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Estimation of Rheological Properties of Ice Cream Unfrozen Liquid Phase by FT-NIR Spectroscopy

Florina A. SILAGHI, Alessandro GIUNCHI, Angelo FABBRI, Luigi RAGNI

Agricultural Economy and Engineering Department, University of Bologna;
p.zza Goidanich, 60 – 47512, Cesena FC, Italy; E-mail: florina.silaghi2@unibo.it

Abstract. The control of ice cream powder mixture production is carried out evaluating the ice cream liquid phase. The present study was conduced on ice cream and unfrozen liquid phase in order to indirectly evaluate the rheological properties by measuring the powder mixture. The calibration set was formed by samples with different percentage of thickeners, maintaining constant the concentration of the other remaining compounds. After the NIR acquisitions the powders were mixed with warm milk, blended and than settled in order to obtain the unfrozen liquid phase needed for the rheological measurements. For each recipe three batches were prepared. The flow curves were evaluated by using the Ostwald de Waele's equation and the goodness of fit was evaluated by the R^2, which was above 0.95. Predictive models of rheological parameters were set up by means of PLS regressions in order to predict the consistency coefficient (K) and the flow behavior index (n) from spectral acquisitions. High correlation of calibration was found for both parameters and NIR spectra obtaining R^2 of 0.884 for K and 0.874 for n.

The good prediction of the models encourages applying them to reduce significantly the time of the powder mixing control during production.

Keywords: Diffuse reflectance, Ice cream powders, Rheological parameters, Calibration, Thickeners.

INTRODUCTION

The production of a grate portion of traditional Italian gelato is obtained hydrating a powder mixture of several ingredients that gives the basic structure to the ice cream. The powder mixture is obtained by mixing in specific proportion dry milk, milk proteins, fat components emulsify, thickeners and aromas.

Ice cream structure determines several important sensorial parameters in the final product such as stiffness, dryness, melt resistance and texture. The setting up of ice cream structure comes from the manufacturing process and from the various components used in the formulation (Granger et al., 2005) In particular, thickeners appears to contribute largely to the properties of ice cream during whipping and freezing. Sommer in 1944 recognized the main functionality of stabilizers, similar to a more recent research (Marshall et al., 2003). Sommer recognizes also the importance of polysaccharides and natural gums as stabilizers of ice cream structure. We now recognize from the literature the importance of freeze–concentration for establishing the unfrozen phase and the behaviour of stabilizers particularly in that phase with regard to entanglement, cryogelation and concentrate solution behaviour (Goff & Hartel, 2004, Regand & Goff, 2002, 2003). The protein/polysaccharide phase separation in the freeze-concentrated unfrozen phase and its effect on ice recrystallization has also been recently studied (Regand & Goff, 2002, 2003), as has the importance of distribution of fat globules, partially coalesced fat and air bubbles into small, stable distributions for control of ice recrystallization (Barford, 2001). Even if the quantity of thickeners in the mixture is very

low if compared to the others ingredients, it plays a main role on stability and textural properties. The production of ice cream powder mixture can be affected by mixing errors. Especially variation of the nominal quantity of thickeners can affect the rheological behaviour of the liquid unfrozen phase and consequently of the ice cream

Because the rheological measurements require a significant amount of time, high cost for the equipment and skilled users, fast and reliable test would be helpful. This problem can be solved by the Near Infrared Spectroscopy (Williams & Norris, 2001) which is almost well-established to control the analytical properties of milk, dairy products, flours and many other food products. In general, NIR can predict composition (protein, sugar, ash, moisture, etc) with high degree of accuracy, as the relevant spectral regions show reasonably clear differences with changing sample composition (Shewry & Tatham, 2000). Some success was achieved even when modelling some rheological parameters (Sinelli et al, 2005).

Diffuse reflectance near infrared spectroscopy is also a suitable and well-established technique for analysis of powders. A NIR analysis can be performed rapidly without sample pre-treatment and the spectra obtained are multivariate fingerprints of the chemical and physical properties of the sample. In addition to off line laboratory analysis, the use of non destructive measurements using integrating sphere enables on line process analysis.

NIR spectroscopy can be used both for qualitative and quantitative analysis of powders. There are numerous reports of powder constituents and qualitative monitoring of powder mixing process by NIR from pharmaceutical field (Bertsson et al, 1998, 2000, 2002).

