Synthesis of new lipopeptide green surfactants from silk by mechanochemistry

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Introduction & Objective

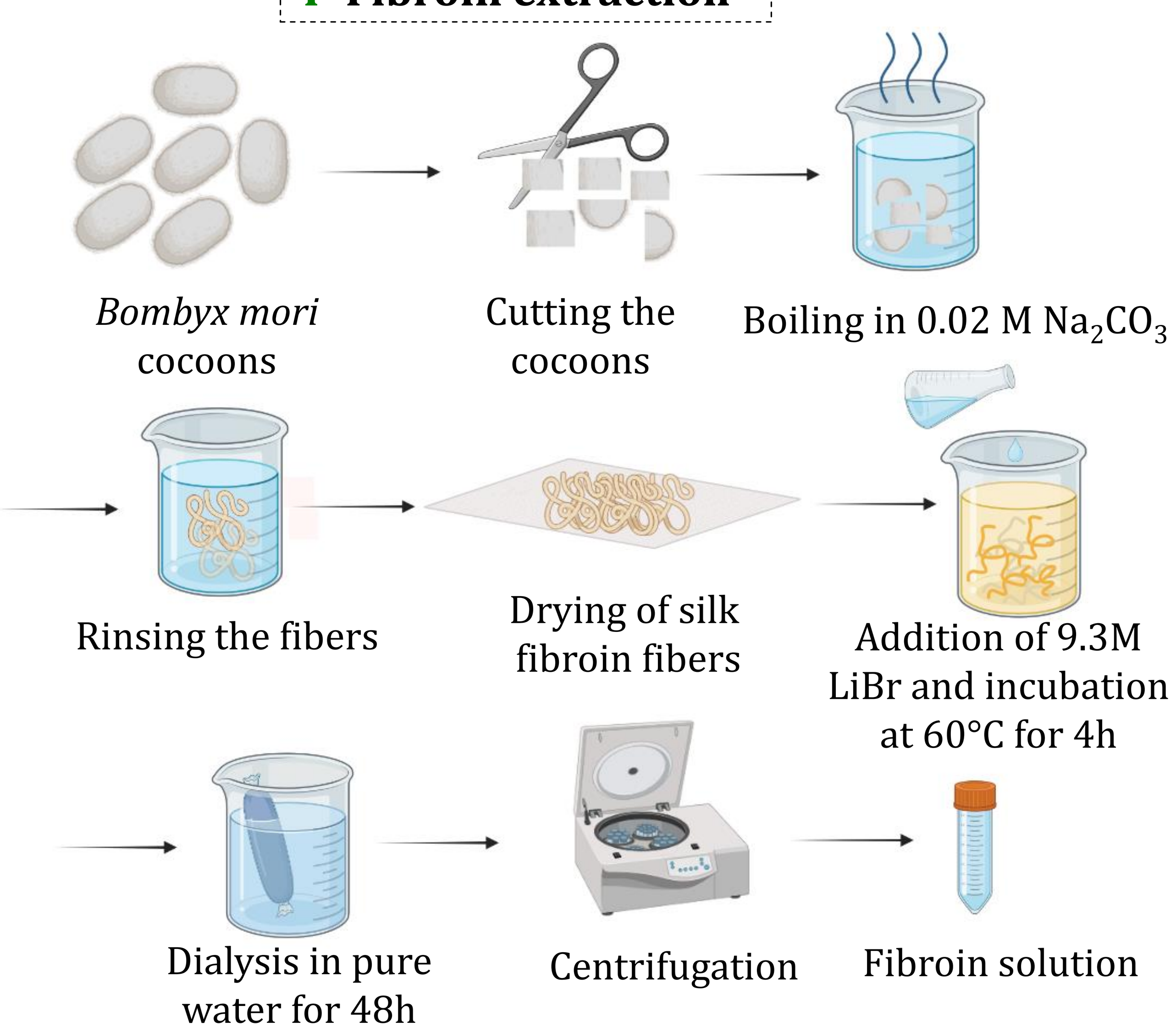
The production of environmentally sustainable amphiphilic molecules from natural origin constitutes one of the major issues for different industries due to the pressure from regulatory legislation and growing consumer trend towards environmentally-friendly chemicals. Natural-based surfactants can be produced from agricultural biomass such as sugars, starches, vegetable proteins and oils. However, these high-quality fractions of biomass are in competition with food and feed industries.[1]

