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Pickering emulsions stabilized by colloidal lipid particles: Potential for high chemical stability?

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Many food, pharmaceutical, cosmetic, and agrochemical products exist as dispersions of immiscible liquids (typically, oil and water), i.e., are emulsions. These emulsion products may undergo a range of physical and chemical destabilization events over their production, storage and end-use. Pickering emulsions have shown to provide definite advantages with respect to physical stability of emulsions compared to conventional emulsifiers, and are emerging in the food area. In addition to controlling the physical stability of food emulsions, preventing adverse chemical degradation is also a challenge, and in particular, oxidation of the unsaturated lipids. Often, lipid oxidation in emulsions is tentatively prevented by using oil-soluble antioxidants (e.g., tocopherols). These components are highly hydrophobic and therefore located inside the oil droplets. However, lipid oxidation is initiated at the oil-water interface, so the efficiency of these antioxidants is far from optimal and could be enhanced when present at the interface [1]. A way to achieve this could be to entrap antioxidants within Pickering particles, thus locating them at the droplet surface. In the present work, we study lipid oxidation in two Pickering emulsions stabilized by colloidal lipid particles (CLPs) [2], with the exact same composition, but with a different physical location of the antioxidant α-tocopherol: either within the CLPs (Figure 1, left), or in the core of the oil droplets (Figure 1, right). Pickering emulsions containing the antioxidant in the CLPs oxidize slower and to a lesser extent compared to Pickering emulsions containing the antioxidant in the core of the droplet [3]. Although, according to our initial hypothesis, the interfacial localization of CLP-entrapped antioxidant may explain these results, other possible mechanisms are currently under consideration, such as the possibility that antioxidant-loaded CLPs would behave as an antioxidant reservoir with progressive release in time. This work opens up new perspectives to develop physically and chemically stable food emulsions with high levels of unsaturated lipids, and optimized levels of antioxidants.

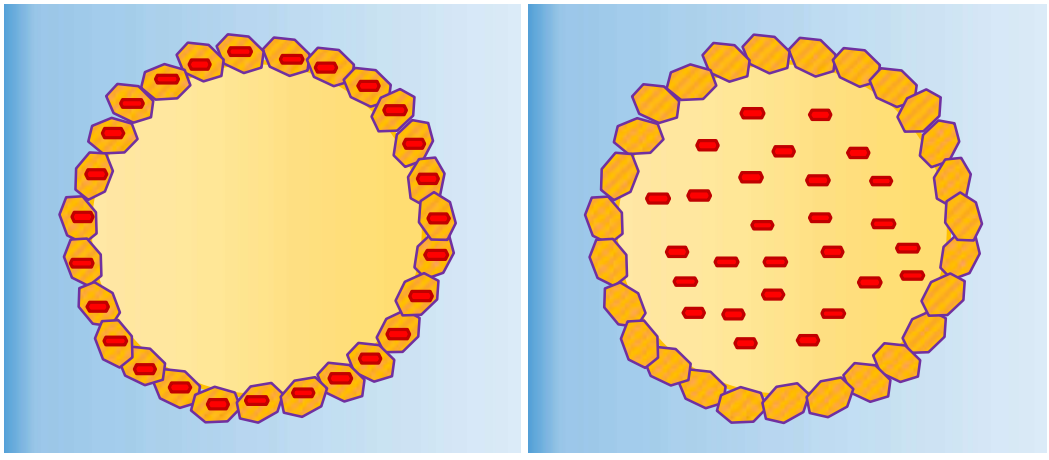

Figure 1: Schematic representation of CLP-stabilized Pickering oil-in-water emulsions: (left) with α-tocopherol incorporated in the particles and (right) with α-tocopherol in the liquid oil droplets.

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Synergistic stabilisation of emulsions by blends of dairy and plant proteins: Contribution of the interfacial composition

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In the food industry, dairy proteins are often used to formulate emulsions. These animal-derived proteins have a high environmental impact and therefore there is a drive to replace them by plant proteins. It is challenging to fully replace dairy proteins by plant proteins in food emulsions, as this will affect the physicochemical stability of the emulsions and the final product quality (e.g., nutritional value and taste). Alternatively, a blend of dairy and plant proteins can be used to improve sustainability, while not compromising on functionality and product quality.

In the present project, the use of blends of pea protein isolate (PPI) with whey protein isolate (WPI) or sodium caseinate (SC) to physically stabilise emulsions has been investigated. Emulsion stability, surface load and interfacial compositions were determined and compared to those of individual protein-stabilised emulsions. The $d_{3,2}$ and surface load measured over a concentration range (0.2-1.6 wt.% protein) were the lowest for SC- and WPI-stabilised emulsions, and the highest for PPI-stabilised emulsions, whereas emulsions stabilised by the blends (1:1 ratio) had intermediate $d_{3,2}$ values and surface loads. Although individual PPI and SC-stabilised emulsions showed some physical destabilisation over 14 days of storage, the WPI-PPI or SC-PPI blends formed stable emulsion systems, suggesting synergistic effects. In the case of the blends, both dairy proteins and plant protein adsorbed at the oil-water interface, but compositional rearrangements at the interface were noticed over three days. More specifically, whey proteins were able to displace pea proteins from the interface, which were themselves able to displace SC. However, such a displacement was possible only when the displacing protein was present in sufficient amount in the system. These effects are important to understand the stabilisation mechanisms of protein blend-stabilised emulsions, and to propose design rules for related applications.

