Online Process Rheometry Using Oscillatory Squeeze Flow

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Abstract:
The flow of complex fluids is routinely encountered in a variety of industrial manufacturing operations. Some of these operations use rheological methods for process and quality control. In a typical process operation small quantities of the process fluid are intermittently sampled for rheological measurements and the efficiency of the process or the quality of the product is determined based on the outcomes of these measurements. The large number of sample-handling steps involved in this approach cost time and cause inconsistencies that lead to significant variability in the measurements. These complications often make effective process/ quality control using standard rheometric techniques difficult. The effectiveness of control strategies involving rheological measurements can be improved if measurements are made online during processing and sampling-steps are eliminated. Unfortunately, online instruments capable of providing sufficiently detailed rheological characterisation of process fluids have been difficult to develop. Commercially available online instruments typically provide a single measurement of viscosity at a fixed deformation rate. This dependence on a single pre-determined shear rate restricts these instruments from identifying changes in the product or the process, especially if the viscosity at the pre-determined shear rate remains unaltered during these changes. We introduce an Online Rheometer (OLR) that uses small amplitude oscillatory squeeze flow to measure the viscoelastic properties of process fluids in-process and in real time under typical processing conditions. We demonstrate that with an appropriate measuring geometry and amplitude of oscillation, the frequency response of typical non-Newtonian fluids can be accurately measured in a process pipe. We also compare our results with other techniques that are typically used for process rheometry, critically evaluating the utility of the OLR technology for advanced process and quality control.

Zusammenfassung:
Das Fließverhalten komplexer Fluide wird gewöhnlich in einer Vielzahl von industriellen Verarbeitungsprozessen wiedergefunden. Bei einigen Verfahren werden rheologische Methoden zur Prozess- und Qualitätskontrolle angewandt. Bei einem typischen Verfahren werden geringe Mengen des Prozessfluids für rheologische Untersuchungen entnommen. Dann wird die Wirksamkeit des Prozesses bzw. die Produktqualität basierend auf den Ergebnissen dieser Messungen bestimmt. Die Vielzahl dieser Testschritte bei diesen Verfahren kostet Zeit und verursacht Inkonsistenzen, die zur signifikanten Schwankung bei diesen Messungen führen. Diese Komplikationen machen oftmals eine effektive Prozess-/Qualitätskontrolle mittels standardisierter rheometrischer Messungen schwierig. Die Effizienz der Kontrollstrategien mit rheologischen Untersuchungen kann verbessert werden, wenn Messungen online während der Verarbeitung durchgeführt werden und dabei die Probenentnahme fortfällt. Jedoch ist die Entwicklung von online-Messgeräten schwierig, die eine ausreichende rheologische Charakterisierung des Prozessfluids durchführen können. Kommerziell erhältliche online-Instrumente führen typischerweise eine Einzelpunktmessung der Viskosität bei einer bestimmten Deformationsrate durch. Die Abhängigkeit von einer einzelnen vorgegebenen Scherrate schränkt diese Messgeräte für die Identifikation von Produkt- oder Prozessänderungen ein, insbesondere dann, falls sich die Viskosität bei der vorgegebenen Scherrate durch diese Schwankungen nicht ändert. Wir stellen ein online-Rheometer (OLR) vor, dass eine oszillatorische Quetschströmung mit kleiner Amplitude ausnutzt, um die viskoelastischen Eigenschaften des Prozessfluids während des Prozesses und in Realzeit unter typischen Prozessbedingungen zu messen. Wir zeigen, dass mit einer adäquaten Messgeometrie und Oszillationsamplitude die Frequenzantwort eines typischen nicht-Newtonschen Fluids in einem Prozess mit einer Rohrströmung genau ermittelt werden kann. Darüber hinaus vergleichen wir unsere Resultate mit denen von anderen Techniken, die typischerweise für online-Rheometrie verwendet werden. Dabei wird der Nutzen der OLR-Technologie für eine anspruchsvolle Prozess- und Qualitätskontrolle kritisch evaluiert.

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Résumé:
Des écoulements de fluides complexes sont souvent générés dans diverses opérations de fabrications industrielles. Certaines de ces opérations utilisent des méthodes rhéologiques pour la mise en forme ainsi que pour le contrôle de qualité. Lors d'une opération de fabrication typique, des petites quantités d'échantillon de fluide sont prélevées par intermittence, pour permettre d'effectuer des mesures rhéologiques. Ces analyses rhéologiques permettre d'évaluer l'efficacité du procéder ainsi que la qualité du produit. Ces approches impliquent le prélèvement d'un grand nombre d'échantillons ainsi que plusieurs étapes de manipulations, ce qui engendre des coûts élevés et conduisent à une variabilité considérable dans les mesures. Ces techniques souvent complexes rendent le rapport entre l'efficacité du procédé et le control qualité difficile en utilisant des techniques de rhéologie standards. L'efficacité de la stratégie de control impliquant des mesures rhéologiques peuvent être améliorées si les mesures sont effectuées sur la ligne de production durant le procédé de fabrication, ce qui supprime l'étape d'échantillonnage. Malheureusement, le développement d'instruments capable de mesurer en direct et de façon détaillés les propriétés rhéologique d'un fluide en cours de fabrication est difficile. Les instruments de mesures en ligne, actuellement disponibles dans le commerce, fournissent généralement une seule mesure de la viscosité à un taux de déformation fixe. Ces instruments sont restreints à un seul taux de cisaillement prédéterminé, ce qui ne permet pas d'identifier des changements dans le produit ou le procédé, surtout si la viscosité à ce taux de cisaillement prédéterminé reste inchangée. Nous introduisons ici un rhéomètre en ligne (OLR) qui utilise des petites amplitudes d'oscillation de compression de fluide pour mesurer les propriétés viscoélastiques des fluides en cours de transformation et en temps réel dans des conditions de fabrication typiques. Nous démontrons qu'en choisissant une géométrie de mesure appropriée et une amplitude d'oscillation adaptée, la fréquence de réponse d'un fluide typique non Newtonien, en cours de transformation dans un tuyau peut être caractérise précisément. Une comparaison de nos résultats avec d'autres techniques usuellement utilisées en rhéologie, ainsi qu'une évaluation critique de l'utilité de la technologie OLR pour des procédés de fabrication complexe et du contrôle de qualité ; sont présentés.