In this context, the development of surfactants from silk proteins as a non-food biomass represents an interesting alternative.
Silk is a biopolymer produced by different varieties of silkworms. Mulberry silk is obtained from the silkworm *Bombyx mori L.*, it is composed of two kinds of proteins: fibroin (≈70%) used in textile industries and sericin (≈30%) eliminated by a degumming process during the production of silk fibers.[2]

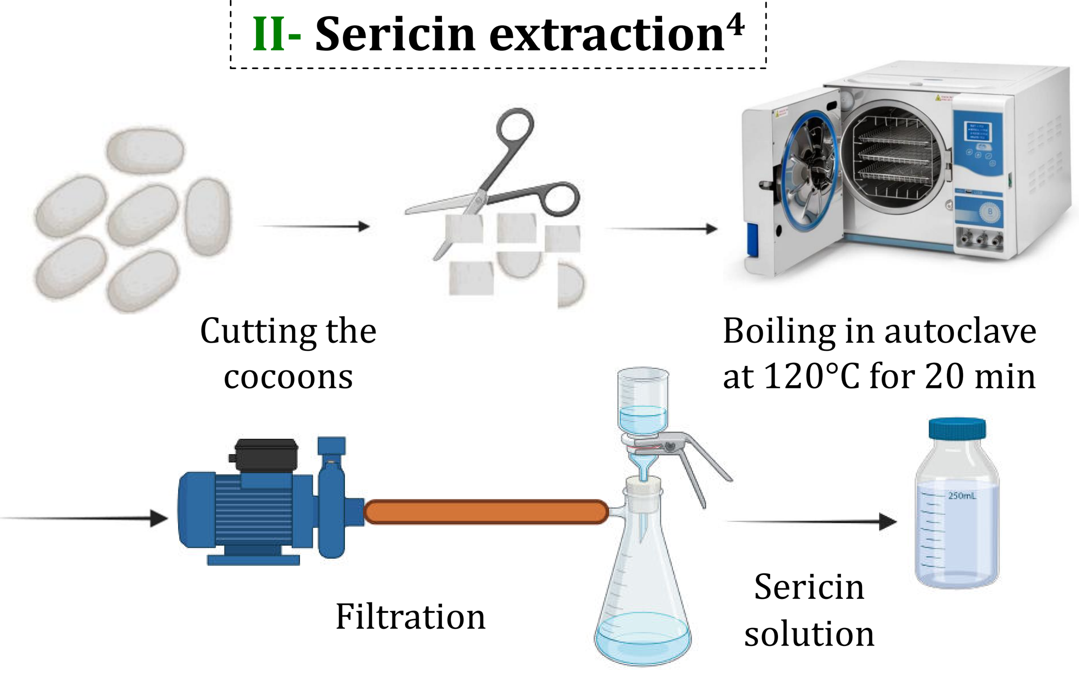
Objectives : Develop an original synthesis to produce lipopeptide surfactants from silk proteins and evaluate their surface activity.

