Quantitative evaluation of rheological properties for complex fluids using ultrasonic spinning rheometry

Taiki Yoshida, Yuji Tasaka, and Yuichi Murai

Graduate School of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo, 060-8628, Japan

We have proposed a novel methodology using ultrasonic velocity profiling for quantitative evaluations of complex fluids in a cylindrical vessel with unsteady rotations. The methodology is expected to acquire various rheological properties in a single run. In this study, enhancement of applicable targets in "ultrasonic spinning rheometry" for measuring various rheological properties was achieved. For the quantitative evaluation, we focus on momentum propagation by unsteady shear flows in an oscillating cylindrical container. The momentum propagation is represented as radial profiles of phase lag of velocity fluctuations in the shear flow. Obtaining the phase lag information using discrete Fourier transform (DFT) on spatio-temporal velocity distributions, it was found that the phase lag changes substantially as rheological properties change in the test fluids. For example, it is possible to evaluate viscosity change and physical property of the test fluid by analyzing the phase lag. In addition, for thixotropic fluids, assuming that a viscosity in pure viscous regime is comparable to Newtonian viscosity, shear stress distributions were calculated using Newton's law of viscosity for the velocity distribution. Since it is possible to distinguish physical properties such as yielded and un-yielded region, we estimated a yield stress by evaluating shear stress distributions.

Keywords: ultrasound, rheometry, viscosity, thixotropy, shear flow

1. Introduction

Rheology dealing with deformational properties of materials has been discussed in the field of chemical engineering, biology, food processing, and dispersion system and so on. In the management of homogeneity and safety of various fluid products, such as highly polymerized compound and plastic processing, it is important to quantitatively evaluate their rheological properties. Most are non-Newtonian fluids, which have various complex behaviors, such as shear-rate-dependent viscosity, shear banding [1], velocity slip on the wall [2] and so on. Therefore, interests in the rheology have been stimulated, in part, by the necessity of measurements in the industry. Conventional rheometers investigating torque response against steady or oscillatory simple Couette-type shear, however, can only evaluate comprehensive physical properties such as apparent viscosity and properties in linear viscoelastic regime. In addition, it is inadequate for multi-phase fluids which have interfaces in physical property distributions. The limitations of rheometry assuming constant shear rate is overcome by solving a problem called "Couette inverse problem" [3]. To solve these problems, another approach of rheometry with considering velocity profiles in test fluids has been proposed as velocity profiling rheometry. Ultrasonic velocity profiling (UVP) [4] is the suitable velocimetry to realize the rheometry because of applicability for opaque fluids such as concentrated suspensions, and this method has been developed [3,5-6]. Shiratori T, *et al*. reported about applicability as a practical method of ultrasonic spinning rheometry by measuring a torque value combined with a widened circular Couette flow. However, there are very little studies of quantitative evaluations of rheolog-ical properties for general complex fluids using UVP.

We have proposed a novel methodology using UVP to quantitatively evaluate viscosity of complex fluids in a cylindrical vessel with unsteady rotations. This methodology has been termed "ultrasonic spinning rheometry" and has major advantages, such as being able to evaluate various rheological properties from single set of velocity distributions measured in test fluids. Hitherto, various approaches have been endeavored for the development of this methodology. Tasaka *et al*. reported that the phase lag of velocity fluctuations from the cylinder wall with a sinusoidal oscillation reflects the changes of the effective viscosity [6]. Shiratori *et al*. proposed 'model-free ultrasonic rheometry', which provides quantitative evaluation of shear-rate-dependent viscosity without using rheology models that are constitutive equations describing relation between stress, strain and strain rate of materials [5]. In these studies, however, there has been little effort to evaluate the properties for complex fluids with yield stress or highly concentrated dispersions.

The purpose of this study is to expand the applicable regime with newly developed methodology for general complex fluids. To obtain rheological properties in these fluids, such as thixotropic fluids and multi-phase fluids, we focused on momentum propagations by unsteady shear flows in an oscillating cylindrical container. The propagations appear with a phase lag of the velocity fluctuation from the wall of the container. This paper attempts to quantitatively evaluate rheological properties by the analysis of obtained velocity distribution of complex fluids.