Keywords: Interfacial displacement, protein mixtures, dairy protein, plant protein, emulsion stability, SDS-PAGE

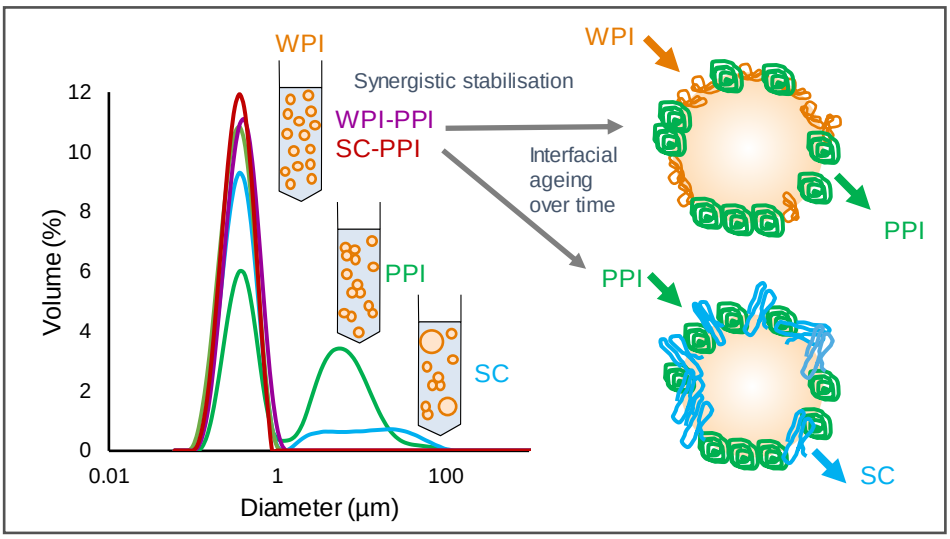

Figure X: Graphical abstract

Nonlinear surface rheology and interfacial microstructure imaging of WPI particles and their constituents

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KEYWORDS: Protein Pickering stabilizer, air/water interface, microstructure, surface rheology, Lissajous plots, atomic force microscopy

In recent years, food-grade Pickering stabilizers have gained great interest, because of their ability to form very stable emulsions and foams. Food-grade Pickering stabilizers are often produced by cross-linking proteins, which typically results in a mixture of cross-linked particles and non-cross-linked proteins. This smaller material could potentially contribute to the interfacial behaviour of the total mixture. The aim of this work was to understand the interfacial properties of air/water interfaces stabilized by whey protein isolate (WPI) particle suspensions. The particles were produced by cold-induced gelation of WPI aggregates, using calcium nanocrystals. To understand the interfacial properties of the total mixture, we have studied the whole hierarchy of structures, including native WPI, WPI aggregates, and WPI particles by combining surface dilatational and shear rheology, and microstructure imaging using atomic force microscopy (AFM).

Air-water interfaces were subjected to large amplitude oscillatory dilatation (LAOD) and shear (LAOS) using a drop tensiometer and a double wall ring (DWR) geometry coupled to a stress-controlled rheometer. The non-linear responses of the LAOD and LAOS experiments were analysed using Lissajous plots of stress versus deformation. Lissajous plots of native WPI- and aggregates-stabilized interfaces in LAOD and LAOS showed a rheological behaviour of a viscoelastic solid, while interfaces stabilized by the particles tended to have a weaker and more fluid-like behaviour.

The microstructure of the interface was analysed by imaging Langmuir-Blodgett films of the three protein systems using AFM. For the WPI interface, we found a highly heterogeneous structure in which the proteins form a dense clustered network. For the WPI particles we observed that they are present in the interfacial film, but are scattered throughout the film, separated by large areas, where smaller material is present. This suggests the presence of smaller material between the particles and also explains the weak layer found in the surface rheology experiments. The smaller material present in this WPI particle suspensions is surface active and plays an important role in interface stabilization, and could also influence the macroscopic properties of foams and emulsions. Based on these observations the WPI particle system does not behave as a classical Pickering system, but instead forms mixed interfaces consisting of particles and non-cross linked proteins.

