Formumetrics

Time enough for Rheology?

Experiments can be designed using shear rheometers which can relate to both material properties and the characteristic times associated with the way a material is used.

We can define the timescales of responses from a material, e.g. the ratio of viscosity to elasticity defines a relaxation time and the inverse a characteristic frequency. We can also define time scales for processes.

The characteristic times can be expressed as follows:

$$\text{time} \equiv \frac{1}{\text{frequency}} \equiv \frac{1}{\text{deformation rate}}$$

since frequency and shear rate are related to reciprocal time.
These informally linked times enable us to make a connection between the commonly encountered viscosity versus shear rate curves and viscoelastic time scales. These times would be characteristic of those that we might encounter when measuring elastic moduli as a function of frequency.

For example, in the diagram (fig1) a range of processes are illustrated from storage stability to spraying. For each, a typical range of shear rates exists.

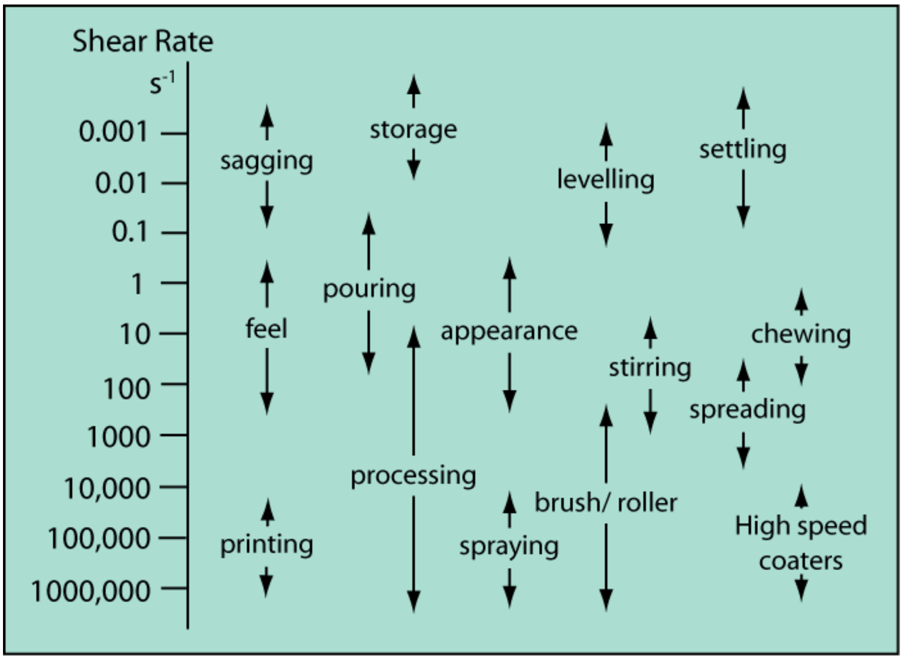

Figure 1. Typical shear rates that are associated with a range of common processes

We can consider two examples of how time scales need to be considered in relation to the type of deformation that is occurring.

When spraying, the very short times and the high shear rates involved result in the break-up of the fluid stream into droplets. In wind tunnel studies, a liquid stream was introduced coaxially into a fast moving air stream. With suitable fluid properties and the correct nozzle design we can produce droplets with a roughly log normal size distribution with a MMD of about 100μm.

The mass median droplet diameter, MMD was adequately described by an expression developed by J. Matta which is:

$$MMD \approx K_1 \left(\frac{Q}{\rho} \right)^{0.1} V^{-1.5} \eta^{0.1} \gamma^{0.9}$$

where
ρ = density of the air
η = viscosity of the liquid
V = air velocity,100ms^{-1}
Q = volumetric flow rate of the liquid, 1 litre min^{-1}
K_1 = a constant for the experimental design

This produces a stream of roughly 30 million drops per second and creates a surface area of 1 square metre per second. These rates dictate that neither surface tension nor viscosity will achieve an equilibrium value. It is clear from Matta's expression[1] that the surface tension of the material has the largest impact on size. For Newtonian materials it was found that the viscosity is much less significant in influencing the particle size.

However if we measure polymer solutions, the expression fails. For example, a 0.5 MDa PEO produces a droplet diameter 2x that of water, whereas a 5 MDa PEO produces a droplet diameter 6x that of water. In the experiments performed in the wind tunnel, calculations suggest a droplet was produced in about 10 μs. Local deformations can be very high indeed. Viscometry measurements show that once shear deformation rates approach 10^5 – 10^6 s^{-1} there are only small viscosity differences between samples, which cannot account for the observed differences in droplet size. Not only is the sensitivity to viscosity greater than that described by Matta's relationship, the relationship to shear viscosity breaks down completely if other polymers are investigated.

