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Adjusting rheological properties of concentrated microgel suspensions by particle size distribution

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ABSTRACT

For concentrated model suspensions consisting of hard spheres, besides the volume fraction, the particle size distribution affects rheological properties, where the relations have been investigated and mathematically described in detail. In contrast, food products often represent complex multiphase systems what demands the consideration of other parameters, e.g., particle interaction and deformation. The principles have been shown to be appropriable to chocolate, which consists of non-spherical, hard particles suspended in a Newtonian fluid (cocoa butter). However, work for concentrated fermented milk products, e.g., fresh cheese, consisting of soft microgel particles with high serum binding is lacking. Therefore, the aim was to produce and characterize different particle size distributions by modifying the post-processing during fresh cheese production (protein content 8.0%). Tempering of the standard generated mainly fine, medium, and coarse particle fractions, and, likewise, increased rheological properties (storage modulus, shear viscosity) and synaeresis. Subsequent blending adjusted intermediate levels. Additionally, with increasing size ratio of the particle fractions generated by tempering, the rheological properties of the blended microgel suspensions were affected differently, e.g., high particle size but low shear viscosity. Besides the size ratio, that was related to the particle properties and fundamentals of multimodal particle mixtures.

1. Introduction

The processing of suspensions with high solid content is challenging in many practical issues counterbalancing economic benefits, e.g., increased process throughput and efficiency, reduced transport and storage costs (Servais, Jones, & Roberts, 2002). However, at high solid content, increasing the solid concentration only by a few percent can modify rheological properties significantly, and may lead to a marked increase in the relative viscosity (Genovese, 2012). Therefore, process steps like mixing, pumping, spraying, or sufficient heat exchange are more difficult to handle. Although modifying the particles' surface properties is possible (Dames, Morrison, & Willenbacher, 2001), this is usually not a desired option for food products (Servais et al., 2002). However, the particle size distribution additionally affects rheological and textural properties making it possible to change these properties by technological means.

The specific volume of particles in soft sphere suspensions is not as well-defined as for hard sphere suspensions, due to effects of the environmental conditions, applied stress and the resulting structural breakdown. The volume fraction ϕ of hard sphere suspensions is replaced by the effective or apparent phase volume

$$\phi_{\text{eff}} = k \cdot \beta = v_{\text{app}} \cdot \rho \cdot w \tag{1}$$

where k (ml g^{-1}) is the specific volume, β (g ml^{-1}) the mass concentration, and v_{app} (ml g^{-1}) is the apparent voluminosity, ρ (g mL^{-1}) the suspension density and w the mass fraction of dry solid (Nöbel, Weidendorfer, & Hinrichs, 2012; Shewan & Stokes, 2015). For model and many real soft sphere suspensions the relation between relative viscosity and volume fraction is well established. Models including high volume fractions up to the effective maximum packing fraction ϕ_m (−), where sticking occurs are classified into three categories: a fundamental approach independently developed by Maron and Pierce (1956) and Quemada (1977)

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$$\eta_r = \left(1 - \frac{\phi_{eff}}{\phi_m}\right)^{-2}, \quad (2)$$

an empirical model by Krieger and Dougherty (1959)

$$\eta_r = \left(1 - \frac{\phi_{eff}}{\phi_m}\right)^{-[\eta]\cdot\phi_m} \quad (3)$$

where $[\eta]$ $(-)$ is the dimensionless intrinsic viscosity, and a semi-empirical model by Mendoza and Santamaría-Holek (2009)

$$\eta_r = \left(1 - \frac{\phi_{eff}}{1 - c\cdot\phi_{eff}}\right)^{-[\eta]} \quad (4)$$

where $c = (1 - \phi_m)/\phi_m$ $(-)$ is a constant at the maximum packing ϕ_m. All models have in common that the maximum volume fraction ϕ_m depends on the shear stress applied while $\phi_{m,0}$ and $\phi_{m,\infty}$ relate to the zero-shear viscosity $\eta_{r,0} = \eta_r(\tau \to 0)$ and the infinite-shear viscosity $\eta_{r,\infty} = \eta_r(\tau \to \infty)$ respectively (Olivares, Berli, & Zorrilla, 2013).

In addition to the properties of the single particles, e.g., serum binding and morphology, the rheological behaviour is also a function of the polydispersity of the suspension. The volume fraction at random close packing ϕ_{rcp} $(-)$ increases with increasing polydispersity σ/r $(-)$ of monomodal spheres from $\phi_{rcp} = 0.64$ $(\sigma/r = 0.00)$ to $\phi_{rcp} = 0.68$ $(\sigma/r = 0.20)$ (Schaertl & Sillescu, 1994) and, hence, a lower relative viscosity at the same total volume fraction. Multimodal mixing of different sized spheres results in lower relative viscosities as well. Small particles become entrapped between large particles increasing the overall random close packing. For a n-modal suspension the total random close packing can be calculated from $0.639 < \varphi_{rcp,n} < 1 - 0.361^n$ (Qi & Tanner, 2012) and the total relative viscosity can be calculated from the product of all single particle fractions (Dames et al., 2001; Dörr, Sadiki, & Mehdizadeh, 2013)

$$\eta_r = \prod_{i=1}^{n} \eta_r\left(\phi_{eff,i}, \phi_{m,i}, \ldots\right) \quad (5)$$

using an appropriable viscosity model Eqs. (2)–(4). In the case of bimodal mixes, the total random close packing ϕ_{rcp} increases with increasing size ratio of large to small particles λ $(-)$ and with increasing fraction of large particles, below $\xi_L = 0.7$ (Dörr et al., 2013). Higher fractions of large particles result in a decrease of the random close packing. The relative viscosity of a soft sphere suspension can be predicted reasonably well from a known particle size distribution if the maximum packing fraction ϕ_m is set to random close packing ϕ_{rcp} (Shewan & Stokes, 2014).

