Journal of Food Engineering 222 (2018) 250–257

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Application of the thixotropic elasto-viscoplastic model as a structure probing technique for acid milk gel suspensions

Marjan Javanmard [a], Edeline Wong [b], Tony Howes [a], Jason R. Stokes [a, *]

[a] School of Chemical Engineering, University of Queensland, Brisbane, QLD 4072, Australia
[b] Fonterra Research & Development Centre, Palmerston North, New Zealand

ARTICLE INFO

Article history:
Received 19 June 2017
Received in revised form
10 November 2017
Accepted 21 November 2017
Available online 23 November 2017

Keywords:
Structural parameter
Thixotropy
Acid milk gel
Rheology
Structure
Particle size distribution

ABSTRACT

The rheology of acid milk gels is investigated as an elasto-viscoplastic thixotropic fluid. The gel is a colloidal protein network that upon shear is transformed into suspension of aggregates where the original rheology of the gel is not recoverable. It is shown that the measured characteristic size of the aggregates is directly proportional to a structural parameter (λ) obtained from rheological measurements. This supports the use of the λ in elasto-viscoplastic constitutive models as a representation of the changing structure in the suspension. λ also correlates to the aggregate particle size after initially breaking down the structure at high shear rate and then allowing the structure to recover at lower shear rates. Following this shear breakdown/recovery, a broader particle size distribution is observed compared with the results obtained during breakdown of the initial set gel. This structural difference may be critically linked to the thixotropic rheological properties of the sheared gels. The outcomes from this research pave the way for mechanistically predicting and quantifying shear processing-structure-property relationships for acid milk gels and other related dairy foods.

1. Introduction

Soft solids display viscoelastic solid-like characteristics at rest, but their structure and rheology is dramatically transformed upon application of shear (Stokes and Frith, 2008). Since their rheology inherently depends on the underlying structure of the material at microscopic length scales, a key challenge in quantifying structure-property relationships arises when shear alters the microstructure that is either non-recoverable or the timescales for recovery to its 'original' state are substantial. This phenomena is commonly exploited during the manufacture of different personal care products, such as skin creams, and soft food, such as dairy products, whereby shear is applied to ensure a consistent microstructure, rheology, texture and stability prior to packaging and consumption. However, whilst this is a common processing step, it is not necessarily well understood to the extent that the shear process is precisely designed to manipulate the properties of the material over its lifetime from storage to consumption. In this paper, we experimentally determine microstructure-rheology relationships for sheared acid-milk gels that serve as a model for yogurts and other dairy foods. This soft matter system also provides a convenient thixotropic elasto-viscoplastic fluid in which to validate the application of proposed structural-kinetic constitutive models.

Under static conditions, elasto-viscoplastic fluids display solid-like viscoelastic behaviour as the result of an interconnected microstructure; either as a gel with interconnections (e.g. attractive surface forces; crosslinks) between colloidal structural entities or as a soft glassy structure with structural entities that are packed tightly together (Nöbel et al., 2016; Ramaswamy and Basak, 1991). From an engineering point of view, the critical shear stress above which the fluid flows is considered to be a yield stress (Stokes and Telford, 2004). As the applied stress increases beyond the yield stress, a transformation in the microstructure occurs that may include breakage of interconnections between the structural building blocks, resulting in viscous shear thinning (pseudoplastic) fluid behaviour. In many instances, the transformation of the microstructure is a time-dependent process and the viscosity decreases with the time of the applied shear; if this time-dependency is reversible, the elasto-viscoplastic fluid is considered thixotropic (de Souza Mendes, 2011).

Different models have been proposed to capture the influence of

* Corresponding author. School of Chemical Engineering, Faculty of Engineering, Architecture and Information Technology, The University of Queensland, Room 308, Don Nicklin Building (74), St. Lucia 4072, Australia.
E-mail address: Jason.stokes@uq.edu.au (J.R. Stokes).

https://doi.org/10.1016/j.jfoodeng.2017.11.031
0260-8774/

shear and time on the rheology and structure of soft materials. These models are divided into phenomenological and theoretical models. Phenomenological models are based on a measureable thixotropic index (Labanda et al., 2004; Tárrega et al., 2004; Weltmann, 1943). The thixotropic index is quantified by a hysteresis loop technique that measures the degree of thixotropic behaviour based on evaluating the enclosed area of a cyclic shear deformation experiment. Nevertheless, the phenomenological models do not reflect the state of the microstructure and the kinetic process of its breakdown and build-up. More models have been developed to overcome these limitations such as the structural-kinetic models that relate the time-dependent rheological properties to changes occurring to the underlying microstructure (Baravian et al., 1996). This type of model was initially proposed by Moore (1959), who introduced a structural parameter, λ, that changes with structure deformation. λ is a non-negative scalar parameter that expresses the structuring level of the microstructure; it ranges in value between 0 and 1, where 0 corresponds to a fully unstructured state and 1 corresponding to a completely structured state.

