Rheological Techniques for Yield Stress Analysis

Keywords: yield stress, structured fluids, rheology, viscoelastic, viscosity

RH025

ABSTRACT

Yield stress analysis is important for all complex structured fluids. It is helpful to better understand product performance in applications such as product shelf life and stability. In theory, the yield stress is the minimum shear stress required to initiate flow. A number of testing techniques are available for measuring and analyzing the yield stress using a rheometer. Three of these techniques, including Steady Stress Sweep (SS), Steady Rate Sweep from High to Low Shear Rates (SR), and Dynamic Stress/Strain Sweep (DS) are introduced in this paper. The SS method was found to be a good approach for yield stress analysis of medium viscosity materials. The SR method was found to be useful for very low viscosity materials as yield stresses can be measured accurately as low as $4x10^{-4}$ Pa. The DS method was found to be useful over a wide viscosity range and was especially practical for testing high viscosity semi-solid materials such as grease.

INTRODUCTION

Yield stress analysis has been widely used in the food, healthcare, pharmaceutical, and paint industries. Many commercial products, such as emulsions, dispersions, pastes, grease and foams, etc., are formulated to display yield stresses. The yield stress is an important characteristic of structured fluids because it helps stabilizing the material. A higher yield stress prevents the material to undergo phase separation, sedimentation or aggregation. It reduces flow under shipping vibrations and gravity. Yield stress studies can help evaluate the product performance and processability and predict product's long-term stability and shelf life[1-5].

A yield stress in rheology is defined as the applied stress at which irreversible plastic deformation is first observed across the sample. It is usually represented as σ_y. Figure 1 depicts some "theoretical ideal" flow models with a yield stress. However in reality, the value of yield stress will depend on the testing method. Therefore, a measured yield stress should be referred to as an "apparent yield stress". One of the most extensively used method to determine the yield stress is probably the continuous shear stress or shear rate ramp, from low to high stress or rate. The yield stress is usually determined by fitting the stress/rate curves with Bingham, Casson or Herschel-Bulkley models. Also manual extrapolation of the stress curve to zero shear rate (shown in figure 1) is frequently used to obtain a yield stress. In a shear stress (rate) ramp, the yield stress can be determined from the transient viscosity maximum in a double logarithmic plot of viscosity versus stress (Maximum viscosity method). Since these test methods are performed under nonsteady state conditions, the measured yield stress value is highly dependent on the experimental ramp rate.

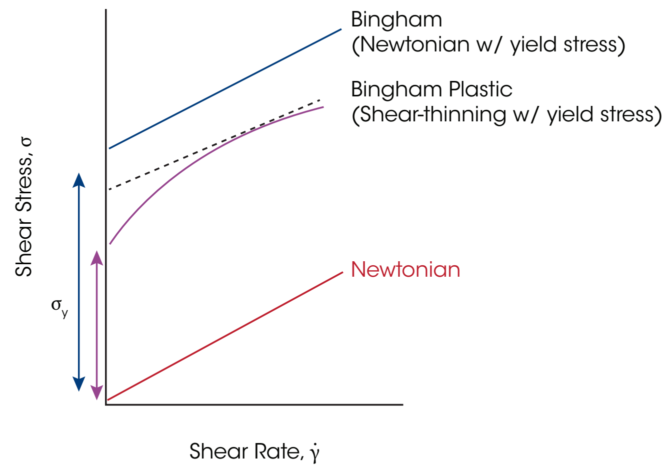

Figure 1: Shear stress- shear rate behavior of some rheological models with a yield stress

In this paper, we introduce three different methods for analyzing the apparent yield behavior of materials using TA Instruments' Combined Motor and Transducer and Separate Motor and Transducer rheometers. The advantages and disadvantages of each analytical technique are also discussed.

STEADY STRESS SWEEP METHOD FOR YIELD ANALYSIS (SS)

A common procedure for yield stress analysis is a steady state stress sweep on a controlled stress rheometer[6-7]. In a SS experiment, a stress or torque is incrementally stepped logarithmically from a minimum value up to a value where the material starts to flow. Each stress is held on the material for a given amount of time. A software algorithm evaluates the data and a data point is taken when the shear rate reaches an equilibrium value. Below the yield point, the change in shear rate with stress is extremely small. The viscosity remains constant with increasing stress and is referred to as the zero shear viscosity. At a given stress, the material starts to flow, the material yields as the viscosity decreases many orders of magnitude over a narrow range of shear stress (Figures 2-5, adapted from Barnes, 2000).

