Rheological models for cultured milk

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ABSTRACT

In this study Ellis, Herschel-Bulkley, Cross and Power law models were tested on rheological data. Ellis, Herschel-Bulkley and Cross model were fitted into rotation viscometry data, while Power law model was fitted into both rotational viscometry data and the frequency sweep data. Of the models tested, it is possible to use modified Cross model with a yield stress ($\tau = \tau_0 + (\eta_0 / [1 + (K\dot{\gamma})^n]) \dot{\gamma}$) and Power law model ($G' = A*f^B$ and $G'' = C* f^D$) to characterize the rheological properties of the cultured milk, which would be used in quality control procedures.

INTRODUCTION

Fermented milk products i.e., yoghurts and cultured milk are classified as non-Newtonian, pseudoplastic and thixotropic fluids, with a yield stress. This means that they have a certain stress limit (yield stress), when exceeded, their viscosity and elasticity decreases, due to microstructure collapse[1], also their viscosity decreases with the increase in shear rate (shear thinning behaviour). The major quality concerns associated with cultured milk are poor texture and higher degree of syneresis. Knowledge related to the rheological properties of cultured milk is important for quality control procedures and product development [2, 3]. Yoghurt and cultured milk possess different textural and flow properties because the former is enriched with dry matter (i.e., skim milk powder, whey protein isolate etc.), this contributes to an increase in elasticity and viscosity and to reduced whey separation (syneresis) in yoghurts compared to cultured milk.

Rheological models i.e. Power law, Herschel-Bulkley, and Cross models have been used in the rheological characterization of various food products [4, 5] and their rheological predictions could also be used in design and optimization of the food process systems[6, 7]. However, these models have been widely applied on yoghurt [4, 6-10]. A study by Zeke et al. [11] characterized the flow properties of cultured milk and other commercial dairy products bought from a food store in Norway using Herschel-Bulkley model.

The present study is aimed at testing the Ellis, Herschel-Bulkley, Cross model on viscometry data and Power law model on both viscometry and oscillation data, to find the model, which should be used in prediction of parameters for the rheological characterization of cultured milk.

MATERIALS AND METHODS
Milk samples

Milk samples were collected in the morning from 18 cows at the Centre for Animal Research (SHF) of Norwegian University of Life Sciences (NMBU). All cows were within 30 and 150 days of calving. The sampling procedure was described by Ketto et al. [12]. Immediately after sampling, milk samples were transported to the pilot plant for milk treatment (i.e., cream

separation, homogenization and heat treatment) and a batch of cultured milk was produced from each sample.

Production of cultured milk

The details on the production of cultured milk were previously described by Ketto et al. [12]. In brief, after heat treatment (95 °C for 5 min), about 5 L of the milk sample were cooled to 22 °C before inoculation with 0.1 % of a frozen direct vat set culture (DVS) mesophilic DL culture (XT-303; Chr. Hansen A/S, Hørsholm, Denmark). The inoculated milk samples were incubated at 22°C until pH 4.5 ± 0.01. The samples were then transferred to the ice water bath for rapid cooling, before storage at 4 °C for 14 d prior to rheological analyses.

Rheological analyses

Rheological analyses were performed on a Physica MCR 301 rheometer (Anton Paar GmbH, Graz, Austria) using a bob-cup measurement system with bob specifications; CC27/Ti with a diameter of 26.657 mm and length of 40.926 mm and cup specifications; C-CC27/T200/Ti with 28.926 mm diameter. Rheological characterization was established in two steps: (1) oscillation (strain and frequency sweep) and (2) rotation viscometry trials according to the method established by Allmere et al. [13], with some modifications as showed by Ketto et al. [12]. Strain sweep was carried out at a constant frequency of 0.5 Hz and strain between 0.0002 and 0.206. The strain value obtained from the strain sweep measurement was sufficient to maintain the structure of the product since it was determined within the linear viscoelastic region (LVR). This value was used in the frequency sweep, at a frequency (*f*) range of 0.1– 0.5 Hz, to determine the values for elastic modulus (*G'*) and viscous modulus (*G''*) within LVR. The rotational viscometry trials were made to determine the flow properties of the product at a shear rate of $0.02 - 1.46 \text{ s}^{-1}$ at a 357 s interval.

