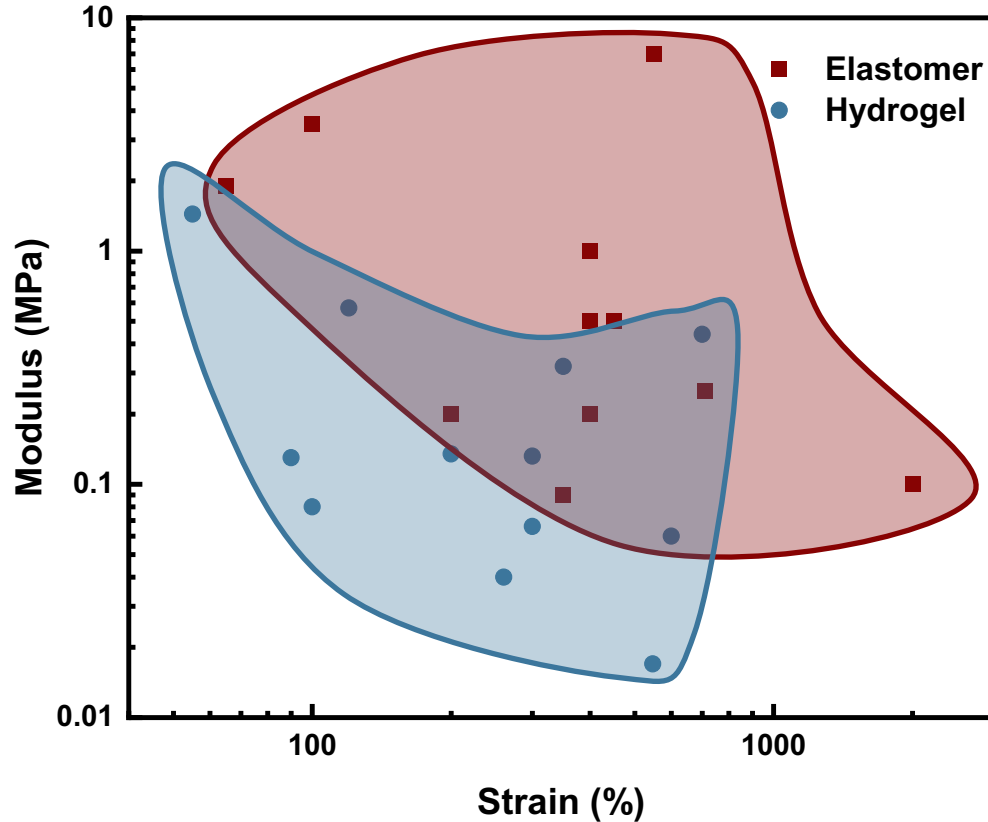
Mechanical properties of polymers



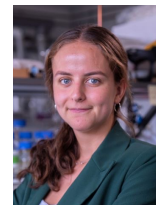
Mechanical properties of 3D printable hydrogels vs. elastomers



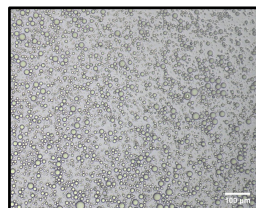
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Baur



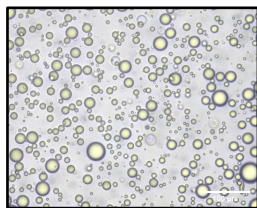
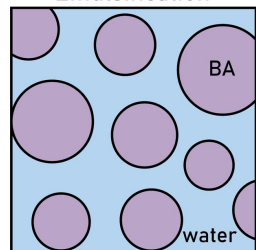
Double network granular elastomers



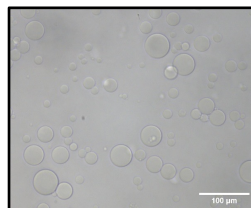
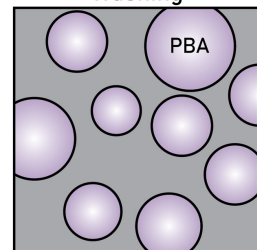
Eva Baur



