Ultrasound based methods for acoustic characterization, in-line viscosity and solid fat content (SFC) measurements of fat blends

Emma Levenstam Bragd[1], Johan Wiklund[1], Paul Wassell[2, 3] and Niall W.G. Young[2, 3]
1. SIK – The Swedish Institute of Food and Biotechnology, P.O. Box 5401, SE-402 29, Gothenburg, Sweden

2. Danisco A/S, Multiple Food Applications, Edwin Rahrs Vej 38, 8220 Braband, Denmark

3. University of Chester, Environmental Quality and Food Safety, Research Unit, Department orf Biological Scence, Parkgate Road, Chester, CH1 4BJ, U.K.

Fat and fat crystallization are today studied by methods that are time consuming, expensive and not optimized for in-line measurements. Therefore, new methods are being developed at SIK (Gothenburg, Sweden). Previously, a method for in-line rheometry combining the Doppler-based Ultrasound Velocity Profiling (UVP) technique with Pressure Difference (PD) measurements, commonly known as UVP-PD, has been developed. In this work, the in-line UVP-PD method was successfully applied to highly concentrated and opaque fat blends. The UVP-PD method could rheologically characterize and differentiate between different fat blends. In addition, new ultrasound based methods have been developed for acoustic characterization, for monitoring crystallization kinetics under dynamic conditions and for determination of the solid fat content (SFC). Experimental results showed, for example, that the SFC can be determined in-line using ultrasonics with good agreement with pNMR. Ultrasound based methods can thus be regarded as rapid and powerful research tools as well as a feasible in-line tool for process monitoring and quality control.

Keywords: Ultrasound, in-line, rheometry, viscosity, SFC

1 INTRODUCTION

Removal and reduction of trans fatty acids (TFA) and saturated fats from foods is becoming increasingly prevalent within the food industry because of the potential dangers these fats can cause in the diet. The problem is to maintain the fat blends' functionality since the TFA and the saturated fats give structure to the fat blends. Successful alternative structurants which have found commercial relevance are based on crystalliser technology, which involves adding small quantities of a long chain hydrophobic moiety that positively affect the fat-crystallization kinetics [1] [2]. Methods available today to monitor crystallisation processes include rheological and microscopic methods, pNMR, DSC and X-ray diffraction. These methods are time consuming, expensive and they are not optimized for in-line measurements. New methods to analyse the crystallisation processes under dynamic conditions are therefore required and are being developed at SIK - The Swedish Institute for Food and Biotechnology (Gothenburg, Sweden). The aim of this work was to evaluate ultrasound based in-line methods for determination of rheological parameters and solid fat content (SFC) in an industrial pilot plant under true dynamic processing conditions, thoroughly described in [1] and [2]. In addition, a light microscopy based method for determining the particle size and particle size distribution of the crystals in different fat blends has been improved and tested. The aim is to replace this method with new ultrasound based methods.

2 MATERIALS AND METHODS

2.1 Materials

The fat blends used for rheology measurements consisted of 25 % Chocofill BR 60, a non-*trans*, vegetable fat filling from Aarhus Karlshamn (Karlshamn, Sweden), in rapeseed oil. To one of the systems 1 % of GRINDSTED® CRYSTALLIZER 110 from Danisco A/S (Copenhagen, Denmark) was added. The fat blends used for SFC measurements consisted of 30% palm stearin (Danisco A/S) dispersed in 70% rapeseed oil. The fat and fat blends used for microscopy studies were Chocofill NH 50, 6 % oil absorber in liquid oil and different concentrations of palm stearin dispersed in rapeseed oil, all from Danisco A/S. The cocoa butter came from Cloetta Sverige AB (Ljungsbro, Sweden).

