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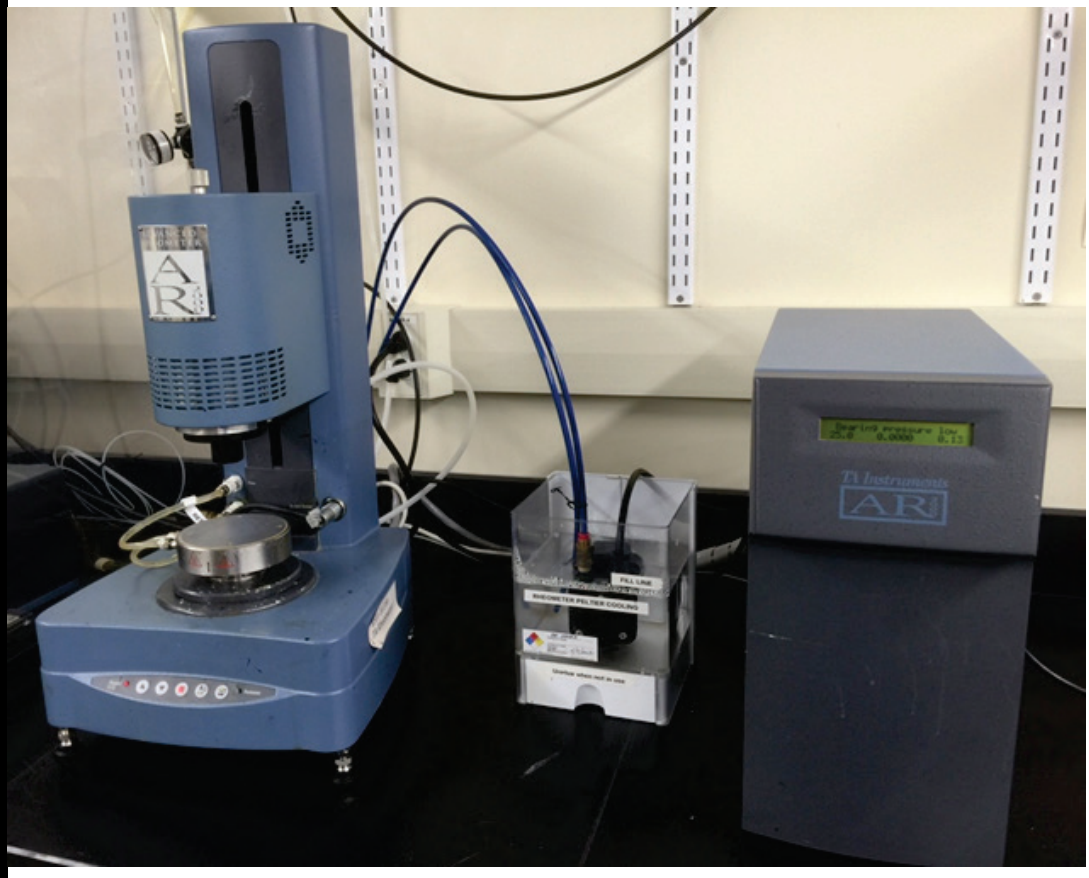
Environmental Consequences of Nanotechnologies

Determination of Nanomaterial Viscosity and Rheology Properties Using a Rotational Rheometer

Qihua Wu, Kathryn Kremer, Stephen Gibbons, and Alan J Kennedy

April 2022



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Abstract

Rheology studies the flow of matter and is one of the most important methods for materials characterization because flow behavior is responsive to properties such as molecular weight and molecular weight distribution. Rheological properties help practitioners understand fluid flow and how to improve manufacturing processes. Rheometers have been extensively used to determine the viscosity and rheological properties of different materials because the measurements are quick, accurate, and reliable. In this standard operating procedure, a general protocol using a rotational rheometer is developed for characterizing rheological properties of nanomaterials. Procedures and recommendations for sample preparation, instrument preparation, sample measurements, and results analysis are included. The procedure was tested on a variety of carbon-based nanomaterials.

