Droplets in emulsion gels: from fillers to networks

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Because of their ability to strongly adsorb at oil/water interfaces and to stabilise oil droplets by steric and electrostatic repulsion, water-soluble proteins are widely used as efficient emulsifiers. At low pH, proteins can aggregate and also form gels, either of protein molecules in solution or of protein-covered droplets.

The soft materials formed from protein-stabilised emulsions are referred to as emulsion gels [1], however, this designation is not precise enough to reflect the variety of composition of these materials. It is thus important to take into account the ratio between adsorbed and suspended proteins in solution before gelation, as during emulsification not all the proteins in solution adsorb at the interface. If the ratio is low, *i.e.* most of the protein is suspended, the system can be seen as a matrix of protein gel with the oil droplets acting as fillers, as in polymeric materials [2]. At a higher ratio the emulsion gel is more of a composite formed of both a protein and a droplet network [3].

Our objective is to study in detail the protein-stabilised emulsion gels considering the full range of their composition. A first step is to characterise separately the gelation of purified suspensions of protein-stabilised droplets, and of suspensions of pure proteins. These components are then combined, resulting in emulsion gels of well-characterised compositions, thus allowing a rigorous approach to these systems.

We use sodium caseinate as a case-study for the protein because of its outstanding properties as a surface-active agent and stabiliser, and because of its well-known ability to form gels [4]. Sodium caseinate-stabilised emulsions are produced using a high-pressure homogeniser, the resulting droplet size is close to the size of naturally occurring caseinate assemblies, *i.e.* 100-200 nm.

We combine rheological and microscopic approaches to characterise the behaviour of the gels, in order to develop our understanding of how the separate networks of droplets and proteins develop and contribute to the overall properties.

We find on Figure 1 that droplet networks exhibit a higher storage modulus than protein networks at an equivalent volume fraction. In both cases, their storage modulus varies according to a power law as a function of the volume fraction ϕ,

$$G'_{t_{gel}+2500s}(\phi) = G'_0 \phi^{\alpha}. \qquad (1)$$

We find that for protein-stabilised droplet gels the exponent is $\alpha_{droplet} = 3.20 \pm 0.09$ and the prefactor is $log(G'_{0,droplet}) = 4.51 \pm 0.07$ while for protein gels $\alpha_{protein} = 3.19 \pm 0.15$ and $log(G'_{0,protein}) = 3.78 \pm 0.10$.

The value for the exponent is consistent with those found in the literature for colloidal gels, either thermoreversible systems, where $\alpha = 3.0 \pm 0.5$ [5] or weak fractal networks, where $\alpha = 3.9$ [6]. Mixtures have an intermediate behaviour, and their storage modulus depends significantly on their composition, described by the ratio $\chi_{protein}$ defined as:

$$\chi_{protein} = \frac{\phi_{protein}}{\phi_{protein} + \phi_{droplet}}. \qquad (2)$$

They tend to be closer in terms of elasticity to a droplet gel if they are mainly composed of droplets, and vice-versa if they are mainly composed of proteins.

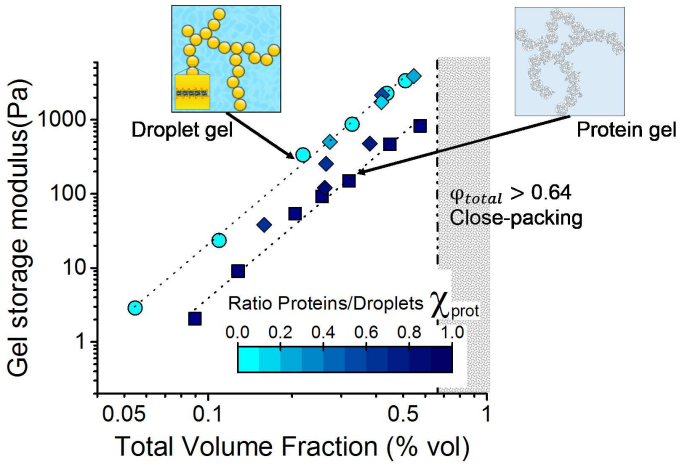

FIG. 1. Storage moduli of gels composed of: only protein-coated droplets (●), only proteins (■), and a mixture of proteins and droplets (◇, the colour indicates the value of $\chi_{protein}$ defined in Eq. (2)) as a function of the total volume fraction.

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