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Characterization of Non-Newtonian Fluids

Introduction

Flow behavior of complex fluids is traditionally characterized employing either sophisticated rheometers or conventional viscometers. The former require profound understanding of the equipment and careful examination of the measurements. Moreover, rheometers tend to be very expensive. On the other hand, conventional viscometers are less refined and often function as viscosity indexers without proper characterization of shear rate and viscosity. RheoSense's *m*-VROC® technology offers a precise and cost effective alternative solution to characterize viscosity of both Newtonian and non-Newtonian fluids. *m*-VROC® precision rivals that of a rheometer and yet it presents straightforward operation and results analysis.

In this application note, we test our system against a certified non-Newtonian standard. Additionally, we present evidence of non-Newtonian behavior in water/cellulose solutions that are commonly used in biopharmaceutical applications. Finally, we review how our technology provides measurements of true viscosity.

Test Materials & Applications

Standard Reference Material (SRM) 2490 (NIST) is a solution of Polyisobutylene in 2,6,10,14-Tetramethylpentadecane which displays a well characterized and certified non-Newtonian shear thinning behavior (i.e. viscosity decreases as shear rate increases).

Methocel™ (Dow Chemical) are mixtures of water-soluble methylcellulose and hydroxypropyl methylcellulose polymers. They are derived from pine pulp and used as thickeners, binders, film formers and for water retention. They also function as suspension aids, protective colloids and emulsifiers.

Testing Protocol:

1. Loading: Test sample is loaded into a syringe and mounted into the syringe pump.
2. Measuring: Using *m*-VROC® software, viscosity is measured as a function of shear rate and/or temperature. For all tested materials displaying a shear-dependent viscosity, the Weissenberg-Rabinowitsch-Mooney (WRM) correction is applied to obtain "true shear rate" and "true viscosity".
3. Cleaning: An appropriate cleaning solvent is run through the flow path between different samples and after testing.

Non-Newtonian Standard

In Figure 1, we present viscosity as a function of shear rate for SRM 2490. A clear non-Newtonian shear thinning behavior is observed (i.e. viscosity strongly decreases with increasing shear rate).

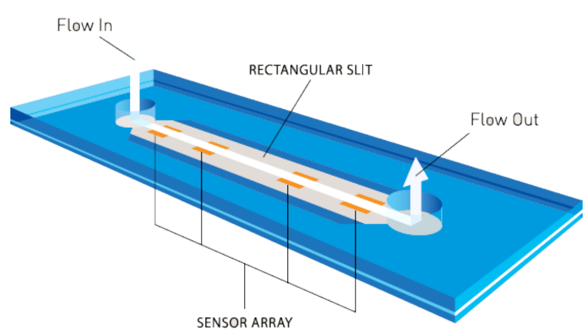
BENEFITS OF *m*-VROC® SOLUTION

m-VROC® offers precise shear viscosity measurements with small sample volume requirements and a wide dynamic operating range. High accuracy and repeatability makes it ideal for R&D and QC applications.

Features include:

- Accuracy: 2% of reading.
- Repeatability: 0.5% of reading.
- Smallest sample volume.
- Shear Viscosity range: 0.2 – 100,000 mPa-s.
- Shear Rate range: 0.5 -1,400,000 s^{-1}
- Temperature control: 4-70°C

VROC® Technology and Principle of Operation



RheoSense's *Viscometer-Rheometer-on-a-Chip* (VROC®) combines a microfluidic channel with a MEMS pressure sensor array to measure viscosity. As the test fluid flows through the channel the sensor array captures the pressure drop, which is proportional to the shear stress at the wall. The shear rate is calculated from the flow rate and the channel dimensions. The viscosity of the test fluid is obtained as the ratio of shear stress to shear rate.

