Rheological effect of particle clustering in gelled dispersions

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ABSTRACT

A theoretical model is presented to describe the effect of particle clustering on the elastic modulus of composite gelled systems. In this model, particle clusters are described as regions with an increased volume fraction of the dispersed particles and with a firmness that is determined by the volume fraction of the particles in the cluster. The firmness of the composite gel is then calculated on the basis of the volume fraction and firmness of these clusters, which are treated as cluster particles. In this way, the Kerner equation (including compressibility, but neglecting the particle surface) and the Palierne equation (including the particle surface, but neglecting compressibility), both corrected for particle crowding at high volume fractions of the dispersed particles by the method of Lewis and Nielsen, are extended to describe the effect of particle clustering. It is demonstrated that, even in the absence of discrete bonds between the particles, clustering considerably amplifies the effect of the dispersed phase on the elastic modulus of the composite gel. This amplifying effect increases for higher volume fractions of the dispersed particles.

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1. Introduction

The textural properties of semi-solid or gelled systems are greatly affected by the inclusion of dispersed filler particles, which can be solid particles, liquid particles (droplets) or gas particles (foam bubbles). Non-food examples of such composite materials are rubber with included carbon particles, plastic with glass fibers and concrete. In some cases air bubbles are incorporated into plastics or rubbers to obtain light weight, soft and heat-insulating materials such as foamed polystyrene, foam rubber, and polyurethane foam. Also in foods composite structures are very common. Examples are chocolate (a solid matrix of crystalline fat, with a dispersion of mainly sugar, cocoa particles), cheese (a semi-solid matrix of proteins, with an emulsion of milk fat) and mousses (a gelled matrix, with included air bubbles).

Our interest in this subject concerns the question to what extent a replacement of saturated fat by liquid oil in an emulsion filled gel affects the rheological behavior, and how this can be compensated by means of a different structuring of the system. Experimental results (Oliver, Scholten & van Aken, 2015; van Vliet, 1988; Yang, Rogers, Berry, & Foegeding, 2011) showed that the apparent gel modulus is increased for an emulsion-filled gel of saturated fat compared to an emulsion-filled gel of a liquid oil at the same volume fraction of the emulsion droplets, which is the expected effect of the higher firmness of droplets. The theoretical equations for unaggregated droplets of partially solid fat correctly predict the increase in composite elastic modulus for whey protein gels and cheese model systems, but underestimate the composite elastic modulus for gelatin, micellar casein isolate and acid-induced milk gels. For example, the commonly applied Kerner model for gels filled with hard particles at a volume fraction $\phi_f = 0.25$ predicts only a moderate increase of the elastic modulus by a factor 1.83 compared to the unfilled gel, whereas an increase by a factor 5–10 is found experimentally for gels of gelatin and Micellar Casein Isolate (Oliver, Scholten, et al., 2015). Several authors have observed

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similar effects and suggested that this enhancement may be caused by an inhomogeneous distribution of the fat droplets, often as a result of droplet aggregation or clustering, thereby including some of the continuous matrix (which includes the gelling agent and solvent), in this way increasing the effective volume fraction of the droplets in the gel matrix (Chen & Dickinson, 1998; Kim, Renkema, & Vliet, 2001; Oliver, Scholten, et al., 2015; Sala, van Aken, Cohen Stuart, & van de Velde, 2007). In some cases, however, the droplets seem to be clustered into denser regions of separate droplets in the composite gel rather than aggregated by direct bonds between the droplets (Oliver, Berndsen, van Aken & Scholten, submitted for publication; Oliver, Scholten, et al., 2015). Fig. 1 shows an example of such an inhomogeneous droplet distribution, in which the droplets are clustered without clear surface bonds between the droplets. The precise cause of this clustering might differ between systems. It can be expected that the properties of the clusters will depend on the way they are formed. The formation of strong bonds between the droplet surfaces can for example be due to bridging of absorbed molecules, isoelectric precipitation or partial coalescence of droplet containing crystalline fat. Fast (or diffusion-controlled) aggregation may lead to more open "fractal" structures (Meakin, 1988), whereas slow (or reaction-controlled) aggregation may lead to compact aggregates (Schmitt, Fernández-Barbero, Cabrerizo-Vílchez, & Hidalgo-Álvarez, 2000). In other cases, clustering of the particles in the gel might be induced by processes during gel formation, for example by stirring (introducing the hydrodynamic effect of shear-induced structuring, "shear-bending") during gelation or an effect of depletion flocculation driven by the presence of growing gel strands of the matrix, without the formation of surface bonds between the droplets.