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Preface

This Standard Operating Procedure (SOP) was developed under Task 2: "Materials process development and characterization" of project "Advancing Carbon Nanomaterials-Based Device Manufacturing through Life Cycle Analysis, Risk Assessment and Mitigation", also known as "SafeRapidNano". The technical monitor was John Ballard (CEERD-EZT). This program was funded by the Engineer Research and Development Center (ERDC) of the U.S. Army Corps of Engineers (USACE), contract number W912HZ-15·2-0032. The program manager was Alan J Kennedy. This work was directed by Rishi J. Patel, Senior Research Scientist at Missouri State University's Jordan Valley Innovation Center. This task is under the direct supervision of Dr. Wu-Sheng Shih, Brewer Science, Inc.

The work was performed by the Environmental Risk Branch (ER-R) of the Environmental Processes Division (EP), U.S. Army Engineer Research and Development Center, Environmental Laboratory (ERDC-EL). At the time of publication, James H. Lindsay was Chief, CEERD-EP-R; Warren Lorentz was Chief, CEERD-EP; and Dr. Elizabeth Ferguson, CEERD-EZT was the Technical Director for Environmental Quality and Installations. The Deputy Director of ERDC-CERL was Dr. Brandon Lafferty and the Director was Dr. Edmond Russo.

COL Teresa A. Schlosser was Commander of ERDC, and Dr. David W. Pittman was the Director.

1 Introduction

This Standard Operating Procedure (SOP) describes how to determine the viscosity and rheological properties of nanomaterials using a rotational rheometer.

Viscosity is a principal parameter for any flow measurement of liquids, solids, and gases. Knowing a material's viscosity and rheological properties is valuable in predicting its behavior during the manufacturing process, and in predicting the performance during a dipping or coating operation. It is also useful in developing the proper procedures for handling and use of materials. Many manufacturers have regarded viscosity measurements as a crucial part of their research, development, and quality control programs (Dealy et al. 2000; Advani 1994; Tabilo-Munizaga et al. 2005).

Background

Rheology describes the deformation of matter, including solids, liquids, or gases, under the influence of stresses (Schowalter 1978). The resistance of a fluid against any irreversible positional change of its volume is defined as viscosity. This resistance becomes apparent when a layer of fluid is made to move in relation to another layer. The amount of force required to move the fluid against the resistance is called shear (Schramm 1994). Isaac Newton was the first to describe this basic law of viscosity

$$\frac{F}{A} = \eta \times \frac{dv}{dx} \tag{1}$$

The term F/A indicates the force per unit area required to produce the shearing action and is referred to as shear stress. Its unit of measurement is dynes per square centimeter (dynes/cm^2). The term η is the apparent viscosity for a given material. The velocity gradient, dv/dx, is a measure of the change in speed at which the intermediate layers move with respect to each other. The term dv/dx describes the shearing the liquid experiences and is thus called shear rate. Its unit of measure is the reciprocal second (s^{-1}).

Thus viscosity (η) can be defined mathematically by

$$Viscosity\ (\eta) = \frac{Shear\ stress\ (\frac{F}{A})}{Shear\ rate\ (\frac{dv}{dx})} \quad (2)$$

To measure viscosity, shear stress and shear rate need to be defined first. Rheometers are operated in both controlled stress and controlled shear rate (which provides a more general capability for rheological evaluation of flow behavior). In a rheometer, the sample is placed in a stationary container and a spindle (referred as the geometry) is attached to the motor. Rotation speed or force (shear stress) of the spindle can be controlled by the motor while the other factor is measured by the instrument. Controlled stress tests are specifically applicable to direct measurement of yield stress and creep. Yield stress measurement can determine the force needed to initiate flow, whereas creep testing measures the flow behavior under a constant force.

Rheometers have been widely used to determine viscosity and rheological properties of many types of samples, including printable inks (Blayo et al. 2001; Phair et al. 2009; Smith et al. 2006; Tuladhar et al. 2008). Phair et al. (2009) measured thixotropic (time-dependent shear thinning) characteristics of concentrated zirconia inks for screen printing by rheometry and imaging methods. A combination of viscosity and yield stress measurements, and creep and recovery analysis were performed by rheometer, and were utilized to assess ink thixotropy (Phair et al. 2009). Smith et al. (2006), characterized low-temperature conversion of conductive silver inks by using a rotational rheometer.

Objectives

The objective of this SOP is to define the operating procedure for measuring the viscosity and rheological properties of nanomaterials using a rotational rheometer.

Scope

This SOP can be applied for measuring apparent viscosity and determining rheological properties, such as shear thinning and thixotropic properties, of nanomaterial solutions using a rotational rheometer. Measurable samples include nanomaterial solutions, solids, or semi-solids. The operation procedure of a TA Instruments AR2000 rheometer is included as an example.