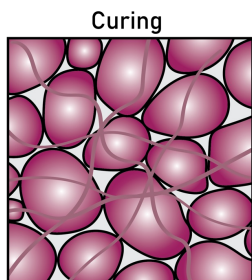
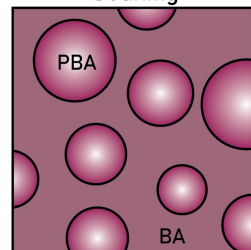
Emulsification



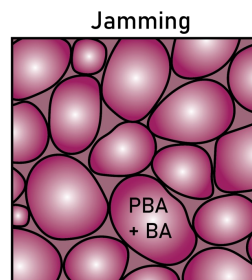
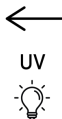
Washing



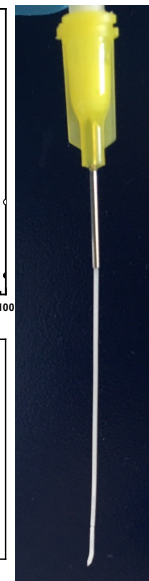
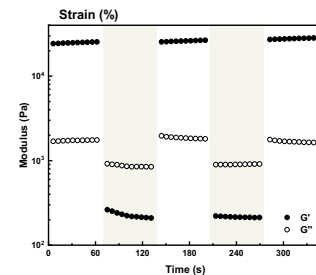
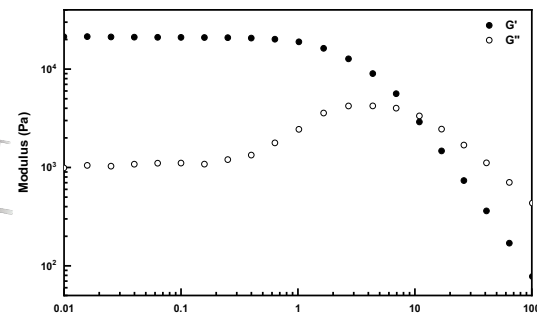
Soaking



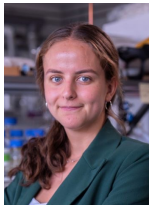
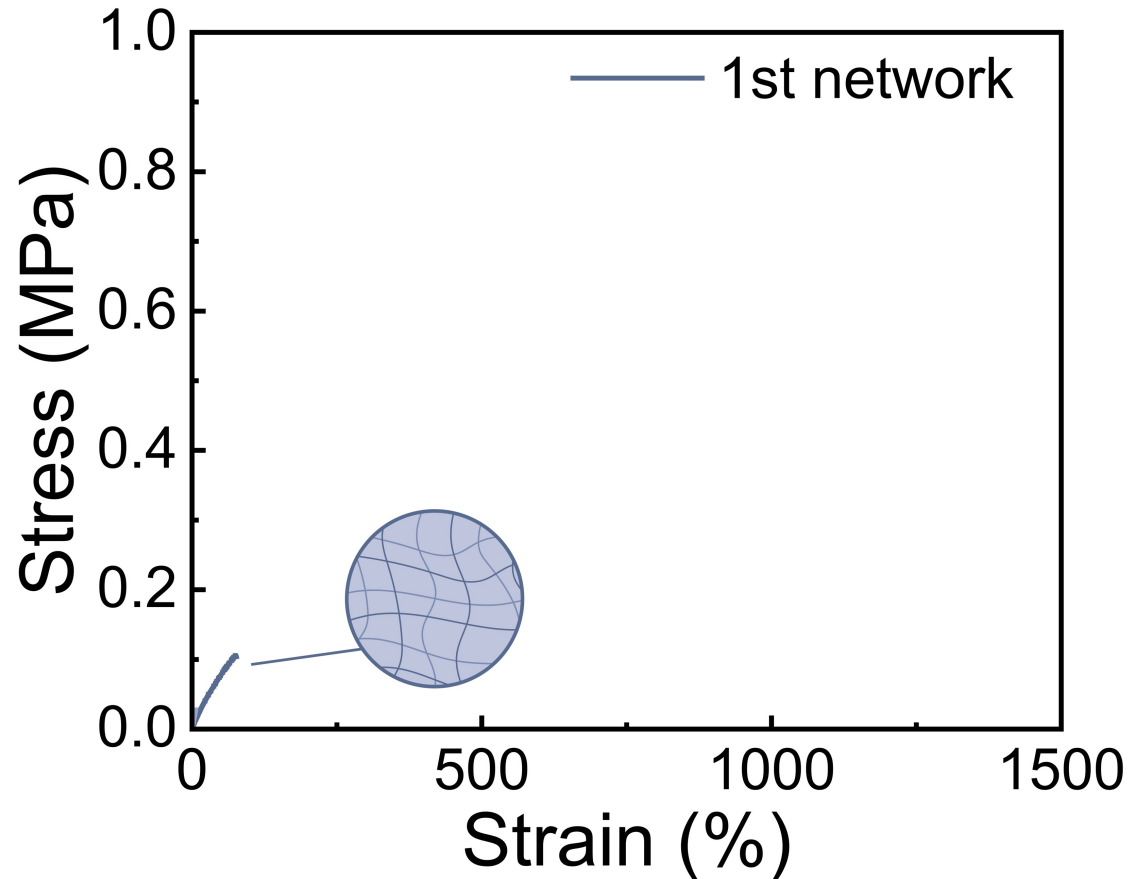
Curing