2.2 UVP technique and the UVP-PD method for in-line rheometry

Ultrasound velocity profiling (UVP) is a technique for measuring an instantaneous velocity profile in liquid flow along the pulsed ultrasonic beam axis. The instantaneous velocity profile is obtained by detecting the Doppler shift frequency of backscattered ultrasound as a function of time. The velocity profiles can then be used for determination of the volumetric flow rate (by integration) and for determination of the shear rate distribution (the velocity gradient). If the UVP technique is combined with pressure difference (PD) measurements, the resulting UVP-PD method can be used for in-line rheometry. The UVP-PD method is well described in literature and allows e.g. real-time measurements of

radial velocity profiles and rheological properties, such as yield stress, directly in-line. If a flow in a tube can be approximated by a power-law model according to Eq. 1, then, the radial velocity profile is given by Eq 2 [3].

$$\tau = K\dot{\gamma}^n \quad (1)$$

$$v(r) = \left(\frac{R\Delta P}{2LK}\right)^{1/n} \cdot \frac{R}{(1+1/n)} \cdot \left[1 - \left(\frac{r}{R}\right)^{(1+1/n)}\right] \quad (2)$$

τ is the shear stress, $\dot{\gamma}$ is the shear velocity, K is the consistency index and n is the power law index. R is the pipe radius, ΔP is the pressure drop and L is the distance over which the pressure drop is measured. The viscosity and the rheological model parameters can be determined by making a non-linear fit of Eq. 2 to the measured velocity profile and pressure drop data.

2.3 UVP-PD System

A custom made UVP-PD testing section comprising a flow adapter cell with ultrasound transducers and a by-pass loop with a differential pressure sensor was developed and is thoroughly described in [2]. The UVP-PD system further comprised a custom pulser/receiver, UVP-DUO-MX with integrated multiplexer (Met-Flow SA, Lausanne, Switzerland). The instrument firmware and driver software were modified to give access to the complex demodulated baseband signal (I/Q). The modified firmware combined with the RheoFlow™ software enabled velocity profile estimation from the UVP-Duo instrument with two options; time-domain algorithmn or fast Fourier transform (FFT). In this work, 4 MHz, 150 V, 2-4 cycles per pulse and 512 repetitions were used and 25-40 profiles were processed and averaged in real-time thus giving a total measurement time of 450 ms per reading. The use of a high-speed digitizer card (Agilent Acquiris, Agilent Technologies Sweden AB) as a part of the data acquisition scheme enabled not only measurements of the velocity profiles, but also the simultaneous determination of the acoustic properties. A high-speed DAQ card from National Instruments Sweden AB (Kista, Sweden) was used for acquisition of data from the differential pressure sensor. The pulser/receiver and the differential pressure sensor were connected to a master PC. UVP data was implemented with an ActiveX library (Met-Flow SA). The novel software RheoFlow™, developed at SIK for in-line UVP-PD based rheological measurements, was used for all data acquisition, processing and analysis.

2.4 Solid fat content (SFC)

The ultrasound based in-line method for determination of the SFC is based on the technique described by McClements and Povey [4-5]. If the sound velocity in a suspension or emulsion is approximately the same as in an ideal solution of the substances, and, if the size of the particles or droplets is much smaller than the wavelength of the sound, then the velocity of sound in the suspension or emulsion is given by Eq. (3) [6].

$$c = \frac{1}{\sqrt{\kappa\rho}} \quad (3)$$

ρ and κ is given by Eqs. (4) and (5) respectively.

$$\rho = (1-\phi)\rho_1 + \phi\rho_2 \quad (4)$$

$$\kappa = (1-\phi)\kappa_1 + \phi\kappa_2 \quad (5)$$

c refers to the velocity of sound, κ to the adiabatic compressibility, ρ to the density and ϕ to the volume percentage of the dispersed phase. The subscripts 1 and 2 refer to the continuous and the dispersed phase respectively. Eq. (3) can be rewritten as a quadratic equation in terms of ϕ that for oils and fats has one solution given by Eq (6) [5]

$$\phi = \left(-B - \left(B^2 - 4AC\right)^{1/2}\right)/2A \quad (6)$$

where A, B, and C are given by Eqs. (7), (8) and (9) respectively.

