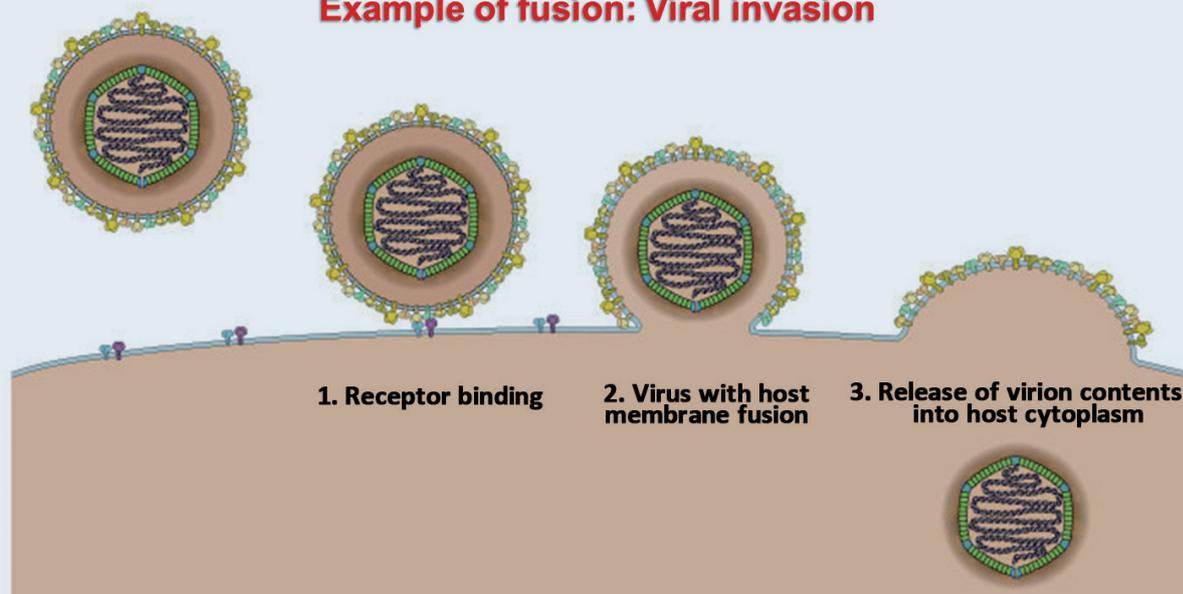


Example of fusion: Viral invasion



Source: Swiss Institute of Bioinformatics

Designing a Starch-Based Active Coating with a pH-Responsive Property

Starch serves as a smart material for food preservation.

Food spoilage due to microbial growth or lipid oxidation occurs commonly in our daily life. The spoilage not only decreases the shelf life of foods but causes serious sickness if toxins are produced by microorganisms and ingested by consumers. The addition of preservatives and antioxidants is the most efficient way to prevent food spoilage from the growth of microorganisms and lipid oxidation. Currently, the direct addition of more than adequate amounts of preservatives and antioxidants in foods is commonly applied, but the spoilage of foods is a gradual process occurring over time during storage; the initial addition of more than necessary amounts of preservatives or antioxidants might be not the best way from concerns about safety, effectiveness and economics. Active package techniques, such as the inclusion of active compounds to prevent microbial growth and to retard lipid oxidation, have hence attracted great attention. A pH-responsive material can not only play the role of a carrier to carry the active compounds but also a controlled release of active compounds when the pH in foods alters during storage. In practice, the minimum dose of antioxidants carried by an active coating of starch film becomes released only when the pH decreases resulting from free fatty acids

released through lipid hydrolysis. How to make the active compounds release from the starch matrix when really needed is a critical technique for the development and applications of a starch-based active coating with pH-responsive property.

Hsi-Mei Lai at Department of Agricultural Chemistry in National Taiwan University is famous in the field of starch chemistry and applications in both academia and food industry. Lai's group sought to design a pH-responsive starch-based thin film that can promise a quick response upon pH altering in food systems.¹⁻³ Charges on the modified starch molecules interact with the negative charges on the additive (citric acid in this case). In detail, the positive charges on the cationic starch (CS) interact with the negative charges on the citrate, which has three carboxyl groups (pK_a 3.14, 4.77 and 6.39), depending on the pH in the food systems.