Quantitative determination with NIR are typically based on multivariate calibration model that establishes a relation between component concentration or properties and the absorbance [log1/R] measured for the same set of samples at different wavelengths. The first step in the calibration process is to select a set of reference samples that is sufficiently large to encompass all of the variations normally expected in the desired application. For quantitative calibration, samples must be analysed by reference method to estimate the true component concentration values (Annual Book of ASTM Standards, 1997). This requirement is problematic if the sample is heterogeneous with respect to content as, for example, powder mixture (Bertsson et al, 2000).

The objective of this work was to develop a NIR spectroscopy model able to estimate the rheological parameters of liquid unfrozen phase by measuring directly the powders mixture. Particularly the effect on rheological properties of the thickeners was considered building specific mixture with different proportion of thickeners leaving the other ingredient constant.

MATERIALS AND METHODS

Basic ingredients

The composition of the tested ice cream powder mix was the following: milk powder, milk protein, dextrose, maltodextrin, whipping agents, emulsifiers, thickeners mix, salt and aroma. The mix of thickeners included sodium carboymethylcellulose, guar gum (extracted from the seeds *Cyamopsis tetragonoloba*), tara gum (extracted from the seeds of *Caesalpina spinosa*), locust bean gum, carragenine. The normal percentage of thickeners in the tested ice cream mix was about 6.2 %.

Sample preparation

In order to build a data set suitable for a strong calibration model a grate range of variability of the sample should be considered. The first step in the calibration of the analysis

of the mixed powder product was to construct the calibration set. The available samples, coming directly from the production, present a very short range of variability in thickeners compounds so it was necessary to rebuild specific recipes of powder mixture, which consisted of samples of compositions spanning from 70 to 130 % of the nominal values of thickeners, maintaining constant the concentration of the other remaining compounds.

For the rheological measurements the powder samples, acquired with the NIR spectrophotometer, were mixed with warm milk in the mass ration 5 to 100, blended at room temperature for 10 minutes and than settled for 20 minutes in order to obtain an ice cream unfrozen liquid phase. For each recipe were prepared three batches.

NIR measurements

Diffuse reflectance spectra were obtained by means of a FT-NIR spectrometer (MATRIX™-I, Bruker Optics, MA, USA) which is equipped with an integrating sphere in the sampling area designed for QA/QC analysis. This method is ideal for measuring large amounts of materials and is particularly useful for analyzing inhomogeneous samples or large particle size items such as grains, seeds or powders.

The spectrum of each sample (results of 100 scans) was recorded in triplicate over the wavelength range 833-2500 nm. Spectra were recorded in reflectance mode, by using standard cups with quartz base. The sample was changed between the three consecutive measurements.

Rheological measurements

Dynamic rheological behaviour of the unfrozen liquid phase was monitored with a controlled stress rheometer, Physica MCR 300 (Anton Paar Ostfildern, Germany) equipped with a TEK 150P circulating bath (Anton Paar Ostfildern, Germany), using a 27 mm diameter coaxial cylinder.

The instrument was measuring the shear rate and the apparent viscosity at 20°C. The apparent viscosity, η, is defined as the ratio of shear stress, τ, to the shear rate $\dot{\gamma}$, ($\eta = \tau / \dot{\gamma}$). This system is usually used for viscosity measurements of medium and high viscosity liquids and pastes such as greases, crèmes, sauces, etc. working in the low medium shear rate range (Alvarez et al, 2004). The rheometer was connected to a computer to control the acquisition data by specific software. The cup of the measuring system was filled up to the index line and let settle for 5 minutes in the rheometer, before each measurement, allowing relaxation of stresses induced during sample loading. Shear rate was increased linearly from 0 to 50 s^{-1}, collecting 30 points of shear rate/shear stress data.

The data were reported as means of measurements made on three samples, where each sample was obtained from a separately prepared batch of ice cream liquid phase of each formulation.

Analysis of the rheological parameters

Most of foods do not have the simple Newtonian rheological behaviour and therefore it is necessary to develop more complex models to describe their behaviour (Holdsworth, 1971, Steffe, 1996).

One of the most widely used rheological model is the Ostwald de Waele (eq. (1)) which describes well many materials.

$$\eta = K \cdot \dot{\gamma}^{n-1} \tag{1}$$

where η is the viscosity expressed in Pa s, K is the consistency coefficient expressed in Pa s^n, $\dot{\gamma}$ is the shear rate expressed in s^{-1} and n is the flow behaviour index, dimensionless.

