A GREEN REVOLUTION IN BIOPLASTICS SILK AND CELLULOSE HYBRID MATERIALS

SOFI² CDT
EPSRC-funded Centre for Doctoral Training in Soft Matter for Formulation and Industrial Innovation

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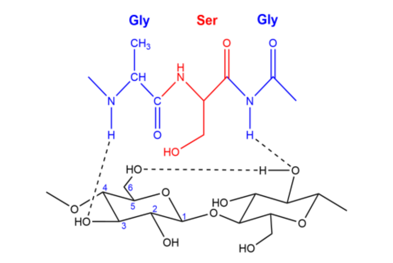
What is the issue?

70 % of all UK waste is from plastic packaging, and the UK is set to mismanage 250,000 tonnes of plastic waste in 2023[1]. Reckless consumption has a huge impact on our world, and new materials must be sustainable to produce, use, and dispose of.

How can we solve this?

- This study investigates the **behaviour of cellulose and silk fibroin polymers to find new materials for sustainable application**.
- **Bioplastics are materials with sustainable sources**, but often have inadequate strength and performance[2].
- **Silk Fibroin and Cellulose** are biopolymers which can be mixed to form **higher performance hybrid materials**[2,3].
- **Understanding hybrid materials could enable creation of new biomaterials and reduce the need for** conventional plastics.



Silk fibroin and cellulose intermolecular interactions

How did we make silk/cellulose hybrids?

Films of various compositions were prepared by dissolving fibres and coagulating polymer mixtures. This formed a gel which dried to form a film.

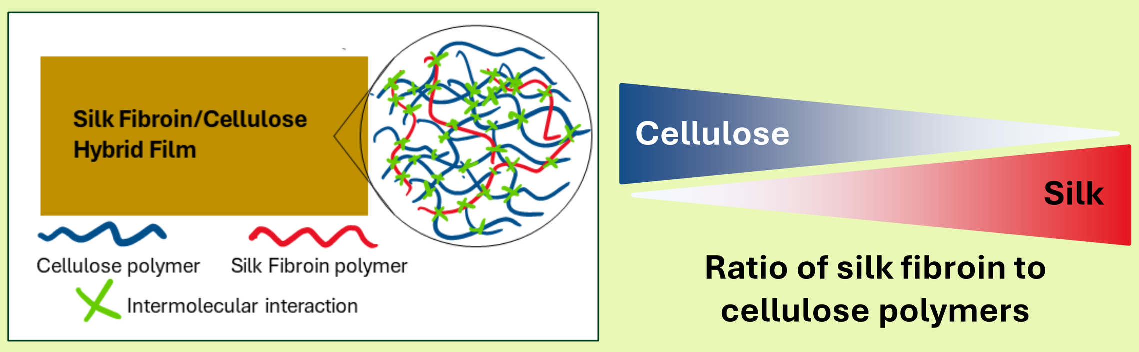
This process uses all **non-toxic and sustainable materials.**

How can we investigate these materials?

A range of techniques were used to **test and optimise the hybrid films.**

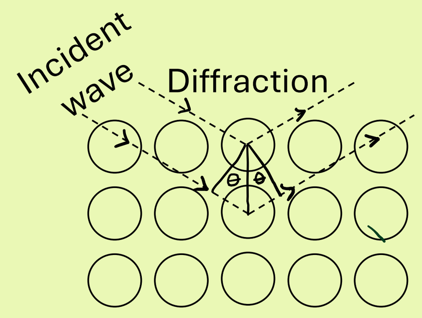
We focussed on how much of each polymer to use!

What ratio of polymers is best?