This approach is widely used for analyzing the yield stress of medium viscosity materials. The yield stress value can be obtained either by taking the very last data point before the viscosity starts to drop significantly, or by taking the onset value from the viscosity curve. It should be noted that the accuracy of the yield stress measured will be dependent on the number of points per decade chosen, when programming the test parameters. For example, when choosing five points per decade in a logarithmic sweep, the successive data points will be much further apart than when

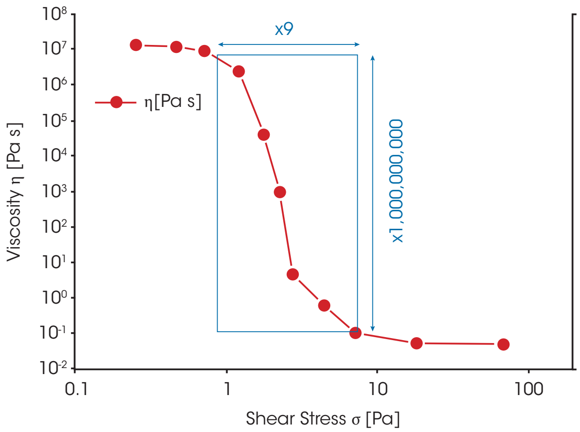

Figure 2: Flow curve of 10% bentonite suspension

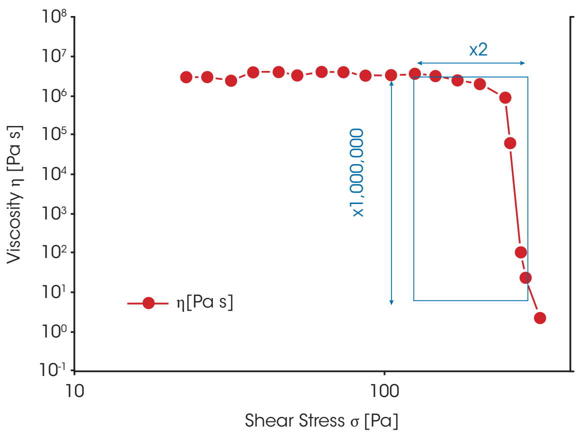

Figure 3: Flow curve of mayonaise

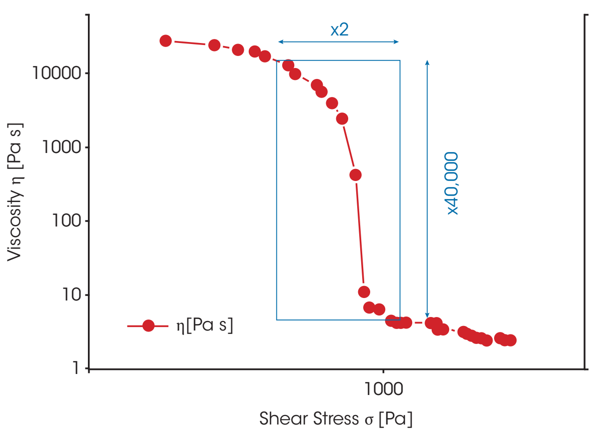

Figure 4: Flow curve of flocculated ink

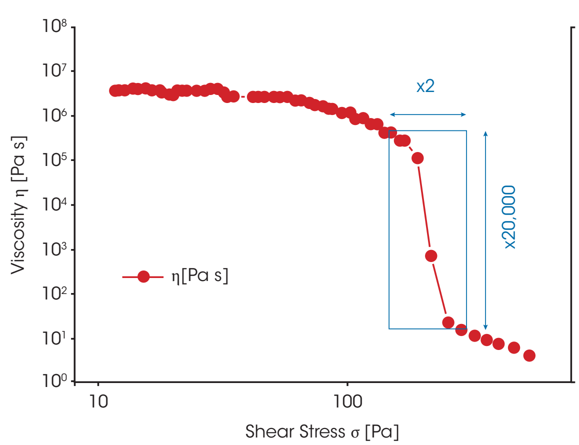

Figure 5: Flow curve of toothpaste

choosing ten points per decade. Therefore, collecting more data points per decade provides a more accurate yield stress, if the material remains stable during the test.