Acid-induced gel properties of an alginate-in-whey protein emulsion

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Water-in-water (W/W) or aqueous two-phase system (ATPS) emulsions are finding increasing applications in diverse fields of technology, for instance as protocells [1], and reactors for the synthesis of hydrogel particles [2], and enzyme-laden microgels [3]. Successful ATPS emulsification depends on thermodynamic incompatibility between two (bio)polymers, causing segregative phase separation [4]. Herein, we demonstrate that hydrophobization of whey proteins, by grafting acetyl moieties and heat denaturation, makes the proteins immiscible with a co-charged polysaccharide solution (alginate). Addition of erythritol, which is a low-calorie and zero-glycemic sugar alcohol, to the hydrophobized protein solution, enhanced emulsification and increased the stability of the resulting emulsion. Subsequently, the acid-induced gel properties of the emulsion was studied by dynamic rheometry and confocal microscopy.
Erythritol addition reduced the surface tension (at the air-water interface) of the hydrophobized protein solution, enhancing the incompatibility between protein and alginate. It also postponed the gelation time of the hydrophobized protein solution and resulted in formation of a softer gel. Confocal imaging of the emulsion gel confirmed micro-phase separation of alginate and the droplets aggregation in the protein-rich matrix.

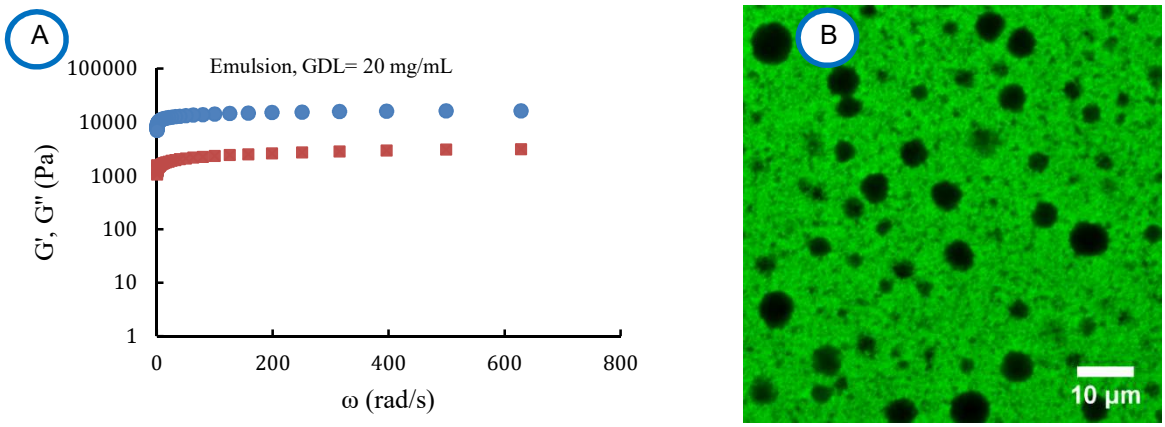

Fig. 1. A: G', storage (circles) and G'', loss (cubes) moduli of the alginate-in-whey protein emulsion gel measured by a frequency sweep test; and B: a typical CLSM image of the emulsion gel.

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Interfacial behaviour of plant proteins

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Challenges of public health and sustainable development require replacing in food products animal proteins by plant proteins. In this optics, it is crucial to understand the structure and kinetic of formation of a film of plant proteins in order to improve the control of emulsions and foams stabilized by these proteins.
In this talk we will present experimental results on the behaviour interfacial properties of wheat gluten, sunflower and rapeseed proteins at liquid interfaces. Thanks to a combination of tensiometry, dilatational rheology and ellipsometry, rational physical pictures of the dynamics of the interfacial properties are achieved, for the various proteins and at both air/water and oil/water interfaces.
For gluten proteins, a time-concentration superposition of the data is evidenced whatever the subphase concentration, which reveals that the kinetics of protein adsorption at the interface is dominated by bulk diffusion. We propose a consistent physical picture of the multistep diffusion-controlled irreversible adsorption of the gliadin proteins at an air/water interface, and evidence surface-induced conformational changes of the proteins followed by film gelation [1].
Sunflower and rapeseed proteins by contrast do not reorganize once adsorbed at an interface and display a simpler dynamics of film formation. In addition the failure at high concentration of the time-concentration superposition of the tensiometry and viscoelastic data strongly suggest a surface-induced aggregation process, which we confirm with turbidity measurements.
By quantitatively comparing the surface pressure dependence viscoelasticity of the various interfaces, we hightlight the crucial role on the behavior of plant proteins at liquid interfaces of the solvent quality and of the protein softness, that is discussed in regard to the protein structure.

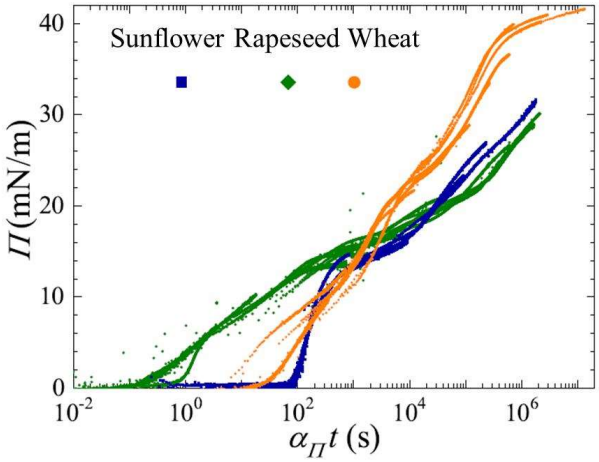

Figure 1: Air-water interface surface pressure master curves obtained for solutions of sunflower, rapeseed and wheat proteins comprised between 10^{-2} and 10g/L.