Jamming

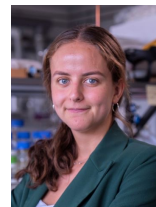


Granular vs. bulk double network elastomers

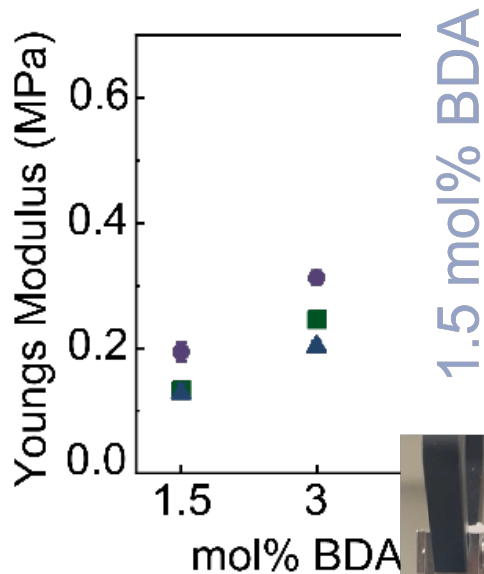


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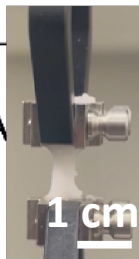
Influence of microparticle stiffness on the mechanical properties of double network granular elastomers



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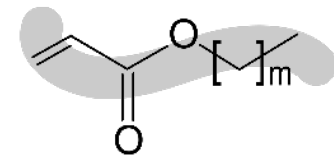
1.5 mol% BDA