The large deviation between experimental results and theoretical predictions motivated us to develop a theoretical construction that extends existing models for the elastic modulus of composite gels by including clustering of the dispersed particles. In this construction the clusters are described as deformable particles embedded in a dilute composite of separate particles in the matrix material. Because in clustered dispersions the volume fraction of the dispersed particles in the clusters as well as the volume fraction of

the clusters can become very high, special attention has been given to the accuracy of the rheological models at high volume fractions.

2. Clustering of the dispersed particles

Clusters of particles in a composite gel will behave as regions in which the rheological properties differ from the average of the composite gel and hence can be viewed as a "cluster particle". The matrix material enclosed within such an aggregate particle contributes to the effective volume of such a cluster particle. This argument is similar to that given previously for correcting the actual volume fraction to the effective volume fraction in unaggregated systems (Lewis & Nielsen, 1970) and in dense aggregates bound by bonds between the particle surfaces (Chen and Dickinson, 1998; Kim et al., 2001), however the effect of the included volume in clusters will already occur at low volume fractions and in the absence of surface bonds.

To estimate the magnitude of this amplification by clustering of the particles the following approach is taken (illustrated in Fig. 2). The matrix material is assumed to be homogeneous throughout the system. Let us assume that all particle clusters are equal and spherical and consist of the "inner" particles, homogeneously distributed at a volume fraction ϕ_{inner} within the particle cluster. The particle clusters themselves are assumed to be homogeneously distributed in the "outer" gelled matrix at a volume fraction of $\phi_{clusters}$. The gel surrounding the particle clusters may moreover contain separate particles, outside the clusters, at a volume fraction ϕ_{outer}. Conservation of mass requires

$$\phi_{clusters} = \frac{\phi_f - \phi_{outer}}{\phi_{inner} - \phi_{outer}}, \tag{1}$$

where ϕ_f is the overall volume fraction of the dispersed particles in the system.

Even in the absence of physical or chemical bonds between the individual particles, the higher volume fraction of the particles within each particle cluster locally amplifies the effect of the filler particles on the elastic modulus of the composite gel compared to the same composite gel with a homogenous particle distribution. Therefore, the particle clusters behave as discrete regions with an altered elastic modulus compared to the surrounding homogeneous composite gel. To calculate the rheological properties (elastic modulus) of the system as a whole, we use an appropriate model for the rheological properties of the outer particle filled gel (containing single particles at a volume fraction ϕ_{outer}) and an appropriate model for the rheological properties of the clusters (containing single particles at a volume fraction ϕ_{inner}). Next we use
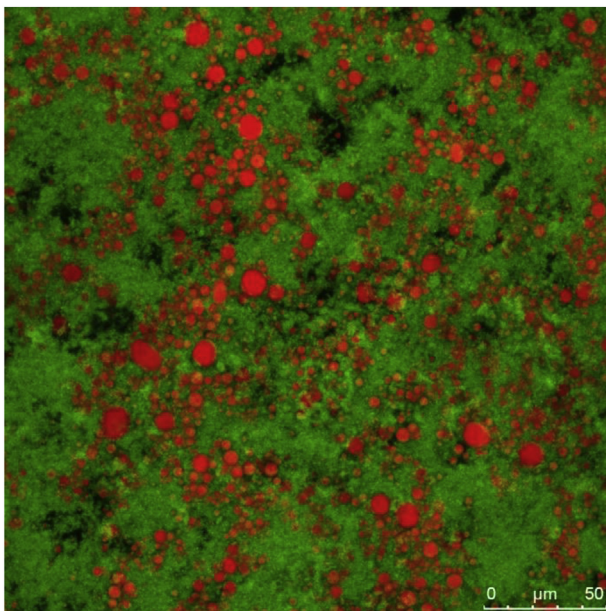

Fig. 1. Example of a composite gel in which the droplets are inhomogeneously distributed. The system is produced by acidification of a emulsion of milk fat in a solution of micellar casein, similar to quark (taken from Oliver, Scholten, et al., 2015).
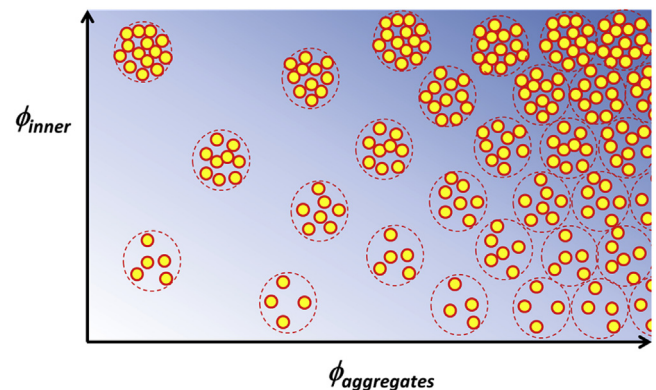

Fig. 2. Schematic representation of the variation in $\phi_{aggregates}$ and ϕ_{inner}, both varied between 0 and random closed packing.