Less work has been published for food products, which, in contrast to model suspensions, often represent complex multiphase systems (Hahn, Krzeminski, Wille, Weiss, & Hinrichs, 2012; Hinrichs, 2000; Hinrichs & Kessler, 1999), and where the particle size is crucial for the sensory perception (Cayot, Schenker, Houzé, Sulmont-Rossé, & Colas, 2008; Hahn, Wachter, et al., 2012; Krzeminski et al., 2013; Sainani, Vyas, & Tong, 2004; Ziegler, Mongia, & Hollender, 2001). Furthermore, other parameters have to be considered, e.g., particle shape, width of the particle size distribution, roughness of the particle surface, particle–particle interaction, particle deformation, or the arrangement of particles (Dames et al., 2001; Servais et al., 2002). Some studies focused on milk chocolate (Aguilar & Ziegler, 1995; Mongia & Ziegler, 2000; Servais et al., 2002; Ziegler et al., 2001) involving non-spherical, hard particles suspended in a Newtonian fluid (cocoa butter). However, soft particles with higher serum binding were rarely investigated, e.g., apple pulp (Missaire, Qiu, & Rao, 1990; Rao, Cooley, Nogueira, & McLellan, 1986) and cassava paste (Ojijo & Shimoni, 2008), where for the latter it was shown that by blending fine and coarse flours a reduction by over 20% of the apparent viscosity was possible. Recently, we showed for fresh cheese, a concentrated microgel suspension consisting of soft spheres with high water binding, that, by tempering, the particle size $d_v\,(0.75)_n$ and storage modulus G'_n, both normalized to the sample tempered for 1 min, increased during tempering (Hahn, Wachter, et al., 2012). However, during subsequent shearing G'_n started on a higher level that enabled us to regenerate a smooth texture ($d_v\,(0.75)_n = 1.0$) with a $G'_n > 1.0$. We proposed that this observation was related to changes in the particle size distributions of the soft microgel particles and the particle properties, e.g., voluminosity.

In order to study the effect of polydispersity and an altered particle size distribution on the rheological properties of concentrated microgel suspensions, fresh cheese samples were tempered and blended aiming to have a median particle size as different as possible. Rheological parameters correlating to the sensory perception of creaminess were chosen for evaluating the samples. The potential to adjust the rheological properties of fermented dairy products, e.g., fresh cheese and greek-style yogurt, by applying the underlying relations of hard and soft sphere model suspensions for concentrated microgel suspensions consisting of soft spheres with high serum binding is assessed in this work.

2. Materials and methods

For this study, the protein content was kept constant. After tempering of the concentrated microgel suspensions, which was carried out to adjust different particle size distributions, the tempered microgel suspensions were blended in different mass ratios, and the rheological properties were ascertained.

2.1. Fresh cheese

Pasteurized milk (<0.1%, w/w fat, 74 °C for 30 s) was used to produce fresh cheese as in detail described by Hahn, Sramek, Nöbel, and Hinrichs (2012). The protein content of the pasteurized milk was standardized to 3.3 ± 0.1% (w/w) by using a reconstituted permeate solution prior to continuously heating the standardized milk in a tubular pilot plant (150 L h^{-1}, ASEPTO-Therm, Asepto GmbH, Dinkelscherben, Germany). After the standardized milk was heated to 95 °C, the temperature was held for 4.3 min, immediately cooled to 20 °C in the tubular pilot plant, conveyed to a sterile tank, and the fermentation was started to a pH of 4.5 by suspending 0.02% (w/w) F-DVS CC06 (Chr. Hansen GmbH, Nienburg, Germany) containing *Lactococcus lactis* subsp. *lactis* and *Lactococcus lactis* subsp. *cremoris*. When the pH reached 6.50, 1 mL per 100 L Chy-Max™ (Chr. Hansen GmbH; minimum activity 190 IMCU per mL) was added. After fermentation, the gel was stirred, and the fermented milk was concentrated at 38 ± 1 °C with a tangential velocity of 7.0 ± 0.2 m s^{-1} and a transmembrane pressure of 100 ± 10 kPa to a final protein content of 8.0% (w/w) (standard, n = 8) as measured by the method of Dumas (Table 1). Concentration was carried out with a cross flow membrane filtration device (model TFF, Pall GmbH, Dreieich, Germany) using a ceramic Membralox gradient of permeability (GP) membrane (type 7P19-40 GP, cut off 0.1 µm, Pall Exekia, Bazet, France). The mean composition and the pH of the high-heated milk, the fresh cheese, and the permeate, which was obtained during membrane filtration, are given in Table 1. Fresh cheese was then pumped with a screw pump (Nemo NM021, Netzsch Mohnopumpen GmbH,