$$A = c_1^2(1-\rho_1/\rho_2) + c_2^2(1-\rho_2/\rho_1) \quad (7)$$

$$B = c_2^2(\rho_2/\rho_1 - 2) + c_2^2\rho_1/\rho_2 \quad (8)$$

$$C = c_2^2\left(1 - c_1^2/c_{total}^2\right) \quad (9)$$

By converting the volume percentage into a mass percentage, the SFC can be calculated according to Eq. (10).

$$SFC = 100\phi\rho_2/\rho \quad (10)$$

Thus, if both the speed of sound in and the density of both the continuous and dispersed phases are known, the SFC can be calculated by measuring the speed of sound in the dispersion. For validation, the SFC, determined with in-line ultrasonic measurements, was compared to the SFC determined off-line with the established IUPAC pulsed nuclear magnetic resonance (p-NMR) technique [7] and calculation principle by van Putte & van den Enden [8]. The densities were determined using a Densito-30PX from Mettler-Toledo (Stockholm, Sweden).

2.5 Microscopy

A light microscopy method, developed and improved at SIK, was used to study fat crystals with polarized light. The method was used for determination of the particle size distribution of the fat crystals. A Nikon Microphot FXA microscope (Japan) was used with a 20x objective. The images were taken with an Altra 20 camera from Olympus. The fat that was to be

studied was melted and allowed to solidify in a schukoff flask. A small sample was taken and placed on a pre-cooled objective glass. Light microscopy images were taken and the diameter of the particles was determined using image analysis.

3 RESULTS AND DISCUSSION

3.1 Velocity profiles and rheology

Figure 1 shows the arithmetic average velocity profile and corresponding power-law fit of the control system (25% Chocofill BR 60 and 75% rapeseed oil) measured in the direction of the flow (flow rate 70 kg/h). The consistency index was calculated to be 6.7 Pas^n and the power-law index was 0.20 (R^2 = 0.998).

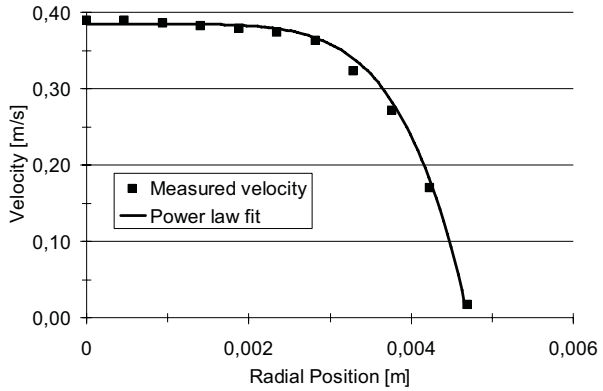

Figure 1. Rheological data and resulting power-law fit for the control system with 25% Chocofill BR 60 and 75% rapeseed oil.

Figure 2 shows the arithmetic average velocity profile and corresponding power-law fit of the blend with 25% Chocofill BR 60, 74% rapeseed oil and 1% GRINDSTED™ CRYSTALLIZER 110, measured in the direction of the flow (flow rate 70 kg/h). The consistency index was calculated to be 14.3 Pas^n and the power-law index was 0.09 (R^2 = 0.983).

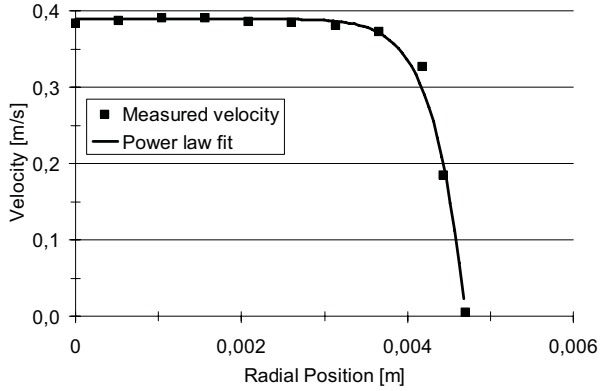

Figure 2. Rheological data and resulting power law fit for the system with 25% Chocofill BR 60, 74% rapeseed oil and 1% GRINDSTED® CRYSTALLIZER.