Materials & Methods

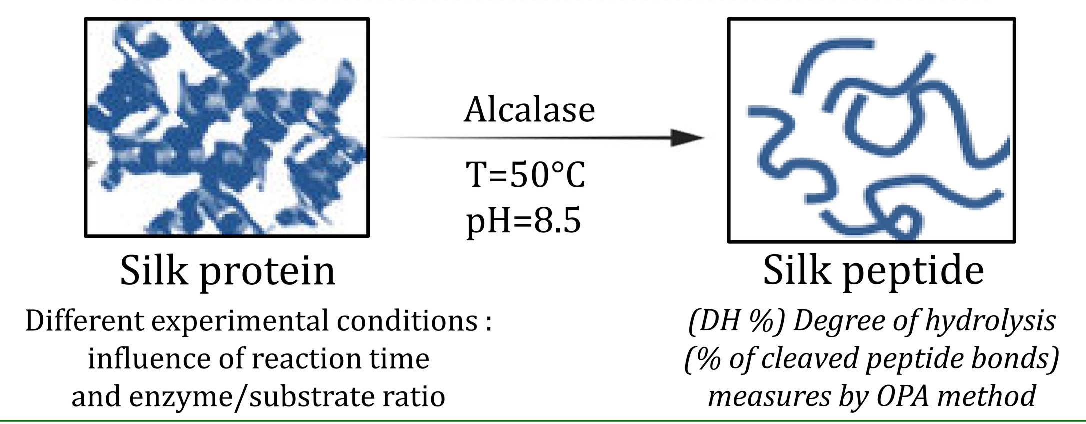
I- Fibroin extraction[3]



II- Sericin extraction[4]

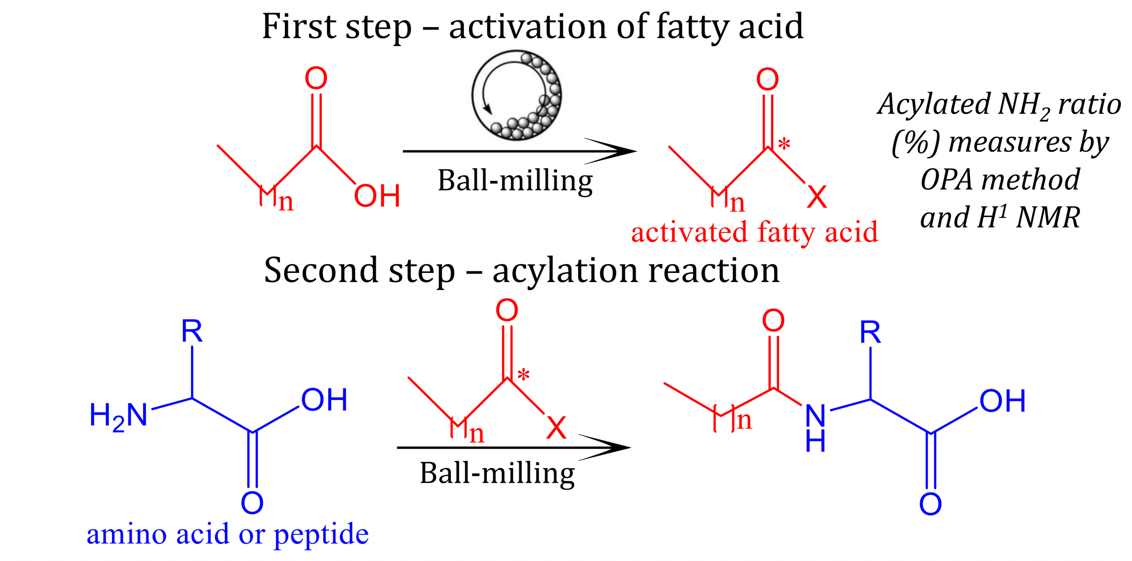


III- Enzymatic hydrolysis of proteins



IV- Chemical modification of silk peptides

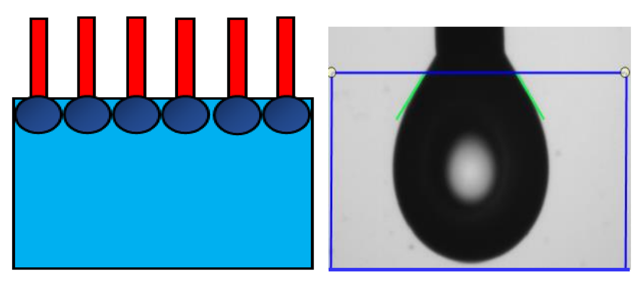
One-pot two step acylation in solventless conditions :