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Viscosity of artificial chewed boluses of cereal foods

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Food Oral Processing (FOP) is a key step for foods assimilation and the benefit of their nutrient properties, especially for elderly whom oral physiology is altered. The main objective of this process is to form a food bolus that can be swallowed safely. Nevertheless, most of the studies about relationships between FOP, oral physiology and food bolus properties focus on particle size and dental status, saliva is only partly considered. However, for cereal products, food bolus viscosity is a function of the added saliva [1], which evidences the interaction between food and saliva. Our aim is to establish a model to determine a coefficient that characterizes this interaction.

To do so, we first study sponge cakes, one sample is standard and the other one is enriched with pea isolates. Artificial boluses composed of crushed sponge cake and a surrounding fluid, representative of saliva, are prepared. Four fluids are used: three of them are Newtonian, water and two Dextran solutions of viscosities 3mPa.s and 10mPa.s. The fourth fluid is shear thinning, composed of different salts and mucin distilled in water, as already used in different studies [2-4]. Viscosity measurements (shear and elongational) are realized using capillary rheometry, including Bagley's corrections. The shear viscosity of boluses follows a power law model from which the consistency K can be derived. A phenomenological model of the consistency is obtained (Figure 1): $K = K_0\, e^{-\alpha\, \Delta WC}$, where α is the interaction coefficient and ΔWC is the difference of water content between the food bolus and the sponge cake. Results also show that the viscosity plays a minor role, compared with its concentration. By varying properties of the surrounding fluid, the interaction between food and saliva can be assessed.

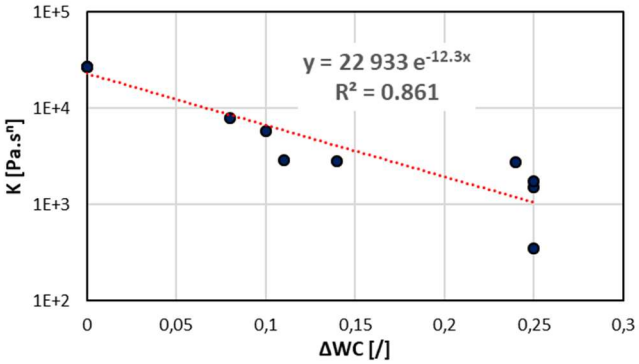

Figure 1: Phenomenological model of the consistency for a standard sponge cake. Red line is a fit by an exponential function that gives the interaction coefficient: α = 12.3.

This study is part of the project "**Mo**delling interactions of **Foo**ds with **SA**liva during oral processing and application to the design of cereal foods enriched with plant proteins (MoFooSA)" that has been supported by the Region Pays de Loire, via the RFI project "Food for tomorrow".

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Microtechnology used as a tool in the development of novel food products

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In this presentation, I will take examples from the work done at the food micro-technology group of Wageningen University, and use them to illustrate how the insights can be used in mild separation technology, and in the production of novel foods.

Ingredients used in food production revolve around a limited amount of crops, and mostly only the fruits of these crops, whereas for example the leaves and stems etc. could also be used. In order to be flexible, separation technology is needed to fractionate the starting materials. Membrane separation will be highlighted using results obtained with miniaturised membranes that help us uncover underlying mechanisms at colloidal scale, which has led to various discoveries for efficient fractionation.

Besides, the functionality of the fractions is key for application. For example, whether animal based proteins can be replaced by their plant based counterparts is highly dependent on their surface activity. We have developed various microfluidic devices with which this can be monitored for small droplets and at short time scales. This allows screening, comparison of ingredients, and even establishing a link with more classic process technology, and also digestive functionality. Also here we started at the colloidal scale and used these insights to design products starting from nano- and micrometer scale.