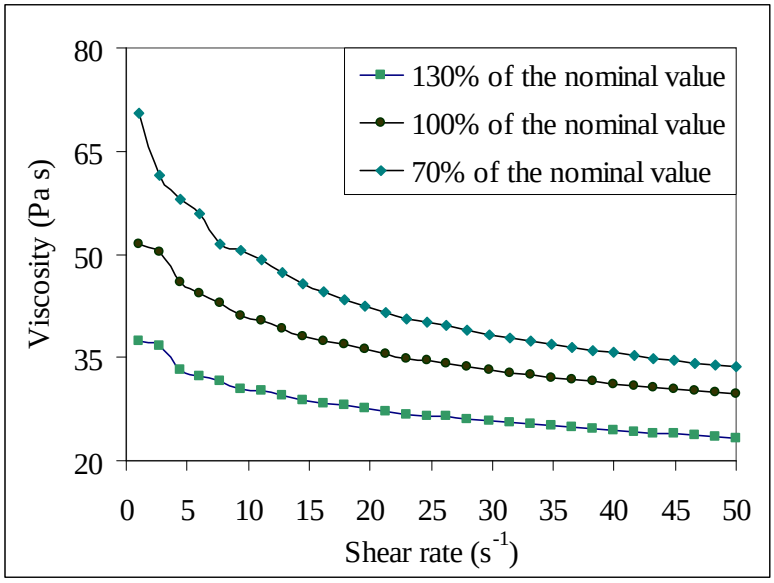

Fig. 1. Viscosity vs shear rate for different concentrations of thickeners in ice cream mixture

The flow curves were evaluated using Ostwald de Waele equation (Abdelrahim et al, 1994). In order to evaluate the goodness of fit, the determination coefficient (R^2) was determined for each batch.

Model calibration

Predictive models of rheological parameters were set up by means of PLS regressions (PLS 2, OPUS ver 5.5, Bruker Optics) in order to predict the consistency coefficient (K) and the flow behaviour index (n) from spectral acquisitions.

During the data processing, the multiplicative scattering correction (MSC) pretreatment was used. In the MSC pretreatment two correction factors are calculated for each spectrum by linear regression of the spectrum on an 'ideal' spectrum which usually is the mean spectrum of the data set. The MSC completely removes additive and multiplicative spectral differences. It should be carried out in direct connection to the PLS calibration or prediction, after splitting the data into calibration set and test set (Esbensen et al., 1998).

In reference to the results of the PCA and the spectroscopic characteristics of the date the best subset of wavelengths were selected.

The subset of wavelengths was further optimized with reference to the best R^2 value and the minimum value of the SECV obtained using the leave-one-out Cross Validation (by using 75% of the data set). These models were then evaluated in terms of R^2 and SEP by performing a Test Set Validation (by using 25% of the dataset). In order to assess the accuracy of the predictive models, the residual predictive deviation for both validations was calculated, by dividing the SD of the reference values by the SECV (RPDCV) or SEP (RPD), (Williams & Norris, 2001).

RESULTS AND DISCUSSIONS

Analysis of the rheological parameters

The flow curves were evaluated by using the Ostwald de Waele's equation. The unfrozen liquid phases were characterized by a consistency coefficient (*K*) from 35.99 to 99.47 Pa s^n, a flow behaviour index (*n*) from 0.736 to 0.85. The determination coefficient (R^2) determined for each batch and used in order to evaluate the goodness of fit was above 0.95.

FT-NIR Spectroscopy

The average spectra related to the ice cream powder mixtures are similar in shape and have absorption bands around 1520, 1730 and 2130 which are mainly related to O-H or C-H functional vibrations and overtones of water, sugars and other substances contained hydroxyl group, and an absorption band around 1935 that corresponds to water bound to protein (Williams & Norris, 2001)

