

Oscillatory Rheology

Measuring the Viscoelastic Behaviour of Soft Materials

Soft materials such as emulsions, foams, or dispersions are ubiquitous in industrial products and formulations; they exhibit unique mechanical behaviours that are often key to the way these materials are employed in a particular application. Studying the mechanical behaviour of these materials is complicated by the fact that their response is viscoelastic, intermediate between that of solids and liquids. Oscillatory rheology is a standard experimental tool for studying such behaviour; it provides new insights about the physical mechanisms that govern the unique mechanical properties of soft materials.

Photo: 108 (photocase)

Soft materials such as colloidal suspensions, emulsions, foams, or polymer systems are ubiquitous in many industries, including foods, pharmaceuticals, and cosmetics. Their macroscopic mechanical behaviour is a key property which often determines the usability of such materials for a given industrial application. Characterising the mechanical behaviour of soft materials is complicated by the fact that many materials are viscoelastic, so their mechanical properties lie between that of a purely elastic solid and that of a viscous liquid. Using oscillatory rheology, it is possible to quantify both the viscous-like and the elastic-like properties of a material at different time scales; it is thus a valuable tool for understanding the structural and dynamic properties of these systems [1, 2].

Oscillatory Rheology

The basic principle of an oscillatory rheometer is to induce a sinusoidal shear deformation in the sample and measure the resultant stress response; the time scale probed is determined by the frequency of oscillation, ω , of the shear deformation. In a typical experiment, the sample is placed between two plates, as shown in figure 1(a). While the top plate remains stationary, a motor rotates the bottom plate, thereby imposing a time dependent strain $\gamma(t) = \gamma \sin(\omega t)$ on the sample. Simultaneously, the time dependent stress $\sigma(t)$ is quantified by measuring the torque that the sample imposes on the top plate.

Measuring this time dependent stress response at a single frequency immediately reveals key differences between materials, as shown schematically in figure 1(b). If the material is an ideal elastic solid, then the sample stress is proportional to the strain deformation, and the proportionality constant is the shear modulus of the material. The stress is always exactly in phase with the applied sinusoidal strain deformation. In contrast, if the material is a purely viscous fluid, the stress in the sample is proportional to the rate of strain deformation, where the pro-



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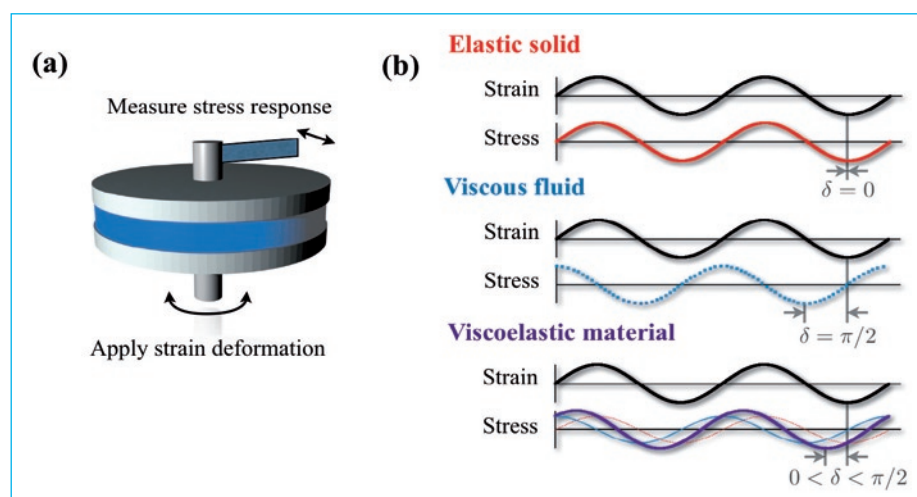


Fig. 1: (a) Schematic representation of a typical rheometry setup, with the sample placed between two plates. (b) Schematic stress response to oscillatory strain deformation for an elastic solid, a viscous fluid and a viscoelastic material.

