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Thermal Analysis & Rheology

ENERGY STORAGE AND DISSIPATION IN VISCOELASTIC MATERIALS

Performing an energy balance on a viscoelastic material undergoing shear can be far from straightforward, a point which is not always recognized in the rheological literature. It is difficult to recommend a text where the matter is dealt with clearly and fully. The most complete analysis is that of Tschoegl [1], from which the following is mainly taken.

During a rheological experiment, a body is supplied with mechanical energy. A full energy balance would consider the resulting in changes in kinetic, surface, potential, thermal and all other forms of energy within the sample. But rheology is concerned only with the deformation and rate of deformation of materials, and the contributions from most of these other forms of energy are considered to be negligible. In other words the sample is considered to have constant volume and surface area. The change in kinetic energy arising from its acceleration from rest is ignored, and it is considered to be in constant thermal equilibrium with its surroundings. The heating effect of the thermal energy generated is also ignored.

In these circumstances it is only necessary to consider the energy stored elastically, as potential energy, or dissipated thermally. In the limiting cases of solids and liquids the analysis is not difficult. If the energy supplied to the material $E(t)$ is considered as a function of time, then for a liquid, the energy dissipated per unit time, per unit volume, $E_d(t)$, is given by:

$$\frac{dE_d(t)}{dt} = \sigma \frac{d\gamma}{dt} \qquad (1)$$

where is σ the shear stress and γ is the shear strain. Since the viscosity, η, is defined as $\sigma/\dot{\gamma}$, where $\dot{\gamma} = d\gamma/dt$, this expression could equally well be been written:

$$\frac{dE_d(t)}{dt} = \eta \dot{\gamma}^2 \qquad (2)$$

or

$$\frac{dE_d(t)}{dt} = \frac{\sigma^2}{\eta} \qquad (3)$$

For liquids the energy stored, $E_s(t)$, is zero.

For solids the energy dissipated is zero, and the energy stored per unit volume is given by:

$$E_s = \frac{\sigma\gamma}{2} \equiv \frac{G\gamma^2}{2} \qquad (4)$$

For viscoelastic materials part of the mechanical energy is stored and part is dissipated, by definition. The energy dissipated under steady state conditions is given by equations 1 to 3, the stored component is obtained from the transient response, i.e. the growth in shear rate to steady state, or its decay after removal of the stress. For low stresses, where the condition of linear viscoelasticity holds, the analysis is relatively straightforward, but in practice at higher stresses it is difficult to separate the elastic (stored energy) response from that due to thixotropic and other time dependent effects.

The analysis of the energy stored and dissipated during oscillation is more complicated than is sometimes recognized. The principle difficulty is that a liquid will continue to dissipate energy continuously during oscillation, but the total energy stored by a solid during a cycle is zero. In the case of the solid, there are two points in the cycle at which the strain is zero, at which points the stored potential energy is also zero. Integrating over the complete cycle, or even half cycle, would not be useful.

The first thought on how to overcome this might be to consider the energy stored at the point of maximum strain, in other words integrate over a quarter cycle, and this is what is sometimes done. But it turns out that this type of analysis is flawed, because the various mechanisms for storing energy do not act coherently. A better way of proceeding is to consider the *average* amount of energy stored during a cycle. It is possible then to make a comparison with the *total* energy dissipated per cycle. This is the approach taken by Tschoegl.

After much analysis, it is found that:

$$E_s(\omega)_{av} = \frac{\gamma_0^2}{4} G'(\omega) \qquad (5)$$

and

$$E_d(\omega)_{cyc} = \pi\gamma_0^2 G''(\omega) \qquad (6)$$

so

$$\frac{E_d(\omega)_{cyc}}{E_s(\omega)av} = 4\pi\tan\delta \qquad (7)$$

Equations 5 and 6 can be checked for liquids and solids for sinusoidal oscillation:

$$\gamma = \gamma_0\sin\omega t \qquad (8)$$

so

$$\dot{\gamma} = \gamma_0\omega\cos\omega t \qquad (9)$$

and

$$\dot{\gamma}^2 = (\gamma_0\omega)^2\cos^2\omega t \qquad (10)$$

For a liquid, combining with equation 2 gives:

$$\frac{dE}{dt} = \eta(\gamma_0\omega)^2\cos^2\omega t \qquad (11)$$

The energy dissipated per cycle is then:

$$E_d(\omega)_{cyc} = \int_0^{2\pi/\omega} \eta(\gamma_0\omega)^2\cos^2\omega t\,dt \qquad (12)$$

$$= \eta(\gamma_0\omega)^2 \int_0^{2\pi/\omega} \cos^2\omega t\,dt \qquad (13)$$

$$= \eta(\gamma_0\omega)^2 \left[\frac{t}{2} + \frac{\sin 2\omega t}{4\omega}\right]_0^{2\pi/\omega} \qquad (14)$$

but $\sin 4\pi = 0$, and for liquids $\eta = G''/\omega$,

so:

$$E_d(\omega)_{cyc} = \pi\gamma_0^2 G''(\omega) \qquad (15)$$

For solids, combining equations 4 and 8 gives:

$$E_s(\omega) = \frac{G\gamma_0^2\sin^2\omega t}{2} \qquad (16)$$

The total energy stored in a quarter cycle is then:

$$= \frac{G\gamma_0^2}{2} \int_0^{\pi/2\omega} \sin^2\omega t\,dt \qquad (17)$$

$$= \frac{G\gamma_0^2}{2}\left[\frac{t}{2} - \frac{\sin 2\omega t}{4\omega}\right]_0^{\pi/2\omega} \qquad (18)$$

which, since $\sin\pi = 0$,

$$= \frac{G\gamma_0^2\pi}{8\omega} \qquad (19)$$

The average energy stored over a quarter cycle, which is equal to the average energy stored over a full cycle, is then:

$$= \left[\frac{G\gamma_0^2\pi}{8\omega}\right] / \left[\frac{\pi}{2\omega}\right] \qquad (20)$$

so

$$E_s(\omega)_{av} = \frac{\gamma_0^2}{4}G'(\omega) \qquad (21)$$

[1]   Tschoegl, N.W., "*The Phenomenological Theory of Linear Viscoleastic Behaviour*", chapter 9, pages 443 - 483, Springer-Verlag, Berlin, 1989.

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