In-line monitoring of chocolate crystallization by UVP-PD technique

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The tempering is one of the most important steps to make chocolate, the goal is to obtain the most stable form of fat crystals (forms V and VI). The in-line monitoring of chocolate crystallization is made by the ultrasonic velocity profiles (UVP) and pressure drop (PD) technique. The velocity profile and the pressure drop allow to calculate the viscosity of the fluid on several decades of the shear rate, which grant to characterize non-Newtonian fluids like chocolate. Moreover a Herschel-Bulkley model also gives the yield stress of the fluid by measuring the plug-flow radius. Two more parameters are taken into account to calculate the solid fat content (SFC), the attenuation of ultrasounds and the speed of sound inside the chocolate. However, the tempering process adds a low concentration of fat crystals (<1%), to the 60% of solid content in chocolate. This change might be too small to be detected by attenuation or variation of the sound speed in the chocolate but a more important effect is expected on the shape of the velocity profile.

Keywords: chocolate crystallization, in-line rheology, UVP-PD, attenuation, sound speed, real time

1 INTRODUCTION

The monitoring of the chocolate crystallization is complex to handle because of the chocolate behavior, which is a living system. During the crystallization process, the amount of fat crystals in the chocolate changes over time and the kinetic of the reaction is affected by different parameters, the most important are temperature and shear stress. By the way it is really difficult to know the degree of temper (i.e. crystallization state) of the chocolate for a given time, especially when an off-line measurement technique is used. The advantage of the in-line rheometry is to measure the properties of a fluid (e.g. chocolate) directly in the pipe and monitor the evolution in real time. Two main issues have been encountered in this project. First one is the capability to measure through the pipe wall: it is known that the wall has an impact on the measured velocity profile [1]. The second issue is to measure in a fluid with high concentration of particles [2]. To understand these disturbances, some trials have been realized with well-known fluids before using chocolate. First experiments have been done with sunflower oil at different flow rates and also different Doppler angles. From these measurements, the best Doppler angle has been chosen to conduct the next trials. The second experiment was conducted to see the influence of the concentration of solid particles (0-40µm) in Sunflower oil. Finally, chocolate is used at different degrees of temper.

2 THEORY

2.1 in-line rheometry

The in-line rheometry is based on the analysis of the shape of the velocity profile and the shear stress in a cylindrical pipe. The velocity profile along the diameter of the pipe is measured by the ultrasound velocity profile (UVP) technique [3] and the shear stress is calculated from the pressure difference (PD) in the pipe [4]. One of the advantages of this method is to be able to measure the viscosity of the fluid over several decades of the shear rate simultaneously. However, it is difficult to reach a desired range of shear rate because it depends on the nature of the fluid (Newtonian, shear thickening or shear thinning), the flow rate and the diameter of the pipe. But the advantage is to be able to reach very low shear rates and shear stresses (theoretically both are null in the middle of the pipe) and this allows to calculate the yield stress of the fluid by measuring the plug flow radius.

2.2 Fitting models

The experiments are conducted with two different kinds of fluids, first one is sunflower oil and then chocolate. In consequences, two models are selected. The Eq (1) represents the theoretical velocity profile in a pipe for a Newtonian fluid.

$$\boldsymbol{V_N(r) = V_{max}\left[1-\left(\frac{r-c_0}{R}\right)^2\right]} \qquad (1)$$

When *R* represents the pipe's radius, *r* is the radial position in the pipe, V_{max} is the maximal velocity, at the pipe's center, and c_0 is the center of the profile. The second model is a Herschel-Bulkley model, which is a power law based model which integrates a plug radius. The Eq (2) describes the formulae used to calculate the velocity profile outside of the center plug (when $|r-c_0| > R^*$).

$$\mathbf{V_{HB}(r)} = \frac{1}{1+\frac{1}{n}}\left(\frac{\Delta \mathbf{P}}{2\mathbf{LK}}\right)^{\frac{1}{n}}\left[(\mathbf{R}-\mathbf{R}^*)^{1+\frac{1}{n}} - (|\mathbf{r}-\mathbf{c_0}|-\mathbf{R}^*)^{1+\frac{1}{n}}\right] \qquad (2)$$

Otherwise Eq (3) is used to calculate the velocity in the plug flow (when $|r-c_0| < R^*$).

$$V_{HB}(r) = \frac{1}{1+\frac{1}{n}}\left(\frac{\Delta P}{2LK}\right)^{\frac{1}{n}}(R-R^*)^{1+\frac{1}{n}} \qquad (3)$$

The new parameters are, R^* the plug radius of the fluid and also, *K* and *n* are parameters of the power-law model, respectively the constancy index and the flow exponent. Finally ΔP is the pressure difference and *L* the length between the pressure sensors. The standard power law model is obtain from the Eq (2) by setting the plug radius R^* to 0.