5 mol% BDA

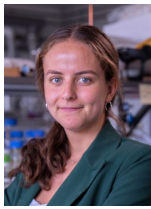


10 mol% BDA

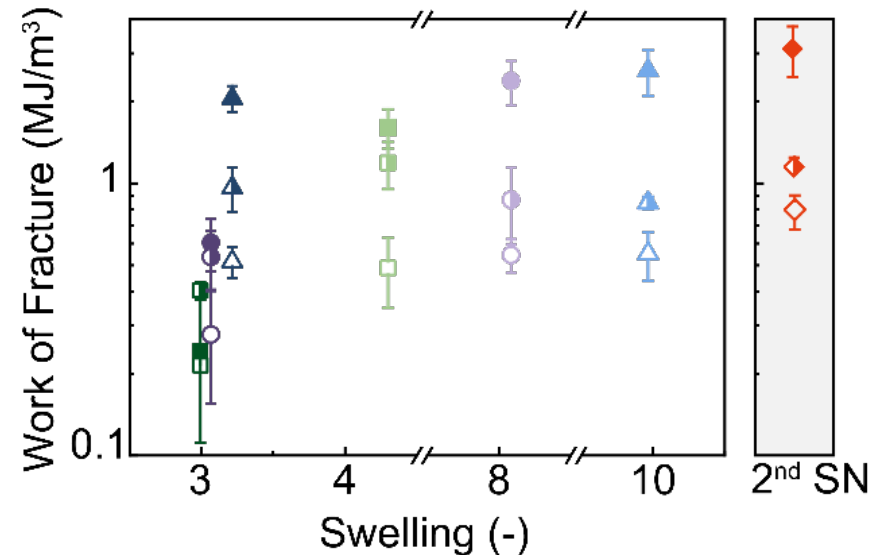
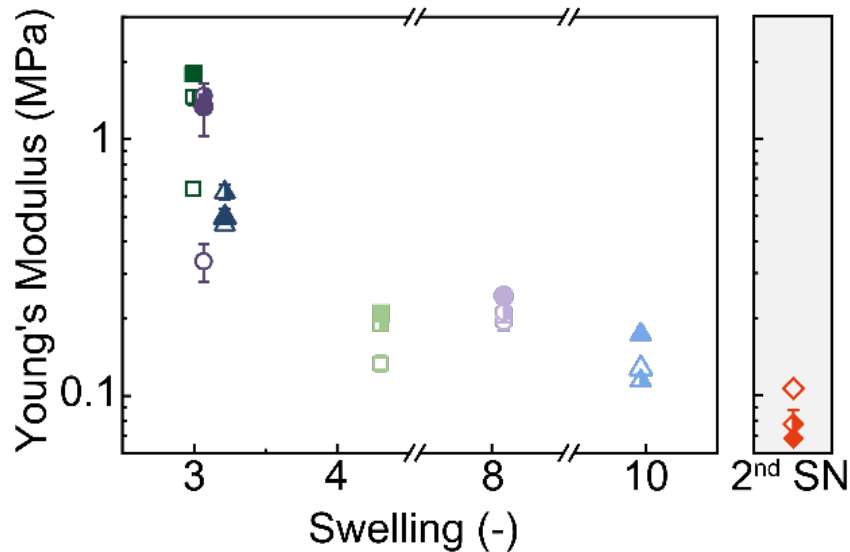


m=3	Butyl	
m=5	Hexyl	
m=11	Lauryl	

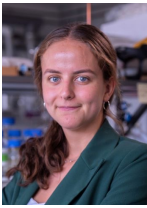
Influence of microparticle swelling on the mechanical properties of double network granular elastomers



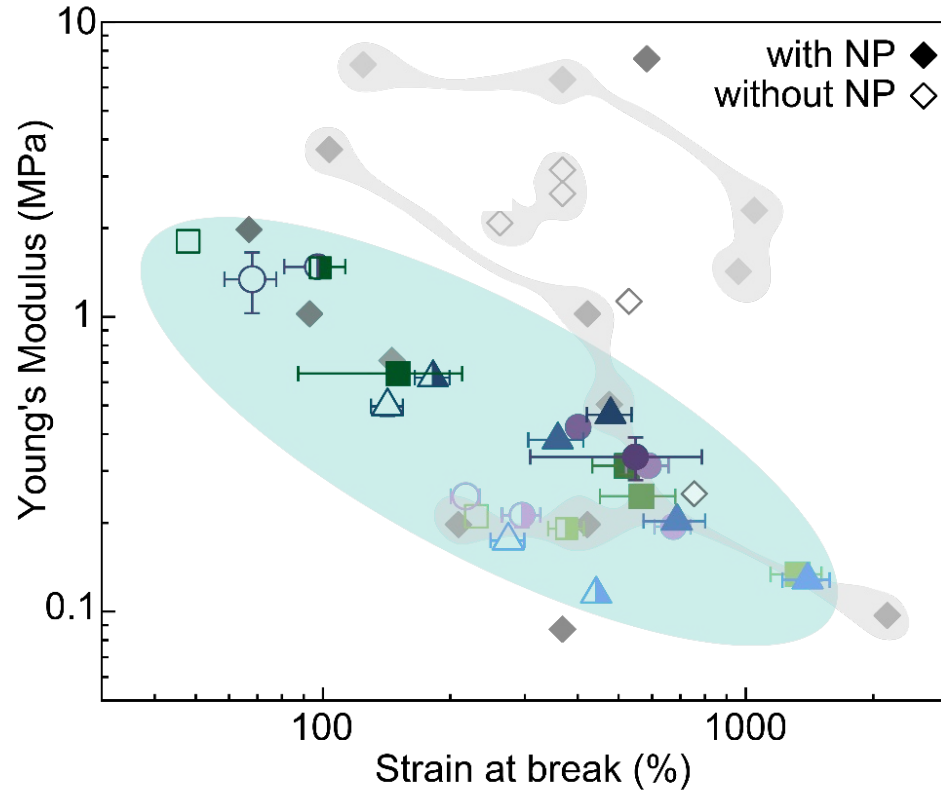
Eva
Baur



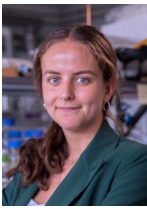
Mechanical properties of double network granular elastomers