Key words: oscillatory, squeeze flow, online, Finite Element Simulation

1 INTRODUCTION

The industrial manufacture of consumer products like pastes, creams, gels and shampoos involves operations on large volumes of non-linear viscoelastic and viscoplastic fluids. The rheological properties of such fluids often affect the efficiency of the processing operations and the quality of the products. Thus, many of these processes employ some kind of rheological testing for process and quality control. In a typical industrial operation, samples of the process fluids are drawn intermittently and rheological characterisations are conducted in a dedicated laboratory rheometer. This strategy, however, can involve a large number of sample-handling steps that impart an unquantifiable history on the fluids before rheological measurements are made and also introduce a time-lag between sampling and obtaining a measurement. The effects of the history make the rheological response of the sampled fluids complicated to the extent that, in many cases, it becomes virtually impossible to correlate the laboratory observations to process behaviour[1]. The resulting inconsistencies affect the efficiency of quality control strategies and ultimately the profitability of the process operations.

One way of circumventing these complications is to perform rheological measurements "insitu" or "in-process" during the manufacturing operation so that the sample-handling steps and associated delays can be eliminated. Not only does this improve the consistency between measurements, it also economizes on the time involved in the decision making process. Thus there has been an ongoing interest in online rheometers and viscometers and several illuminating reviews[2–6] exist that discuss the attributes a process rheometer should possess. On-line viscometers that are now commercially available for the continuous measurement of viscosity only partly satisfy these requirements. For instance, one of the most popular viscometric instruments used in the industry are of the immersion type which consist of a vibrating element that is immersed in the fluid of interest and both generates the deformation and senses the response of the process fluid. The deformation is limited to a thin layer of the fluid that is adjacent to the surface of the probe. These instruments typically measure viscosity at a single pre-determined shear rate, and are particularly well suited for monitoring quasi-steady state viscosity in process fluids whose responses are not very sensitive to the rates of shear. The fluid properties characterised therefore represent elements that adhere to the small surface of the vibrating probe which can be substantially different from that of the bulk. Thus, while these instruments are useful for characterisation of Newtonian fluids they are typically insufficient for characterising complex fluids whose microstructure evolves continually during processing for which a single point measurement is insufficient. A number of related technologies have been proposed to overcome the above limitation of process viscometers including adaptation of popular laboratory techniques to online applications. In recent times more elaborate configurations that use ultrasonic vibrations have also been used [7–14]. Despite this progress a survey of the recent literature concerning online viscometry/ rheometry shows that an overwhelming majority of the available technologies provide a measurement which relates only to the dynamic viscosity[15, 16]. While these measurements can provide an estimate of viscosity, they do not necessarily allow access to certain important material properties, the elastic modulus for instance, unless a constitutive behaviour is assumed. Additionally, some of these techniques require substantial time for accurate measurements which is detrimental if integration with some sort of feedback process control or monitoring is desired.

In this paper we test the performance of an Online Rheometer (OLR) that uses oscillatory squeeze flow between two parallel plates submerged in a fluid of interest to provide viscoelastic measurements of process fluids in real time and in typical conditions encountered in industrial processes. Our preliminary studies have assumed that the fluids under consideration are homogeneous and that any particles are sufficiently small (less than 1/10 the gap between the plates) such that they do not affect the flow field. The theoretical underpinnings of the instrument have been previously discussed [17] and a correlation between the measurements of the OLR and laboratory rheometers have also been reported [18] using a standard reference viscoelastic material (NIST 2490). Additionally an attempt has been made to demonstrate the operation of the instrument in a simulated process situation through the use of a bench-scale pipe loop[17]. During these validation tests significant deficiencies were identified that lead to unreliable data quality over a localized band of frequencies. Thus while adequately demonstrating the concepts and the benefit of the technique with regard to online rheometry at an industrial scale, the instrument used in these preliminary studies was largely unsuitable for real-world industrial operations. The technology has since been substantially refined and now warrants a fresh evaluation particularly on industrial-scale flow processes. The focus in this paper therefore, is the evaluation of the performance of the OLR in conditions that are representative of industrial production facilities. A comparison of the measurements made by the OLR with those made using commercially available process viscometers will also be presented under identical process flow conditions so as to clearly demonstrate the advantage of using the OLR for process operations.

