Importance of Oscillatory Time Sweeps in Rheology

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ABSTRACT

Oscillatory time sweeps are important when testing materials, such as dispersions and polymers, that may undergo macro- or micro-structural rearrangement with time. These rearrangements directly influence rheological behaviour. Oscillatory time sweeps directly provide the necessary information about how a material changes with time. Depending on the sample tested, information on polymer degradation, solvent evaporation, dispersion settling, cure information and/or time dependant thixotropy, can be found. By determining the time for polymer degradation, solvent evaporation and dispersion settling, information related to the maximum time of any analytical test can be measured. Once any of these cases occur, the material properties change so drastically that accurate and reproducible measurements becomes difficult.

INTRODUCTION

Dispersions are discrete substances that are randomly distributed in a fluid medium. There are three categories of dispersions:

- Suspensions - solid particles in a liquid medium.
- Emulsions - liquid droplets in a liquid medium.
- Foams- a gas in a liquid medium.

Some materials, however, consist of all three types.

Many factors influence the rheological behavior of dispersions including:

- Volume concentration of the dispersed phase
- Viscosity of suspending medium
- Size of the dispersed phase
- Size distribution of the dispersed phase
- Surface chemistry of the dispersed phase
- Shape of the dispersed phase

These variables give rise to many interesting rheological behaviors.

However, the true behavior of a material can only be observed if the system is in a steady state. Therefore, the first consideration when testing dispersions is to determine if the material is stable before data collection. That is, the network structure due to rearrangement of the dispersed phase is unchanging before beginning the experimental procedure, assuming thermal equilibration of the material has been attained. This requires that the time dependant structural effects, due primarily to the microscopic interactions of the dispersed phase with the liquid medium and itself, to be tested.

A simple test to determine if a system has time dependent rheological properties is an oscillatory time sweep. This test monitors if and how the material properties change after it has been loaded, by monitoring certain viscoelastic parameters as time advances. By selecting the appropriate conditions for the parameters of the control variable (a value of either oscillatory stress or strain found within the linear viscoelastic region), the frequency and the temperature of interest, evaluation of the material's behavior with time can be monitored directly.

EXPERIMENTAL

The AR2000 Rheometer, using a Smart Swap™ Peltier plate temperature system with a 40 mm parallel plate, is used for all testing. The temperature was maintained at 25 °C for all tests. Solvent traps were used to ensure that no evaporation or drying takes place during each procedure. The oscillation procedure uses a conditioning step that applied a pre-shear controlling shear rate at 100 1/s for 30 seconds. The oscillatory time sweep applied a constant oscillation stress of 0.2 Pa at a frequency of 1 Hz. The oscillatory stress sweep varied the stress from 0.2 Pa until the material yielded at a constant frequency of 1 Hz.

RESULTS AND DISCUSSION

An automotive ink is used as an illustrative example. An example of an oscillatory time sweep on automotive ink is shown in Figure 1 in which elastic modulus (G') is displayed on a logarithmic scale on the Y-axis versus time on the X-axis. This figure shows in that after pre-shearing, the material's properties constantly increase until a steady value is obtained near 120 s. This is illustrated by the increase of the elastic modulus. This indicates that the material's structure has reached an equilibrium state. Once this time is determined, any subsequent tests on this material should be set up with the same pre-shear conditions, followed by the required equilibration time, in this example 150 seconds.

Figure 2 illustrates the case when the structure is allowed to rebuild to an equilibrium state. This figure consists of two oscillatory stress sweeps that further characterize the ink sample used in Figure 1. Each test, where the material is pre-sheared, differs only by the amount of equilibration time allowed after the pre-shear ceased. One sweep is started directly after the pre-shear stopped, labeled 'time after pre-shear = 0 seconds', and the other stress sweep allows the material to build a steady structure, labeled 'time after pre-shear = 150 seconds'. The oscillatory stress sweep performed on the sample causing structure to form, shows a relatively steady linear viscoelastic region followed by a gradual breakdown of the structure. This steady linear viscoelastic region at low applied stresses indicates that little or no change in structure is occurring, as determined by the oscillatory time sweep.

The oscillatory stress sweep labeled 'time after pre-shear = 0 seconds', which does not allow any time for the structure to form, clearly leads to erroneous information about the sample's rheological properties. This is compared to the oscillatory stress sweep that was delayed by the correct amount of time. After the pre-shear finished and the oscillatory stress sweep test is initiated, the material begins to form a structure, shown by an increase in elastic modulus, regardless of the stress applied to the material. This indicates that the energy necessary to inhibit bond formation is larger than the oscillatory stress that is being applied. As the stress increases, the amount of applied stress gradually becomes equal to the amount of energy required to maintain or form any new structure. Eventually, the structure cannot resist the applied stress and it begins to yield. Therefore, by not allowing the structure to come to a steady state, the measured material properties were grossly underestimated, shown by the reduced elastic modulus and yield stress.