New approach for the characterisation of dairy protein foams stability

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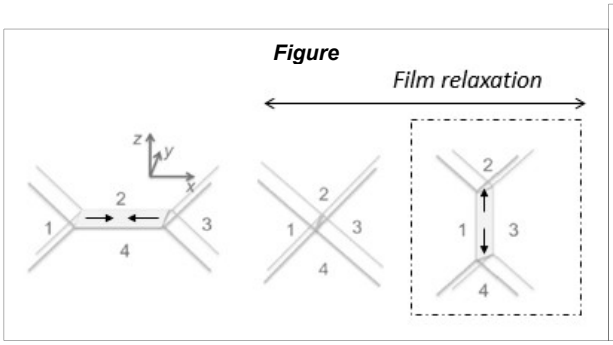
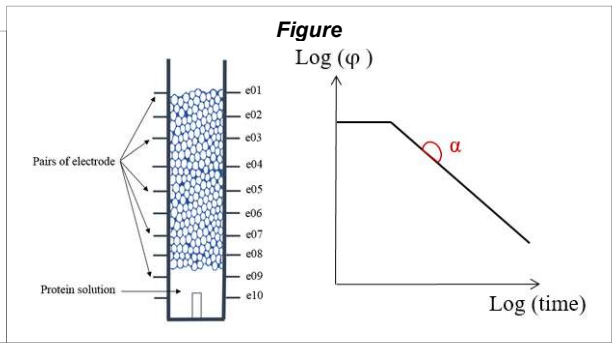
The main destabilisation processes in aqueous foams are liquid drainage, coalescence and disproportionation. In food sciences, the measurement of protein foam stability generally integrates all of them in a "global stability", and a challenge is to correlate the stability and rheology of foams to the properties of interfaces.

We adopted a multi-scale approach by combining the interfacial rheology of proteins adsorbed at the air–water interface, the dynamics of protein films after T1 topological rearrangements (Fig. 1), and macroscopic foam characterisations: the foam stability against drainage was evaluated by following the evolution of the liquid fraction as a function of time and height (Fig. 2) [1], and the foam complex modulus and yield stress were measured under oscillatory shear. We investigated the behaviour of dairy proteins (whey protein isolate and purified β-lactoglobulin), either in the native state or after modification by dry-heating and/or pH adjustment prior to dehydration.

Our results show that small-extent structural modifications of proteins have a dramatic impact on interfacial rheology, liquid film dynamics, foam stability and foam rheology.

This approach, correlating multiple investigation scales, sheds light on the contribution of the interfacial rheology to protein foam properties, in particular through the involvement of film relaxation dynamics.





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Influence of kinetic and shear rate on whey protein aggregates structure: a small-angle x-ray scattering study

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Whey proteins are of interest because of their nutritional and functional properties in food application. Heat-induced aggregation coupled with process conditions of whey proteins gives them new functional properties that can be used to impart specific structural and physical properties of food products. Then, aggregation process needs to be well understood and controlled to design specific functional whey protein aggregates.

Most of previous studies has focused on the role of the physicochemical conditions on the structure and size of protein aggregates [1], whereas process parameters have not been clearly investigated. In this study we will study the role of process parameters, i.e. shear rate, heat treatment and time on the size and structure of protein aggregates to control the aggregation process.

However, the main difficulty to understand the respective role of each parameter is to separate the kinetics of denaturation and aggregation and the flow from the thermal history. In this study, we have developed a continuous process of aggregation at small-scale (<1 mm) to have laminar flow conditions for various shear rates and a fine control of the thermal history. Thermal and flow conditions can thus be controlled independently. This feature is clearly a novelty compared to previous studies [2] in which aggregation was limited by heat transfers. This small-scale continuous process allows us to vary, in one hand, the residence time and thus to establish the kinetics of aggregation, and in the other hand, the shear rate up to 500s-1.
This set-up has been used to test the role of several process parameters on the kinetics and structure of whey protein aggregates by small angle X-ray scattering (SAXS) techniques for given physicochemical conditions (pH and ionic strength) leading to sub-micrometric aggregates. We follow the kinetics of aggregation from the protein scale (few nanometres) to the aggregate scales (< 1 µm). Structure of whey protein aggregates larger than few micrometres are also investigated by quantitative fluorescent microscopy and image analysis methodology developed for this purpose.

We show that the kinetics leads to the formation of new aggregates and not to their enlargement. Secondly, we show that the flow process has a large impact on the size and structure of the aggregates: the size of the aggregates is increased by a factor 3 when comparing the ones obtained under static conditions and the ones obtained under flow, whereas their internal structure remains unchanged. The shear rate, on the other hand, leads to an increase of the size of the aggregates without increasing their density.

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Understanding of structural heterogeneities in the starch hydrogels

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Abstract

As an easily accessible, renewable and environmentally friendly material, and a pivotal part of the human diet, starch holds great promise for a wide variety of structural, pharmaceutical and biomedical applications. Starch hydrogels are unique three-dimensional, semi-solid structures able to hold a large amount of water and other solvents with unique rheological, physicochemical and biochemical properties. As representatives of molecular gels, starch hydrogels simultaneously feature domains with highly distinct manner of organisation, packing and molecular mobility, which introduces considerable difficulties to their full experimental characterisation.

In this project, we have applied NMR methods specifically tailored to the identification of rigid and mobile components, such as ^{1}H-^{13}C CP and CPSP-MAS NMR[1–6], which are novel to the field of starch hydrogels. Hydrogel materials were produced by different hydrothermal treatment methods using five separate maize cultivars, featuring different levels of composite glucans, degree of modification and resistant starch character.