2 THEORETICAL BACKGROUND

For oscillatory squeeze flow between two parallel plates with the gap z varying about an equilibrium position h with an angular frequency ω in time t, as $z = h + \epsilon e^{i\omega t}$, Bell et al. [19] show that for small strains which are a fraction of the separation between the plates, $\epsilon = \epsilon h$, the total normal force, $p = p_o e^{i(\omega t + c)}$, oscillates with the imposed deformation with an amplitude p_o and with a phase lag c, and p takes the form [19].

$$p = \frac{3\pi i\omega\varepsilon a^4 \eta^* e^{i\omega t}}{2h^3}\left\{1 - \frac{(\alpha h)^2}{10}\right\} \quad (1)$$

In the above equation a is the radius of the top plate, η^* the complex viscosity, and $\alpha = \sqrt{(i\omega\rho/\eta^*)}$. The second term within the braces accounts for inertial contribution when α^2 is small but not negligible. Field et al. [20] also provide an identical expression for normal force. The expressions for the storage G' and the loss modulii G'' then take the following forms.

$$G' = \frac{2h^3 p_o \cos c}{3\pi\varepsilon a^4} + \frac{\omega^2 \rho h^2}{10}$$
$$G'' = \frac{2h^3 p_o \sin c}{3\pi\varepsilon a^4} \quad (2)$$

Thus knowing the geometric parameters h, a, and ϵ along with the upper plate displacement profile and measuring p_o and c, the storage and loss modulii can be estimated using oscillatory

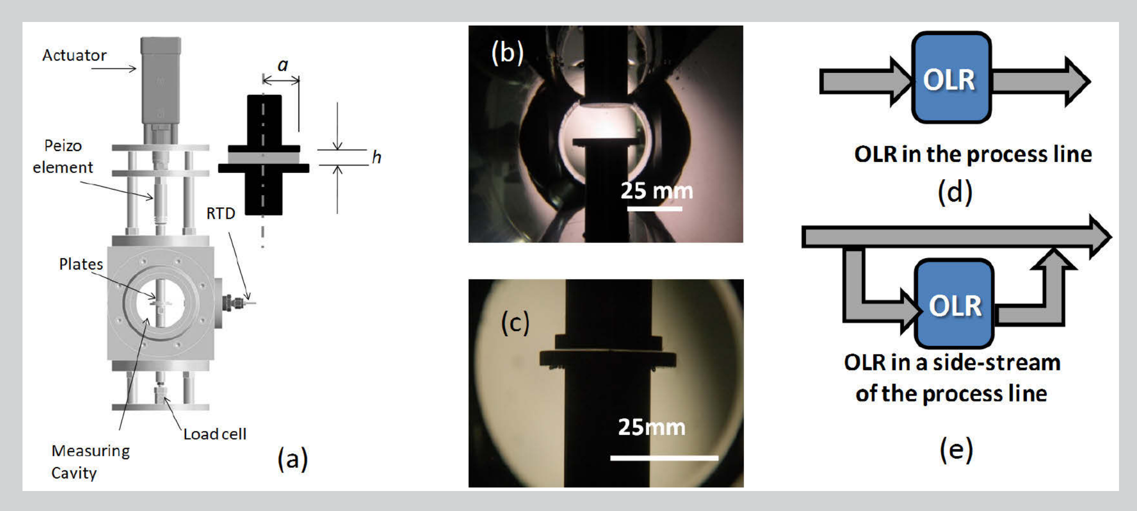

Figure 1: (a) A picture of the Online Rheometer (OLR) which was used in this work. The central cavity allows the fluid to flow through. The instrument contains two end-plates of which the top plate imposes the deformation and the bottom plate records the load. Under idle condition the top plate is retracted as shown in (b) and brought into position (at a given gap h) (c). The OLR can be operated in the inline mode (d). However it is possible to install the instrument on a side-stream (online mode) for intermittent measurements if required (e).

squeeze flow. The upper plate motion can have a complex character including that of a pseudo random noise [20]. However for the present measurements we use a swept sine wave of the format $y = A\ sin[(ai/2 + b)i]$, with amplitude A and number of samples n where i = 0, 1, 2... (n-1), $a = 2(f_2 - f_1)/n$ and $b = 2f_1$, where f_2 and f_1 are the final and initial frequencies in units of cycles/sample, respectively. A similar wave form was also used by Glasscock et al. [17] in initial studies using an earlier version of the OLR.

In a typical experiment the time history of the oscillatory variation of the gap h between the two parallel plates (displacement) and the corresponding variation of the measured normal force p are recorded. Both the displacement and the force are decomposable in harmonic components and the ratio of the Fourier transform of the force $P(\omega)$ to the displacement $H(\omega)$ provides the transfer function which includes a component that is dependent on the geometry Q and another on the complex modulus G^*.

$$TF = \frac{P(\omega)}{H(\omega)} = QG^*(\omega) \tag{3}$$

Since the ratio of the transforms (transfer function, TF) and the influence of the geometry are known, the complex modulus can be easily determined. Clearly, obtaining reliable estimates of the transfer functions is essential for accurate measurements using the above scheme. To increase the signal to noise ratio, the measurements may be repeated a number of times N to allow the average transfer function to converge to a steady state value which is subsequently used for calculations. The effects of the instrument response, which will be convolved with the test fluid response, are accounted for by measuring a Newtonian calibration fluid of known viscosity. Further details regarding the procedure are available in the original work of Field et al. [20] and, in the context of the OLR, in Glasscock et al. [17].