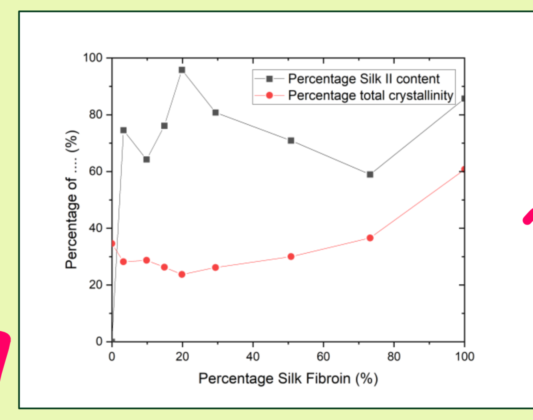


Ratio of silk fibroin to cellulose polymers

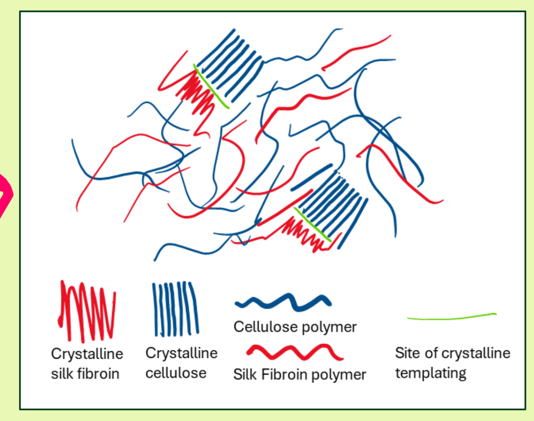
Internal Structure



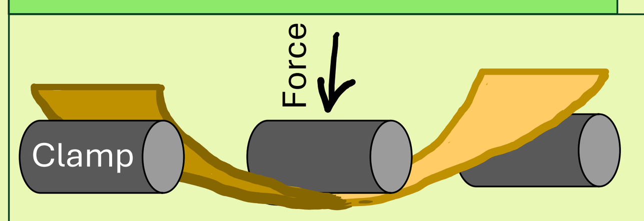
X-Ray Diffraction



Adding 10-25 % silk encourages polymers to align, forming crystals.

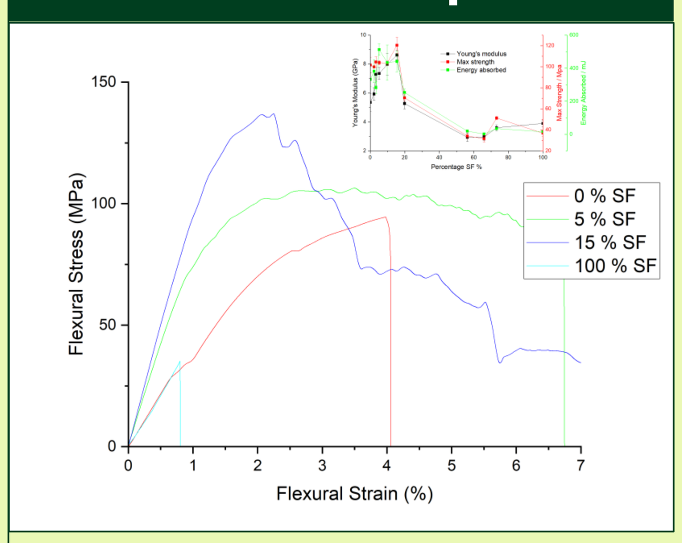


Stiff cellulose 'templates' flexible silk polymers, improving overall strength.



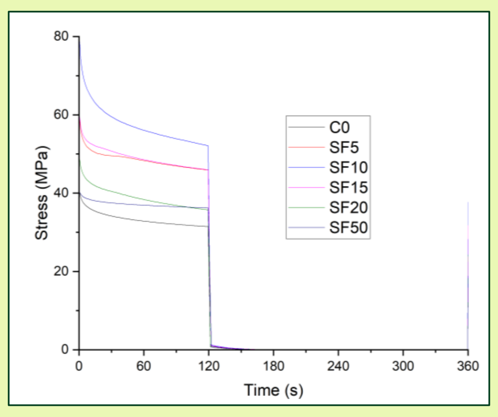
Bending/Flexural Testing

Mechanical Properties



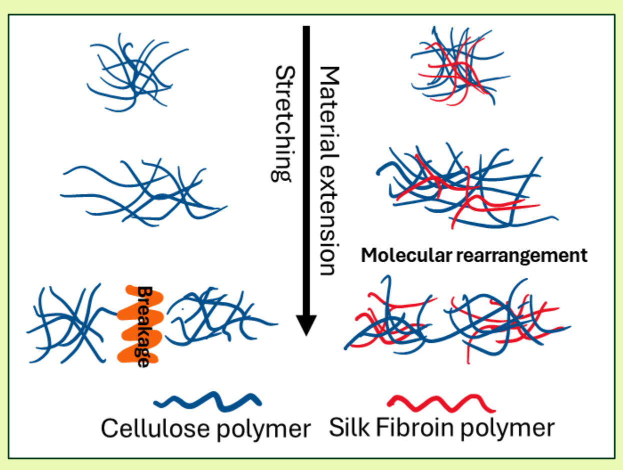
Strength, stiffness, and flexibility are maximised with 10-15 % silk content.

Molecular Movement



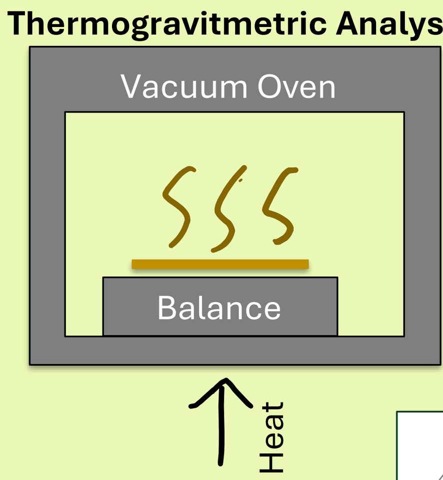
When flexed for a long period, hybrid samples relax quickly and will permanently deform.