2 Terminology

Related documents

- ASTM D2196 (2015) *Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational Viscometer*.
- ASTM D7867 (2013) *Standard Test Method for Measurement of the Rotational Viscosity of Paints, Inks and Related Liquid Materials as a Function of Temperature*.
- Instrument operation manual provided by the instrument's manufacturer (e.g., TA Instruments AR2000 Rheometer manual).

Definitions

- Dynamic Viscosity: This term expresses a fluid's resistance to shearing flows, where adjacent layers move parallel to each other with different speeds.
- Kinematic Viscosity (also known as momentum diffusivity): This term is the ratio of the dynamic viscosity to the density of the fluid.
- Newtonian Fluid: This term describes a fluid in which the viscous stresses arising from its flow, at every point, are linearly proportional to the local strain rate (the rate of change in its deformation over time).
- Non-Newtonian Fluid: This term describes a fluid having a variable viscosity, depending on applied stress or force.
- Shear Rate ($\dot{\gamma}$): This symbol is the rate at which a progressive shear deformation is applied to the material.
- Shear Stress (τ): This symbol is defined as the component of stress with a material cross section.
- Thixotropic Mixture: This term describes a mixture that will become less viscous over time when introduced to a steep change in shear rate and then will take a fixed time to return the equilibrium viscosity.

3 Materials and Apparatus

Materials

- Nanomaterial samples
- Deionized (DI) water
- National Institute of Standards and Technology (NIST)-traceable viscosity standard (available from various vendors)
- Calibrated rotational geometry (different sizes and types available from various vendors)
- Plastic spatula for sample handling
- Disposable pipette for sample handling
- Paper towels for cleaning purposes

Apparatus

Rotational rheometer with the following capabilities: 1) performs unidirectional rotational displacement to the sample, 2) accurately and precisely measures the torque developed by the sample to the rotational displacement, 3) collects and analyzes data, and 4) measures temperature and has a unit to control the temperature within desired range and precision (e.g., TA Instruments AR2000 Controlled-Stress Rheometer with Peltier plate temperature control).

4 Procedure

Experiment preparation

Sample preparation

Most liquid samples can be tested without modification. Ensure that the selected sub-sample is representative of the entire specimen, shake or vortex the sample if necessary to ensure homogeneity. Most solid samples can also be directly tested with special geometries, such as rectangular torsion geometry. If samples need to be pretreated (such as with heat or mechanical treatment) prior to testing, record the treatment in the proper notebook.

Instrument preparation

Selecting measuring geometries

The following types of geometries (spindles) are commonly available: 1) cone and plate, 2) parallel plate, and 3) cup and bob. Each type has its own advantages and disadvantages. This list is non-exhaustive.

Cone and plate geometries may be preferred in some cases due to their wide viscosity measurement range AND uniform strain and shear rates across the test geometry. The measured viscosity is determined by the cone diameter and angle geometry. Cone and plate geometry is not, however, recommended when performing temperature sweeps because the thermal expansion of materials may introduce errors as this type of geometry is sensitive to gap changes. Also, materials with a high concentration of solids (or in semi-solid form) tend to be expelled from the gap at high shear rate testing, therefore, cone and plate geometries should be avoided for those types of materials.

The parallel plate geometry is suitable for most applications. It is easy to clean and requires only small sample volumes (depending on the size of the geometry). The parallel plate geometry is not as sensitive to gap settings as cone and plate geometry. Thus, parallel plate geometry is ideal for testing samples through temperature gradients as minimal or no compensation is needed for gap changes caused by material thermal expansion. Corrections are needed for shear rate sweeps. It may be used for samples with suspended solids.

The cup and bob geometry type has different shapes of spindles, is generally more difficult to clean, and requires large sample volumes. Advantages include better sensitivity for low-viscosity materials (such as low-concentration nanomaterial solutions).

The proper geometry needs to be selected before starting the experiments. For thick nanomaterial paste or solid samples, a parallel plate may be selected. For low-viscosity materials, a cup and bob type is best. Be sure to check the measurement range of the selected geometry. Small-sized geometries should always be used for thick samples.