3 EXPERIMENTAL METHODS AND MATERIAL

The general construction of the OLR is shown in Figure 1a. A magnified view of the measuring cell is provided in Figure 1b. Prior to measurements the top and the bottom platens are brought close together using a pneumatic actuator such that the separation between the two plates is between 0.5 and 1 mm in order to optimise signal from the load cell. The movement sandwiches a sample of the fluid of interest between the platens. The configuration with the platens in position and ready for measurements is shown in Figure 1c. In this work an oscillation amplitude of about 3 μm was used in measurements which results in an average strain range of about 0.15 to 3 %. It is possible to vary either the gap between the platens or the amplitude of motion to alter the strain amplitude. The force is measured by a load cell connected to the bottom platen while the temperature is measured by a resistive thermal device (RTD) mounted on the body of the instrument. The instrument is calibrated using a standard Newtonian calibration fluid to eliminate contributions to the force response arising from the OLR itself in the form of internal friction or inertia. The equations used to analyse the response assume no-slip on the surfaces of the plates, and to ensure this platens can be roughened if slip at the interface is expected. However, this was not found necessary for experiments reported here.

The OLR can be installed in a process pipe in any of the two configurations shown in Figures 1d and e. In the following the configuration in Figure 1d in which the OLR is directly placed in the pipeline will be referred to as the “in-line” mode of operation. When it is placed in a side-stream as in Figure 1e it will be referred to as the “on-line” mode of operation. These definitions are in accordance with those proposed by the U.S. Food and Drug Administration [21]. While operating in the on-line mode the OLR can be completely isolated from the main flow by the use of isolation valves and fluid can be intermittently routed through the side stream at convenient intervals for measurement purposes. Once the fluid is isolated the measurements occur in a geometry where the platens are completely submerged in the fluid of interest and there is no flow.

Experiments using the in-line configuration were conducted in a pipe-loop built at Rheology Solutions' Melbourne laboratory using a 2.5 % solution of carboxymethyl cellulose (CMC) in water. The pipe-loop used consisted of a stainless steel tube of 70 millimetre internal diameter and rated to a maximum pressure of 10 bars. The loop was equipped with a flow meter (Proline-Promass 83, Endress and Hauser, Switzerland) that also allowed the measurement of viscosity and mass flow rate and the density of the fluid. Additionally a separate inline viscometer (VA-Series, Marimex, Canada) was also integrated into the pipe-loop for an independent verification of the viscosity of the fluid. The VA-Series is an immersion type viscometer and operates at an effective shear rate of $\dot{\gamma} \approx 3500\ s^{-1}$. The effective shear rate used by the Proline Promass flowmeter is around $\dot{\gamma} \approx 4500\ s^{-1}$. The loop is also equipped with several RTDs and pressure gauges for monitoring the temperature and the pressure of the fluid during flow. A schematic diagram of the piping and instrumentation set-up is shown in Figure 2. As is shown the OLR was configured directly in the flow path (inline mode) for the experiments that follow. Experiments were conducted at various flow rates and the results were compared with measurements made using a laboratory rheometer (Haake MARS III, Thermo Electron, USA) on samples drawn from the flow stream on each flow rate. In addition to the above measurements the viscosity values measured by the VA-Series and the Proline-Promass flowmeter were also noted.

The pipe-loop shown in Figure 2 also allows the estimation of the viscosity using the measurement of the flow rate and the pressure drop. In experiments the fluid was pumped through the loop at various flow rates and the pressure drop over a known length of pipe-line (1320 mm) was calculated. The pressure transducers were located at 10, 16, 23 and 29 pipe-diameters away from the nearest bend to guarantee fully developed flow [22]. The wall stress τ_w was calculated as $\tau_w = D\Delta P/4L$ where D is the diameter of the pipe, ΔP is the pressure drop over the known section of the pipe, and L is the length of the pipe. The absolute value of the rate of shear at the wall $\dot{\gamma}_w$ was calculated as $\dot{\gamma}_w = ((1 + 3n')/(4n'))8V/D$, where $V = 4Q/(\pi D^2)$ is the average velocity, Q being the volumetric flow rate. The factor n' was evaluated from experimental data using the following expression.

$$n' = \frac{d\,ln(\Delta P)}{d\,ln(Q)} \tag{4}$$

The factor n' defines the degree of non-Newtonian character [23] in the fluid of interest; for a power law fluid this is equal to the power-law index. Since the fluid tested is non-Newtonian we use the generalized Reynolds number suggested by Metzner and Reed [23] which is given by the following equation.

$$Re_{MR} = \frac{D^{n'} V^{2-n'} \rho}{K' 8^{n'-1}} \tag{5}$$

where K' is a parameter that in the words of Metzner and Reed [23] "... defines its (fluid's) consistency: the larger the value of K' the 'thicker' or 'more viscous' the fluid." For a power law fluid, where $\tau = K\dot{\gamma}^n$, K' is equal to the prefactor K. The data from the OLR for the CMC solution was independently verified using an oscillatory Haake MARS III laboratory rheometer (Thermo Corporation, U.S.A). To evaluate the operation of the OLR in the "on-line" mode with no flow the instrument was isolated and the measuring cavity filled with a fluid of interest such that the platens were completely submerged. Two fluids were used, a commercial hand-soap (Dettol®, Reckitt and Benkiser) and a solution of 10 % by weight of polystyrene (M_w = 290000 g/mol) in diethylphthalate. The properties of these were measured in an oscillatory ARES rheometer (TA Instruments).