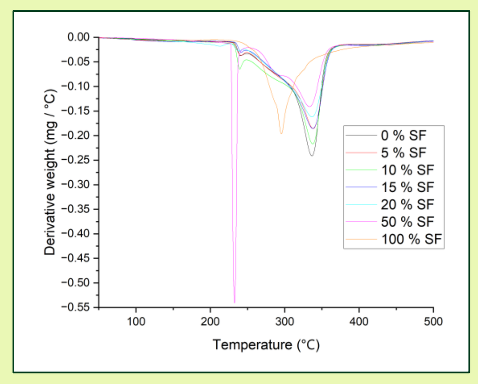
Cellulose-silk interactions act as weak 'sacrificial bonds' that break before the whole network[5], letting it stretch due to 'polymer slippage'[3].



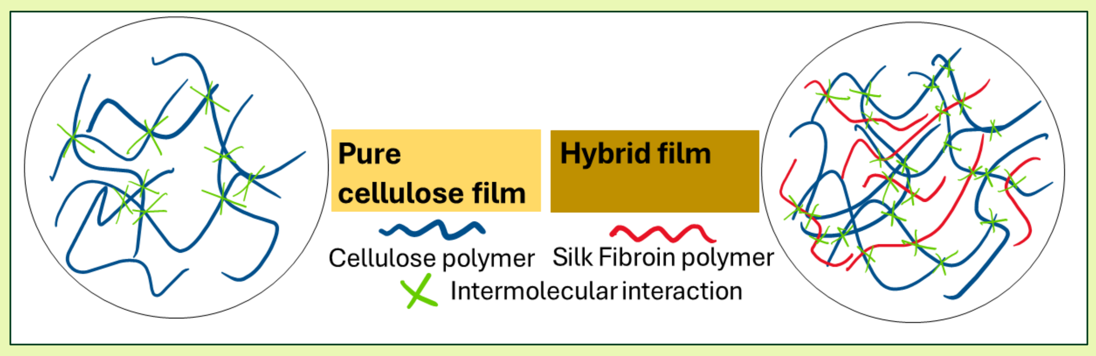
Phase Separation

Thermogravimetric Analysis





Mixed polymers decay at lower temperatures than pure phases[4].



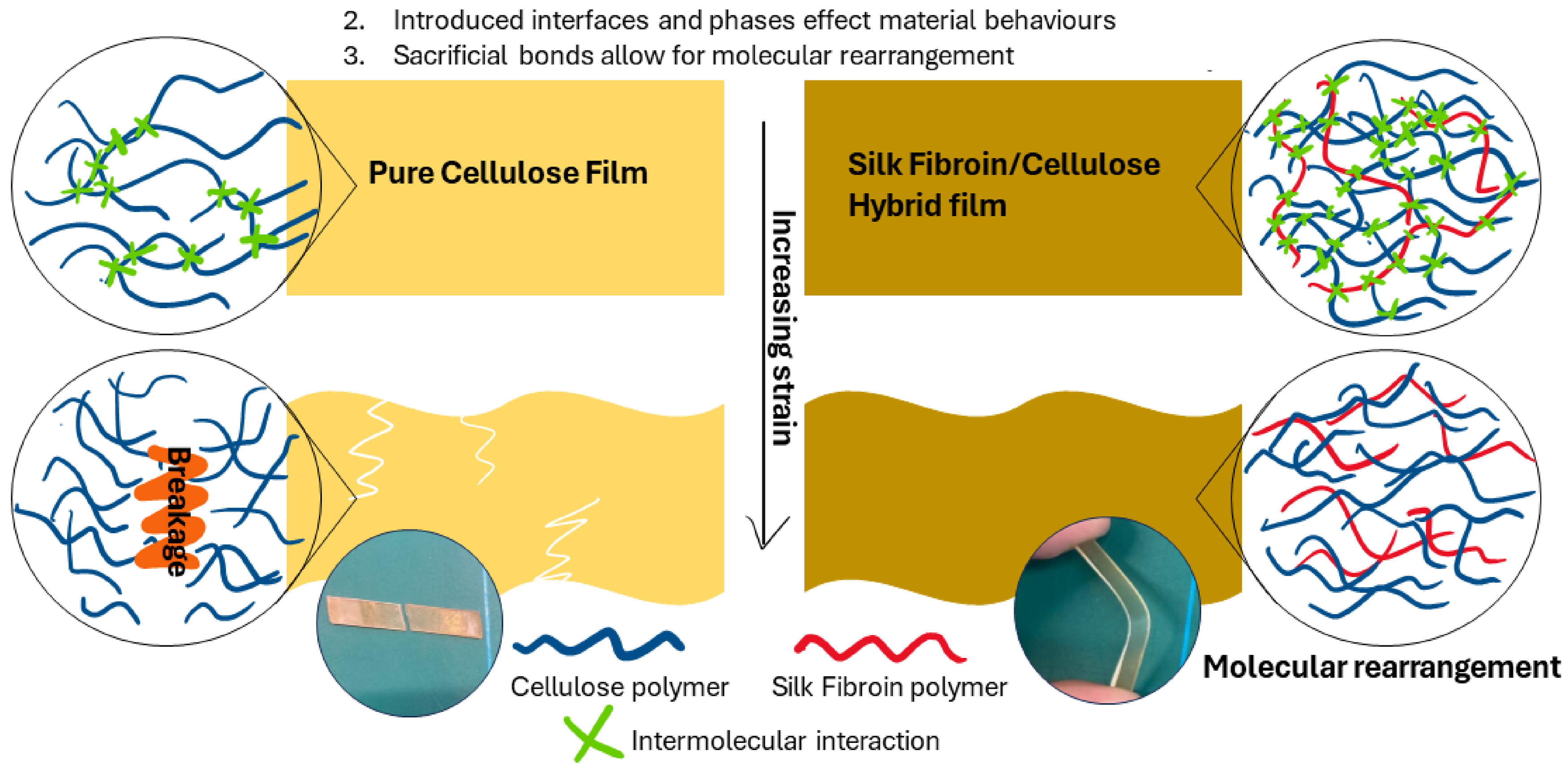
Silk and cellulose are mixing at the molecular level forming a dense network[6].

