Determination of the Linear Viscoelastic Properties of Materials Using Non-Viscometric Geometries

Bernard Costello

TA Instruments Ltd. Fleming Way, Crawley, RH10 9NB, U.K

ABSTRACT

The correspondence principle states that a class of viscoelastic problems may be solved, provided that the solution of the corresponding elastic problem is known[1]. Here it is shown that one of its consequences is that the linear viscoelastic properties of a material can be obtained using a non-viscometric geometry.

INTRODUCTION

The correspondence principle has been widely used in rheology, and in mechanical engineering generally. Its use has recently been extensively discussed by Hilton[2], who described four classes of the principle, and the conditions under which these apply. These classes refer to the nature of Poisson's ratio, ν, which is the ratio of the transverse contraction strain to the extensional strain when a rod is stretched.

For no volume change on extension, Poisson's ratio would be 0.5, for no transverse dimensional change, it would be zero. For many engineering materials such as many metals and concrete, a value of between 0.2 and 0.4 is often quoted, although Poisson's ratio is known to be a complex function, that varies with frequency in both magnitude and phase[3]. Little information is available in the scientific literature on the phase of Poisson's ratio, presumably because of the difficulty of making the measurements, but for many of the types of soft materials that rheologists are used to dealing with, Poisson's ratio is close to 0.5 over a broad frequency range. Since this amounts to a condition of incompressibility, it seems reasonable to assume that there is no phase difference between the extensional and transverse strains. These conditions correspond to the third of Hilton's classes. One consequence of the conditions is that, for a linear viscoelastic material in the absence of inertia, if an oscillating stress of any form is applied to a sample, the phase lag between the stress and the strain will be the same at every point in the sample. For a linear viscoelastic material, Trouton's ratio, the ratio of extensional to shear viscosity, is also constant, with a value of 3. According to the correspondence principle, therefore, the ratio of the complex shear viscosity, $\eta*(\omega)$, to the complex extensional viscosity, $\eta_E*(\omega)$ must also be constant with a value of 3. This means that an arbitrary set of stresses can applied to sample to provide its linear viscoelastic properties, provided that the result has previously been obtained for a known sample.

VISCOMETRIC GEOMETRIES

Viscometric measuring systems (geometries) are those for which the stress and strain fields are well defined. Such geometries include the small angle cone and plate and the narrow gap concentric cylinder system, and the reason for their use by

rheologists is that they enable the sample material functions to be readily calculated.

The operating variables of a rotational rheometer are the torque, M, and the angular displacement, ϕ, or angular speed, Ω, where $\Omega = d\phi/dt$. These are converted to the rheological variables, stress, σ, and strain, γ, or strain rate, $\dot{\gamma}$, through factors which depend on the measuring system type and dimensions. Thus $\sigma = F_\sigma M$ and $\gamma = F_\gamma \phi$. For a small angle cone and plate, for example, $F_\sigma = 3/2\pi R^3$ and $F_\gamma = 1/\beta$, where R is the plate radius, and β is the cone angle[4]. For a Hookean elastic material, since the ratio of stress to strain is constant, the two factors can be replaced by a single measuring system factor, $F_g = F_\sigma / F_\gamma$. For the cone and plate $F_g = 3\beta/2\pi R^2$. For viscometric geometries, the various factors have been derived analytically for the full viscoelastic case. However, if the correspondence principle can be relied on, then the full viscoelastic solution is not necessary. We can simply write that, since the Hookean elastic shear modulus $G = F_g M / \phi$, the (linear) complex shear modulus $G^* = F_g M^* / \phi^*$, and the (linear) complex viscosity $\eta^* = F_g M^* / \Omega^*$. For the usual rheological case of Hilton's class 3, these relationships apply whatever the nature of the deformation: whether shear, extensional or a mixture of both.

NON-VISCOMETRIC GEOMETRIES

None of the above discussion would matter much if the properties of all samples of rheological interest could be determined using the standard geometries, but of course they cannot. Some samples have large particles, others may sediment or slip at the geometry wall. Moreover, it is difficult to take a specimen of, for example, a set yogurt, from its container and load it onto a rotational rheometer without damaging it. If the correspondence principle can be invoked, then a non-viscometric geometry of suitable form can be used. All that is required is calibration of the geometry with a material of known properties to provide the measuring system factor, F_g.

Calibration of the measuring system

This can easily be done using, for example, a standard Newtonian oil, since $F_g = \Omega \eta / M$ (of course, it would be wise to check the calibration using several oils, each over a range of torques). Calibration of this type does not provide the stress or strain factors, only the ratio of the two.

STARCH

Starch is used as a rheology modifier in many foodstuffs. As a raw material, it is normally supplied in the form of approximately spherical granules, with diameters between about 1 μm and 100 μm. To be used as a rheology modifier, starch must undergo gelatinization, which occurs when the granules are disrupted in aqueous environments, to swell and eventually release the constituent molecules. The temperature at which this process commences will depend on the nature of the starch, but it is usually above about 60°C. The process is thermally irreversible, and when the temperature is reduced, the system remains gelatinized, although some slow de-gelatinization (retrogradation) may occur.