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[1] *J. Matta, private communication, also see: J. Matta & R.P. Tytus, J. Appl. Polym. Sci., 1982, 27, 397-405.*

In producing droplets, liquid is pulled from the surface creating very high stretching (extensional) fields[2,3] rather than shearing fields (fig 2).

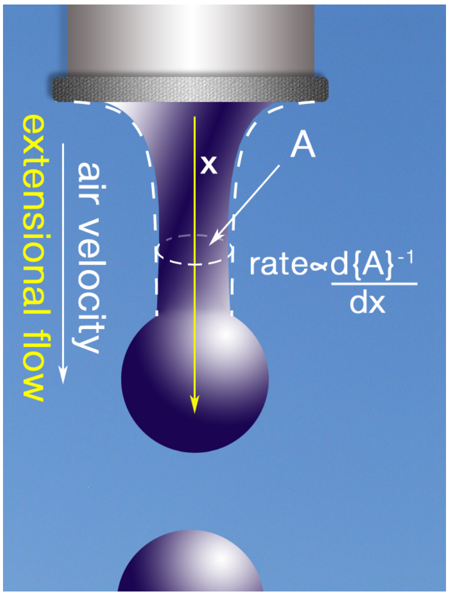

Figure 2. An idealised schematic of a single drop forming indicating the extensional rate

The high extensional viscosity seen with the high molecular weight PEO was found to control droplet formation. This viscosity was greater than that seen with lower molecular weight PEO's or other aqueous polymers which were tested. This is a case where rate, or timescale can only illustrate the difference when the appropriate type of deformation is used.

Another example where deformation and timescales must be carefully considered is chewing. The type of movements that occur in the mouth during chewing are extremely complicated. Suitable choices of standard test protocols on rotational rheometers enable the rheological quantities that are measured to be related to a consumer's experience.

Let us take soft cheese as an example. To mimick the 'mouthfeel', a typical test is where the cheese is placed between two parallel plates and subjected to a sinusoidal oscillation in the linear viscoelastic range. Hence rendering the characteristic moduli a function of time alone and not the magnitude of stress or strain. It is important to recognise that this is 'mouthfeel'. Chewing, on the other hand, is a destructive process with typical shear rates of 10^1 - 10^2 s^{-1} (fig 1). This shear rate is easily accessible on a viscometer. Whereas the initial texture of the cheese may be perceived below the yield stress, imitating the chewing process requires the sample to be subjected to stresses / strains in excess of the yield value. Flow results from the

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[2] *H. Huang, NAW, 2005, 5/6, 63-68.*

[3] *A.N. Rozhkov, Fluid Dynamics, 2005, 40, 835-853.*

structural breakdown of the Casein gel matrix.

The onset of flow has been studied using a transient test conducted at high strains e.g. a creep recovery test. Here, a constant stress was applied to the cheese for a fixed time and then suddenly removed. This experiment produces a creep and a creep recovery curve, with the resultant strain being measured as a function of time to give viscoelastic-like (elastic) or liquid-like (viscous) responses (fig 3).