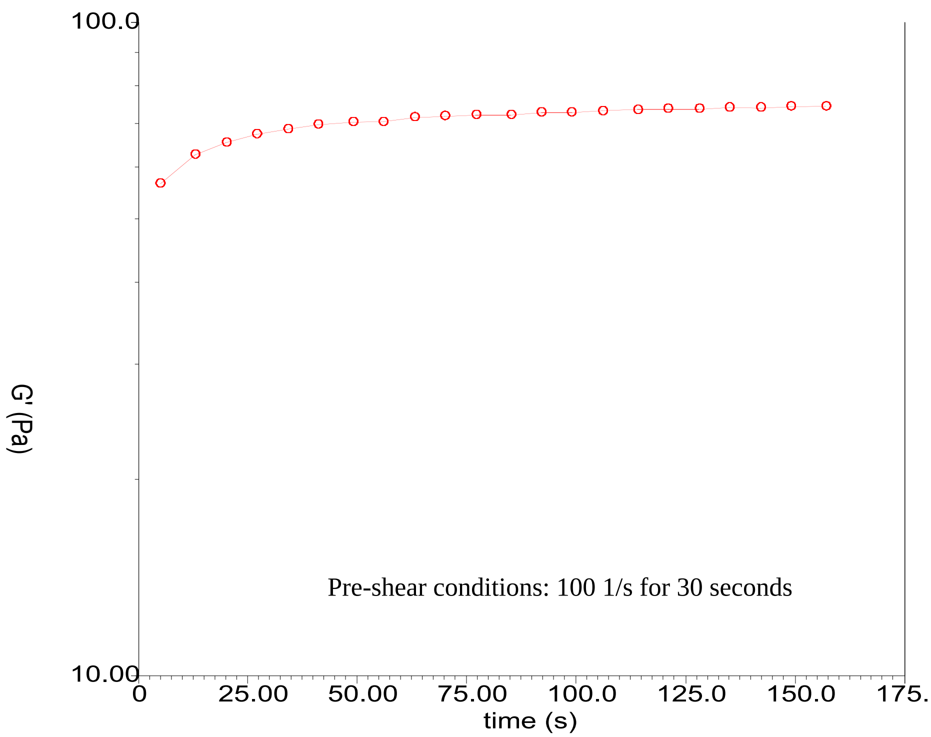

Figure 1 – Automotive Ink Showing Changing Modulus with Time

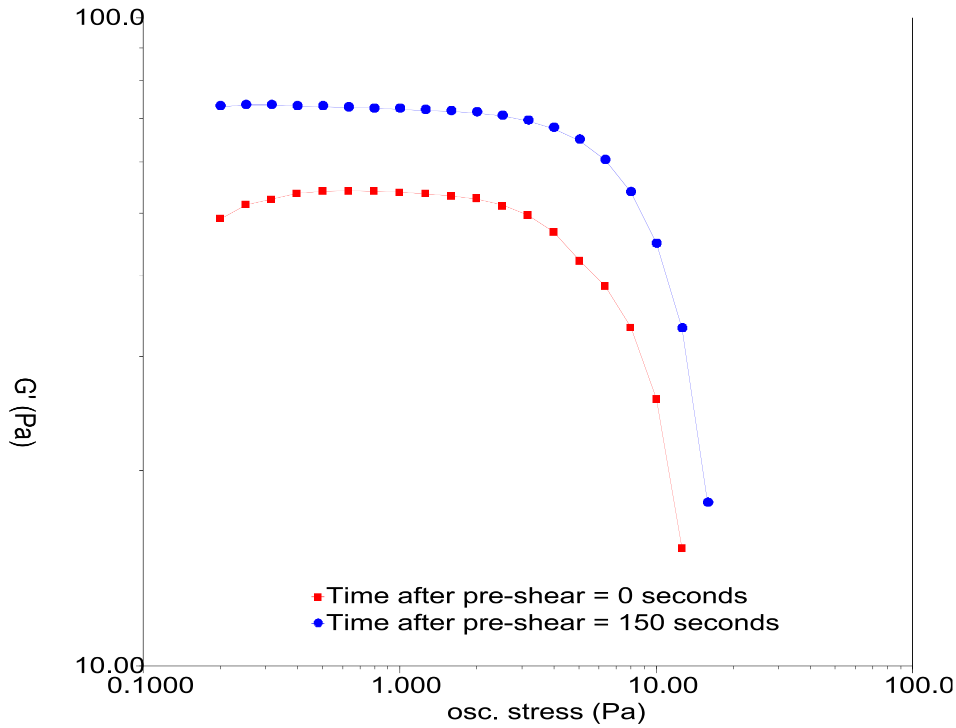

Figure 2 – Effect of Pre-Shear

SUMMARY

The importance of an oscillatory time sweep before running the oscillatory stress sweep is demonstrated using dispersions as an example. The collected time information is useful for other materials, such as polymers, and will carry over into all subsequent rheological tests, such as creep/recovery, stress relaxation, flow and other oscillatory tests. This equilibration time is only associated with the particular material being measured. Once any component within the material has been changed or adapted, another oscillatory time sweep is required. Accurate and reproducible information on a material's rheological properties becomes routine when taking *time* to tailor one's experiment.

KEYWORDS

Rheology, Oscillation