Our initial investigations resulted in the identification of previously unpublished distinct carbon sites exhibiting increased mobility in low amylose starch hydrogels, when compared to their high amylose counterparts. Data obtained from these investigations were cross-referenced with rheological and thermal analyses of the maize hydrogels. These findings were hypothesised to be a consequence of the predominantly linear structure of amylose, compared to its highly branched glucan analogue, facilitating inter-chain association during the period of gelatinisation.

We aim to use our findings for the development of previously unexplored starch hydrogel-based materials for applications in the pharmaceutical and biomedical sphere, as novel biocompatible prosthetic implants and “smart” drug delivery methods as targeted, stimuli-responsive and controlled drug release loading materials.

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Model of the swelling of protein gels in simulated gastric juice

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Soy gels at different crosslink densities has been subjected to immersion in a simulated gastric juice. Via titration the pH of the juice is kept at pH=2 level. Due to strong buffering effect of the soy protein the pH inside the gel is only slowly changing. Soy protein is a polyelectrolyte gel, whose charge depends on pH due to dissociation of acidic and basic groups.

We have modelled the experiments via extending Flory-Rehner theory with Donnan-equilibrium, to account for the ionic contribution to the swelling pressure, cf.[1]. The swelling pressure is plugged into Darcy's law to describe swelling kinetics. Furthermore, the kinetics in the total of bound and free protons inside the gel has been modelled, taking into account diffusion of free protons, convection of protons due to swelling, and the buffering capacity of the soy gel.

The experiment and model show a rich dynamics of the gel, which shows shrinkage after an initial swelling stage. This indicate also a rich dynamics inside in-vivo gastric environment, where also the action of pepsin enzyme has to be added to the system. Its activity is strongly dependent on pH, and its diffusion is modulated by the mesh width of the shrinking/swelling gel.

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Dry heating of β-lactoglobulin generates microparticles: role of pH and lactose

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Heat treatment of whey proteins is known to increase the functionality of these high nutritional proteins such as their viscosity or gelling properties [1]. While heating a whey protein solution is a widespread practice, heating them as a powder, or dry heating, is a less known process. We have experimented the dry heating at 100°C of whey proteins with traces of lactose. Dry heating of a whey protein powder at pH 9.5 has been shown to generate microparticles [2,3]. Is has been demonstrated that crosslinks of whey proteins in the powder during its dry heating make the powder partially insoluble, leading to microparticles having a shape close to that of the powder. Due to the porous structure of the powder, the microparticles formed by dry heating are able to entrap a huge amount of water (20-40 g water/g microparticle), with a yield of formation > 0.5 g microparticle/g of powder. They could be used as a 100% dairy ingredient in food products to increase their viscosity

With the aim to understand the process of formation of these microparticles, experiments were performed with pure β-lactoglobulin (β-Lg) in solution stored at 4°C with or without lactose, at pH 9.5 or 6.5, then freeze-dried and finally dry heated.

Analyses were performed at 3 steps, during storage of the β-Lg solution before its drying, after its drying and after dry heating of the β-Lg powder. Residual native proteins and secondary structures of proteins, the browning of powders, the yield of conversion of β-Lg into microparticles and their ability to entrap water were measured along the process.

In conclusion, the alkaline pH and the presence of lactose are crucial for the production of microparticles, but these two factors act at different steps of the process. The alkaline pH is only required during the storage of the β-Lg solution before drying and hardly plays a role during dry heating, while the presence of lactose is only crucial during the dry heating and is useless during the storage of β-Lg solution.

These results help understanding the formation of microparticles by dry heating.

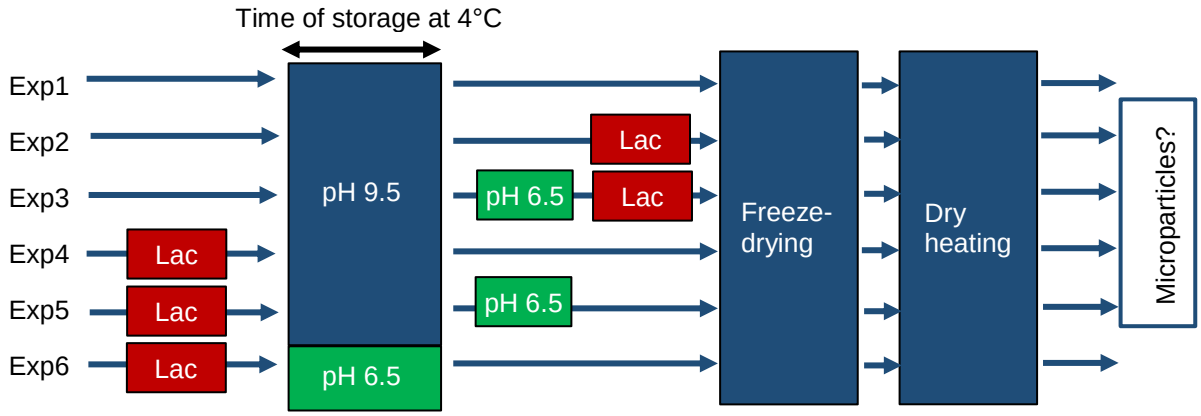

Figure 1: experiment plan

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Heat-induced gelation of mixtures of casein micelles with whey protein aggregates

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In this study we explore the functional properties of whey proteins found in the milk serum. Whey proteins are well known for their texturizing properties such as gelation, stabilization of foams and emulsions, film formation (Nicolai, Britten, and Schmitt, 2011). Current consumer demand for heathier, simpler ingredients in foods produced the terms such as “clean label” and “clean eating”. Whey proteins can be considered as an excellent “clean label” alternative to traditional E-number texturizing ingredients used in products, such as gelatine or modified starches, because they are percieved as healthy by most consumers and do not require approval by the European Food Safety Authority.