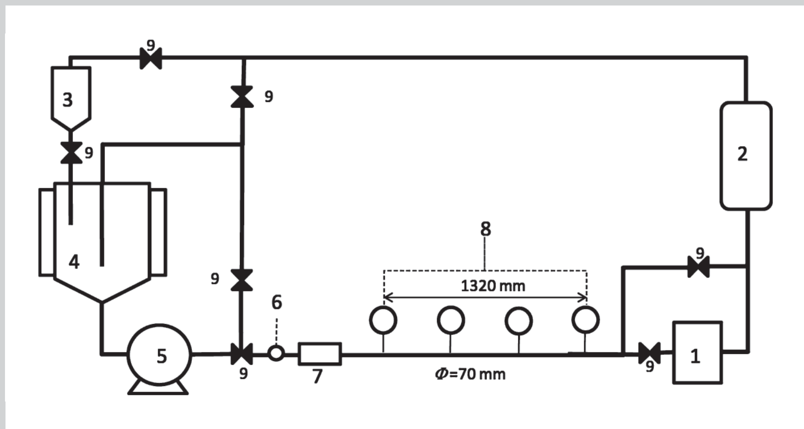

Figure 2: Schematic of the pipe-loop arrangement 1: OLR, 2: Flowmeter, 3: Measuring tank, 4: Bulk tank, 5: Mono pump, 6: Online Viscometer, 7: Inspection window, 8: Pressure transducers, 9: Valves.

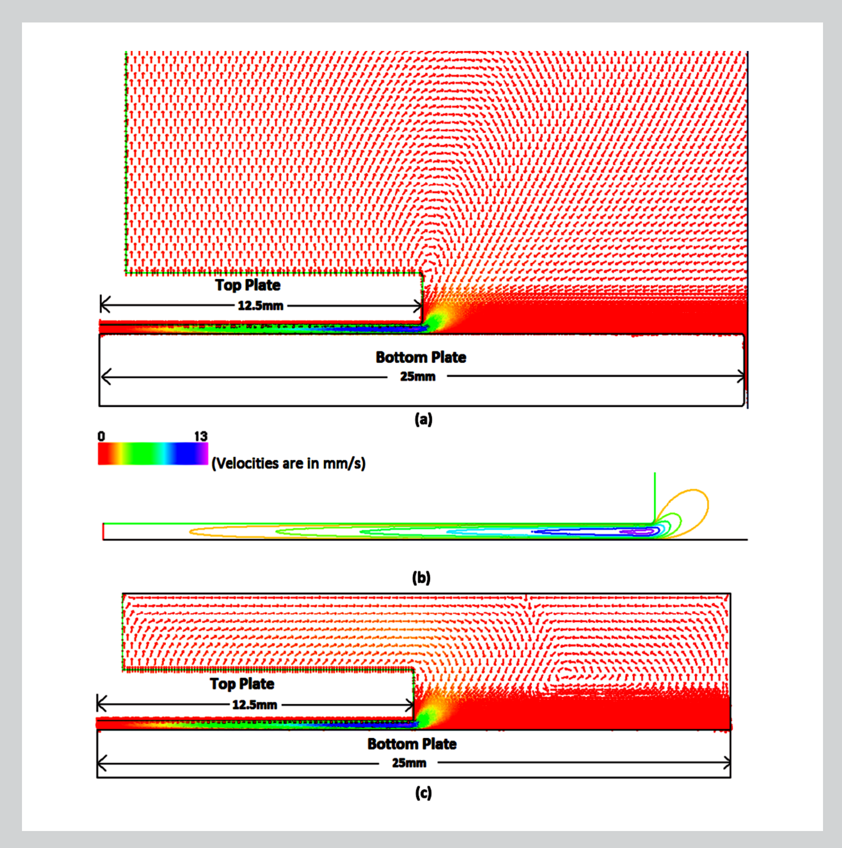

Figure 3: Above diagrams show the flow of fluid within the OLR as the top plate moves up. (a) Vector flow field for Dettol hand soap in in a squeeze flow rheometer with a sufficiently large cavity (identical to the one used in the physical OLR). Note: with this larger cavity there is no longer a recirculation and the viscosity measured is nearly identical to that of the open OLR model with an infinite volume. (b) Contour plot showing the velocity of the Dettol between the two plates of the OLR as modelled in Figure 3a. (c) Vector flow field for Dettol hand soap in a squeeze flow rheometer with an overly confined cavity. Note: the restricted space causes a recirculation of the fluid leading to incorrect viscosity measurements (see table 1).

4 COMPUTER SIMULATION

The equation used by the OLR to calculate sample properties make a few assumptions about conditions within the OLR including a) that the flow between the plates is viscometric b) that the force on the bottom plate will be the same whether or not the plates are submerged (as the calibration is routinely performed in an unsubmerged configuration) and c) that the OLR's cavity is sufficiently large to allow for this submerged flow not to be over confined, with the flow being affected by the chamber walls [19]. The OLR was therefore modelled using a finite element simulation to validate these assumptions.