2. Experiments

2.1 Experimental apparatus

The experimental apparatus is shown in Fig. 1. The experiments were conducted in a rotating cylinder whose inner diameter is 145 mm (= $2R$), height is 65 mm and thickness of the lateral wall is 2.0 mm. The cylinder is made of acrylic resin and is filled with test fluids. The cylinder has no lid and thus the top surface of fluid layer is stress free. The cylinder was mounted at the center of a water chamber to keep uniform temperature and to allow transmission of ultrasonic wave from the outside of the cylinder. The oscillation of cylinder is controlled by a stepping motor, where its oscillation angle and oscillating frequency are defined as $\theta = 90$ degree and f =1.0 Hz, respectively.

During the cylinder oscillation, velocity distributions of the fluid are measured by UVP. The obtained ultrasonic echo signals were processed by UVP monitor model Duo (Met-Flow S.A.) into spatio-temporal velocity distribution. An ultrasonic transducer with 4 MHz resonance frequency was fixed in the chamber with a horizontal displacement Δy from the center line of the cylinder to obtain the azimuthal velocity component. Velocity fluctuations are measured on the UVP measurement line ξ at each measurement point and the velocity component u_ξ is parallel to the measurement line ξ. Assuming that the axisymmetric flow field and the velocity component in the radial direction are negligibly small compared to the azimuthal velocity component, the component u_θ is obtained as

$$u_\theta = \frac{u_\xi r}{\Delta y} \qquad (1)$$

at a radial position r.

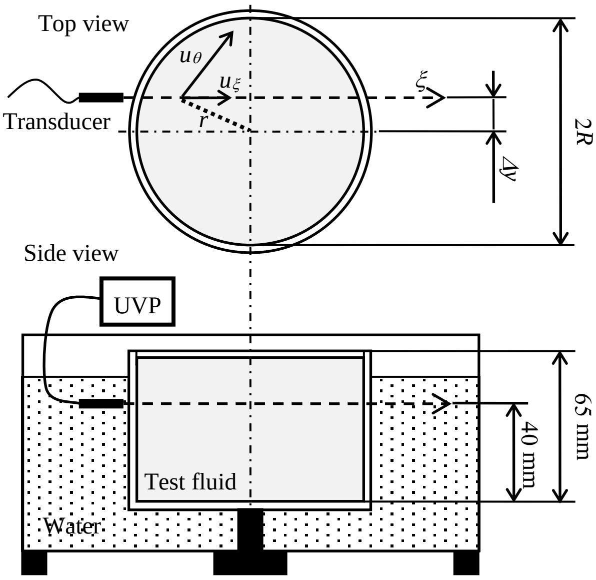

Figure 1: Schematic diagram of experimental setup and arrangement of the measurement line.

Empirically, Δy = 15 mm was selected based on the results of previous studies [5-6] with consideration of incidence of ultrasonic wave against curved cylinder wall and suitable velocity range of projection component of the velocity. The transducer was set 40 mm from the bottom of the cylinder to avoid effects of shear stress due to oscillation at the cylinder bottom plate. Table 1 summarizes the setting parameters of UVP measurement in this study.

Table 1 Setting parameters of UVP

Base frequency	4.0	MHz
Temporal resolution	25	ms
Spatial resolution	0.74	mm
Velocity resolution	1.304	mm/s
Number of cycles	4	-
Number of repetitions	32	-

2.2 Test fluid

In this study, a montmorillonite suspension was examined to demonstrate the applicability of the present rheometry. Montmorillonite is a kind of clay mineral having a deviation of electric charges between an edge and face in the particle. In the left illustration of Fig 2, we show the schema of stable structure dispersed montmorillonite particles in the solvent. The structure is termed “Card house structure”, and is kept stable by interaction between particles such as Coulomb force. The interaction forms clusters of the particles with leaving the suspensions at rest.

In the schematic illustration shown by the others illustrations in Fig. 2, these clusters become smaller influenced by disturbances such as shear stress. Decrease of the cluster size accompanies decrease of a viscosity in the suspension. As the results the suspension has complex behaviors like time-dependent gelling behavior and high shear thinning flow behavior. In case the card house structure of the suspension keeps stable the structure, the suspension has viscoelastic behaviors against a disturbance such as shear stress. These behaviors are termed thixotropy. To attain details for thixotropy refer to past studies [7]. As yet, nothing is established to evaluate these behaviors quantitatively in a single run. However, the behaviors of suspensions have been estimated by results attained from various investigations in the past. So, we demonstrate the applicable methodology using this suspension.