V- Evaluation of surface activity of lipopeptides

Surface tension measurements

Pendant drop method (Tracker – Teclis)



Laplace-Young relation :

$$\gamma = \frac{\rho \times g \times z}{\frac{2}{b} - \left(\frac{1}{R_1} + \frac{1}{R_2}\right)}$$

Results & Discussion

I- Fibroin hydrolysis

❖ *Influence of reaction time* ❖ *Influence of enzyme/substrate ratio*

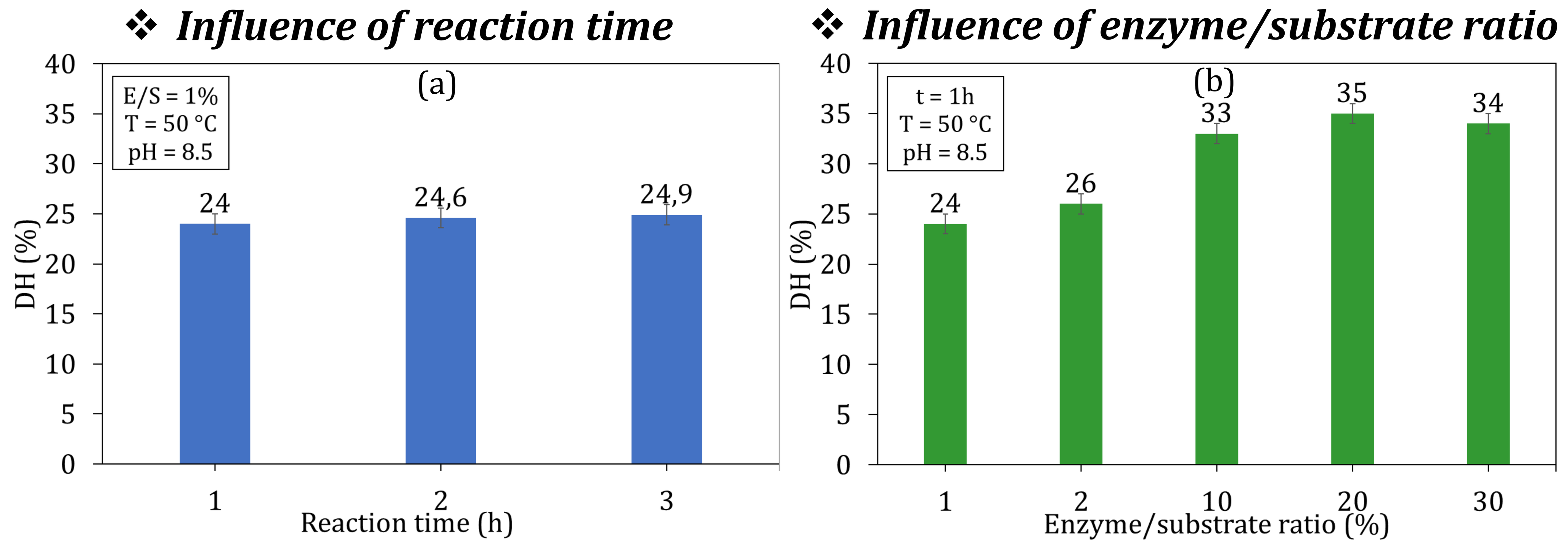


Fig 1 : DH (%) at different (a) reaction time (h) and (b) enzyme/substrate ratio (%)

At constant enzyme/substrate ratio (1%), reaction time has no significant influence on DH (25 ± 1 %) (Fig 1-a). At constant reaction time (1h), DH increases for low enzyme/substrate ratio (1, 2 et 10%), and remains constant for high enzyme/substrate ratio (Fig 2-b).