Instrument start-up and calibration

Switch on the instrument power and open the control software. Ensure the instrument is functioning correctly per directions. Set the desired measurement temperature in the control software. The rheometer needs to be calibrated before use and between each geometry change while in use. Follow the instrument operation manual for the detailed calibration procedure (e.g., TA Instruments AR2000 rheometer manual). Use NIST-traceable standards for calibration and verification.

After calibration, set up the proper method based on what needs to be measured. Generally, there are two types of characterization for viscosity. The first one is stepped shear stress/shear rate, and the second is ramped shear stress/shear rate. In the stepped shear method, individual shear values are selected and each shear is applied for a set time. Shear rate, shear stress, and viscosity are recorded. In the ramped shear method, the shear is increasing or decreasing continuously and measures are taken at defined time intervals through the shear gradient.

Sample analysis

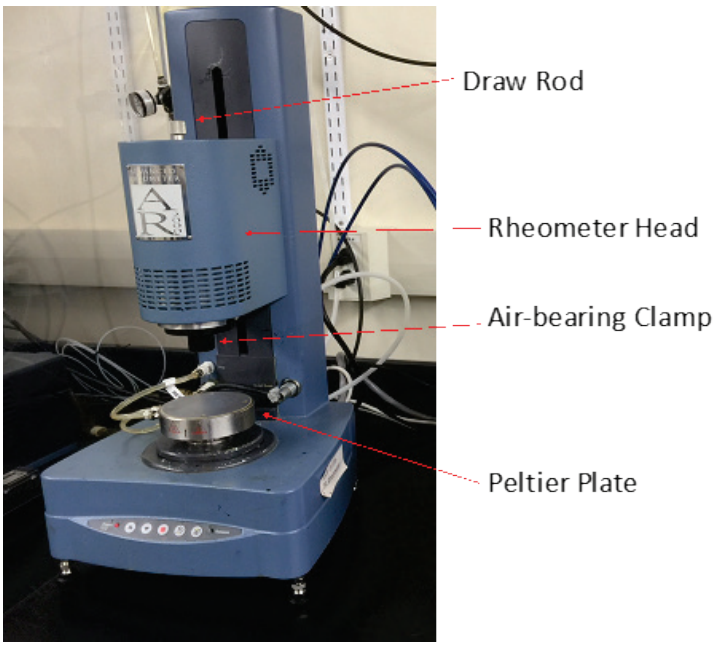
This section describes the general operation procedure of a TA Instruments AR2000 rheometer as an example for sample analysis.

Start-up

Connect the Peltier cooling pump power source and turn on the compressed air. The pressure gauge should read 30 pounds per square inch (psi). Remove the air-bearing clamp (which covers the drive shaft and draw rod) by turning the knob counterclockwise (Figure 1.). Ensure that

the red power light on the instrument is illuminated. If it is not, turn on the power button on the back of the electronics control box. Ensure that the Peltier cooling pump is submerged in DI water to the line indicated on the submersion tub.

Figure 1. TA Instruments AR2000 rheometer.



Log into the computer and load the "TA Rheology Advantage" shortcut. Click on the AR2000 tab on the right side of the screen and enter the required temperature, ensuring that the temperature remains constant while the other values are continually changing. Load the appropriate measuring geometry in the software by selecting it under the "**Geometry**" tab at the top of the screen.

Instrument parameters

Select the desired testing method in the software under the "Method" tab. Table 1 shows an example of available methods for various types of printable nanomaterial samples.

Table 1. Example of AR2000 rheology methods.

Methods	Ink Printing Type	Typical Geometry
10HzHold_10min	• Ink jet • Aerosol Jet® • Drawbar	• 60-mm 2° aluminum cone • 40-mm aluminum parallel plate
2HzHold_10min	• Ink jet • Aerosol Jet® • Drawbar	• 60-mm 2° aluminum cone • 40-mm aluminum parallel plate
ScreenPrint_Hold	• Screen	• 25-mm aluminum parallel plate

Instrument inertia can be calibrated via the following path: "Options" tab → Instrument → "Inertia" tab → Calibrate → Next. Once the Instrument Inertia is calibrated, attach the appropriate measuring geometry by turning the knob clockwise.

Calibrate the geometry inertia via the following path: Geometry Name → Settings → Calibrate → Next.

Calibrate the air bearing friction via the following path: "Options" tab → Instrument → "Miscellaneous" tab → Calibrate (next to bearing friction) → Next.