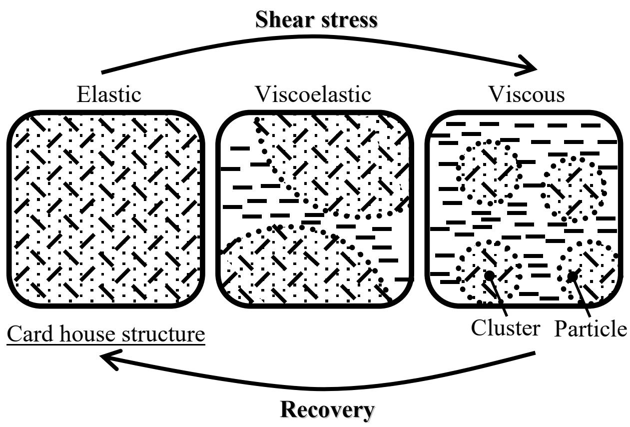

Figure 2: Schema of breakdown in the card house structure

Montmorillonite suspensions were prepared by adding the 4.0 wt. % powder to 0.01 mol/L NaCl aqueous solutions: rheological properties relating card house structure strongly depends on concentration of NaCl. Abend and Lagaly have studied the dependence of viscosity changing in salt concentration of montmorillonite suspensions [8]. In order to fully swell the suspension, it was left for over a day before measuring began. After filling the cylinder with the suspension, the suspension was stirred vigorously to abolish shear stress history. The structural recovery time of the suspension was defined as T = 100 min.

3. Results and discussions

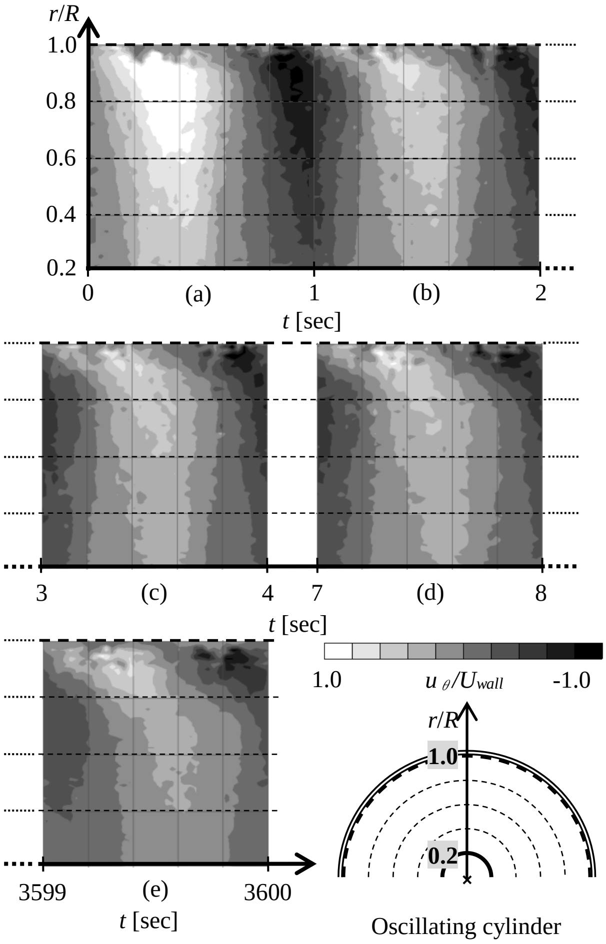

Figure 3: Spatio-temporal velocity distributions changing with spin-cycle time and schematic illustration of the cylindrical configuration

With the assumption of axisymmetric, one-directional flow in the azimuthal direction, the spatio-temporal velocity map obtained by UVP can be converted into radial-temporal distribution of the azimuthal velocity component. In Fig. 3, the vertical axis indicates the radial positions normalized by radius of the cylindrical container (= R) and the horizontal axis indicates the spin-cycle time. The shades of black-and-white represent the spatio-temporal distribution of the azimuthal velocity normalized by maximum azimuthal velocity at the cylinder wall, U_{wall} (= $2\pi fR$). Oscillation of the azimuthal velocity propagates from the wall to center of the cylinder as a damping wave.