What does this tell us?

- Adding **10-15 weight % silk to cellulose** improves the **material strength** and **flexibility**.
- Material strength is encouraged due to **increased silk crystallinity, and dense interactions in the hybrid phase.**
- Hybrid films show **time-dependant deformation due to 'polymer slippage' for this behaviour.**
- Polymer slippage is allowed due to **weak 'sacrificial bonds' at interfaces.** When deformed these break to allow molecular mobility.

How do hybrid materials improve material strength and flexibility

1. More intermolecular interactions increase strength and stiffness
2. Introduced interfaces and phases effect material behaviours
3. Sacrificial bonds allow for molecular rearrangement



What's the impact?

- **This new optimal material provides strength and flexibility without pollution in production, use, or disposal. Letting us design new materials for more specific applications!**
- **Reducing the cost of choosing green materials makes it commercially viable, without which materials won't be used.**

Mixing silk and cellulose offers a new way to make sustainable high performance biomaterials. Understanding why they perform will encourage hybrid material development in ecofriendly industries!

References

1. Wrap, https://wrap.org.uk/taking-action/plastic-packaging
2. Kostag, M.; Jedvert, K.; El Seoud, O. A. Engineering of sustainable biomaterial composites from cellulose and silk fibroin: Fundamentals and applications. *International Journal of Biological Macromolecules* 2021, 687-718, 167. https://doi.org/10.1016/j.ijbiomac.2020.11.151
3. Mohammadi, P.; Aranko, A. S.; Landowski, C. P.; Ikkala, O.; Jaudzems, K.;Wagermaier, W.; Llinder, M. B. Biomimetic composites with enhanced toughening using silk-inspired triblock proteins and aligned nanocellulose reinforcements. *Science Advances* 2019, 5, 9. https://doi.org/10.1126/sciadv.aaw2541
4. Hadadi, A.; Whittaker, J. W.; Verrill, D. E.; Hu, X.; Larini, L.; Salas-de La Cruz, D. A Hierarchical Model to Understand the Processing of Polysaccharides/Protein-Based Films in Ionic Liquids. *Biomacromolecules* 2018, 3970-3982, 19, 10. https://doi.org/10.1021/acs.biomac.8b00903
5. Tasuka Nakajima. Generalization of the sacrificial bond principle for gel and elastomer toughening, *Polymer Journal* 2017, 477-485, 49. https://doi.org/10.1038/pj.2017.12
6. Tian, D.; Lia, T.; Zhang, R.; Wu, Q.; Chen, T.; Sun, P.; Ramamoorthy, A. Conformations and Intermolecular Interactions in Cellulose/Silk Fibroin Blend Films: a Solid-State NMR Perspective. *Physical Chemistry B* 2017, 6108-6116, 25, 121. https://doi.org/10.1021/acs.jpcb.7b02838