Model fitting

After rheological characterization, the frequency sweep data (i.e., *G' vs. f* and *G'' vs. f*) were fitted with the Power law model (Eq. 1 and 2) [13, 14]. The rotation viscometry data (τ *vs.* $\dot{\gamma}$) were fitted with the Power law (Eq. 3), the Herschel-Bulkley (Eq. 4), the conventional Cross model [15] (Eq. 5) and the modified Cross model with yield stress [16] (Eq. 6). The Ellis model was also fitted into the rotational viscometry data as shown in Eq. 7. All models were fitted using non-linear regression, *nlinfit*, in MATLAB [17].

$$G' = A f^B \qquad (1)$$

Where G' = elastic modulus (Pa), A = structure constant (Pa s^n), B = structure index and *f* = frequency (Hz).

$$G'' = C f^D \qquad (2)$$

Where G'' = viscous modulus (Pa), C = viscosity constant (Pas^n)), D = viscosity index and *f* = frequency (Hz).

$$\tau = K \dot{\gamma}^n \qquad (3)$$

$$\tau = \tau_0 + K \dot{\gamma}^n \qquad (4)$$

Where τ = shear stress (Pa), τ_0 = yield stress (Pa), $\dot{\gamma}$ = shear rate (1/s), K = consistency index (Pas^n) and n = exponent related to shear thinning behaviour.

$$\eta = \left(\eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + K \dot{\gamma}^n} \right) \qquad (5)$$

Where η = apparent viscosity ($\tau/\dot{\gamma}$), η_∞ = viscosity at infinity shear rate (Pas). η_∞ was very low close to zero ($\eta_\infty \sim 0$) and difficult to estimate from the model. Modified Cross model with yield stress was proposed as follows:

$$\tau = \tau_0 + \left(\frac{\eta_0}{1 + K \dot{\gamma}^n} \right) \dot{\gamma} \qquad (6)$$

Where τ = shear stress τ_0=yield stress (Pa), $\dot{\gamma}$ = shear rate (1/s), η_0 = viscosity at zero shear rate (Pas), K = structural relaxation time and n = exponent related to shear thinning behaviour.

$$\tau = \left(\frac{\eta_0}{1+\left(\frac{\sigma}{\sigma_{1/2}}\right)^{\alpha-1}} \right) \dot{\gamma} \qquad (7)$$

Where τ = shear stress (Pa), η_0 = zero shear viscosity (Pas), $\dot{\gamma}$ = shear rate (1/s), while σ and α are the model fitting constants.

RESULTS AND DISCUSSION

Frequency sweep data

Figure 1 shows the frequency sweep results for the G' vs. f and G'' vs. f, before and after Power law model fitting. It shows a slight increase in G' and G'' when the samples oscillated at a frequency range of 0.1 to 0.5 Hz. During the entire frequency range, the values of G' were greater than G'' ($G' > G''$), this shows that the material expresses more elastic properties than viscous properties [18]. However, the values for G' and G'' were lower than the values reported in other food products, e.g. yoghurts[19]; this is because of the nature of cultured milk. In fact, cultured milk possesses a weaker texture compared to yoghurt, as the fortification of yoghurts contribute to more cross-linking and a denser network between the aggregating particles [19, 20].

Model fitting of the frequency sweep data using the Power law model gave a good fit ($G' = A*f^B$, $R^2 = 0.98$ and $G'' = C*f^D$, $R^2 = 0.99$). By using the Power law model, it was possible to estimate the important parameters from the model for all samples i.e., G', G'', A, B, C, and D. A previous study by Allmere et al. [13] obtained a good fit on the frequency sweep data with the Power Law model in chemically acidified milk gels (using glucono-δ-lactone) and it was possible to compare different samples based on the predictions from this model. Hence, it is possible to study the structural properties of cultured milk using the Power law model.
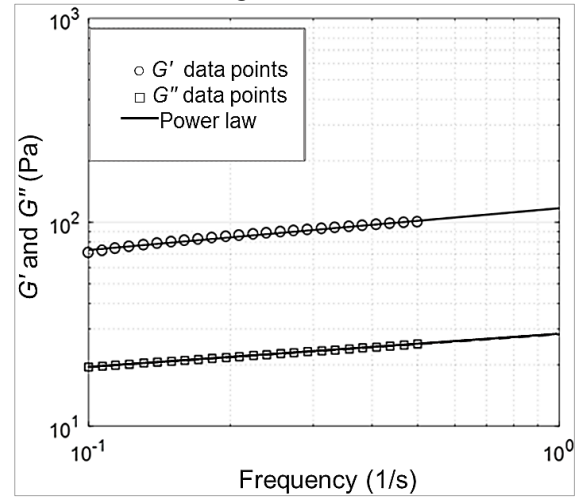

Figure 1: Power law model fitting on frequency sweep data (G' & G'' vs. f). (G' = elastic modulus, G'' = viscous modulus, f = frequency).