As shown in Fig. 3, phase lag from the cylinder wall to inner suspensions occurs on the velocity distribution. Since the suspensions have thixotropic behaviors such as decreases of viscosity by shear stress, the phase lag appears as the time-dependent viscosity decrease in the suspensions by shear stress oscillating the cylinder wall. To quantify and clarify the phase lag, the velocity distributions were analyzed by time-directional discrete Fourier transform (DFT) for 1 s measurement. The analysis results are shown in Fig. 4. The axes represent the radial positions normalized by R and the phase lag of the local velocity fluctuations from a cylinder wall. Different symbols labelled (a) to (e) represent time steps corresponding to spatio-temporal velocity map in Fig. 3.

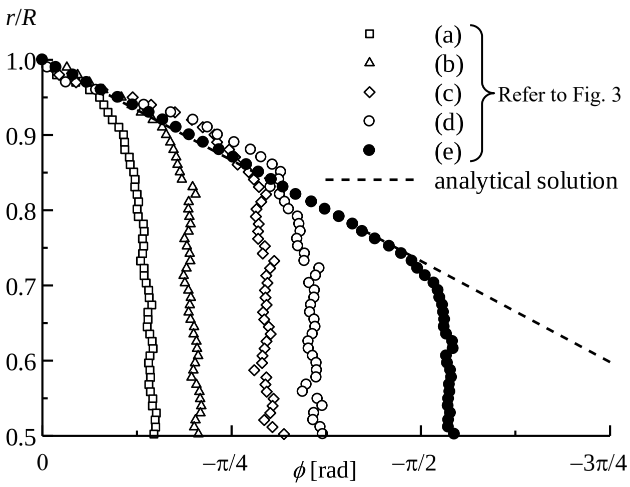

Figure 4: Phase lag of the local velocity fluctuations from a cylinder wall for different waited cycles

In the result of (a) in Fig. 4, the phase lag has almost constant value except near the wall, r/R = 1.0. With increasing oscillation time, however, the curve of the phase lag from the cylinder wall changes progressively. This is because the viscosity of suspensions in the cylinder was decreased by shear stress acting on the fluid from the oscillating cylinder. Eventually, the curve of the phase lag converges at time step (e). Also information included in Fig. 4 is the dependence of viscosity on a gradient phase lag from the cylinder wall. This result is shown in short dash line of Fig. 4. The line was provided by comparing analytical solution in Newtonian fluids [6] and the best given gradient of phase lag at $0.8 < r/R < 1.0$ by least squares method. By this methodology, we obtained the viscosity, μ = 0.489 Pa・s. This methodology is based on the assumption that behavior of test fluids is nearly that of Newtonian fluids. In addition, these results can be used to distinguish physical properties such as yielded and un-yielded region. A knee in the curve as shown in each plots of Fig. 4 has been suggested to indicate a boundary between yielded and un-yielded region.

In a past study [9], the value was estimated as 0.528 Pa･s using a conventional rheometer. One of the uncertainties of this measurement is estimated as 20 % measurement error, and it is thought to be due to the influences by shear banding, slip on the wall, and so on [10]. Since the viscosity value obtained by our rheometry is observed by velocity distributions of experimental results, this value is superior to the viscosity value from results obtained by the conventional rheometer.

Furthermore, to discuss deeply, we focus here on only the analysis result of Fig. 4 (e). In the Fig.4, the phase lag of the experimental and analytical results coincides with the curve approximately above 0.7 < *r*/*R*. Therefore, it is reasonable to assume that the viscosity of test fluids behaved like Newtonian viscosity in the region, which is defined as the pure viscous region. Here it is possible to use Newton's law of viscosity for this region. The law is given by

$$\tau(r,t) = \mu\left(\frac{\partial u_\theta(r,t)}{\partial r} - \frac{u_\theta(r,t)}{r}\right). \quad (2)$$

By using the law for measurement results of the velocity distribution, it is possible to measure shear stress distribution only in the range of this region. In Fig. 5, the vertical axis indicates the radial position normalized by radius of cylindrical container (= *R*) and the horizontal axis indicates shear stress τ. Here plots of maximum shear stress value at each radial point in the time series are shown in Fig. 5. We compare the experimental results to the result obtained by analytical solution applying estimated viscosity. Near the cylinder wall, they do not agree with the curve and plots because of high velocity fluctuations. In contrast, near the cylinder center, they mostly coincide with the curve and plots.