These models are fitted on the measured velocity profile with the Levenberg-Marquardt algorithm through a least-square function. The parameters which are optimized are (for both models) V_{max}, *R*, R^*, c_0, *K* and *n*. Two geometrical parameters are left free for the fit. The first one allows the algorithm to correct the positioning error of the profile with c_0. Moreover the fitted radius *R* is also free to estimate the velocity slip on the wall, when the fitted radius is higher than the pipe radius. In that case, the velocity given by the fluid model at the position of the real wall gives the velocity slip.

2.3 Shear stress

The shear stress is calculated along the radius with the Eq (4).

$$\tau(r) = \frac{\Delta P\,|r-c_0|}{2L} \tag{4}$$

The shear stress is only known by the pressure difference. This pressure measurement is a key parameter to calculate the viscosity but it is not so easy to measure a pressure in a pipe, a lot of parameters can influence the measurement. First, the hydrodynamic flow in the pipe as to be laminar to get a stable pressure in the pipe. Moreover, the pump as also an influence on the pressure. As I am using a volumetric pump, the variation on the pressure in the pipe are directly influenced by the fluctuation of pump's flow rate.

2.4 Shear rate

There are two different ways to calculate the shear rate of the velocity profile. The first solution is to use the mathematical derivative of the velocity function. So Eq (5) represents the shear rate of the Newtonian fluid and Eq (6) is the formulae used for the Herschel-Bulkley model.

$$\dot{\gamma}_N(r) = \frac{2 * V_{max} * (c_0 - r)}{R^2} \tag{5}$$

$$\dot{\gamma}_{\mathbf{HB}}(\mathbf{r}) = \begin{cases} -\left(\frac{\Delta P}{2LK}\left(|r-c_0| - R^*\right)\right)^{\frac{1}{n}} & if\ |r-c_0| > R^* \\ 0 & if\ |r-c_0| < R^* \end{cases} \tag{6}$$

The other solution is to compute the approximate spatial derivative of the flow profile by iterating the Eq (7) over the different points of the curve, with a regular radial step h between two data points.

$$\frac{\partial V(i)}{\partial r} = \frac{V(i+1) - V(i-1)}{2h} \tag{7}$$

2.5 Viscosity

To compute the viscosity, first, 300 velocity profiles are measured and averaged. From this mean profile, the appropriate fluid model is fitted with the Eq (1) or (2) and then the shear rate is computed with Eq (5) or (6). Next step is to calculate of the shear stress from the Eq (4), this one is aligned with the center of the fluid model to be able to calculate a correct flow curve. Finally the viscosity is calculated with the ratio shear stress over shear rate.

3 MATERIAL AND METHODS

3.1 UVP measurement device

The profiler used to perform the UVP measurement is an UB-lab, from the UBERTONE Company based in Strasbourg, France. The transducers are from IMASONIC (Reference TX4-5-8).

3.2 Measuring cell

The cell used includes 4 pairs of holes, able to determine the optimal Doppler angle. Moreover, the near field is placed into the PVC due to a distance between the sensor and the edge of the pipe of 13mm. The Doppler angles, defined from the normal to the flow direction, are 20°, 25°, 30° and 35°. In addition, there is a pair of holes on the radial axis, with a gap of 5mm between the sensor and the pipe, for the measurement of time of flight. Last point, each pair of hole are not aligned but shifted in order to correct the refraction of the ultrasound beam in the fluid and to measure properly the ultrasound attenuation. The celerity used to calculate these shifts are 2250 m/s in the PVC and 1550 m/s in the fluid, which give the values, respectively for each Doppler angle, 2.9 mm, 3.8 mm, 4.7 mm and 5.7 mm.

3.3 Pressure sensors

The pressure sensors are from the company Kulite, based in Loenia, New Jersey, USA. The model used is a XTL-190M, pressure measurement is based on a sealed gaged geometry, up to 3.5 bar. The accuracy on pressure drop with these sensors is around 2%, with a precision of 5mbar. Therefore, to process the viscosity measurement, the pressure drop in the pipe is set around 500mbar to minimize the repeatability error. In facts, this is only achievable with the chocolate, because the viscosity of the oil is not high enough to produce a pressure drop of 500mbar in the pipe with a reasonable flow rate.

