From Fibril Formation to Fibril Properties and Rheology of Food Materials

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ABSTRACT

For control and design of food properties it is important to understand how molecules and their interactions give rise to formation of microstructures and resulting rheological properties. This will be illustrated by discussing the formation and properties of fibrils in aqueous and non-aqueous (model-) systems and the consequent rheological properties.

INTRODUCTION

Foods exhibit different micro-structures, with their sizes ranging between nanometers to millimeters. The form of the microstructures can range from fibrillar, plate-like, spherical, to topologically more complex, like e.g. bi-continuous ones. In aqueous surroundings fibrillar structures may be e.g. polysaccharides like xanthan, triple helices of gelatin, carrageenan bundles, or thin protein strands. The functionality of fibrillar structures ranges from thickeners and stabilisers to depletion agents of emulsions but they can also be used as gelators. The properties of the gels depends on the length distribution of the fibrils and their aspect ratio (length versus diameter). A high aspect ratio leads to space filling network at low volume fractions, i.e. weight efficient gels. We will address two different types of gel systems that contain fibrils. One with the aqueous phase as continuous phase, and the other with an oil phase as the continuous phase.

For the aqueous continuous phase, we distinguish between gelatin (composed of triple helices) and supramolecular aggregates formed by proteins or peptides. For the oil continuous phase many organo-gelators are available to structure, but only few of them are food-grade. Several have been proposed, amongst which mixtures of plant sterols with γ-oryzanol deserve special attention (see for example Bot et al.[1]).

The insights are not only applicable to foods. Supramolecular assembly is an important subject of study in various other research fields. It is relevant in biomedical sciences regarding so-called amyloid fibrils, being associated with several neurodegenerative diseases [2]. In the field of material sciences they are used for fabrication of metal nanowires, bio-nanotubes, nanometer thick coatings, three-dimensional peptide scaffolds, and vehicles for bioactives[3]

AQUEOUS FIBRIL SYSTEMS

To prepare aqueous fibril systems based on globular proteins, different conditions apply for different proteins. Several food-grade proteins have been used (egg proteins [4, 5], soy proteins[6] , kidney bean proteins[7] and milk proteins[8-12].

For beta-lactoglobulin (β-lg), fibrils are formed while heating at pH 2 and 80 °C for

several hours. These fibrils are several micrometers long and only nanometers thick, making them indeed highly suitable for structuring at low weight fractions[8]. The fibril formation process has been discussed in detail[13-15]. It was found to be entropy-driven in its initial assembly phase. Flow is found to affect the fibril growth[16]. Once fibrils exist, they make contact one another above a certain concentration, due to their random orientations. Once the excluded volume yields three or four points at which one fibril touches another, one has reached the critical gelation concentration[17]. The concentration in excess to this gelation concentration determines the elasticity, with a scalar percolation exponent[18,19-21]. The magnitude of the elasticity in the percolation regime (0.1%-1 %) also follows from excluded volume arguments. It amounts to about 100 Pa. For stiff rods, the relevant lengthscale is the length of the rod. For semi-flexible fibrils, the relevant lengthscale turns out to be the persistence length, the lengthscale on which the fibril is essentially rodlike. At higher concentrations, the elasticity is determined by a lengthscale that arises due to the interdependencies of fluctuations throughout the entire system. This is referred to as the deflection length[22] . Also in the higher concentration regime, excluded volume effects are dominant. The transition regime between low and high concentration can be well described by a simple additivity law[23]. The elasticity of the two classes of these fibril based aqueous gels (gelatin and supramolecular aggregates) is dominated by entropy.

NON-AQUEOUS FIBRIL SYSTEMS

It was found that mixtures of γ-oryzanol with β-sitosterol are capable of forming firm, thermo-reversible organogels that are quite transparent up to high concentrations of structurants[24]. The aggregates are characterized by X-ray scattering and scanning electron microscopy (SEM) as hollow tubules that can be up to micrometers long, but have a thickness in the nanometer range[1] . The organogel at a total structurant concentration of 10% has a strength of G'~100 kPa [25].

COMPARING AQUEOUS AND NON-AQUEOUS FIBRIL SYSTEMS

Comparing the fibril formation in aqueous and oil continuous systems, the formation of protein fibrils in water is entropy-driven[14] ($\Delta H \sim 0$, $\Delta S < 0$) and the fibril formation results from a quite complicated process in which the acid hydrolysis of the protein into peptides plays an important role[6]. The resulting aggregates are irreversible in the sense that they are stable against temperature changes and dilution. In comparison we find that the tubules formation in the oil phase by mixtures of phytosterols is an enthalpy-driven process[24] ($\Delta H < 0$, $\Delta S < 0$) and the aggregation into tubules is thermo-reversible. Although in both systems the aspect ratio is large, the tubules are hollow cylinders with a diameters estimated to be ~10-fold larger than the diameters of the solid protein fibrils.

It is interesting to note that the typical pure organogel is much stronger (G'~100 kPa) than the fibrillar gels (G' ~ 1 kPa) [5], at comparable volume fraction.

FUTURE CHALLENGES

One of the future challenges is to better understand interdependent dynamics at different scales in relation to non-linear rheology and fracture. Another challenge is to better understand the interdependencies among different scales in more complex systems.

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