Rotation viscometry data

Only the modified cross model with yield stress showed a good fit ($R^2 = 0.99$), while the Power law, Ellis and Herschel-Bulkley models did not give a good fit on the rotation viscometry data (Figure 2). Others have shown good fit on the rotation viscometry data of yoghurts with the Power law, Herschel-Bulkley and conventional cross models [5, 8, 21]. The flow properties of cultured milk in the present study showed low values of yield stress (τ_0), lower than the τ_0 values reported in yoghurts and cheese [11, 22]. Krulis and Rohm [5] reported the viscosity of yoghurts at infinity shear (η_∞) to be 0.054 Pa, higher than η_∞ from the present study, which were very low close to zero. Hence, η_∞ was excluded from the modified Cross model. Despite the fact that the two models (Power law and Herschel-Bulkley models) have been successfully used in the rheological characterization of yoghurts, their usability is limited at very low shear rate values compared to the Cross model, which can be used at a wide range of shear rates[4].
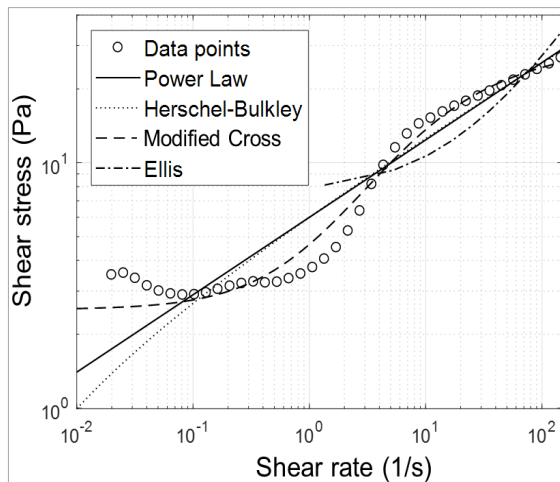
Figure 2: Power law, Herschel-Bulkley, Ellis and modified Cross model fitting on rotational viscometry data (τ vs. $\dot{\gamma}$). τ = shear stress and $\dot{\gamma}$ = shear rate.

Yield stress obtained from modified the Cross model was negatively correlated (r^2 = -0.80) with the degree of whey separation in the cultured milk[12]. This means that, the samples with lower value of yield stress would have a weaker network between aggregated particles, lower elasticity, thus easily release the weakly entrapped whey[12,23]. The use of modified cross model in the prediction of yield stress may give information how different the samples are susceptible to syneresis. Hence, it may be possible to predict whey separation in the samples of cultured milk indirectly using the yield stress values from the model prediction. This would save time and costs to quantify the whey separation, by the suggested methods[24]. This study showed that the modified Cross model could be used to study the flow properties of fermented milk with a slightly weaker structure than yoghurt, like cultured milk.

CONCLUSIONS

The Power law model and the modified Cross model with yield stress were successfully fitted into the oscillation and rotational viscometry data, respectively, of cultured milk. The current findings provide information, which could be used by the dairy industry to study structural and flow properties of cultured milk. This information could be used as a tool in product development and quality control procedures for cultured milk, since its consumer acceptability may be limited by textural defects and high extent of whey separation.

REFERENCES

1. de Souza Mendes, P. R. (2009), "Modeling the thixotropic behavior of structured fluids", *Journal of Non-Newtonian Fluid Mechanics.*, **164**, 66-75.

2. Benezech, T. and Maingonnat, J. F. (1994), "Characterization of the rheological properties of yoghurt-A review", *Journal of Food Engineering.*, **21**, 447-472.

3. Vélez-Ruiz, J. F., Barbosa Cánovas, G. V,. and Peleg, M. (1997), "Rheological properties of selected dairy products", *Critical Reviews in Food Science and Nutrition.*, **37**, 311-359.

4. Mullineux, G. and Simmons, M. J. H. (2008), "Influence of rheological model on the processing of yoghurt", *Journal of Food Engineering.*, **84**, 250-257.

5. Krulis, M. and Rohm, H. (2004). "Adaption of a vane tool for the viscosity determination of flavoured yoghurt", *European Food Research and Technology.*, **218**, 598-601.

