Rheological characterization of oil saturated powder blends based on experimental design and multivariate analysis

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ABSTRACT

This study presents results from rheological measurements of mixtures containing edible oil, microcrystalline cellulose powder, water and buttermilk powder. Experimental design and multivariate analysis were used to study and test the effect on the responses.

INTRODUCTION

The marked for food products enriched with health beneficial polyunsaturated fatty acids (PUFAs) is expanding[1]. Different enrichment strategies such as microencapsulation and emulsification are well-known for incorporation of these PUFAs[2,3,4]. Cellulose derivates are commonly used regarding microencapsulation[5] and as an application in food products[6]. Microcrystalline cellulose (MCC) is derived from cellulose by acid depolymerisation of α-cellulose yielding crystalline bundles which can further be processed by two routes, resulting in 1) powdered or 2) colloidal microcrystalline cellulose. Drying crystalline bundles results in powdered MCC. Co-processing the crystalline bundles with a soluble hydrocolloid gives colloidal MCC[7]. As food application MCC are used as a dietary fiber source, bulking agent, and stabilizer[8]. Buttermilk powder is the spray dried aqueous phase of buttermilk released during churning of cream into butter[9]. It contains material derived from the milk fat globule membrane, which is mainly composed of proteins and phospholipids[10]. The high content of surface-active phospholipids gives buttermilk powder emulsifying properties[11].

In this study three major ingredients were utilized to compose paste-like mixtures. Texture and properties of pastes are dependent on the functionalities and the amounts of the ingredients. The rheological properties are important for consumer and producers evaluation of the overall quality of such product. By changing the mixture composition and using multivariate analysis, it is possible to explore how such changes affect the mixture properties, which factors have most influence, the interaction between the factors and so on[12].

The objective with the study was to;

- Utilize rheological measurements to characterize mixtures containing polyunsaturated edible oils, microcrystalline cellulose powder and water.
- Study the effects from rheological characterization, using experimental design and multivariate analysis.

MATERIALS AND METHODS

Materials

Crude, cold pressed oil from Camelina seeds (CAM) was provided by Bioforsk Øst (Apelsvoll, Norway). TINE EPADHA Oil 1200, refined and deodorized cod liver oil (CLO) and spray dried buttermilk powder was supplied by TINE SA (Oslo, Norway). Microcrystalline cellulose (MCC) powders Avicel GP 1030 (co-processed with approximately 11% carboxymethyl cellulose) and Avicel PH 101 (pure MCC) were obtained from FMC Biopolymer (Philadelphia, PA). Throughout the letters "–c" (colloid) and "–p" (powdered) were used indicating Avicel GP 1030 and PH 101 respectively.

Sample preparation and experimental design

An experimental design was constructed in Unscrambler (v. 9.7; Camo AS, Trondheim, Norway) to obtain different mixture ratios between oil, MCC and water. Limits were set at 35-60% for oils, 10-35 % for MCC, and 30-55% for water. From here on MCC powder will be denoted as powder. The 22 different combinations of mixture ratios of oil, powder and water are presented in Figure 1.

Preparation of the samples was carried out by the following procedure; Oil and buttermilk powder was mixed together with a spatula (20% buttermilk powder was added in proportion to the amount of oil in grams. From here on oil means; oil + buttermilk powder), before adding MCC and water. The mass was mixed together with a hand blender (Philips, HR1364, China) for 10 s, and then stirred with a spatula before another 10 s with the hand blender until homogeneous. Each sample batch was on a total of 40 g. The same procedure was performed, using both oils and both MCC powders in turn. Consequently there were four different combinations of oil and MCC powders; CAM/-c, CLO/-c, CAM/-p and CLO/-p. Each sample was prepared just before the analysis.