II- Acylation of amino acids and silk peptides

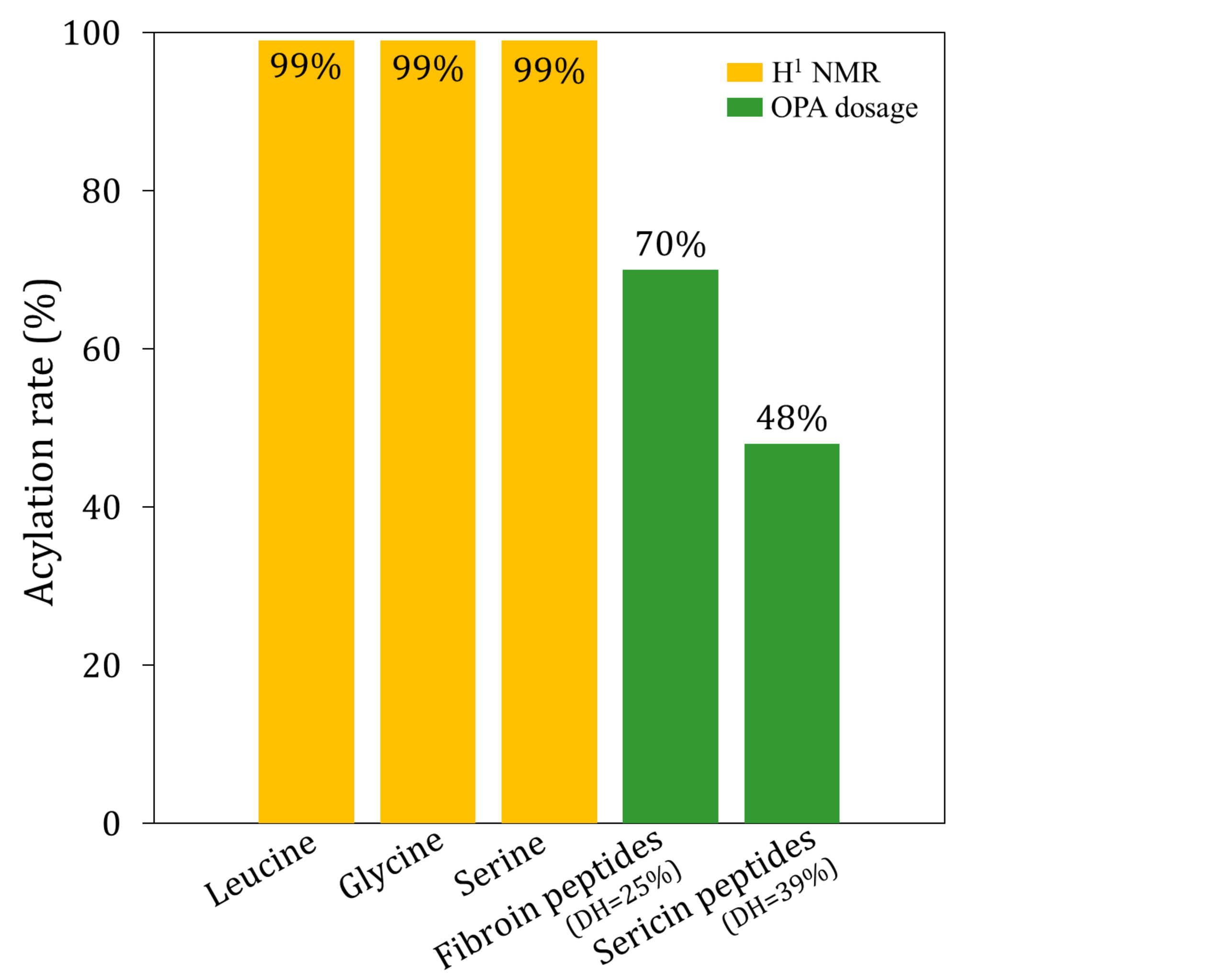


Fig 2 : Acylation rate (%) of amino acids *(by H^1 NMR)* and silk peptides *(by OPA dosage)*

In optimized conditions, the grafting of fatty chain (C14) on model amino acids (Leucine, Glycine and Serine) in solventless conditions by ball-milling reached an acylation rate of 99% estimated by NMR. Extended to silk peptides, an acylation rate of 70% for fibroin peptides having a DH=25%, and an acylation rate of 48% for sericin peptides having a DH=39% were obtained by OPA dosage (Fig 2).