The challenge for the steady state stress sweep method are low and high viscosity materials. The yield stress of some low viscosity suspensions/dispersions (e.g., orange juice) can be extremely low and the smallest incremental amount of stress added might dramatically alter the measured result. In a stress sweep test, it is possible to step beyond the yield stress of the sample from one data point to the next (Figure 6). In addition, while testing high viscosity semisolid materials, such as grease or paste, wall slippage might occur between the geometry and the sample. This greatly affects the measurement accuracy and reproducibility (Figure 7), and is difficult to eliminate even if serrated or crosshatched test fixtures are used. Therefore, two other analytical techniques for yield analysis are discussed and compared to the stress sweep method.

STEADY RATE SWEEP METHOD FOR YIELD ANALYSIS (SR)

Some low viscosity suspensions or dispersions (e.g., orange juice, ink, or milk) have very low yield stress values that require the rheometer to operate close to the low-end torque specification. These yield stress values cannot be easily determined using the stress sweep method, even if small torque increment steps were applied. Furthermore, can loading of the sample damage the weak structure before the test begins.

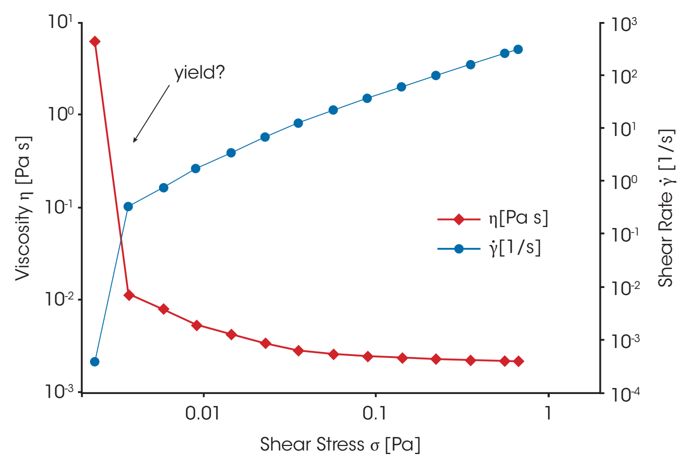

Figure 6: Flow curve of an orange juice

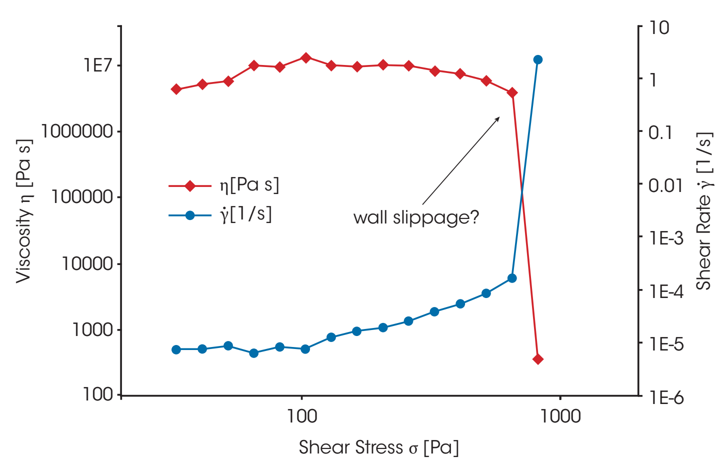

Figure 7: Flow curve of grease

To overcome these limitations, a steady state flow shear rate sweep test can be used to analyze the yield behavior of these materials. When performing this test, the sample can be loaded either onto a cone-plate, parallel plate or cup/bob geometry. The shear rate is controlled during the test, and is stepped down logarithmically from high (e.g., 10 1/s or 100 1/s) to low (e.g., 10^{-5} 1/s) values. When the yield point has been reached, the stress on the sample reaches a plateau and becomes independent of rate. Concomitantly, the "apparent" viscosity (η_a) of the sample goes to infinity with decreasing shear rate (Figure 8 and Figure 9).

The viscosity is defined as:

$$\eta = \frac{\sigma}{\dot{\gamma}} \qquad (1)$$

When $\sigma = \sigma_y$ (yield stress), then

$$\eta_a = \sigma_y \frac{1}{\dot{\gamma}} \qquad (2)$$

and in the double logarithmic plot

$$\log \eta_a = k - \log \dot{\gamma} \qquad (3)$$

the "apparent" viscosity decreases with the rate at a slope of -1.