Eva
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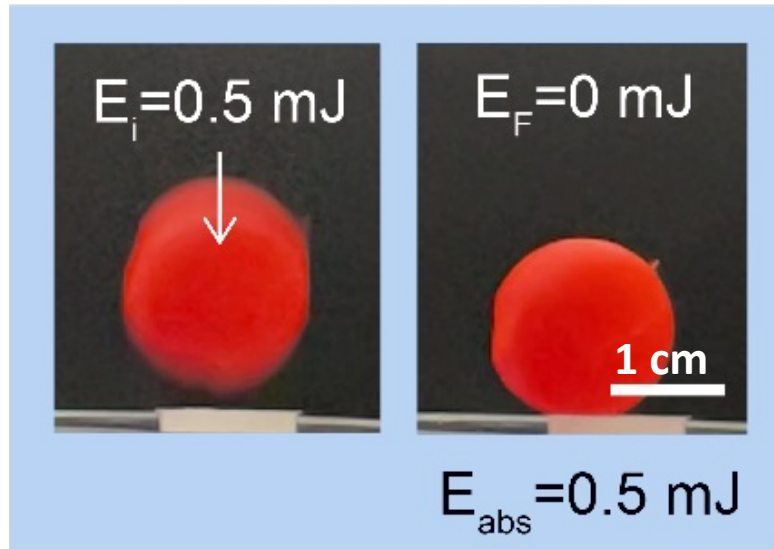


Damping properties of double network granular elastomers

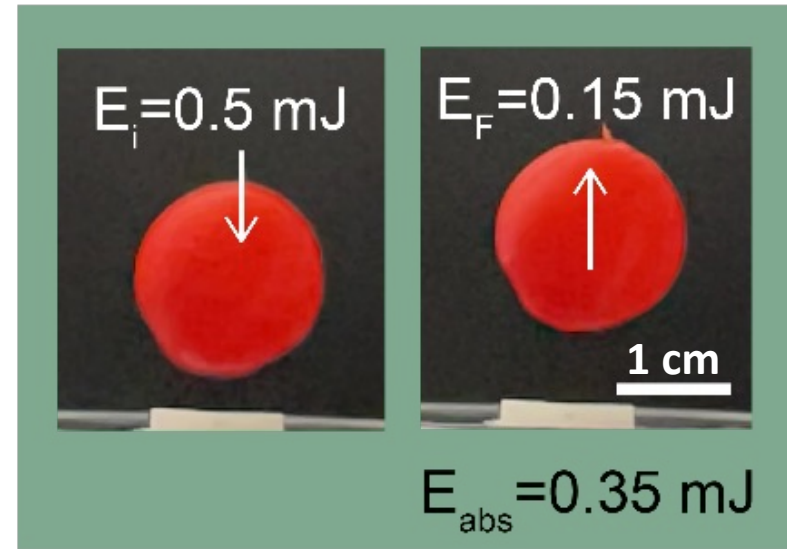


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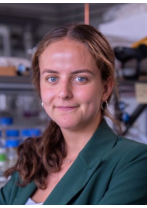
$\triangle$ LA 1.5 BDA



