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.