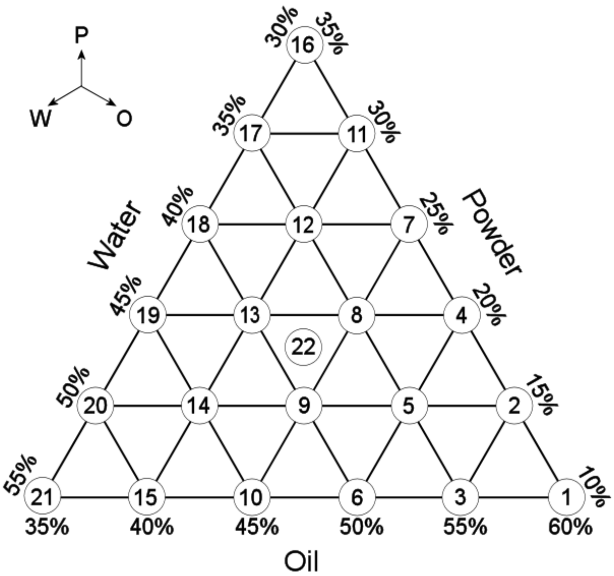

Figure 1. A simplex coordinate system for the mixture proportions of oil, powder and water in percent, outlined from preliminary experiments. Sum of the components are 100%.

Rheological measurements procedure

The samples were analyzed on a Physica 200 UDS rheometer (Paar Physica, Anton Paar, Germany, 2003) fitted with a MP31 top plate and a Peltier bottom plate. The instrument was programmed to perform controlled amplitude sweeps from 0.01-10.0 % strain at 10 Hz with a constant temperature of 20°C and a gap between the plates of 1.0 mm, during the study. 22 samples were analyzed to determine the characteristics of oil, powder and water mixtures at different mixture combinations. The following modules were registered; $G_0^{'}$, $G_0^{''}$, strain (γ) at $G_{0.95}^{'} = 0.95 G_0^{'}$ and stress (τ) at $G_{0.95}^{'} = 0.95 G_0^{'}$. $G^{'}$ is denoted as the elastic or storage modulus and is a measure for the solid nature of the mixture. On the contrary, the viscous or loss modulus $G^{''}$ is a measure of the fluid character.

$G'_{0.95}$ and $G''_{0.95}$ is where the elastic modulus has a 5% reduction, and this is considered to represent the upper limit of the linear viscoelastic range (LVR). Each sample was analyzed in quadruplicate and in randomized order.

Statistical treatment and data analysis

The statistical analysis was performed in R ver. 2.12.0, which is a free software environment maintained by the R Development Core Team (http://www.r-project.org/). The mixtures of powder, oil, and water were analyzed using multiple linear regression, applying both main effect and interaction models (Eq. 1 and 2 respectively). For G'_0, G''_0 and stress the responses were transformed using the natural logarithm because of the extreme spans and logarithmic nature of the responses. Estimated coefficients of all main effects and two-way interactions were calculated, fitted values were plotted as mixture response surfaces, and predicted values (cross-validated mixture by mixture) were plotted against measured values.

$$\hat{y} = b_1O + b_2P + b_3W \quad (1)$$

$$\hat{y} = b_1O + b_2P + b_3W + b_4OP + b_5OW + b_6PW \quad (2)$$

Where O = oil, P = powder and W = water

RESULTS

In Figure 2 and 3 images of samples number 19 and 2 are shown to illustrate the effect of different mixture ratios of oil, powder and water on the properties of the samples. All samples except from sample nr. 16 (35 % oil, 35 % powder and 30 % water) gave measurable results. Sample nr 16 was therefore taken out from the analysis after preliminary experiments, resulting in 21 samples for each of the four mixture combinations (CAM/-c, CLO/-c, CAM/-p and CLO/-p).

Figure 2. Sample nr. 19 (35 % oil, 20 % powder and 45 % water).

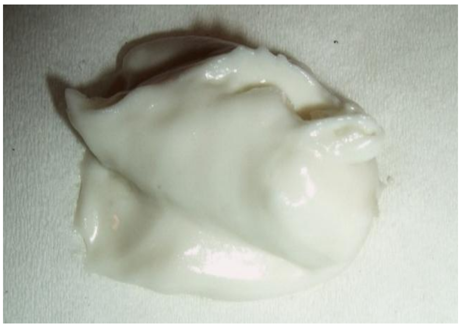

Figure 3. Sample nr. 2 (55 % oil, 15 % powder and 30% water).