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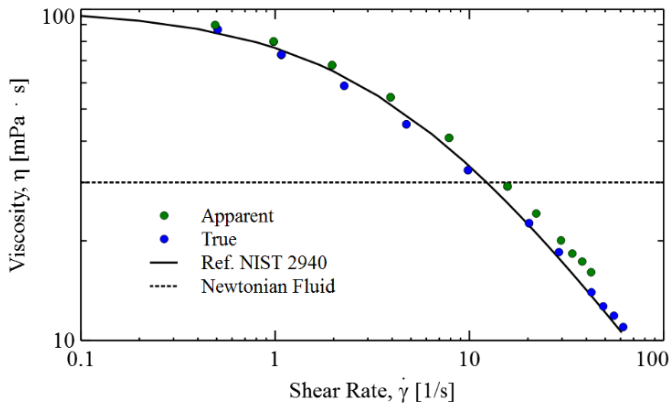

Figure 1. Characterization of a non-Newtonian standard using *m*-VROC®. Measurements of apparent viscosity (green) and true viscosity (blue) compared to certified NIST certified viscosity non-Newtonian standard 2490 (solid black). The behavior of an ideal Newtonian fluid is given by the dashed line.

For non-Newtonian fluids, the viscosity dependence on shear rate causes the velocity profile inside the VROC® channel to be non-parabolic. In that case, the true shear rate at the wall $\dot{\gamma}$ is necessary to obtain true viscosity as:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

where τ is the shear stress at the wall, which is measured precisely by *m*-VROC®. Using the WRM correction the true shear rate at the wall is obtained as [1]:

$$\dot{\gamma} = \frac{\dot{\gamma}_{app}}{3}\left(2 + \frac{d\ \ln \dot{\gamma}_{app}}{d\ \ln \tau}\right) \qquad (2)$$

where apparent shear rate $\dot{\gamma}_{app}$ is given by the flow rate and the microfluidic channel dimensions. More details on the WRM correction are given in the Appendix.

As anticipated, the correction improves the agreement with the reference viscosity profile (see Figure 1). The dashed line shows the typical behavior of a Newtonian fluid (i.e. Viscosity is independent of shear rate). These results confirm not only the high accuracy of VROC® technology but also its suitability for the characterization of the viscosity of both Newtonian and non-Newtonian fluids.

Cellulose Water solutions

As shown for SRM 2490, non-Newtonian fluids can present significant dependence of viscosity on shear rate. However, it is important to note that this dependence might not be observed at low or moderate shear rates. For some systems, non-Newtonian effects might only appear at high shear rates [2]. Therefore, testing the viscosity of these fluids at shear rates that are relevant for the specific application is essential for the proper characterization of viscosity that is needed for process modeling. Table 1 presents a collection of common applications and their associated shear rates.

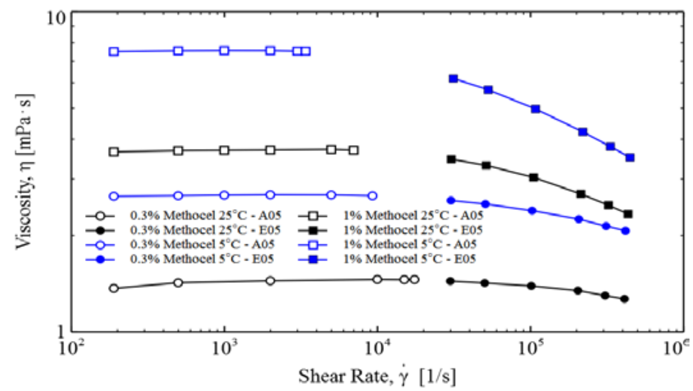

Figure 2. Measurements of true viscosity versus true shear rate for 0.3% (circles) and 1% (squares) Methocel™ water solutions. Samples were tested at 5°C (black) and 25°C (blue) for a wide range of shear rates (200-400,000 1/s) using A05 (open) and E05 (filled) VROC® chips. Comparison of measurements between chips shows excellent agreement.

Table 1. Common applications and characteristic shear rates. *m*-VROC® can measure viscosity between $\mathbf{0.5}$ and $\mathbf{1.4{\times}10^6}$ [1/s].