Structural-kinetic models have been described by coupling a constitutive model for the shear stress in terms of viscometric functions and a shear rate-dependent structural parameter λ, and a kinetic model that expresses the rate of the change in λ (Dullaert and Mewis, 2005; Labanda and Llorens, 2006; Moore, 1959; O'Donnell and Butler, 2002; Steffe, 1996; Tiu and Boger, 1974; Cheng and Evans, 1965). For example, Tiu and Boger (1974) apply this approach to study the shear and time-dependent rheology of mayonnaise; they capture the shear-dependency using the Herschel-Bulkley model multiplied by a structural parameter λ that is represented using a second order kinetic model, as shown by equations (1) and (2).

$$\sigma = \lambda\,(\sigma_0 + K_H\dot{\gamma}^{n_H}) \tag{1}$$

$$\frac{d\lambda}{dt} = -K_1(\lambda - \lambda_e)^2\ ,\ \lambda > \lambda_e \tag{2}$$

K_1 is a function of shear rate, σ_0 is the yield stress, $\dot{\gamma}$ is the shear rate, K_H is the fluid consistency index and n_H is the flow behaviour index, and they are all determined from experimental data. For a particular shear rate, λ is the instantaneous value at a particular time and λ_e is its value when steady state (equilibrium) is reached. λ is equal to 1 before the sample is subject to any shear. This approach has also been successfully applied to characterise the structural-kinetic characteristics of buttermilk (Butler and McNulty, 1995).

Baravian et al. (1996) considered how the structural parameter relates to shear-thinning for dispersions of aggregating solid particles. Their simple model includes the limiting Newtonian viscosities, zero-shear viscosity (η_0) and infinite-shear viscosity (η_∞), and is defined as follows:

$$\eta = \frac{\eta_\infty}{(1 - K\lambda)^2}, \tag{3}$$

where

$$K = 1 - \sqrt{\frac{\eta_\infty}{\eta_0}} \tag{4}$$

In this model, λ is expressed as a function of viscosity as follows:

$$\lambda = \frac{1}{k}\left(1 - \sqrt{\frac{\eta_\infty}{\eta}}\right) \tag{5}$$

Therefore, once the η_0 and η_∞ are measured, λ can be calculated using Equation (5) (Baravian et al., 1996). Note, for thixotropic fluids both η and λ are dependent on shear rate (or shear stress) and time.

The λ used in these and other relevant models that have been proposed is generally only determined empirically from rheological measurements. The value obtained is rarely cross-checked against actual changes to the microstructure. However, there is an abundance of techniques to characterise structure and particle size *ex situ* of shearing experiments, whilst there are many emerging techniques, such as x-ray scattering, small angle neutron scattering (Kim et al., 2014) and confocal microscopy (Xu and Gilchrist, 2014) to measure microstructural changes directly under flow. To our knowledge, no quantifiable microstructure measurement has been produced to demonstrate the predictive capability of the empirically determined λ value. This is particularly important, as λ is be used to evaluate the state of the structured fluid, thus it should be relatable to changes occurring in the measurable structure.

In this paper, the effect of shear on the rheology and structure of acid milk gels is evaluated, and the hypothesis to be tested is that λ is related to a characteristic size of the shear gel's microstructure. For this we applied the model of Baravian et al. (1996); this model is chosen due to its simplicity and limited number of material functions, and because we consider our system to be dispersions of aggregating particles; a recent review (Javanmard, 2017) highlighted that most other models include more fitting parameters that make their use in practice difficult to validate. The effect of shear on characteristic size within the system is evaluated using light scattering technique and this is related to λ as a function of shear rate and shear-recovery time.

2. Materials & methods

2.1. Preparation of sheared acidified milk gels

Samples were prepared by recombination of skim milk powder (13.8% w/w) supplied by Fonterra (Palmerston North, New Zealand) in distilled water and sodium azide (0.02% w/w) stirred for 2 h at room temperature. The skim milk powder composition is given in Table 1. The milk solutions were heat treated in a water bath at 85 °C for 30 min. Then, they were cooled to 22 °C in ice water and left overnight in a refrigerator at 4 °C. The next day the hydrated samples were warmed to 42 °C in a water bath. Samples were then acidified using glucono-δ-lactone (GDL) in powder form, supplied by Sigma-Aldrich. 1.6% w/v GDL was added to the solutions to give a final pH of 4.3. This amount was based on their final weight of the solutions after the heat treatment. Samples were then incubated (Heratherm incubator, Thermo Scientific) at 42 °C for 4.5 h. Following incubation, samples were cooled to 20 °C and stored at

Table 1
Composition of skim milk powder used to prepare acid milk gels in this study.

Ingredient	Protein (%)	Milk solid Non-fat (%)	Casein (%)	Whey Protein (%)	Fat (%)	Carbohydrate (%)	Ash (%)	Ca (mg/100 g)	Na (mg/100 g)	K (mg/100 g)	PO4 (mg/100 g)
Skim Milk Powder	33.4	94.4	26.7	6.7	0.8	54.9	7.9	1234	390	1813	2200