In the case of on-line operation, axial symmetry of the OLR can be assumed allowing a two-dimensional simulation to be employed. A flow solver code developed at the University of Leeds [24] was employed. This is a Lagrangian finite element code employing a Delauney mesh that is embedded in the fluid, such that the elements carry their strain history with them. The method combines a finite element solution of the momentum and continuity equations with a method-of-characteristics solution of the constitutive equations and thus produces a time dependent solution of the flow; which is assumed to start from rest. Whilst this program can account for mesh distortions by reconnecting points as required to preserve the Delauney triangulation, in the simulations reported in this paper this, with the resulting diffusion of stress, was not required. A Maxwell constitutive equation was used for the fluid, with the necessary parameters obtained from oscillatory measurements conducted on an ARES rheometer. The geometric domain was constructed incorporating all key dimensions (plate diameters, plate thicknesses, shaft diameters, and cavity size), with no-slip boundary conditions imposed on the plates. A sinusoidal movement at fixed frequencies was imposed on the upper plate and the simulation run for at least three cycles to obtain a steady state. To speed up the simulations the mesh density was varied from a fine mesh in the areas of the simulation where more flow and stress was expected (between the plates) to a more coarse mesh in areas where the stress and strain were lower. The mesh density between the plates was optimised to find the maximum density such that increasing the density further did not change the calculated results – this was approximately 8 elements across the gap.

In order to analyse the effect of submerging the plates, additional simulations were run with only the area between the two plates filled with fluid. The effect of the OLR's internal volume was investigated by running simulations with various cavity diameters as well as with unconstrained boundaries such that the model closely represented plates submerged in an infinite fluid bath. The force on the lower plate was measured from the simulation by integrating the pressure and normal stress over the elements adjacent to the plate. From this the force, amplitude and phase were calculated, and the viscosity of the test fluid was then calculated using Equation 1. The resulting flow field for the full submerged OLR geometry is shown in Figure 3a. As expected, the simulation showed that the velocity profile of the sample adhered to that proposed by Bell et al. [19], i.e. $\upsilon_r = ue^{i\omega t}$, $\upsilon_z = we^{i\omega t}$ where *u* and *v* are complex functions of *r* and *z* (Figure 3b). Comparing simulations with both submerged and unsubmerged plates showed a difference in force on the lower plate of approximately 1 %. As the rheological parameters are directly proportional to this force (see Equations 1 and 2), this implies that the difference between submerged and un-submerged operation would create a difference in calculated viscosity of approximately 1 % (See Table 1) which is less than the experimental error observed and thus justifies the use of the unsubmerged mode for the measuring the calibration data. Figure 3 illustrates the flow fields for both a large (a) and small cavity (c). It can be observed that changing the size of the cavity affects the flow field in the cavity and hence the measured force on the lower plate. In the case of the overly confined small cavity (Figure 3c) there is an area of recirculation observed that results in the incorrect calculation of sample viscosity. Table 1 lists the calculated viscosities for the various models simulated. It was found that as the size of the cavity increased, the viscosity converged to a value similar to that calculated with the plates operating unsubmerged. The difference between the viscosity for unconstrained outer boundaries was within 0.5 % of that for the actual OLR geometry and so it can be assumed that the OLR chamber is sufficiently large.

Figure 4 summarises the results of simulations made at a range of plate frequencies for both Dettol and the PS solution. They are compared with experimental measurements made on the OLR in on-line mode (as discussed below) and show a close correlation which confirms that the theoretical basis of the calculations performed in the OLR is sound.

5 RESULTS AND DISCUSSION

We now discuss the results of experiments conducted under no-flow conditions. This configuration also mimics the online mode of operation when the OLR is in a side-stream between isolation valves. Initial experiments were performed using Dettol hand soap and the results are presented in Figure 4a where they are compared to both measurements made in an ARES oscillatory rheometer and our computer simulations. It is evident that there is qualitative agreement between the laboratory oscillatory rheometer results and the OLR data, however the lack of temperature control in the OLR in this configuration leads to a variation in the data between subsequent experimental trials due to the thermal sensitivity of our test material. A close inspection of the data taken in both instruments on the same day in the same laboratory condition reveals a good correlation between the two devices. The design of the OLR does not include a method for temperature regulation. This affects it performance in standalone mode but would be of little consequence in process operations as it is assumed a manufacturing process stream is sufficiently uniform thermally. Also included on the figure is a data set taken with the OLR in unsubmerged mode and, as predicted by our computer simulations, a close correlation was observed.

The overlap between frequencies accessible between the ARES (from 0.1 to 100 rad/s, 0.015 to 15.9 Hz) and the OLR (1 to 100 Hz) is not as large as would be desired to validate the OLR as a rheometer. Therefore a second test fluid was employed. A 10 % by weight solution of polystyrene of molecular mass M_w = 290000 g/mol in diethyl phthalate was characterized on the laboratory rheometer at different temperatures and the overall response shifted to room temperature using time-temperature superposition (TTS). Thus it was possible to test the dynamic response of the polystyrene solution between ω = 1 and 10^5 rad/s, allowing sufficient overlap with the frequency range accessible by the OLR, $6 < \omega < 600$. In Figure 4b the measurements made by the OLR at various frequencies are shown in terms of the complex viscosity and compared to the measurements made on the laboratory rheometer and our computer simulations and again show good correlation with results within approximately 10 % of those measured on the ARES.

