Cambridge Polymer Group

Yield Stress Rheometry

By Dr. Gavin Braithwaite

Introduction

Yield stress in solid materials occurs when the material strength is exceeded, and the material permanently deforms. However, in a material where the component molecules are "associated" rather than permanently bound, yield stress is a more dynamic property. In these materials, the yield stress can be rate (speed) and stress (force) sensitive and is frequently vital to the function of the material. Ubiquitous examples would be hair gel, meringue, ointment and adhesives. In all cases, the material will hold its shape until a critical force is applied. If an ointment applied to a child's cut knee did not have a yield stress, it would flow off the knee and be ineffective. Industrial examples include gravitational sagging of coatings such as paint, settling of suspensions, and power requirements for pumping polymer solutions and melts through pipelines, extruders, or injection molders. A variety of techniques can be employed to measure a material's yield stress, and an equally extensive range of values can be obtained, depending on how the testing is conducted. The suitability of a particular test depends on the final application for the material. This application note discusses two of the more common techniques.

Applied Stress

The most common method for determining yield stress is to experimentally apply an increasing force until the material begins to "flow." Specifically, a known stress is applied to a sample while monitoring the resultant strain. In a rheometer, this experiment can be performed with a variety of geometries, including cone-and-plate and Couette cells, but must be performed with a controlled stress rheometer. In general, when the applied stress τ_a is below the yield stress of the material τ_y, the material will not flow, and the strain will never rise above zero, as shown in Figure 1b. When the stress is greater than the yield stress, the fluid can either show (a) a gradual rise in strain (rigid-plastic response); (b) a sudden step strain followed by a gradual rise (elastic-plastic response); or (c) a steady rise in strain at a constant strain rate (Bingham plastic, or viscoelastic response). Typically, a rheologist will perform a stress sweep while monitoring the strain in order to determine the approximate range of the yield stress. This test will be followed by transient studies, in which the response from a single stress step is monitored as a function of time, as shown in Figure 1 and Figure 2.

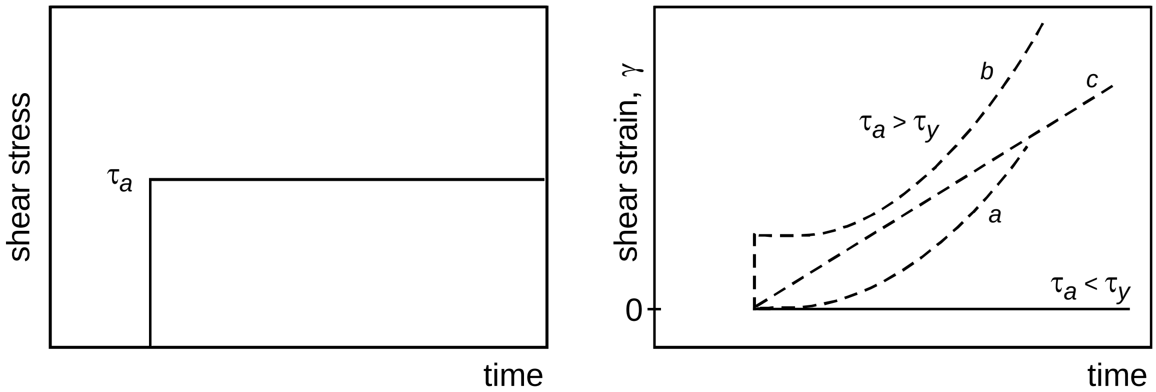

Figure 1: Behavior of material under a step change in stress. Dashed lines in resultant shear strain are for cases where the applied stress is greater than the yield stress. Left figure 1a (applied stress), right figure 1b (resultant strain possibilities).

Cases exist where the sample can exhibit an initial creep response, then attain a steady strain value γ_e (τ_a). As the applied stress increases, the strain will increase indefinitely, eventually attaining a constant strain rate $\dot{\gamma}_e$. The experiment is complicated by not knowing how long to monitor the experiment to determine if the sample has finished deforming. The longer the measurement period, the lower the reported yield stress. As shown in Figure 2, a range of yield stress values could be obtained depending on how long the researcher waited. If the period is too short, it appears that the yield stress is the applied stress τ_2. However, if the researcher waits a longer period, they will notice that the strain is continuing to rise. Therefore, the yield stress will be closer to τ_1. The test at τ_4 is well above the yield stress, and the strain increases steadily at a constant strain rate.

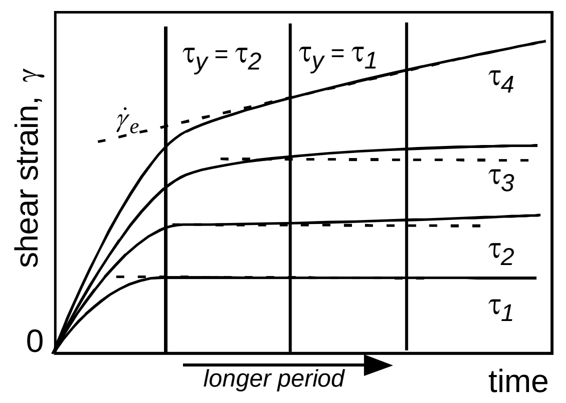

Figure 2: Yield stress measurements of a viscoelastic fluid conducted with different applied stresses and varying measurement periods. If the measurement period is too short, the reported yield stress will depend on the measurement time, due to an initial transient response resulting from creep.