This process is not easy to monitor using standard geometries. At low temperatures the granules sediment, and a impeller-in-cup measuring system has been developed for use in the food industry, that prevents this from happening (Fig. 1) This geometry is designed to be used in constant rotation, which means that the sample is always being subjected to shearing, and as the geometry is non-viscometric, the shear rates and stresses involved are not known.
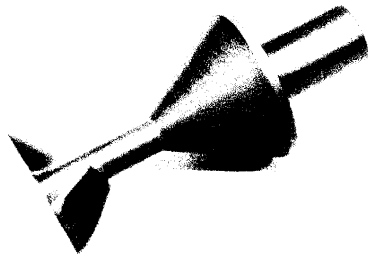
Figure 1: impeller designed for use with starch

A more useful way of monitoring the kinetics of starch curing would be to use a viscometric geometry with low amplitude oscillation. The principle discussed here allows this. The starch is held in suspension by the paddle at constant rotation, until the unset of gelation, when the operating mode is switched to low amplitude oscillation.

RESULTS

Shower gel

Fig. 2 shows the results obtained for a commercial shower gel using the impeller-in-cup measuring system designed for use with starch samples, compared with those obtained using a standard 40 mm diameter parallel plate. F_g for the impeller-in-cup was found to be 11020 m^{-3}. Data are shown as the magnitude of the complex modulus, $|G^*(\omega)|$ and phase angle, δ, plotted against angular frequency. If the correspondence principle holds, the phase angle at each frequency will be the same for the two geometries. Correspondence between the $|G^*(\omega)|$ values is achieved by using the appropriate value for F_g.

There is good agreement between the two data sets, apart from at high frequencies, where the inertia of the sample becomes significant (this shows one possible source of error of the method).
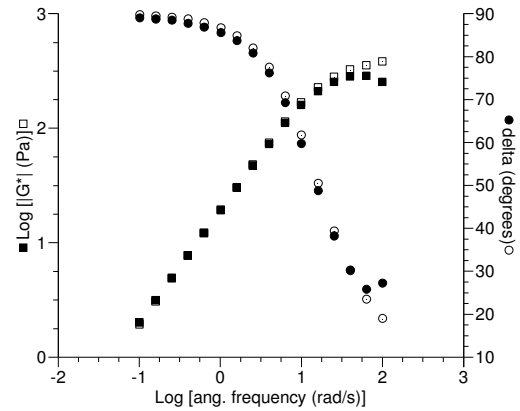

Figure 2: log $|G^*(\omega)|$ (squares) and δ (circles) for shower gel using impeller-in-cup (filled symbols) and parallel plate (open symbols)

Starch

Results for a hydroxethylated dent corn starch are given in Fig. 3, which shows log $G'(\omega)$ and log $G''(\omega)$ plotted against global time, i.e. time after commencement of the experiment. Oscillation frequency was 1 Hz. Temperature profile was: hold at 35°C for 1 minute, raise to 95°C over 4 minutes, hold for 6 minutes, reduce to 35°C over three minutes, and hold for 7 minutes. The impeller was rotated at a constant angular velocity of 16.8 rad s^{-1}, until the starch started to gel, at about 3.9 minutes.
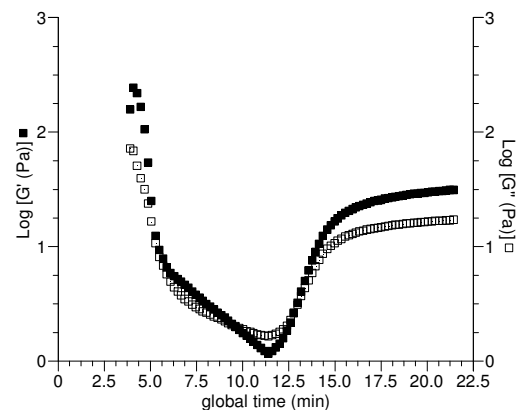

Figure 3: log $G'(\omega)$ and log $G''(\omega)$ against time for a a hydroxethylated dent corn starch

CONCLUSION

It has been shown that the correspondence principle can be used to allow the linear viscoelastic properties of materials to be detrmined using non-viscometric geometries.

REFERENCES

1. Tschoegl, N.W., (1989), "The Phenomenological Theory of Linear Viscoelastic Behavior", Springer-Verlag, Berlin, pp. 509-513.

2. Hilton, H.H., (2001), "Implications and Constraints of Time-Independent Poisson Ratios in Linear Isotropic and Non-Isotropic Materials", *J. Elasticity*, **63**, pp 221-251.

3. Tschoegl, N.W., (1998), "Time Dependence in Material Properties: an Overview", *Mech. of Time-Dependent Materials*, **1,** pp. 3-32.

4 Macosko, C.W., (1993), "Rheology: Principles, Measurements, and Applications", VCH, New York, p 206.