6. Fangary, Y. S., Barigou, M., and Seville, J. P. K. (1999), "Simulation of yoghurt flow and prediction of its end-of-process properties using rheological measurements", *Food and Bioproducts Processing.*, **77**, 33-39.

7. Mullineux, G. and Simmons, M. J. H. (2007), "Effects of processing on shear rate of yoghurt", *Journal of Food Engineering.*, **79**, 850-857.

8. Aportela-Palacios, A., Sosa-Morales, M. E., and VÉLez-Ruiz, J. F. (2005), "Rheological and physicochemical behaviour of fortified yoghurt, with fiber and calcium", *Journal of Texture Studies.*, **36**, 333-349.

9. Hassan, A. N., Ipsen, R., Janzen, T., and Qvist, K. B. (2003), "Microstructure and rheology of yogurt made with cultures differing only in their ability to produce exopolysaccharides", *Journal of Dairy Science.*, **86**, 1632-1638.

10. Behnia, A., Karazhiyan, H., Niazmand, R., and Nafchi, A. R. M. (2013), "Rheological properties of low fat yogurt containing cress seed gum", *Agricultural Sciences.*, **4**, 29-32.

11. Zeke, I. C., Juhász , R., Schüller, R. B. & Rukke, E. O. (2010), "Flow properties of common norwegian dairy products", *Annual transactions of the Nordic rheology society.*, **18,** 117-121.

12. Ketto, I. A., Øyaas, J., Ådnøy, T., Johansen, A.-G., Schüller, R. B., Narvhus, J., and Skeie, S. B. (2018), "The influence of milk protein genetic polymorphism on the physical properties of cultured milk", *International Dairy Journal.*, **78**, 130-137.

13. Allmere, T., Andrén, A., Lindersson, M., and Björck, L. (1998), "Studies on rheological properties of stirred milk gels made from milk with defined genetic variants

of κ-casein and β-lactoglobulin", *International Dairy Journal.*, **8**, 899-905.

14. Ramaswamy, H. S., Chen, C. R., and Rattan, N. S. (2015), "Comparison of viscoelastic properties of set and stirred yogurts made from high pressure and thermally treated milks", *International Journal of Food Properties.*, **18**, 1513-1523.

15. Cross, M. M. (1965), "Rheology of non-Newtonian fluids: A new flow equation for pseudoplastic systems", *Journal of Colloid Science.*, **20** , 417-437.

16. Rayment, P., Ross-Murphy, S. B., and Ellis, P. R. (1995), "Rheological properties of guar galactomannan and rice starch mixtures-I. Steady shear measurements", *Carbohydrate Polymers.*, **28**, 121-130.

17. MATLAB. (2003). *MATLAB*. Version 6.5.1 ed. Natick, Massachusetts: The MathWorks Inc.

18. Skriver, A., Rømer, H., and Qvist, K. B. (1994), "Rheological characterization of stirred yoghurt. Viscometry and oscillation", *Annual Transaction of the Nordic Rheology Society.*, **2**, 38-40.

19. Chua, D., Deeth, H. C., Oh, H., E. and Bansal, N. (2017), "Altering the casein to whey protein ratio to enhance structural characteristics and release of major yoghurt volatile aroma compounds of non-fat stirred yoghurts", *International Dairy Journal.*, **74**, 63-73.

20. Laiho, S., Williams, R. P. W., Poelman, A., Appelqvist, I., and Logan, A. (2017), "Effect of whey protein phase volume on the tribology, rheology and sensory properties of fat-free stirred yoghurts", *Food Hydrocolloids.*, **67**, 166-177.

21. Domagala, J. and Juszczak, L. (2004), "Flow behaviour of goat's milk yoghurts and bioyoghurts". *Electronic Journal of Polish

Agricultural Universities., **7**, article 9, (7 pages).

22. Holdsworth, S. D. (1993), "Rheological models used for the prediction of the flow properties of food products", *Transactions of the Institution of Chemical Engineers., Part C.*, **71**, 139-179.

23. Lucey, J. A., van Vliet, T., Grolle, K., Geurts, T. and Walstra, P. (1997), "Properties of acid casein gels made by acidification with glucono-δ-lactone. 2. Syneresis, permeability and microstructural properties". *International Dairy Journal.*, **7**, 389-397.

24. Lucey, J. A., Munro, P. A. and Singh, H. (1998), "Whey separation in acid skim milk gels made with glucono-δ-lactone: effects of heat treatment and gelation temperature". *Journal of Texture Studies.*, **29**, 413-426.