III- Measurement of the surface tension of silk peptides and lipopeptides

The surface tension of air/water can be reduced by the absorption of fibroin and sericin peptides. After acylation, the surface activity has been improved. Indeed, the surface tensions obtained with lipopeptides are lower than those obtained with non-acylated peptides. Fibroin peptides and lipopeptides have better surface activity than those of sericin (Fig 3).

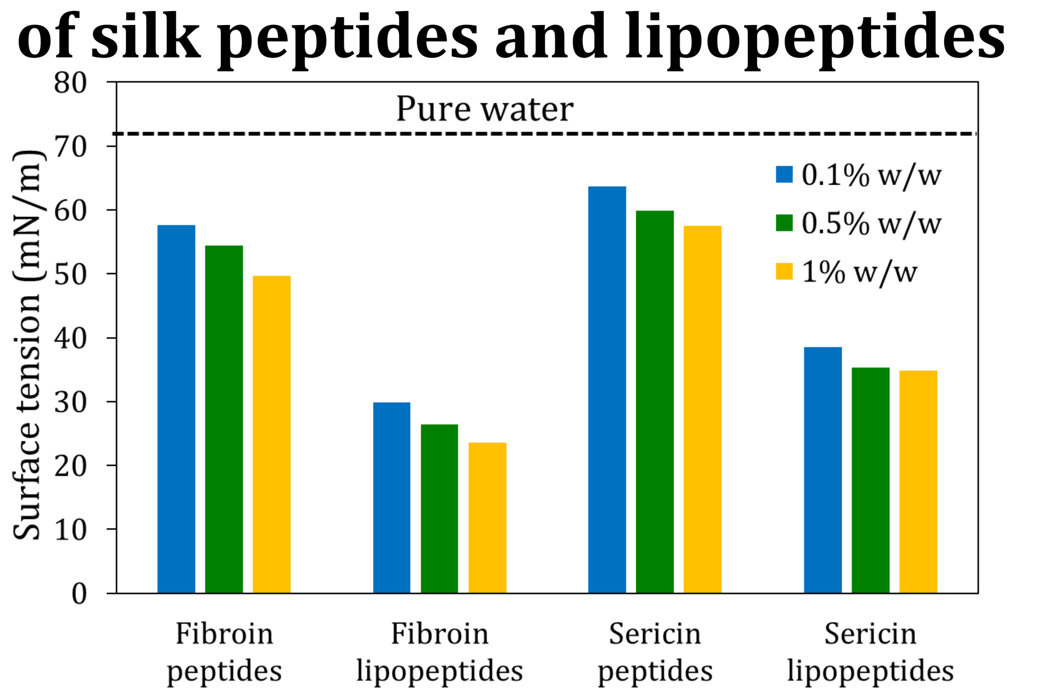


Fig 3 : Surface tension of silk peptides and lipopeptides

References

[1] Clark J.H., Green Chemistry, 2019, 21, 1168-1170.
[2] Vepari C. and al., Progress in Polymer Science, 2007.991-1007.
[3] Rockwood D.N. and al., Nature Protocols, 2011.6.1612-1631.
[4] Bascou R. et al., Mater Today Com, 2022, 33, 104491.

Conclusion & Perspectives

✓ The preliminary results showed that the proposed acylation strategy gives silk lipopeptides having a good ability to reduce the air/water surface tension, this underlines the interest of their potential use as amphiphilic molecules.

➢ **Perspectives :**

- ❑ Functionalization of silk peptides by other grafting strategies in solventless conditions.
- ❑ Synthesis of lipopeptides with different structures.
- ❑ Investigation on the relationships between structure, physicochemical properties and functional properties.