The low power-law indices indicate that both blends are shear-thinning which is in accordance with the shape of the velocity profiles, showing close to plug-flow. The consistency index for the fat blend with added crystallizer is higher than the consistency index for the control system, even though the composition essentially is the same. The viscosity of the sample with added crystallizer at a shear rate of 1 s^{-1} is about double the viscosity of the sample without added crystallizer. Hence, the viscosity of a fat blend can be significantly increased by addition of a small amount of crystallizer.

3.2 Solid fat content (SFC)

Following results comes from in-line SFC measurements during true dynamic processing conditions without the need of a calibration curve. The density of palm stearin was 899 ± 1 kg/m³ and the sound velocity at 10ºC was determined to be 1548 ± 5 m/s. The density of rapeseed oil was 916 ± 1 kg/m³ and the sound velocity was determined to vary with temperature according to the equation c=1536.4–3.487×T (R^2 = 0.997). Figure 3 shows how the SFC in a blend consisting of 30% palm stearin and 70% rapeseed oil varies with temperature. The SFC is measured both with the standard p-NMR method and with the ultrasonic method.

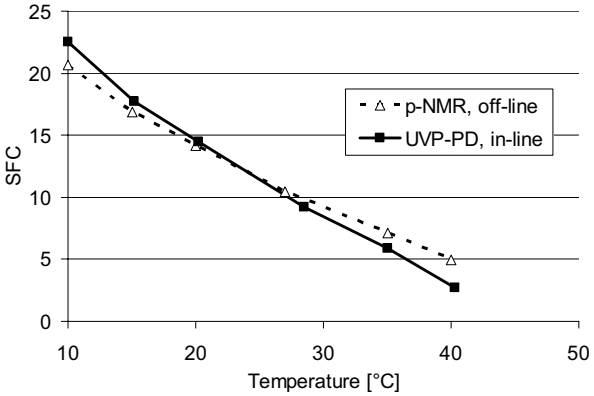

Figure 3. Solid fat content measured with ultrasonic's and p-NMR.

Figure 3 shows that there is a good correlation between the measurements made with the ultrasonic method and the measurements made with the standard IUPAC p-NMR method. The ultrasound based method can thus be used as a non-invasive in-line method for measuring SFC.

3.3 Microscopy

Light microscopy images were taken of the different fat or fat blends (not shown) and the images could be used to determine the size distribution of the fat crystals. Figure 4 shows an example of how the PSD was determined from light microscopy images. The microscopy based method works well but it is time consuming. A new method for determining the PSD using ultrasound is under development at SIK.

The method is based on measurements of the ultrasound velocity and attenuation over a wide frequency range, typically 0.5-100 MHz and the PSD can be calculated using multiple scattering theory [9]. The method is rapid and has good chances of in the future replacing the more time consuming microscopy method.

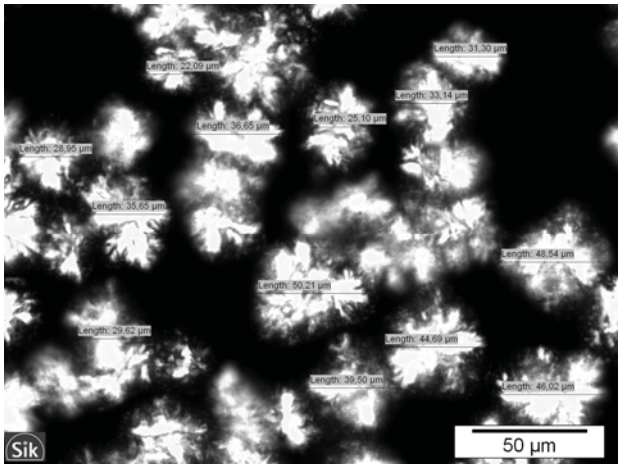

Figure 4. Fat crystals in Chocofill NH 50. The particles sizes are determined with the light micrscopy based method.

Nevertheless, the microscopy images give us insights of the structure of the fat crystals in a way not possible with ultrasonic techniques. Figure 3 shows a microscopy image showing crystals of palm stearin in rapeseed oil.