$\blacksquare$ BA 10 BDA



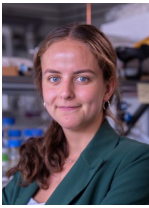
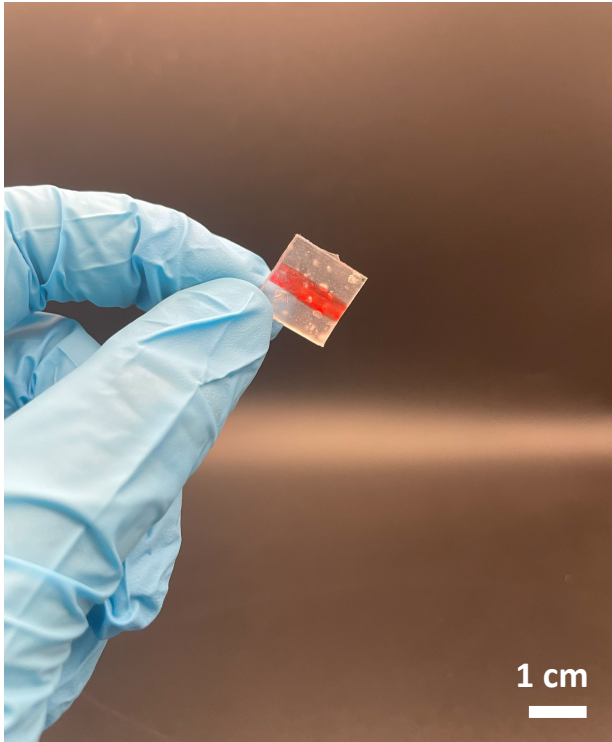
Mechanically anisotropic 3D printed elastomers



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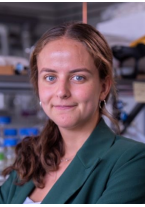