As Fig. 1 shows, there is no significant difference in the size of starch granules embedded in a CS thin film between pH 3.0 and 5.5 in NaCl solution (0.01 M) (Figs. 1(a) and 1(b)). Once citric acids are added to the CS starch film forming a solution, the citrate-CS

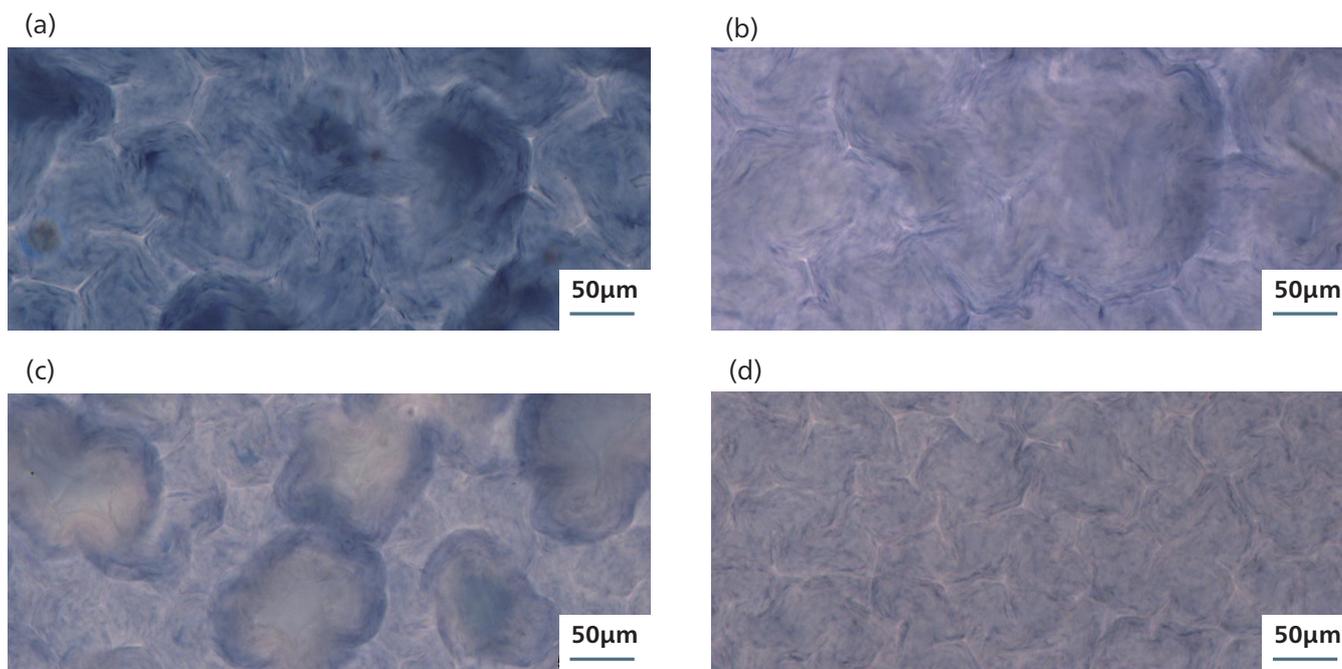


Fig. 1: (a)-(b) Morphology of swollen CS ($R = \infty$); (c)-(d) citrate-CS ($R = 2$); (a) and (c) thin films at pH 3.0; (b) and (d) pH 5.5. R is the number ratio of positive charge to negative charge. [Reproduced from Ref. 3]