Moreover, new pressure sensors from the same Company was ordered for the chocolate trials. These have a flat membrane, model XTM-190M 1.7 bar, because of the holes in the model XTL-190M, which are blocked by the solid particles of the chocolate.

3.4 Measurement loop

The pipes used for the loop have a diameter of 25 mm. The length of the straight section before the measurement cell is 90 cm and there is a distance of 145 cm between the two pressure sensors. The pump used for the oil calibration is a lobe pump from Waukesha and allows a flow rate up to 2000 L/h for fluids with a viscosity under 10 Pa.s. Then to perform the trials on the chocolate, the pump was change for a gear pump, which allows a range of flow rate from 100 L/h to 700 L/h.

3.5 Data post-processing

The post processing of the data is made with python 2.7, with the libraries Numpy and Scipy. The data are recorded on text files and computed on a PC under Ubuntu 12.04 LTS, with a quad core processor at 2.4 GHz, and 2 GB of RAM.

3.6 Method

The trials start with sunflower oil, which is a Newtonian fluid, in order to compare the results with the theory. Later on, plastic particles were added to the oil at different mass concentrations, from 0.3% to 25%, to see the influence of the particles on the fluid behavior and the disturbance on the ultrasound signal. The properties of the particles are listed in the table 1. The particles are from Potters Europe, with the reference Sphericell 110P8. These particles are selected because of their properties close to the particle size distribution of chocolate [5], which should have a size under 50µm. The idea is to get a model of chocolate which is liquid at room temperature. The particle size analysis was performed with a Beckman Coulter LS133201.

Table 1: Particle size distribution by DLS of the particles used to modify the behavior of the sunflower oil.

Density (kg/m^3)	D10 (µm)	D50 (µm)	D90 (µm)
1100	3.66	12.3	25.0

4 RESULTS AND DISCUSSION

4.1 Calibration by oil

Table 2 shows the trials done with different quantities of particles added to the oil. For the trials 1 the minimal quantity of particles is added in order to have an echo strong enough to be able to measure the velocity (Signal to noise ratio, SNR, around +5dB). Then a larger quantity of particles is added gradually to reach a SNR of more than +10dB for trial 4, nevertheless the concentration of particles stays under 1%. Moreover, the temperature of the different trials changes from 20°C to 22°C because of the thermal dissipation of the pump and also the viscous frictions in the fluid. The emission frequency for UVP is set to 3.41 MHz and the pulse length, and also the measurement distance, are 0.43mm with the celerity set to 1460m/s. The pulse repetition frequency (PRF) is set to 2068Hz. The emission voltage is 30V and the gain is set to +62dB. Finally, the throughput of the pump is set around 800L/h.

Table 2: Resume of the viscosities (in mPa·s) obtained for the pure sunflower oil by in-line rheometry for a shear rate of 100 1/s at room temperature. The viscosity of pure sunflower oil measured on a rheometer at 20°C is 59 mPa·s

Angle (°)	Trial 1	Trial 2	Trial 3	Trial 4
20	64	61	61	63
25	57	58	61	63
30	58	58	62	63
35	59	57	62	64

The lowest particle concentration (Trial 1) shows the largest variation for the smallest angle compare to the higher one. This can be explained by the small Doppler angle, which is around 10° inside the fluid. Indeed for very small Doppler angles, the measured velocity is very sensitive to the variation of this angle. When the particles concentration increases, the differences between the different angles decreases but the viscosity increases at the same time, which makes sense according to the theory but the concentration is not known precisely enough to make assumption about the viscosity error on these data. The figure 1 shows the velocity and the shear rate measured and fitted, by the Eq (1) for the trial 2 at 35°. The disturbances close to the walls are not taken into account to process the fit of the model.