Multivariate analysis

Data from the rheological measurements were used to fit empirical models and to test their adequacy. The models were used to plot response surfaces to illustrate the effect of the three components.

Mixtures with CAM/-c and CAM/-p showed the highest cross-validated coefficients of determination (R^2) in the main model for G'_0 and G''_0. The values were 0.84 and 0.85 for G'_0 and G''_0 respectively. There were no considerable differences in cross-validated coefficients of determination between the two powder types "-c" and "-p". For stress, the interaction model of CAM/-p gave the highest R^2 value of 0.78.

In mixtures with CLO/-c and CLO/-p, the main effect models of G'_0 and G''_0 gave the highest R^2 values of 0.86 and 0.87 respectively.

No considerable differences were found between the two powder types "-c" and "-p". For stress, the interaction model of CLO/-p showed the highest R^2 value of 0.73. None of the models for strain had high enough cross-validated coefficients of determination to be of practical use.

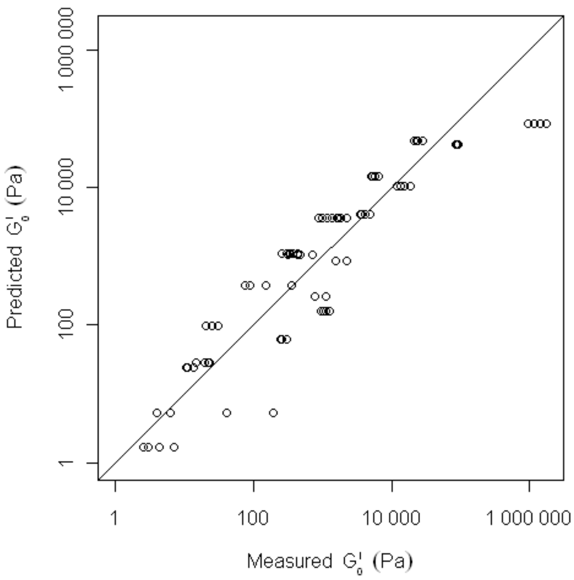

Figure 4. Main effects of measured storage modulus G_0' plotted against predicted G_0'. 21 samples, each in four replicates gives 84 individual samples. (R^2 = 0.84 for CAM/-p.

CAM/-p and CLO/-p were used to illustrate the main model of G_0' and G_0''. The models (from Eq. 1 and 2) corresponding to the highest validated coefficients of determination for CAM/-p were;

- $G_0' = 0.11\,O + 0.37\,P - 0.12\,W$
- $G_0'' = 0.10\,O + 0.28P - 0.10\,W$
- $\tau = 1.15\,P - 0.18W$
  $- 0.01OP + 0.01OW - 0.01PW$

For CLO/-p the models were;

- $G_0' = 0.11\,O + 0.39\,P - 0.14\,W$
- $G_0'' = 0.10\,O + 0.31\,P - 0.12W$
- $\tau = 1.08\,P - 0.21W$
  $- 0.01OP - 0.01PW$

Only design variables having significant effect ($p < 0.05$) are expressed in these models.

To illustrate the multivariate regression model of the main effects, measured G_0' versus predicted G_0' for CAM/-p is plotted in Figure 4.

In Figure 4 the storage moduli between the different mixtures are shown to vary to a great extent. E.g. mixture number 15 and 21 gave low measured G_0' values, while high values were found for sample number 11 and 17.

A response surface plot of the main effect model of G_0' is shown in Figure 5. Mixture proportions of oil, powder and water are given in percent, while predicted G_0' values are given in Pa.