The rheologist can select the appropriate measurement time based on the final application of the material.

Applied Steady Shear Rate

An alternative approach to measuring the yield stress is to apply a steady shear rate to the material and monitor the resultant stress. Depending on the nature of the material, the stress will rise gradually to, overshoot and decay to, or immediately attain, a constant stress that does not change with strain. This behavior is shown in Figure 3. This constant stress level will, however, depend on the applied shear rate.

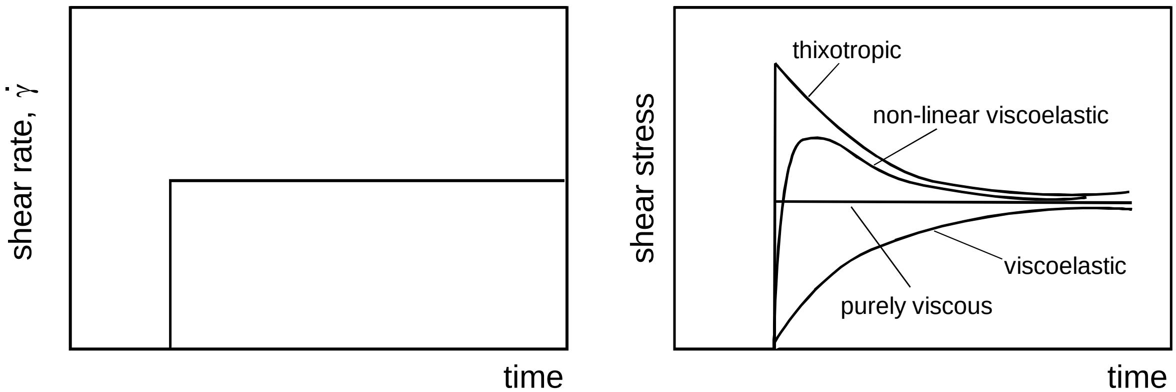

Figure 3: Responses of various materials to a step change in steady shear rate.

By performing a series of measurements at different steady shear rates, a curve such as that shown in Figure 4 can be constructed. To determine the yield stress, the curve has to be extrapolated to zero shear rate. The yield stress will be the intercept of the y-axis. The lowest measured shear rate from which the extrapolation is made will dictate the magnitude of the yield stress. If the extrapolation is made from the linear portion of the plot, then a Bingham yield stress τ_B will be reported. As the extrapolation is made from lower and lower critical shear rates, lower yield stresses will be determined. In general, the lowest shear rate should be determined from the characteristic time scale expected in the flow application of the material, and the extrapolation should be made from this value.

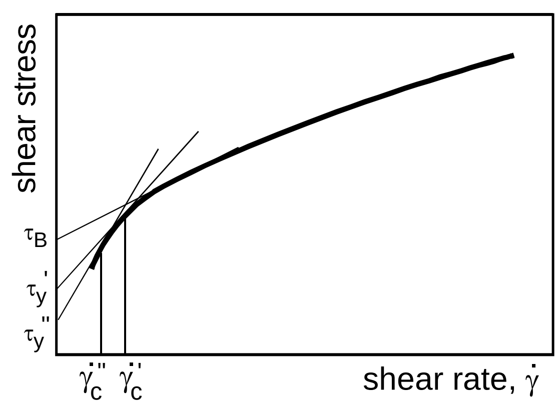

Figure 4: Extrapolation of constant shear stress values to zero shear rate in order to calculate yield stress. The value of the yield stress will depend on the shear rate from which the extrapolation is made.

Conclusions

Care must be taken when performing yield stress measurements. The rheologist needs to determine the appropriate battery of tests to conduct based on the final application of the material and the properties of the material. In controlled stress measurements, it is usually recommended to perform a stress sweep up and down, in order to approximately determine the yield stress range and the level of thixotropy. The decreasing stress ramp is usually lower than the increasing stress ramp due to disruption of structure formed in the material. To avoid erroneous results, this test is usually followed by a series of step changes in stress, as shown in Figure 2. Controlled rate experiments can be conducted similarly, with a steady shear rate sweep up and down, followed by more careful experiments at individual rates as a function of time. Controlled stress experiments tend to be less accurate than controlled stress experiments when measuring yield stress. In either case, the validity of the results will depend on the care taken to collect the raw data, sample loading procedure, and other factors.

About Dr. Gavin Braithwaite

Dr. Gavin Braithwaite is the CEO of Cambridge Polymer Group, Inc. He received his BS in Physics from Edinburgh University, his MS in Electrical Engineering from Southampton University, and his Ph.D. in Chemical Engineer from Imperial College. He was a post-doctoral fellow at Harvard University and the Massachusetts Institute of Technology, where he designed and tested a micro-shear rheometer. At Cambridge Polymer Group, Dr. Braithwaite handles day-to-day operational concerns and guides the overall strategic direction of the company. He is also actively involved in project work. Dr. Braithwaite is an author on multiple technical publications ranging from the use of atomic force microscopy in colloid stability to measurement and modification of native tissue for biomedical purposes. In addition, he holds multiple patents on hydrogel formulations, biomedical materials and analytical instrumentation.

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