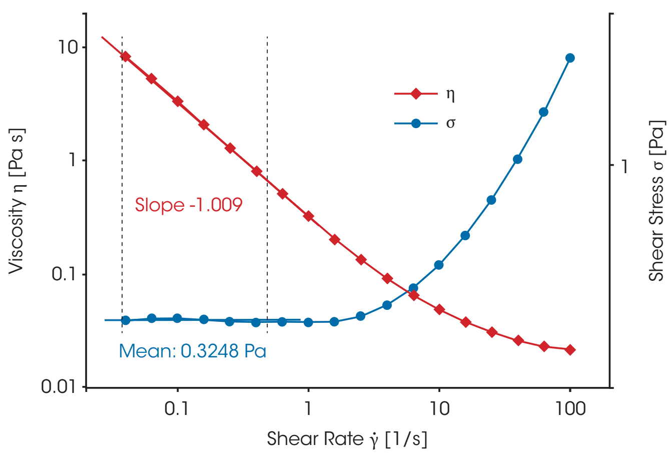

Figure 8: Yield stress analysis of blue ink

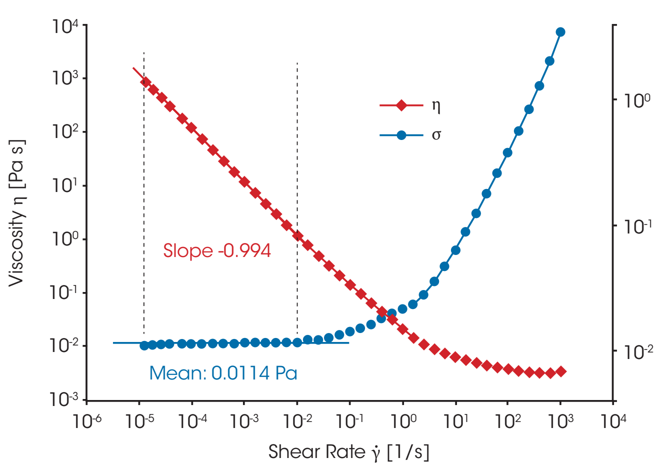

Figure 9: Yield stress analysis of orange juice

The shear rate sweep test can be easily performed on both CMT and SMT rheometers and shows excellent performance when analyzing the yield behavior of low viscosity materials. The benefit of this test method is that by sweeping the shear rate from high to low, all sample history from loading is eliminated. The measurement results show good reproducibility. Table 1 lists the yield stresses of some low viscosity samples. The yield stress can be measured accurately as low as $4x10^{-4}$ Pa.

Table 1: Yield stress of some low viscosity materials

SAMPLE	YIELD STRESS [Pa]	YIELD TORQUE [μNm]
Blue ink	0.3	18.0
Orange juice	0.01	0.6
Fat free milk	0.00044	0.02
Pectin Solution 0.1%	0.04	1.5
Xanthan gum 0.1%	0.01	0.4

DYNAMIC STRESS/STRAIN SWEEP METHOD FOR YIELD ANALYSIS (DS)

The conventional stress sweep test method for determining yield stress is challenged by high viscosity materials such as greases and pastes. With increasing stress wall slippage is observed, even when crosshatched or serrated plates are used. Many publications in the literature deal with the problem of wall slippage during yield stress analysis [8-12]. When slippage occurs, the measured yield stress is lower than the actual yield stress of the sample and the test results are usually poorly reproducible.

The dynamic oscillation stress/strain sweep test is an alternative method to analyze the yield behavior of high viscosity materials. To perform this test, cone-plate or a plate-plate geometries are used predominately. The results are best viewed in a double logarithmic plot of the storage modulus (G') as function of oscillation stress. The yield stress is the critical stress at which irreversible plastic deformation occurs. In figures 10-13 the yield stresses are taken as the onset value of the modulus curves.

The dynamic stress/strain sweep method can be used for materials with wide ranges of viscosities. The test can be performed on both controlled stress and controlled strain rheometers. Since the measurements are mostly done in the linear viscoelastic region of the material, the wall slippage problem is minimized, especially when crosshatched, serrated or sandblasted test fixtures are used. In general the dynamic strain/stress sweep shows excellent reproducibility.