Application	Shear rate [1/s]
Sag and Leveling	10^{-2}-10^{0}
Flow coating, mixing	10^{0}-10^{2}
Brushing, roll coating	10^{2}-10^{4}
Injectability, Lubrication	10^{4}-10^{7}

In Figure 2, we present results for two different concentrations of Methocel™ at two different temperatures. As expected, viscosity decreases with increasing temperature. We tested two different shear rate ranges and observed that at low shear rates Methocel™ solutions act as Newtonian fluids while at high shear rates they display non-Newtonian behavior.

As a result of the small scale of the flow channel, *m-VROC®* allows measurement of viscosity at much higher shear rates than what is achievable with conventional rheometers, for which shear rate is limited by the appearance of flow instabilities [1].

Summary

In this technical note, we demonstrate *m*-VROC® suitability for the characterization of complex fluids over a wide range of (3)
shear rates. Our technology is able to successfully reproduce the shear rate-dependent viscosity of a certified non-Newtonian standard. VROC® technology is a powerful tool in the rheological characterization of the behavior of fluids at high shear rates that are not accessible by convectional rheometers and viscometers. As an example of *m*-VROC® capabilities, we present results for two cellulose water solutions present in many applications.

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Appendix: WRM Correction Protocol

m-VROC® software includes an optional feature to automatically apply WRM correction and obtain measurements of true viscosity. The only requirement is to perform measurements of viscosity at three or more shear rates. However, some applications might require comparison of viscosity at specific shear rates (i.e. compare different samples). In this appendix, we present the steps necessary to obtain true viscosity at specific/target shear rates from the shear stress and apparent shear rate measurements that result from a shear rate sweep.

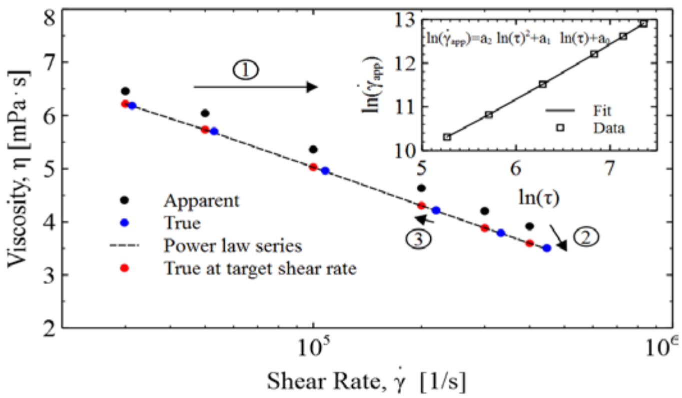

Figure A1. Shear thinning measurements of viscosity on 1% Methocel solution. Apparent viscosity results (black circles) are corrected to (steps 1&2) true viscosity results (blue circles) using WRM correction in Eqns. 1 and 2. The corrected true viscosity is fitted to a power law series that is used to obtain true viscosity at the target shear rates (step 3).

First we perform a rate sweep using *m*-VROC® software automatic function (See Figure A1). Ideally, we want to cover a slightly wider range of shear rates than the one covered by the target shear rates.

Then, we use shear stress and shear rate from the results report to create the inset in Figure A1 (step 1). We fit these results to a second order polynomial and obtain from it the first order derivative of the logarithm of the shear rate with respect to the logarithm of the shear stress:

$$\frac{d \ln \dot{\gamma}_{app}}{d \ln \tau} = 2a_2 \ln \tau + a_1$$

To obtain true shear rate, we apply the WRM correction in Eq. (2). True viscosity is then calculated using Eq. (1). Note that the correction is done through the shear rate. As a result, the obtained true viscosity values (blue circles) are displaced to the right (step 2 in Figure A1).

Finally, we fit a power law (or power law series) to the true viscosity data and apply this law to calculate viscosity at the target shear rates (step 3 in Figure A1).

References

[1] C. Macosko, Rheology: Principles, Measurements and Applications, Wiley, 1994.

[2] C. J. Pipe, T. S. Majmudar and G. H. McKinley, "High Shear Rate Viscometry," *Rheol. Acta,* 2008.