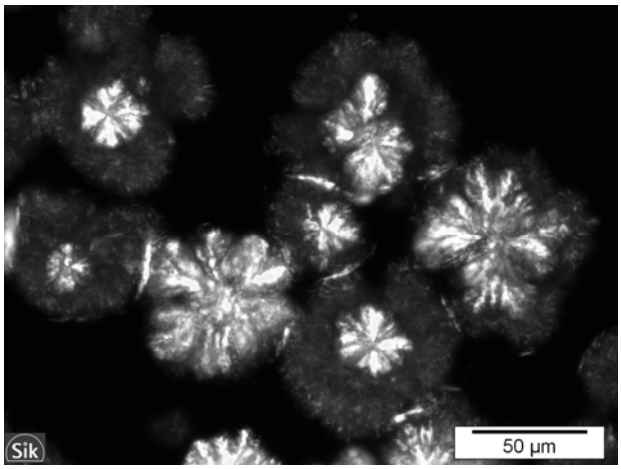

Figure 5. Growing fat crystals in a blend with 30% palm stearin and 70% rapeseed oil.

The light microscopy image in Figure 5 is taken soon after the sample preparation. Some crystals are assembled into diffuse clusters while others can be found in more compact, ordered structures. Light microscopy images of the palm stearin/rapeseed oil samples taken a longer time after sample preparation show that the palm stearin with time becomes arranged into smaller and more ordered structures.

4 CONCLUSIONS

The results show that the developed UVP-PD system and ultrasound based methods can be used to study both the rheology and SFC of opaque fat blends in-line and under true dynamic processing conditions. The SFC measured with the ultrasonic technique showed a strong correlation with the SFC measured with standard p-NMR. The UVP-PD method is an attractive tool for monitoring and characterization of fat blends in-line. The next step is to be able to measure the size and size distribution of the fat crystals with ultrasound in order to replace the time consuming microscopy techniques.

ACKNOWLEDGEMENTS

Graham Bonwick, Christopher Smith and Eva Almiron-Roig, University of Chester, U.K. are acknowledged for scientific collaboration. Lisbeth Dahl Pedersen, Danisco A/S, Braband, Denmark is acknowledged for experimental assistance. Met-Flow SA, Lausanne, Switzerland is acknowledged for technical support.

REFERENCES

[1] Young N et al.: Monitoring struturants of fat blends with ultrasound based in-line rheometry (ultrasonic velocity profiling with pressure difference), International Journal of Food Science and Technology 43 (2008) 2083-2089.

[2] Wassell P et al.: In-line viscosity and solid fat content (SFC) measurement of fat blends with ultrasound based in-line rheometry. International Journal of Food Science and Technology 45 (2010) 7 pages (doi: 10.1111/j.1365-2621.2010.02204.x).

[3] Wiklund J & Stading M: Application of in-line ultrasound Doppler-based UVP–PD rheometry method to concentrated model and industrial suspensions, Flow Measurement and Instrumentation 19 (2008) 171–179.

[4] McClements & Povey: Solid fat content determination using ultrasonic velocity measurements, International Journal of Food Science and Technology 22 (1987) 491-499.

[5] McClements & Povey: Comparison of pulsed NMR and ultrasonic velocity techniques for determining solid fat contents, International Journal of Food Science and Technology 23 (1988) 159-170.

[6] Urick RJ: A sound velocity method for determining the compressibility of finely divided substances, Journal of Applied Physics 18 (1947) 983-987.

[7] IUPAC: 2.150 - Solid content determination in fats by NMR (low resolution nuclear magnetic resonance) (ex 2.323). In: Standard Methods for the Analysis of Oils, Fats and Derivatives, 7th Edition, Blackwell Scientific Publishing, Oxford (1987).

[8] Van Putte K & van den Enden J: Fully automated determination of solid fat content by pulsed NMR, Journal of the American Oil Chemists' Society 51 (1974) 316-320.

[9] McClements DJ & Coupland JN: Theory of droplet size distribution measurements in emulsions using ultrasonic spectroscopy, Colloids and Surfaces A. Physicochemical and Engineering Aspects 117 (1996) 161-170.