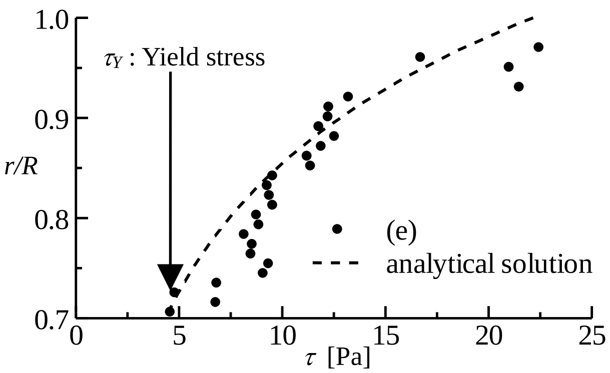

Figure 5: Radial profile of maximum shear stress detected

As written above, these results can be used to distinguish physical properties such as yielded and un-yielded region. Therefore, there are boundary regions between yielded and un-yielded region and for this experimental condition, the boundary region is present in the vicinity of *r*/*R* = 0.7. From Fig. 5, the shear stress value at *r*/*R* = 0.7 may suggest the yield stress value of the suspension, τ_Y = 4.57 Pa. This is indicated by the arrows in Fig. 5. Thus, even though it is difficult to evaluate the yield stress value for conventional rheometer, our rheometry has the ability to measure this value.

4. Conclusions

We proposed a novel methodology using UVP to quantitatively evaluate various rheological properties of complex fluids in a cylindrical vessel with unsteady rotations. Oscillation of the azimuthal velocity propagates from the wall to center of the cylinder as a damping wave. In this study, a montmorillonite suspension which has various complex behaviors was used to demonstrate as test fluids. Since the suspensions have thixotropic behaviors such as decrease of viscosity by shear stress, the phase lag appears as the time-dependent viscosity decrease in the suspensions affected by shear stress due to oscillating the cylinder wall. In this experimental result, viscosity was estimated as μ = 0.489 Pa･s. This value may be more reliable than that determined by a conventional rheometry because of inverse problem algorithm such as measuring from velocity fluctuations. Since the phase lag of the experimental results agrees well with analytical solutions assuming ideal Newtonian viscosity in a range of 0.7 < *r*/*R*, it is reasonable to assume that the viscosity of test fluids behave like Newtonian viscosity in the region, which is defined as the pure viscous region. Thus shear stress distributions were measured using Newton's law of viscosity for this region. In addition, since there are boundary regions (*r*/*R* = 0.7) between yielded and un-yielded region and for this experimental condition, the shear stress value τ at r/R = 0.7 may suggest the yield stress value τ_Y of the suspension. In this experimental result, the yield stress value τ_Y obtained are as follows: τ_Y = 4.57 Pa.

References

[1] Divoux T, *et al.*: Shear banding of complex fluids, Annu. Rev. Fluid Mech., 48:81-103 (2016).

[2] Rodrigez-Gonzalez F, *et al.*: Rheo-PIV analysis of the slip flow of a metallocene linear low density polyethylene melt, Rheol. Acta., 49:145-154 (2010).

[3] Shiratori T, *et al.*: Ultrasonic velocity profiling rheometry based on a widened circular Couette flow, Meas. Sci. Technol., 26:085302 (2015).

[4] Takeda Y: Ultrasonic Doppler velocity profiler for fluid flow, Springer, (2012).

[5] Shiratori T, *et al.*: Development of ultrasonic visualizer for capturing the characteristics of viscoelastic fluids, J. Visualization, 16.4:275-286 (2013).

[6] Tasaka Y, *et al.*: Estimating the effective viscosity of bubble suspensions in oscillatory shear flows by means of ultrasonic spinning rheometry, Exp. Fluids, 56:1867 (2015).

[7] Haward A B: Thixotropy – a review, J. Non-Newtonian Fluid Mech. 70.1:1-33 (1997).

[8] Abend S & G Lagaly: Sol–gel transitions of sodium montmorillonite dispersions, Applied Clay Sci, 16.3:201-227 (2000).

[9] Suzuki K, *et al.*: Factors affecting to the viscosity of montmorillonite/water suspension: 2. Relationship between aspect ratio of montmorillonite particles and viscosity of aqueous suspensions, 50.3:162-174 (2012).

[10] Shimizu M & Sato F: Repeatability and reproducibility on measuring of viscosity (Properties of instruments), Miyazaki prefecture foods development center study report, 54:9-14 (2009).