Anisotropic bending

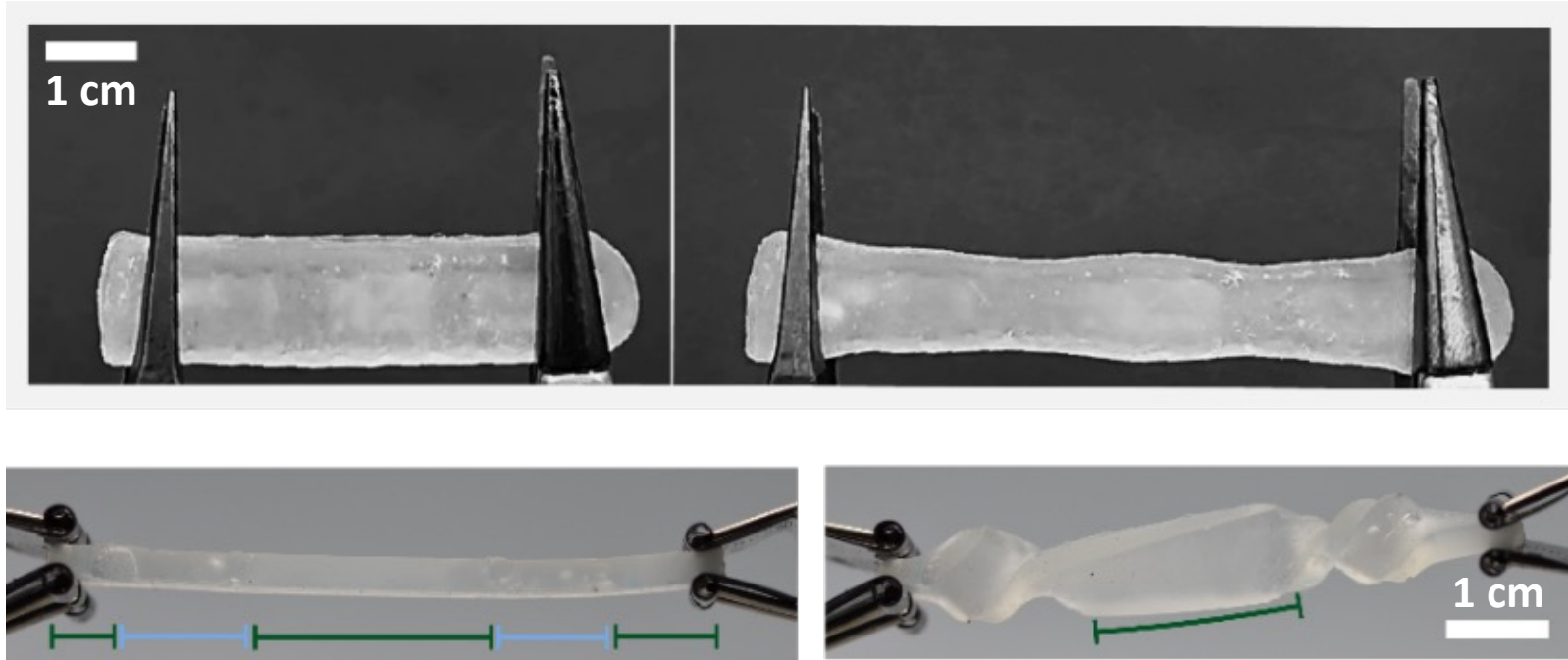


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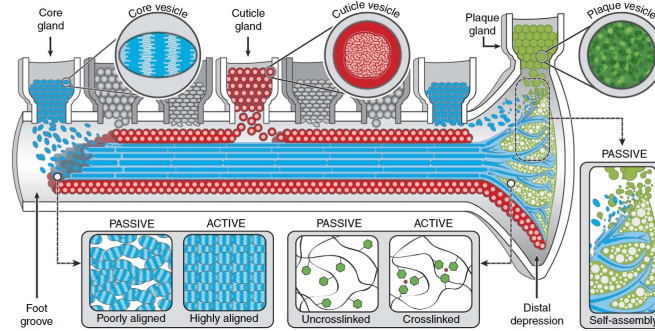
Anisotropic twisting



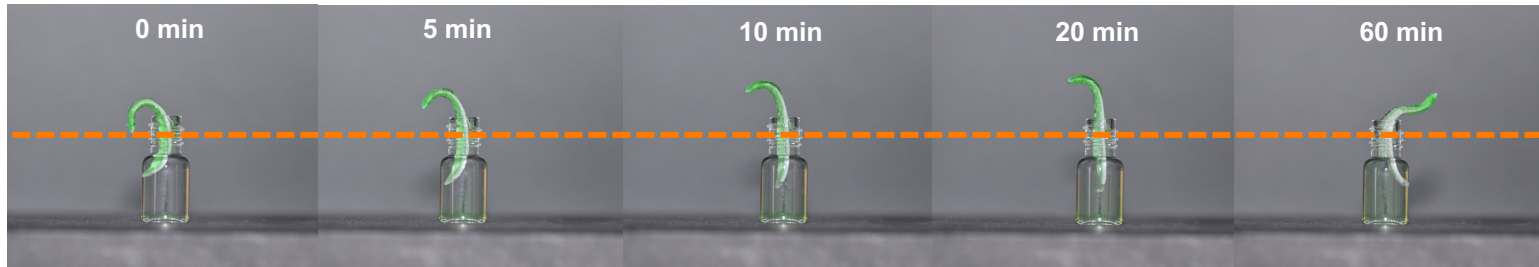
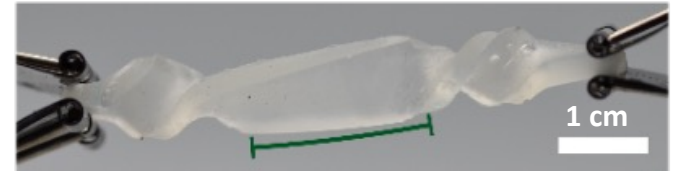
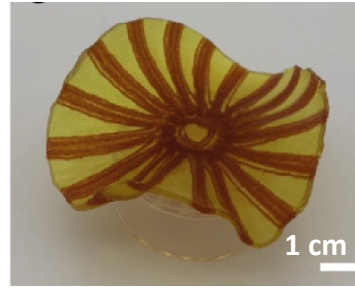
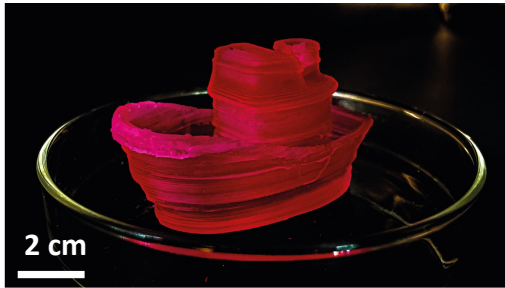
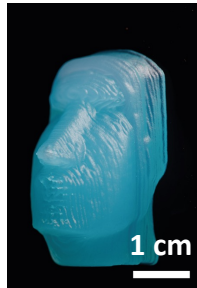
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Conclusions



T. Priemel, E. Degtyar, M.N. Dean, M.J. Harrington, *Nat. Comm.* **2017**, 8





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