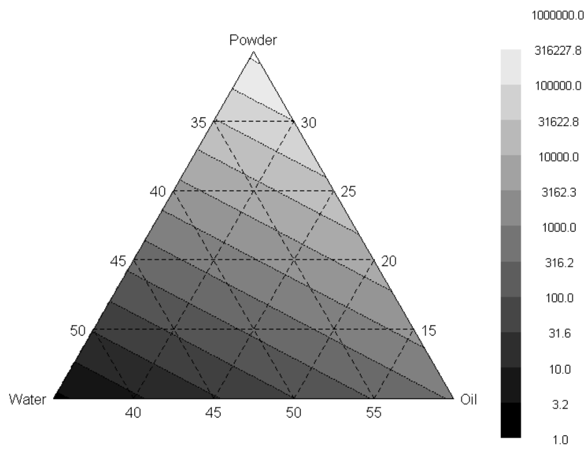

Figure 5. Response surface plot of the main effect model of G_0'(CAM/-p). The gray scale indicates the predicted G_0' value (Pa) at the different mixture ratios of oil, powder and water.

To illustrate the multivariate regression model having interaction effects, CAM/-p is shown. Measured stress versus predicted stress is plotted in Figure 6.

As seen in Figure 6 there are variations in stress between the samples. E.g. sample number 15 gave low measured stress values, while sample 11 and 17 gave the highest stress values. This indicates that more force is applied to sample number 11 and 17.

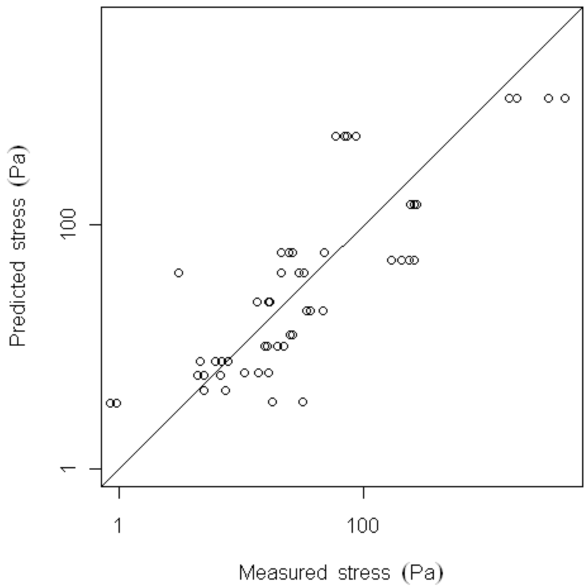

Figure 6. Measured stress plotted against predicted stress. The interaction model is shown. 21 samples, each in four replicates gives 84 individual samples. (R^2 = 0.78 for CAM/-p) The unit of stress is (Pa).

A response surface plot of the interaction effect model of stress is shown in Figure 7. Mixture proportions of oil, powder and water are given in percent, while predicted stress values are given in Pa.

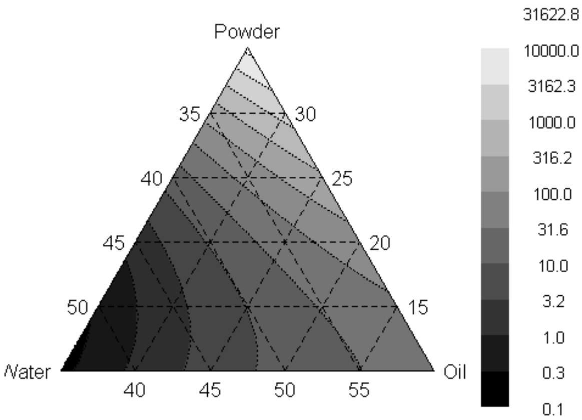

Figure 7. Response surface plot of the interaction model of stress for CAM/-p. The gray scale indicates the predicted stress value at the different mixture ratios of oil, powder and water.

DISCUSSION

The rheological properties of the oil-in-water emulsion with powdered MCC (-p) and colloid MCC (-c) were examined using oscillation methodology which is a common method for investigating gels and dough's [12]. The practical range of proportions of the component variables was established based on preliminary work to yield mixtures with measureable and acceptable properties. Hence, the constrained region is a sub-region of the initial simplex described by an equilateral triangle of smaller dimensions. In mixture design the components add up to 100 % [13].