It was previously established that during heating at certain conditions whey proteins form suspensions of stable aggregates. Three types of aggregates with different functionality have been discribed in the literature – fractal aggregates, microgels and fibrils, with fractal aggregates having the most interesting functional properties for applications in food products. In particular, stable suspensions of fractal aggregates can form gels at ambient temperatures upon acidification or addition of salt – a process known as “cold gelation”. Cold gelation of whey protein fractal aggregates was previously studied in detail in our resarch group. It was found that cold gelation is a thermally activated process with an activation energy of 210 kJ/mol for gelation induced by addition of calcium chloride and 155 kJ/mol for acid-induced gelation (Kharlamova, Nicolai, and Chassenieux, 2018 a&b).

On the other hand, gelation of complex association colloids called casein micelles, that represent the major protein fraction in milk, was found to be characterized by a critical gelation temperature t_c. Gelation of micelles in water suspensions does not occur even after prolonged heating at tempratures below t_c, while happens almost immediately at and above t_c (Thomar & Nicolai, 2016).

In presented talk we discuss gelation of mixtures of casein micelles with whey protein fractal aggregates (Fig. 1). We show that addition of fractal aggregates to micelles results in formation of a hybrid protein network at a lower temperature. The mechanism of gelation of such systems is suggested. The results of the study can be used as a benchmark for application of whey protein aggregates as a gelling agent in more complex dairy systems.

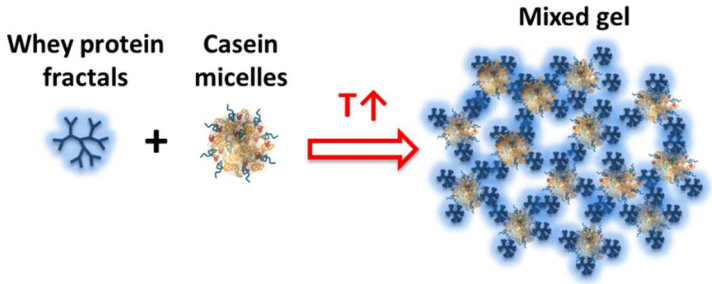

Figure 1: Schematic representation of gelation in mixtures of micelles with fractal whey protein aggregates.

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Gelation kinetics of sodium caseinate induced by continuous acidification

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Sodium caseinate is a milk protein which is used in pharmaceutical products and food. This protein is stable in water at pH=7 due to surface charges that induce an electrostatic repulsion. However, as the pH decreases and reaches this isoelectric point, pI=4.6, electrostatic repulsions vanish and the Van der Waals forces induces the flocculation of the caseinates. Here, we add GDL to the caseinate dispersion, a molecule that slowly and homogeneously reduces the pH from 7 to 3 and therefore leads to gelation [1]. Using a combination of rheology, X-ray scattering and confocal microscopy we study the gelation process.

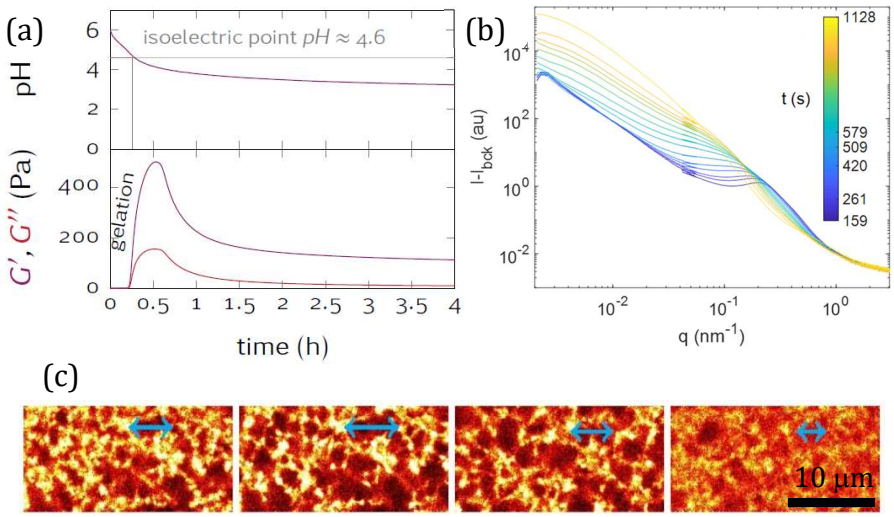

Figure 1: (a) rheology: evolution of the elastic G' and loss G'' modulus as a function of time and pH. (b) Saxs: evolution of the scattering intensity as function of the wave number q and time. (c) Confocal microscopy: snapshot of the gel at different times.