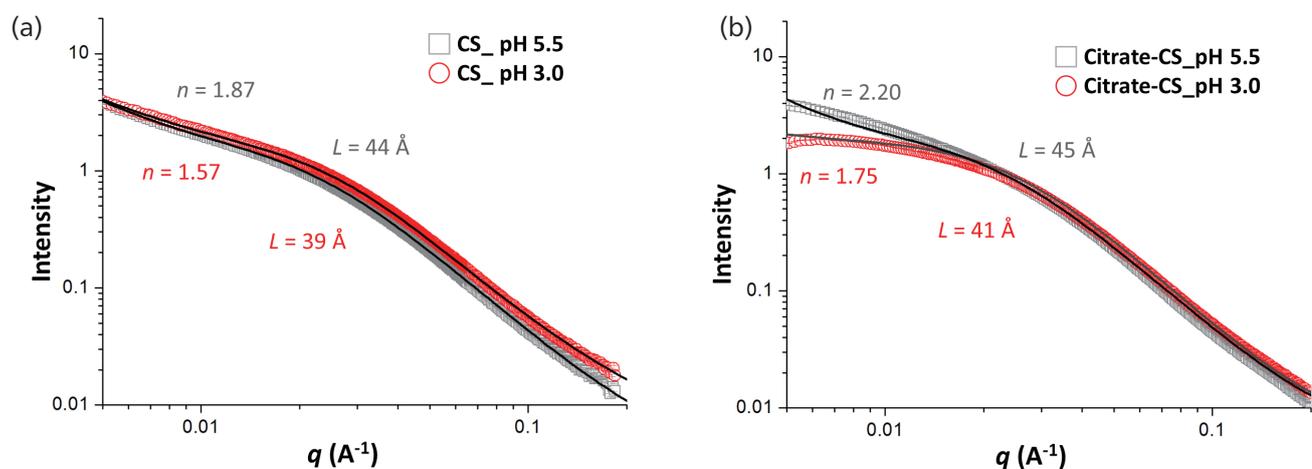


Fig. 2: Observed (open squares) and calculated (solid line) SAXS profiles of CS (a) and citrate-CS thin films with $R = 2$ (b) after swelling tests in solutions of pH 3.0 and pH 5.5. The main structural change responsive to pH in citrate-CS thin films depends whether large aggregates are formed or not. [Reproduced from Ref. 3]

starch thin film shows a swelling or collapsing transition across pH 3.0 in NaCl solution (0.01 M) in a swelling test. At pH 3.0, the swollen CS granules were investigated due to few negative charges available for attraction to the opposite charges (**Fig. 1 (c)**), whereas at pH 5.5 the starch granules embedded in the citrate-CS starch thin film shrank because much negative charge on the citrates plays the role of cross-linker to bring the chains of starch molecules together (**Fig. 1(d)**). This mechanism explains how the citrate-CS starch thin film possesses a pH-responsive character. To incorporate the active compounds in a starch-based thin film, the active compounds

can be initially added into the film forming solution. The starch granules with a greater degree of swelling thus retain greater amounts of active compounds in the film. During releasing test, the active compounds entrapped in the swollen starch granules become released only when the swollen starch granules collapse. In practice, for a fresh food with pH greater than pK_{a1} of citrate, an electrostatic interaction between cationic groups on CS and the pH-tunable anionic groups of citrate (carbonyl groups) occurs so that the swollen starch granules are protected and prevented from collapsing. When the pH of the stored food falls below the pK_a of citrate, the protec-

tion of the swollen starch granules from the citrate disappears; the active compounds are thus released from the collapsed starch granules.

Small-angle X-ray scattering (SAXS) is a powerful tool to determine, on a nanometre scale, the mesh size of soft matter, such as starch and its derivatives. SAXS at **TLS 23A** is used to examine how the citrate constrains the network inside swollen CS starch granules. The small- q scattering exponent (n) attributed to scattering from aggregated CS chains in a network of size exceeding the resolution of SAXS ($> 200 \text{ \AA}$ given by $2\pi/q$) from the SAXS data is fitted with a correlation-length model (**Fig. 2**). The largest n found in the swollen citrate-CS thin films at pH 5.5 is due to the ionic crosslinking. At pH 3.0, as the protonated citrate can no longer interact with the charged CS chains; n is similar to that in CS thin films (**Fig. 2 (a)**). The shoulder-like feature about 0.03 \AA^{-1} in all SAXS patterns characterizes the correlation length ($L = 41\text{--}44 \text{ \AA}$) in the starch network. Regarding the hierarchical structure of starch, the calculated L is much smaller than the gyration radius (312 nm) of corn starch amylopectin.⁴ In the semi-dilute starch concentration, the correlation length is recognized as the mesh size of amylopectin. The reason that the thin film with a lesser degree of swelling forms a larger mesh size (larger L) and aggregate (larger n) (**Fig. 2**, pH 5.5) is attributed to the uneven distribution of cationic charges on amylopectin during cationization.² The amylopectin clusters embedded in crystalline regions are the least reactive regions that remain neutral, and the meshes (polymer-poor region) lie inside the neutral part of one amylopectin.¹ As the intermolecular attractive forces (ionic crosslinking) among amylopectin molecules are introduced, an intermolecular aggregation occurs, responding to the enlarged mesh size within one expanded amylopectin molecule. The contrary

findings are, as expected, that the mesh size decreases under repulsion by the repulsive forces among the amylopectin molecules, which occurs in either the fully ionized quaternary amine in CS or ionic crosslinking-free citrate-CS thin films at pH 3.0.

This work shows us the possibility to prepare a pH-responsive coating with citrate and cationic starch. Most of all, SAXS helps us to unveil how the cationic starch structure alters in the presence of ionic crosslinking. There is no doubt that SAXS will be an important tool to probe the structural changes of a starch network in related research work, including active compounds in loading and releasing experiments. (Reported by Hsi-Mei Lai, National Taiwan University)

This report features the work of Hsi-Mei Lai and Shing-Yun Chang published in Food Hydrocolloids, 56, 254 (2016).

TLS 23A IASW – Small/Wide Angle X-ray Scattering

- SAXS
- Materials Science, Chemistry, Condensed-matter Physics, Soft Matter

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