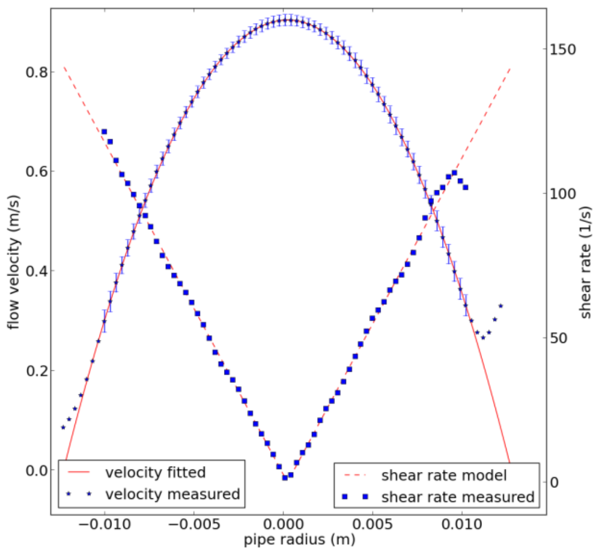

Figure 1: Velocity profile measured and fitted by a Newtonian model, and the shear rate associated for sunflower oil with a Doppler angle of 35°, transducer on left side.

The Trials conducted to optimize the Doppler angle show less disturb shape of the profiles and less sensitivity to the Doppler angle inside the fluid for the highest angles (30° and 35°). Moreover, a relatively strong echo is seen by the transducer on the walls for the angles from 20° to 30°, but not for the 35° as displayed on the figure 2. These echoes can disturb the velocity profile, so the 35° angle seems to be the optimal angle to conduct the next trials.

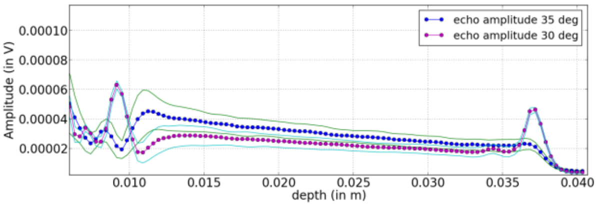

Figure 2: Echo amplitude in the cell with sunflower oil, for 30° (blue line) and 35° (purple line)

4.2 Oil and plastic particles

For this experimentation, plastic particles have been added to the oil at different concentrations. The setup was running one night before the measurement in order to stabilize the temperature at 23°C. For each particle concentration, a sample is taken to do the measurement of viscosity with the rheometer. All particle concentrations are given in volume. The frequency used for the UVP measurement is 3.41 MHz, pulse length and the measurement distance are 0.43mm for a given celerity of 1480m/s and the PRF is set to 1364Hz. The emission voltage is 30V and the signal received is amplified with a gain of +62dB. Moreover the throughput of the pump is set to 210L/h.

Table 3: Results given by in-line rheometry compared to off-line rheometry (for a shear rate of 100 1/s) for different particle concentrations in volume. The temperature of the trials is 23°C

Particle conc. v/v (%)	Viscosity in-line (mPa·s)	Viscosity off-line (mPa·s)	Error (%)
0.25%	57.3	57.4	0.2%
0.41%	57.4	57.7	0.5%
0.83%	58.3	58.6	0.5%
4.31%	66.7	65.1	2.5%
9.09%	78.8	75.5	4.4 %
20.5%	114	107	6.5%
27.3%	125	134	6.7%

The influence of the particles on the viscosity is relevant over a concentration of 1%. Concerning the velocity profile, the exploration depth is long enough to fit a model with a concentration under 10% (more than 70% of the profile). For 20% and 27%, the measured velocity profile didn't reach the middle of the pipe. So accordingly to the table 3, we can see that the maximal error is under 5% for particles concentration lower than 10% and goes up to 7% for higher concentration. Additionally, the frequency drive generates a lot of noise on the measurement of the velocity profiles and reduce by the way the depth exploration in the pipe.

This limited exploration depth is critical for the next step, where the solid concentration of the chocolate reaches at least 60% in volume. The solution chosen for the UBERTONE device is to increase the emitted voltage up to 60V and reduce the emission frequency because the attenuation is proportional to the square of the frequency even if the spatial resolution is lower. Last point is to reduce the noise as much as possible, especially from the frequency converter by plugin it on a different power source than the UVP device.

5 CONCLUSION

The principle of in-line rheometry in a pipe is feasible with an accuracy of 5% for fluids with low particles concentration (less than 10% in volume) without the correction of the velocity behind the wall by deconvolution processing [6]. For higher particle concentrations, like chocolate, this is much more challenging. For a frequency of 4 MHz, the dampening of the ultrasound in the chocolate is too high to expect the measurement of the velocity profile over the pipe radius. Nevertheless, the ongoing trials on the chocolate shows that reducing the frequency to 2MHz and increasing the power of the emitted signal, allows to measure the velocity profile over half of the pipe.

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