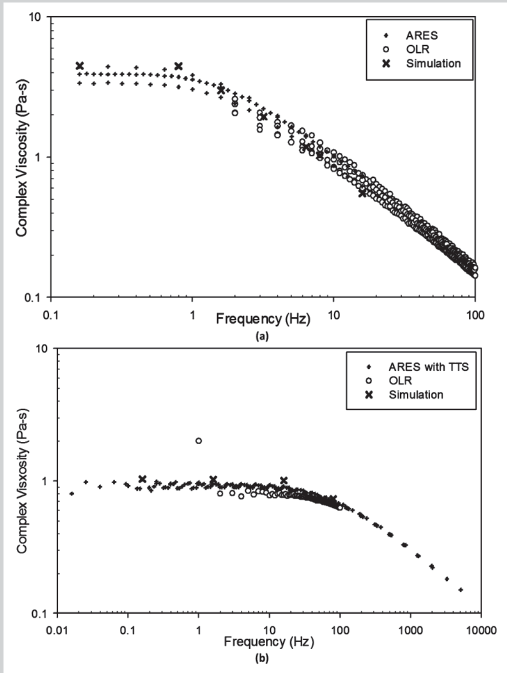

Figure 4:
(a) Viscosity of Dettol hand soap as a function of frequency as measured by squeeze flow rheometer, rotational rheometer, and simulation respectively.
(b) Viscosity of 10 % Polystyrene Diethyl Phthalate solution as a function of frequency as measured by rotational rheometer, squeeze flow rheometer and simulation, respectively.

Table 1:
Measured viscosity of fluid using various model geometries.

Model Name	Model Description	Viscosity of Dettol @ 100 rad/s [Pas]	Difference from OLR model [%]
OLR	Full 2D model of OLR	0.550	-
Open OLR	OLR with external walls as free surface	0.553	0.5
Small Cavity	OLR with external walls closer to plates	0.494	- 10.2
Un-Submerged	OLR plates without surrounding fluid	0.556	1.1

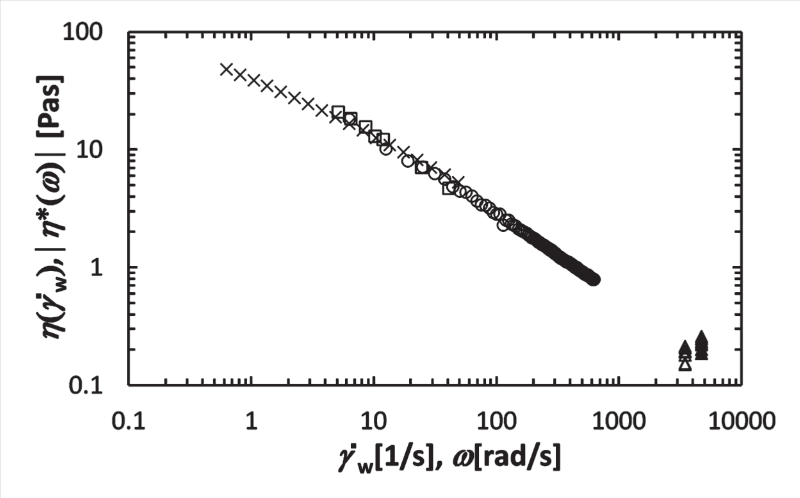

Figure 5: Viscosity of a 2.5% solution of carboxymethylecellulose in water measured in Rheology Solutions' pipe loop using pressure drop measurements (□), a process viscometers (Marimex Viscoscope) (△) and a E&H Proline range flowmeter (▲), compared with the complex viscosity measured on a laboratory scale rotational rheometer (Haake MARS III) (X) as well as those made on the OLR (○).

We will now discuss the results of the experiments performed with the OLR in "in-line mode" in the pipe-loop introduced above using a 2.5 % solution of carboxymethylcellulose in water as our test fluid. The linear viscoelastic response of the fluid was measured by a Haake MARS III over a frequency range of 6 to 100 rad/s. This frequency range was chosen to allow for appropriate overlap between the measurements made on the laboratory rheometer and the OLR. Pressure drop data ΔP measured at the wall over a known distance can be used to calculate the viscosity provided the flow conditions are laminar and elastic effects invoked by flow are unimportant [25]. Typically in steady laminar flow of non-Newtonian fluids the elastic effects can be neglected [26]. We calculated the Fanning friction factor f, which is related to the wall stress via $\tau_w = f\rho V^2/2$, and found that for all conditions at which the pipe-loop was run $f = 16/Re_{MR}$ suggesting that the flow remained laminar in these experiments.

In Figure 5 we present the viscosity calculated from pressure drop in our pipe-flow experiments $\eta(\dot{\gamma}_w) = \tau_w/\dot{\gamma}_w$ against the wall shear rate $\dot{\gamma}_w$ using unfilled squares as makers. The viscosity is observed to decrease with increasing shear rate. On the same plot the complex viscosities obtained from our oscillatory rheometer characterisation are included as circles. The good correspondence between these indicates that the empirical Cox-Merz rule ,which suggests that the magnitude of the complex viscosity in polymeric fluids can be compared with the viscosity at equal values of angular frequency and shear-rate, holds [27]. Also shown in Figure 5 are the viscosities measured by the two commercially available online-viscometers. It can be observed that the viscometers operate at much higher values of shear-rate and measure a viscosity that is at least an order of magnitude lower than those measured by the laboratory rheometers and the pipe-flow experiments, however these data appear to follow the same trend as observed by the pressure drop measurement.