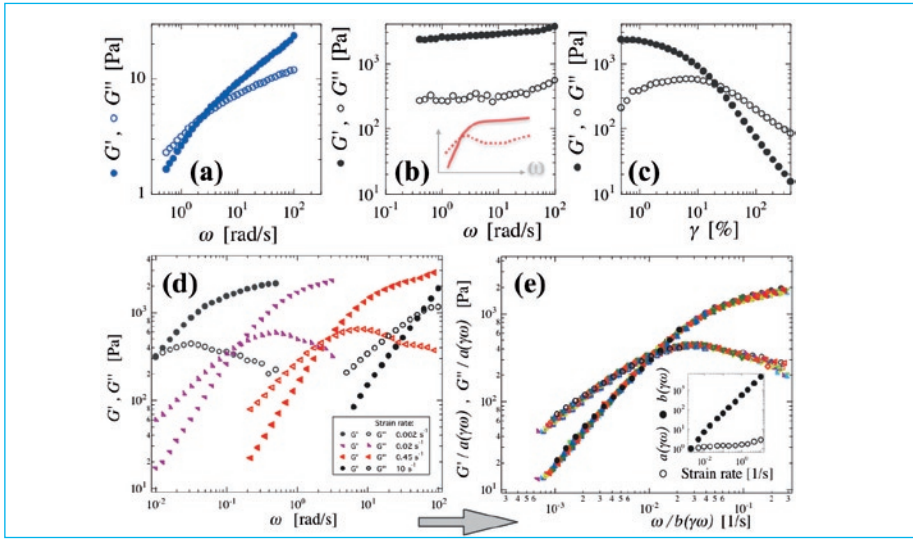


Fig. 2: Frequency dependence of G' and G'' for (a) a suspension of hydrogel particles and (b) for the elastomer blend DC-9040 (Dow Corning), a typical additive in cosmetic and pharmaceutical formulations. Further measurements of DC-9040: (c) Strain dependence of G' and G'' , (d) Constant-rate measurements at strain rates 0.002 s^{-1} , 0.02 s^{-1} , 0.45 s^{-1} and 10 s^{-1} , (e) master curve of constant-rate measurements that were scaled both in magnitude and frequency.

portionality constant is the viscosity of the fluid. The applied strain and the measured stress are out of phase, with a phase angle $\delta = \pi/2$, as shown in the center graph in figure 1(b).

Viscoelastic materials show a response that contains both in-phase and out-of-phase contributions, as shown in the bottom graph of figure 1(b); these contributions reveal the extents of solid-like (red line) and liquid-like (blue dotted line) behavior. As a consequence, the total stress response (purple line) shows a phase shift δ with respect to the applied strain deformation that lies between that of solids and liquids, $0 < \delta < \pi/2$. The viscoelastic behaviour of the system at ω is characterised by the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, which respectively characterise the solid-like and fluid-like contributions to the measured stress response. For a sinusoidal strain deformation $\gamma(t) = \gamma_0 \sin(\omega t)$, the stress response of a viscoelastic material is given by $\sigma(t) = G'(\omega)\gamma_0 \sin(\omega t) + G''(\omega)\gamma_0 \cos(\omega t)$.

In a typical rheological experiment, we seek to measure $G'(\omega)$ and $G''(\omega)$. We make the measurements as a function of omega because whether a soft material is solid-like or liquid-like depends on the time scale at which it is deformed. A typical example is shown in figure 2(a), where we plot $G'(\omega)$ and $G''(\omega)$ for a suspension of hydrogel particles [3]; at the lowest accessible frequencies the response is viscous-like, with a loss modulus that is much larger than the storage modulus while at the highest frequencies accessed the storage modulus dominates the response, indicating solid-like behaviour.

Linear and Nonlinear Rheology

It is important to recognise that the frequency-dependent moduli G' and G'' probe the behaviour of a material in an undisturbed state, where

the applied strain deformations are sufficiently small so as not to affect the material properties. Many soft materials show a strikingly nonlinear stress response as the strain deformation is increased; this behaviour suggests a fundamental change of the material properties under shear from the equilibrium properties at rest. However, such nonlinear data are often disregarded because the physical origins of this behaviour remain poorly understood.

New Developments in Nonlinear Rheology

Nonlinear viscoelastic measurements have the potential of revealing new information about the behavior of soft materials. Recent studies [4, 5] suggest that such nonlinear data provides valuable information about the properties of a wide range of soft materials, called soft glassy materials [6]. The underlying physical picture suggests an intrinsic link between the slow structural relaxation of such glassy systems and their linear and nonlinear viscoelastic response.

