Introduction

Amongst the several small strain experiments used in rheometry, including stress relaxation and creep, sinusoidal (or oscillatory) rheometry is often most commonly used to characterize the frequency-dependence of polymer solutions, melts, suspensions, and emulsions. In this test, a sample is deformed in an oscillatory shearing flow when placed in a cone-and-plate, parallel plate, or couette geometry. In one test procedure, the rheometer will oscillate one part of the geometry to a preset strain γ_0 and monitors the time-dependent stress $\tau(t)$ that arises because of the deformation. In a related test procedure, the geometry is oscillated to a preset stress, and the resultant time-dependent strain is monitored. Both procedures yield the same result.

Mathematical Representation

Mathematically, the controlled strain experiment is represented as follows:

$$\gamma = \gamma_0 \sin \omega t \tag{1}$$

$$\tau = \tau_0 \sin(\omega t + \delta) \tag{2}$$

In general, the resultant stress will be delayed in time by a phase angle δ. As shown in the plot below, the stress wave can be deconvoluted into two waves of frequency ω, with one wave in phase with the strain wave and one 90° out-of-phase. In other words,

$$\tau = \tau' + \tau'' = \tau_0' \sin \omega t + \tau_0'' \cos \omega t \tag{3}$$

From trigonometry, it can be shown that the phase angle can be written as

$$\tan \delta = \frac{\tau_0''}{\tau_0'} \tag{4}$$

From the relationship between stress and strain, the two dynamic moduli can thus be defined:

$$G' = \frac{\tau_0'}{\gamma_0} \quad \text{elastic or in-phase modulus} \tag{5}$$

$$G'' = \frac{\tau_0''}{\gamma_0} \quad \text{viscous, loss, or out-of-phase modulus} \tag{6}$$

Alternatively, these experiments can be thought of in terms of an oscillating shear rate, $\dot{\gamma}$, which leads into a definition of a *dynamic viscosity*. The strain rate is simply the derivative of the strain, or

$$\dot{\gamma} = \frac{d\gamma}{dt} = \gamma_0 \omega \cos \omega t = \dot{\gamma}_0 \cos \omega t \tag{7}$$

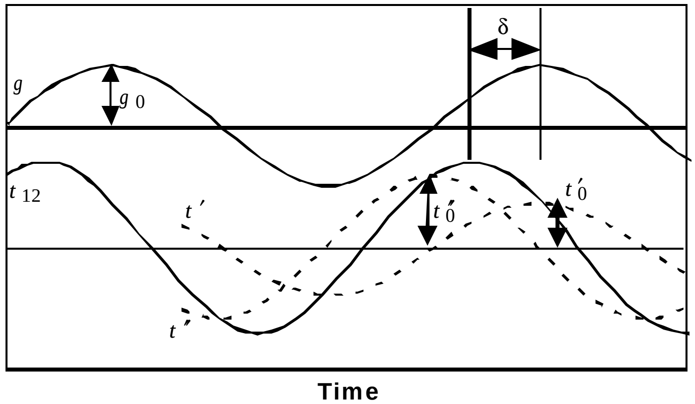

Figure 1: Relationship between imposed strain γ and resultant stress τ_{12}, showing the phase lag δ between the two. The stress is deconvoluted in the in-phase τ' and out-of-phase τ'' components of stress.

The viscosity function is the ratio of the stress to the strain rate, so that the following relationships can be obtained:

$$\eta' = \frac{\tau_0''}{\dot{\gamma}_0} = \frac{G''}{\omega} \quad \text{viscous portion of complex viscosity} \tag{8}$$

$$\eta'' = \frac{\tau_0'}{\dot{\gamma}_0} = \frac{G'}{\omega} \quad \text{elastic portion of complex viscosity} \tag{9}$$

The overall magnitude of the complex viscosity is defined as

$$|\eta^*| = \left(\eta'^2 + \eta''^2\right)^{1/2} \tag{10}$$

Table 1 lists the usual information obtained from oscillatory tests on various types of materials. A typical result for a frequency sweep on a polymer solution is shown in Figure 2. The plots show the transition from a viscous material to an elastic material, and indicate the critical crossover frequencies. For example, an approximate relaxation time λ can be obtained from the inverse of the frequency where the material goes from being viscous to being rubbery, $\lambda = 1/\omega_c$.

Table 1: Values obtained from oscillatory rheometry

Newtonian Liquid	$G' = 0$	$\eta' = \mu$	$\delta = \pi/2$
Hookean Solid	$G' = G$	$\eta' = 0$	$\delta = 0$
Viscoelastic Material	$G'(\omega) > 0$	$G''(\omega) > 0$	$0 < \delta(\omega) = \pi/2$

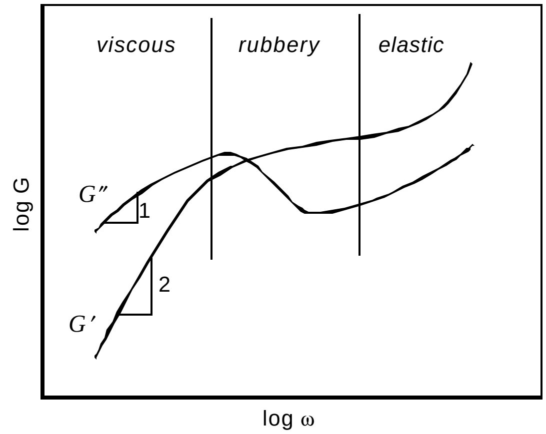

Figure 2: Typical viscoelastic spectrum for a polymer solution when subjected to an oscillatory frequency sweep.

Applications

Small amplitude oscillatory shear flows are used in many applications. They can be used to examine irreversible structure development and destruction in gels, curing systems, paints, etc. The use of multiple harmonics applied simultaneously, termed *multi-harmonic frequency analysis*, is particularly useful when examining mutating systems, i.e. systems undergoing a transient phase change, chemical change, or solvent loss. Oscillatory shear flows probe discrete relaxation time scales λ in the polymer system, where $\lambda=1/\omega$, and can show the frequency regime where the material departs from an essentially Newtonian, or viscous, response to a more elastic response to the deformation.

The amplitude of the oscillatory test must be selected with care. If the strain is too large, the material will be deformed beyond its linear viscoelastic regime, where the measured component becomes dependent on the extent of the deformation. For this reason, a strain sweep should always be conducted prior to a frequency sweep (or a series of individual tests at an individual frequency) to determine the strain where the material function, such as the viscous portion of the viscosity, becomes dependent on the strain. An example of this phenomenon is shown in Figure 3. Without this measurement, erroneous interpretation of data can result.

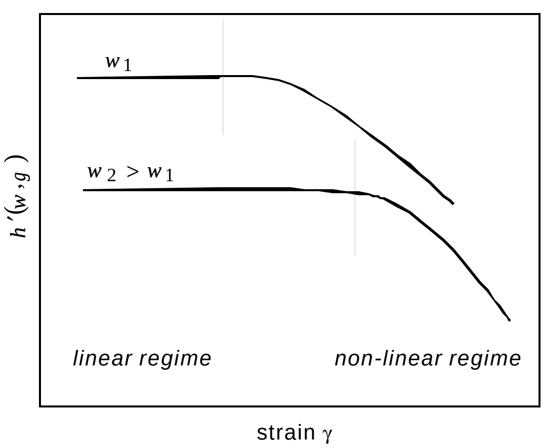

Figure 3: Linear viscoelastic regimes for a polymeric material as a function of strain amplitude and frequency. For accurate interpretation of data, the strain amplitude must be small enough to be in the linear regime, but high enough to generate a measurable torque.

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