All the studied mixtures had higher $G_0^{'}$ than $G_0^{''}$ in the strain-rates range investigated. However mixtures with low quantities of powder (10-15%) and high water resulted in a 10^4-10^5 lower $G_0^{'}$ than those of high powder (30%) and gave increase of tendency from elastic to viscoelastic character. Compositional properties of the mixtures can be altered according to desired application, using the different combinations in Figure 1.

Buttermilk powder functioned as an emulsifier and was added to prevent the oil and water phase from separating and to make relatively stable mixtures. Oil had to be mixed with the buttermilk powder in order to create the samples. The value of 20 % buttermilk powder in proportion of the oil in gram was established during preliminary experiments and resulted in an oil-buttermilk mixture referred to as oil.

Sample 19 and 2 shown in Figure 2 and 3, respectively are examples of mixtures obtained in the experiment. Mixture ratios in sample 2 resulted in a more paste-like mixture with a $G_0^{'}$ value around 10^3 while sample 19 had a $G_0^{'}$ value around 10^2 and was more viscous because of a lower content of buttermilk powder added to the oil phase and a higher content of water. Sample 16 resulted in a granular, hard mixture which gave no measurable results.

From the multivariate analysis, the main effect model for $G_0^{'}$ gave the highest cross-validated coefficient of determination (R^2). Therefore this model was used for further interpretation. The multivariate model of $G_0^{'}$ is interpreted as follows; when increasing the relative amount of oil in the mixtures, an increase in the storage modulus was detected. However, increasing the amount of powder had a significantly higher effect on $G_0^{'}$ compared to the two other mixture components. This is also shown in the response surface plots in Figure 5 where the alteration in shading from black to a brighter shade illustrates an increase in $G_0^{'}$ when the amount of powder was increased. When increasing the relative amount of water in the mixtures, the storage modulus decreases, resulting in more viscous samples. This can also be seen in Figure 5, indicated by darker shading. Since there were no considerable differences in cross-validated coefficients of determination between the two powder types "-c" and "-p", the interpretation of $G_0^{'}$ was considered equivalent for the four combinations CAM/-c, CLO/-c, CAM/-p and CLO/-p.

As for $G_0^{'}$, the main effect model of the loss modulus $G_0^{''}$ gave the highest cross-validated coefficients of determination. The model interpretation of $G_0^{''}$ was equal to $G_0^{'}$ where an increase in oil gave an increase in the loss modulus, increasing powder had the highest effect, and water affected the $G_0^{''}$ value negatively.

The interaction model for mixtures with CAM/-p gave the highest cross-validated coefficient of determination for stress. This model was therefore chosen to express how different mixture ratios of oil, powder and water effected stress in the samples.

The multivariate model demonstrated; increasing the amount of powder gave an increase in stress (more force was applied to the samples). Powder had the highest effect and therefore influenced the most on the response, which is also shown in Figure 7. Increasing the relative amount of water decreases the stress in the samples. A positive interaction effect was shown between oil×water while negative interaction effects were shown between oil×powder and powder×water. This indicates that when increasing one constituent the effect of the other will decrease and vice versa. E.g. if oil is increased with one unit, the effect of powder will decrease with the coefficient value per unit. Also, when increasing (or decreasing) both constituents with one unit, the response will follow and respond by decreasing (or increasing).

The interaction model of CLO/-p showed the highest cross-validated coefficients of determination for stress. The interaction model was interpreted as follows; the amount of powder had the highest effect on stress. When increasing the relative amount of water, a decrease in stress was shown.

The interaction effects of oil×powder and powder×water were the same as for the interpretation of CAM/-p. No adequate cross-validated models were found for strain, in either of the models.

CONCLUSIONS

Rheological measurements of different combinations of oil, microcrystalline cellulose and water, outlined by an experimental design, were characterized using multivariate modelling. The conclusions can be summarised as follows;

- From the cross-validated coefficients of determination (R^2), the main model of $G_0^{'}$ and $G_0^{''}$ was used to explain the effect of the variables, while the interaction model was used for stress.
- None of the models for strain had high enough cross-validated coefficients of determination to be of practical use.
- The relative amount of powder had the strongest effect on the responses.
- Incorporation of more dry matter in less fluid naturally gave mixtures with more elastic behaviour.

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