The linear viscoelastic response of soft glassy materials is often rather featureless within the accessible range of frequencies, as shown in the example in figure 2(c); the storage modulus is typically larger than the loss modulus and depends only weakly on frequency. However, the typical nonlinear response shows more pronounced features: A robust hallmark of these systems is that as the strain increases at fixed ω , the loss modulus initially increases to a peak before ultimately decreasing at the largest strains, as shown in the example in figure 2(c). This unusual behaviour can be explained as a natural consequence of a slow structural relaxation process that is expected in these materials at very low frequencies [6, 7], as shown schematically in the inset of figure 2(c). Importantly, the time

scale of this relaxation is expected to depend on the strain rate of deformation; the relaxation speeds up if the system is subjected to shear [4, 8–10]. As the strain amplitude of deformation is increased in a strain-sweep measurement, the strain rate increases and the characteristic frequency of the slow relaxation process moves towards higher frequencies. As a consequence, a peak in the loss modulus is observed at the point where this characteristic frequency becomes comparable to the oscillation frequency of the strain deformation, ω . Thus, the observed behaviour at large strains directly reflects the structural relaxation of the material.

This behaviour is exploited in a new approach to oscillatory rheology, Strain-Rate Frequency Superposition (SRFS) [5], where the amplitude of strain rate is kept constant as ω is varied. Examples of such measurements are shown in figure 2(d) for different strain rate amplitudes of shear deformation. At all strain rates, the frequency dependence of the response shows the behaviour expected for a slow structural relaxation process, with a pronounced peak in the loss modulus. The data show that with increasing strain rate amplitude the response moves towards higher frequencies; however, the general shape of the response is surprisingly insensitive to strain rate, as shown in figure 2(e). By scaling the frequency and the magnitude of each data set, we collapse the data recorded at different strain rates onto a master curve with the corresponding scaling factors shown in the inset. While the magnitude scaling factor, $a(\gamma\omega)$, depends only weakly on the applied strain rate, the frequency scaling factor $b(\gamma\omega)$ shows a linear dependence on $\gamma\omega$; thus, within the range studied, the characteristic relaxation frequency is proportional to the applied strain rate. Surprisingly, notable differences in the shape of this shear-driven relaxation are observed between different samples [5]. Thus, the shape of the relaxation is not governed by the single time scale induced by the shear but is instead governed by a sample-dependent spectrum of relaxation times. In the example shown the unusually broad shape of the peak indicates that the relaxation spectrum of this system contains a remarkably broad range of time scales.

The behaviour observed suggests that valuable information about the structural relaxation of soft materials can be accessed from such nonlinear viscoelastic measurements, even if the relaxation occurs at time scales that are not accessible to linear oscillatory rheology.

Conclusions

Oscillatory rheology is a valuable tool for studying the mechanical behavior of soft materials. Recent studies suggest that the nonlinear viscoelastic behavior contains valuable information about the dynamics of these systems. Thus measurements at large strain deformations should lead to a better understanding of the physical mechanisms that govern their behaviour.

References

- [1] W. Macosko: *Rheology: Principles, Measurements and Applications*, Wiley-VCH, New York, 1994
- [2] Larson R.G.: *The structure and rheology of complex fluids*, Oxford University Press, New York, 1999
- [3] Hu Z. and Xia X.: *Adv. Materials* 16, 305 (2004)
- [4] Miyazaki H.M. *et al.*: *Europhys. Lett.* 75, 915 (2006)
- [5] Wyss H.M. *et al.*: *cond-mat/0608151* (2006)
- [6] Sollich P. *et al.*: *Phys. Rev. Lett.* 78, 2020 (1997)
- [7] Cates M.E. and Sollich P.: *J. Rheology* 48, 193 (2004)
- [8] Fuchs M. and Cates M.E.: *Phys. Rev. Lett.* 89 (2002)
- [9] Fuchs M. and Cates M.E.: *Faraday Discuss.* 123, 267 (2003)
- [10] Miyazaki K. *et al.*: *Phys. Rev. E* 70, 011501 (2004)

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