In Figure 6 we present the data measured by the OLR operated as a part of the pipe-flow experiments for three separate trials, in an in-line configuration, and compare them with the complex viscosity. The complex viscosity of a sample of the fluid was measured separately using the laboratory rheometer (Haake MARS III) every time a pipe-flow experiment was performed at a temperature identical to that measured by the RTDs in the pipeline. This way the possibility of differences resulting from the processing history and temperature on the measurements made by the OLR and the laboratory rheometer were minimised. The mass flow rate $\dot{m}$ and the velocity v are also indicated in the caption of the figure. Repeated measurements using the OLR at the same flow conditions were consistent, differing by at most 2.5 % at all but the lowest frequencies (< 3 Hz). It can be observed that the measurements from the OLR agree well with the measurements performed in a laboratory rheometer. In all cases the differences were less than 10 % which was of the same order as the differences observed in the MARS rheometer at the differing temperatures. It was observed that the force measurements from the OLR became increasingly noisy beyond a maximum flow rate of approximately 3000 kgs/hr (which correspond to an average flow velocity of about 0.2 m/s) for the experiments conducted here. This was especially apparent in frequencies beyond 16 Hz as observed in Figure 6c. The exact origin of the noisy data is yet unclear. However this aspect is not further investigated here since it is envisaged that in actual practice the problem could be easily circumvented by placing the OLR in a side-stream equipped with isolation valves and adopting a strategy where the measurements are conducted intermittently by diverting the process flow through the side-stream (online mode).

6 CONCLUSIONS

The emphasis on understanding of the scientific underpinnings of the manufacturing processes has driven much of the innovation and policy initiatives in the food and pharmaceutical sectors after the release of a roadmap by the U.S. FDA in 2004 [21]. This roadmap urges the industry to

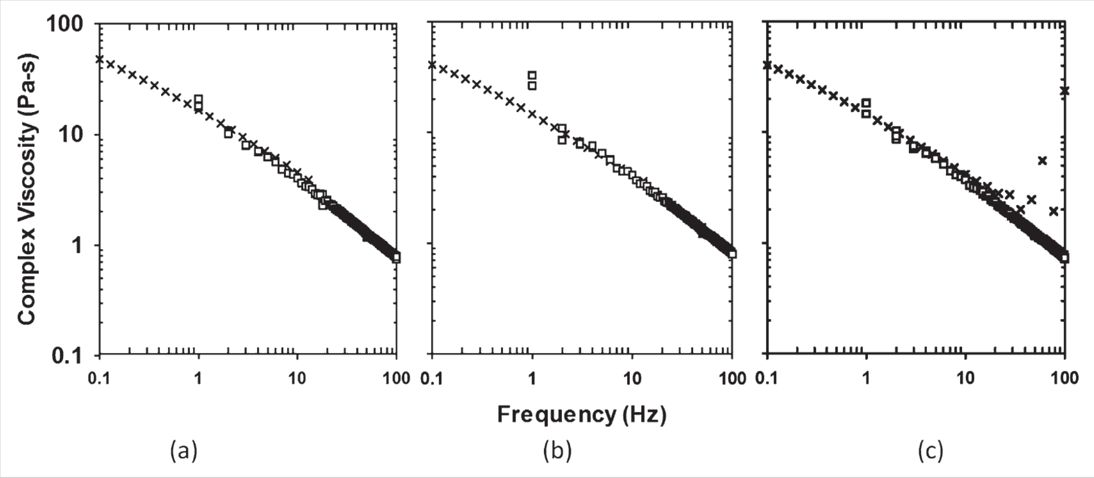

Figure 6: Viscosity measurements of 2.5 % solution of carboxymethylcellulose in water measured at various flow rates in the pipe loop. For comparison, measurements on a laboratory rotational rheometer are included using cross symbols (X). The other symbols represent measurements made by the OLR for repeated experiments at a fixed flow-rate. Results from three representative flow rates are shown: (a) $\dot{m}$ = 1500 kgs/hr (v ~ 0.1 m/s), (b) $\dot{m}$ = 1900 kgs/hr (v ~ 0.13 m/s) and (c) $\dot{m}$ = 2900kgs/hr (v ~ 0.2 m/s).

adopt technologies that can be used to design, analyse and control manufacturing through timely measurements of critical quality and performance attributes of raw and in-process materials with the goal of ensuring final product quality. These “Process Analytical Technologies” or PAT are expected to improve product quality, reduce waste and improve the productivity of lean manufacturing operations. Following the release of the roadmap industry practitioners have included a wide variety of instruments that enable them to monitor and control processes better. We believe that the OLR can contribute to this effort. In a review of the available instruments for process viscometry completed over a decade ago Zimmer et al observed that the process viscometers provided “grossly inaccurate” results when non-Newtonian fluids were of interest and suggested methodologies for correcting for the inaccuracies. Unfortunately the performance of process viscometers has not improved much since that appraisal. In this paper we have presented the performance of an OnLine-Rheometer (OLR) that provides accurate data for a range of non- Newtonian fluids and which provides measurements that agree quantitatively with measurements made on research-grade laboratory instruments. We have defined the flow configurations in which the instruments are likely to be used and have provided representative measurements for each scenario. In all cases a single calibration of the instrument is sufficient to provide effective and accurate characterisation of the process fluid in on-line and in real time.

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