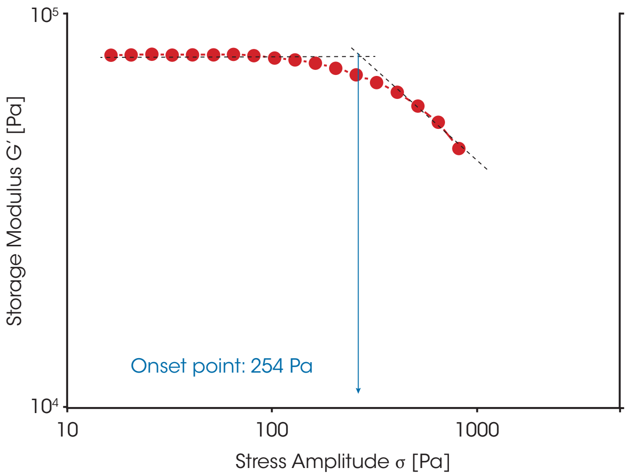

Figure 10: Yield stress of a skin ointment

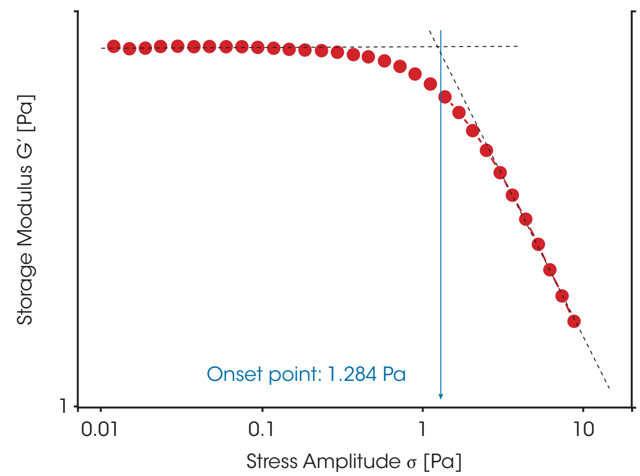

Figure 12: Yield stress of a paint

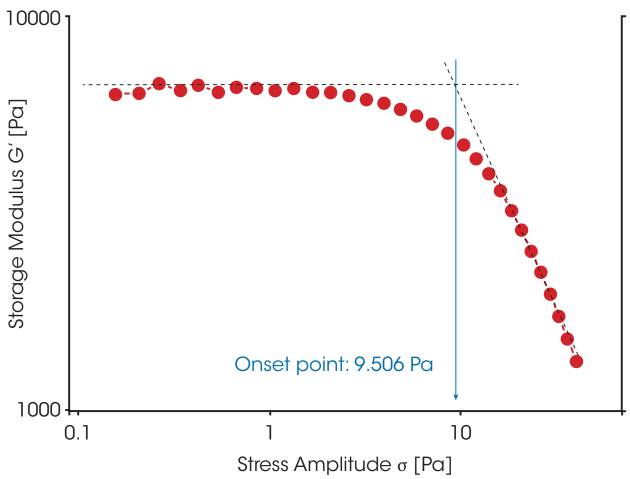

Figure 11: Yield stress of a toothpaste

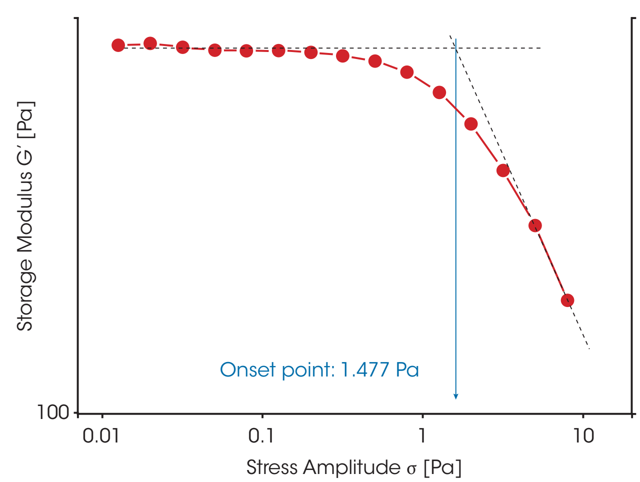

Figure 13: Yield stress of a sun lotion

CONCLUSIONS

Yield stress analysis is important in many areas such as the food, paint, and pharmaceutical industries. The traditional approach to measure yield stress is to run a steady stress sweep experiment on a controlled stress rheometer. This test method performs well for medium viscosity suspensions and dispersions. However, it has certain limitations when testing low and high viscosity materials.

The steady state shear rate sweep method allows good yield stress measurements to be performed with excellent reproducibility on low viscosity solutions.

Dynamic oscillation stress/strain sweeps are another option for yield stress analysis. This method minimizes wall slip effects and provides good measurement reproducibility.

Even though yield stress determinations by different methods give different results and these can only be viewed as "apparent yield stress values", yield stress test methods are still a valuable tool to characterize structured fluids. Yield stress values can be correlated to material processing and end use properties and can be used to rank products' performance. Additionally, yield stress test methods are easily performed within a reasonable time frame, and in general show good reproducibility.

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