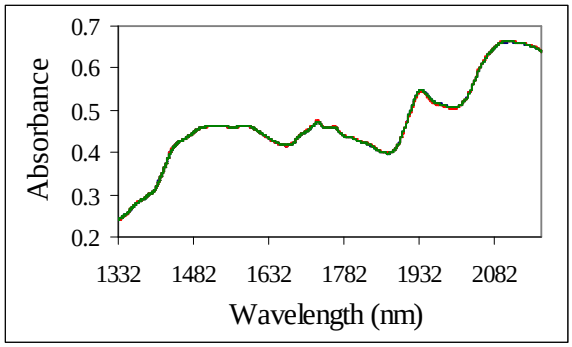

Fig. 2. Raw NIR spectra of ice cream mixture

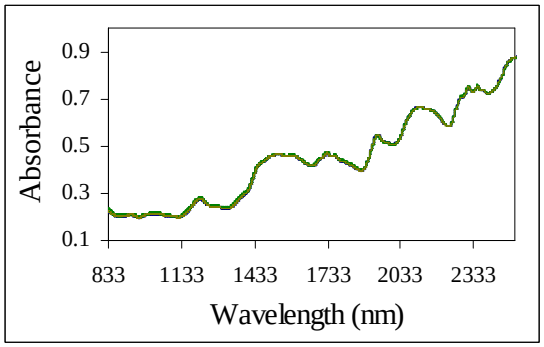

Fig. 3. Spectra of ice cream mixture after MSC pretreatment in the considerate subset of wavelength.

Model calibration

In diffuse reflectance spectrometry, the spectrum of a powder is affected by both the concentration of the chemical constituents and the physical properties of the powder. The measured reflectance is the result of absorption, refraction and scattering of the incident light. A multiplicative correction (MSC) was performed to reduce the effect light scattering that varies according to particle shape and size, particle distribution and chemical constitution (Berntsson et al., 2000).

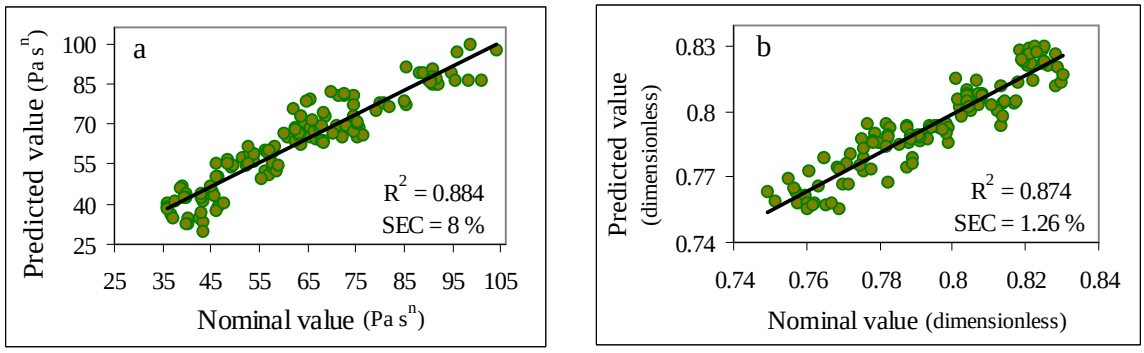

Fig 4. Predicted values vs. nominal values in Cross Validation for *K* (a) and *n* (b)

Statistical parameters were obtained by means of PLS regression analyses in the spectral range of 1330-2180 nm on the MSC preprocessed spectra. A high correlation of calibration was found between the NIR spectra and the consistency coefficient (*K*) and flow behaviour index (*n*), with a determination coefficient (R^2) of 0.884 and 0.874, respectively, and a standard error of calibration (SEC) of 8 % of *K* and 1.26% of *n*, respectively. When the model was applied to predict other unknown samples, the prediction results were similar for *K* with R^2 of 0.865, and lower, with R^2 of 0.698, for *n*. Cross and test set validation showed residual predictive deviation values around 3, which means that the regression model can be used for screening purposes (Williams & Norris, 2001).

CONCLUSIONS

Ostwald de Waele's model is capable of simulating the rheological properties of ice cream mixtures with a very good fit (R^2 above 0.95). NIR technique was used to develop calibration models for the prediction of rheological properties of unfrozen liquid phase by using PLS regression. Diffuse reflectance, conduced by means of integrating sphere on powder mixture, appears to be able to correlate the spectroscopic answer to physical properties of ice cream liquid phase. Good prediction accuracy comparable to the reference method was obtained for both consistency coefficient and flow behaviour index giving a screening performance. The application of these models can reduce significantly the time of the mixing control which is mainly conduced by making and testing the ice cream or evaluating the textural properties of the unfrozen ice cream liquid phase.

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