Once all calibrations are completed, zero the geometry gap by clicking the control button in the software. Lower the geometry until the lower end touches the Peltier plate, then raise the head with geometry. Perform rotational mapping by selecting "Instrument rotational mapping" from the icon bar on the left side of the screen and select "Perform mapping" when the Rotational Mapping dialog box appears.

Perform measurement

Load the appropriate amount of the sample so that the geometry will rest using a disposable 1 milliliter (ml) pipette (for low-viscosity materials) or a small plastic spatula (for high-viscosity materials). Lower the geometry to a set gap once the sample is loaded. If the sample spreads outside the geometry area, wipe away the excess material using a paper towel and/or a plastic spatula. If necessary, raise the geometry to the back-off distance and wipe the excess from the edge of the geometry and/or increase the sample amount. Once the sample is correctly loaded, the measurement can be started.

Shut-down

When measurement is completed, raise the geometry by clicking the "Raise head" icon in "TA Rheology Advantage." Save the results and close the program. Clean the Peltier plate by wiping with a paper towel and any necessary solvent. Remove the geometry by turning the knob counterclockwise. Clean with a paper towel and any necessary solvent (e.g., DI water). Replace the air-bearing clamp (Figure 1) by turning the knob clockwise, and turn off the compressed air.

5 Reporting

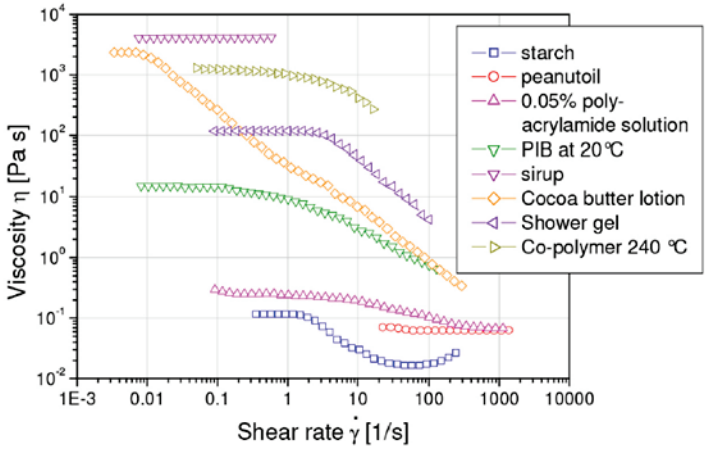
Results analysis and report format will vary for different types of instruments and software. Refer to ASTM D2196 for raw data calculation and interpretation. This section demonstrates results analysis for data obtained by TA Instruments, AR2000 rheometer.

Analysis of results

When the run is complete, minimize the screen and open "Rheology Data Analysis." Select the "File" tab and choose "Open" to locate the folder in which the results were saved. Double-click the file to open it. The file name will appear on the left side of the screen. Double-click the file name to open the graph of the file. Select the "View" tab and choose "Table" to view the tabulated data from the graph. Record the data in the appropriate notebook or report form.

Figure 2 illustrates an example of viscosity vs. shear rate results for different types of materials (Franck 2004). From the plot, some materials such as polymer solutions (polyisobutylene, shower gel, and polyacrylamide solution) do not behave linearly and do not have a yield stress. These materials appear to be shear thinning and are considered pseudoplastic. Starch is another example of a non-Newtonian fluid that shows both shear thinning and shear thickening depending on the shear rate range. When starch is slowly stirred, that is, it is undergoing a low shear rate, the starch suspension will look milky, and when it is stirred at a high speed, it will become thicker.

Figure 2. Viscosity versus shear rate for different types of materials (Franck 2004).



QA/QC Considerations

To ensure the quality of data, the instrument should be calibrated and NIST-traceable standards should be measured routinely. Refer to the manufacturer's operating manual for the calibration procedure. Duplicated runs can be performed to estimate reproducibility from the standard deviation. However, there is no general specification or controlled range that applies to all samples and rheometers.

6 Summary

Viscosity and rheology properties of nanomaterials are of great interest and value for industrial manufacturing and applications. This SOP describes the use of a rotational rheometer to determine viscosity and rheological properties of nanomaterial samples. A general procedure and considerations for specimen preparation, instrument preparation, sample testing, and results analysis are included. The operation procedure of a TA Instruments AR2000 rheometer is also included as an example. The SOP can be used for most nanomaterials solutions, and semi-solid, and solid samples.

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14. ABSTRACT

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