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Stable oil-in-water emulsions using an hydrophobically modified xanthan

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Polysaccharides are widely employed in many industries such as food or cosmetic mainly to stabilize oil-in-water emulsions and to control their rheological properties. Among the others, xanthan gum is the most used due to its outstanding thickening properties of aqueous solutions. However, because of its poor interfacial properties, it requires the addition of an emulsifier to disperse and stabilize the oil droplets. Unfortunately, the use of low molecular weight surfactants has many disadvantages related to toxicological and environmental considerations. On this basis, macromolecular surfactants have been developed during the last decades, most being synthetics while the nowadays demand of natural ones is considerably growing. To overcome this problem, octyl residues were grafted onto the backbone of xanthan to confer new amphiphilic properties[1]. Moreover, xanthan can adopt two different conformations[2], with distinct rheological properties[3] depending on the experimental conditions: an ordered semi-rigid helical structure or a disordered flexible coil.

The objective of the present work is to study and understand the phenomenon involved in the stability of oil-in-water emulsions containing amphiphilic xanthan.

Oil-in-water emulsions using no surfactant but containing pristine or modified xanthan have been studied and compared. As expected in emulsion, unmodified xanthan is not able to stabilize the emulsions as phase separation occurred within only few hours. Oppositely, emulsions obtained with modified xanthan are stable over months (see fig. 1).
These results clearly demonstrate the high potential for hydrophobically modified xanthan as emulsion's stabilizer which has been studied as a function concentration and grafting density.

***Figure 1**. Oil in water emulsions containing 1g/L of pristine xanthan one day after preparation (left) and modified xanthan 2 months after preparation(right)*

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Gelation of mixture of iota and kappa carrageenan

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We will discuss the rheological properties and microstructure of mixture of native kappa carrageenan (κ-car) and iota carrageenan (ι-car) in the presence of salts ($CaCl_2$ and/ or KCl). For κ-car solution, increasing the $CaCl_2$ between 5 and 40 mM increased the elastic modulus (G_{el}) and the gelling temperature (T_g). However, further increase of the $CaCl_2$ concentration did not lead to a further increase of the elasticity. Adding $CaCl_2$ between 5 and 20 mM to ι-car also enhanced T_g and G_{el}, but in this case G_{el} remained constantly above 20 mM $CaCl_2$. Mixtures of κ-car and ι-car showed a two-step gelation process at temperatures that coincided with the one of pure κ-car and ι-car solutions, respectively. However, the elastic modulus of the mixtures at low temperatures was much higher than the sum of those of the pure systems within the same conditions.

For the gelation of mixed gel in presence of both KCl or $CaCl_2$, G_{el} was higher than samples with just one type of salt at the same concentration. G_{el} increased when increasing the fraction of $CaCl_2$ in mixed salt up to 50%, further adding $CaCl_2$ led to a decrease of the storage modulus. However, T_g increased gradually with increasing fraction $CaCl_2$. At a fixed ratio of KCl and $CaCl_2$ of 50:50, G_{el} of mixed carrageenan increased with increasing total salts up to 40 mM and remained the same at higher concentrations (Fig.1).

In parallel, the influence of these salts on the structure of mixed gels was studied by confocal laser scanning microscopy (CLSM). In the mixtures, κ-car and ι-car could be distinguished because they were covalently labelled with different fluorescent dyes. CLSM images show that ι-car in pure or mixed gel is distributed more homogeneously than κ-car both in presence of KCl and/or $CaCl_2$. However, κ-car appears more homogeneously distributed in the mixed gel than in the individual gels. In addtion, κ-car in the mixed gels with mixed salts appear more homogeneous than that in presence of $CaCl_2$. Furthermore, the tubidity of mixed systems was evaluated as a function of temperature and time. The results showed that there are synergistic effects between κ-car and ι-car in mixed gels and between KCl and $CaCl_2$ in gels with mixed salts.

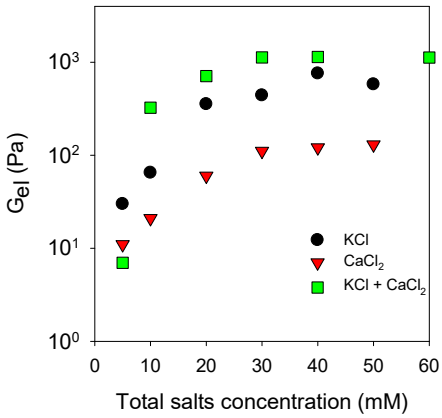

Fig 1. Elastic modulus of mixed carrageenan at 5-5 g/L after one hour at 5 °C as a function of total $CaCl_2$ and/ or KCl concentration.