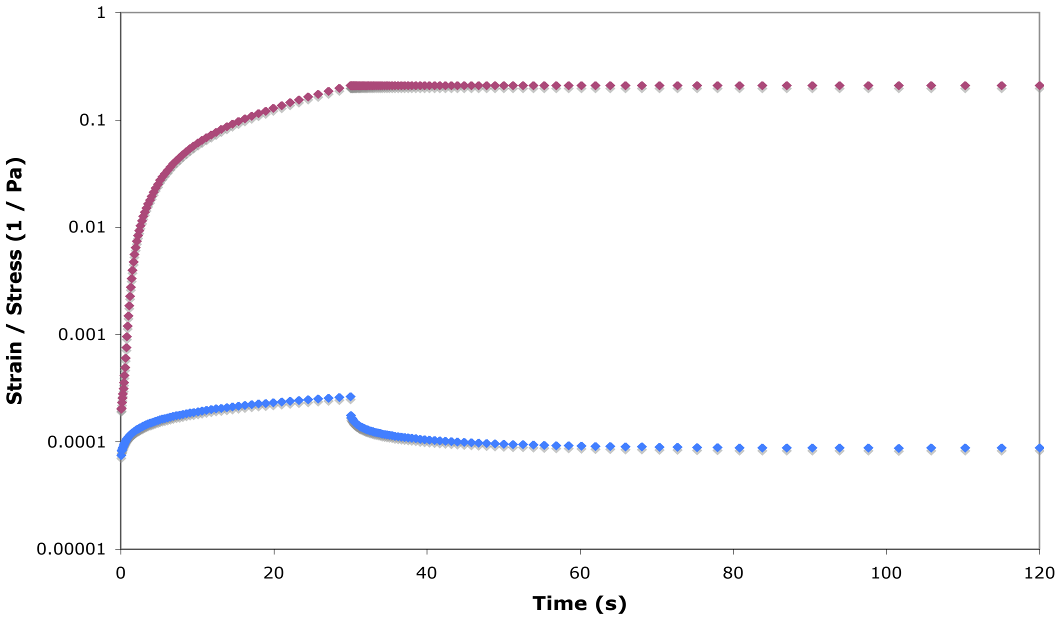

Figure 3. A creep test on soft cheese at low and high applied stress.

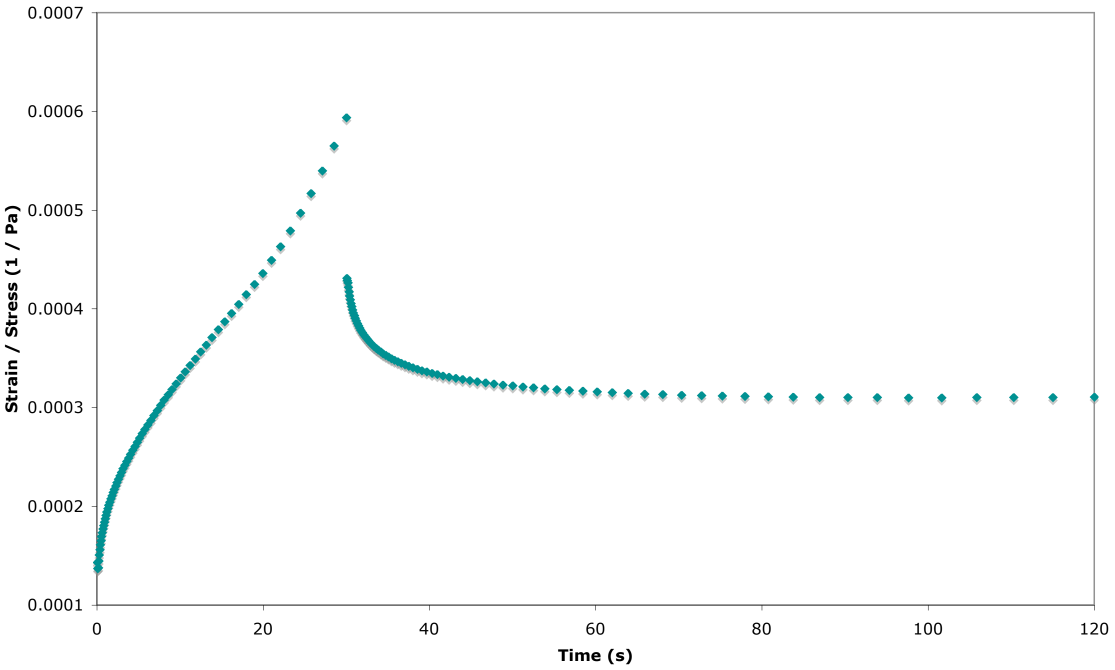

Figure 4. A creep test on soft cheese close to the yielding stress.

By choosing an appropriate experiment with the correct timescales, the properties that are obtained e.g. yield stress, shear viscosity, and the viscoelastic properties can be related, in some manner, to the textural properties of the semi-solid cheese. The behaviour is complex close to the point of yielding (fig 4) where the degree of flow is sensitive to the timescale of the experiment. So just as with spraying, not all the appropriate rheological properties will be defined by simple shear tests. Food developers need to pay close attention to the food's rheological properties and be aware of textural, temporal and structural changes, a difficult task.

We have illustrated that it can be misleading to consider rates and time scales without considering the type and magnitude of the deformation. Non-linear responses that occur in chewing or extensional flow fields that occur in drop formation, should play an influential role in experimental design, its limitations and interpretation. Sometimes, time alone is not enough!