



Normal stresses in shear flow

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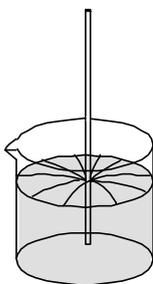
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INTRODUCTION

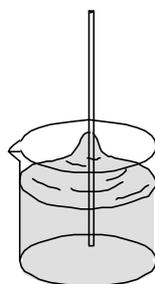
Historically, normal stresses in shear flow were the first evidence of elasticity in liquids. However today, due to the wide availability of more convenient measurements like the elastic modulus, G' , via sinusoidal oscillations, few normal stress measurements are made. Yet there are many applications where shear normal stresses can be very important. Whenever shear strains are large, measuring normal stresses is both appropriate to the problem and sensitive to the microstructure generated by the large strain. /1/ This review describes shear normal stresses and what causes them. More details on actually making normal stress measurements can be found in the Product brief: "Measuring Normal Forces /2/.

WHAT ARE NORMAL STRESSES?

During World War II it was observed that high polymers like natural rubber when dissolved in



Newtonian fluid
Inertia causes the fluid to flow away from the center



Viscoelastic fluid
Elastic forces cause the fluid to climb up the rod

Figure 1. A rod is rotated in a beaker of motor oil on the left and in a solution of 1% polyisobutylene in oil on the right.

gasoline (to make flame thrower liquids) exhibited very unusual flow behavior. When such solutions were mixed they climbed up the stirrer shaft (see Figure 1) and even out of the container! Karl Weissenberg /3/ (1947) reported this and showed that rod climbing was caused by normal stresses generated by the shearing.

These same shear normal stresses cause a cross-linked rubber rod to get *longer* when it is twisted. Figure 2 illustrates a rod twisted by a torque M . Each element of the rod is acted upon by a shear stress, T_{zq} or T_{21} , and also experiences normal stresses T_{22} and T_{33} . Because the rod is curved, T_{11} is a hoop stress, which squeezes around the rod circumference and forces the material to deform along the z axis. To prevent the rod from elongating in z direction a force F must be exerted on the ends

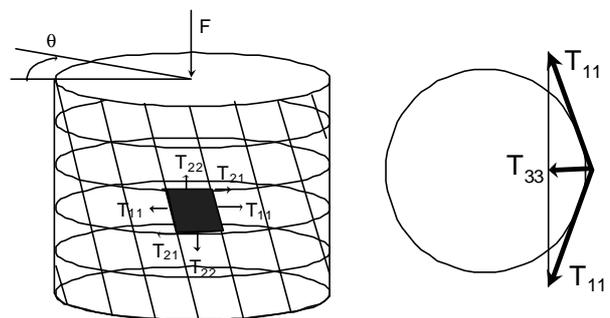


Figure 2. Torque and normal forces are generated when an elastic rod is twisted. The direction of the deformation is q (or x_1). Thus the stress component in the direction of twisting acting on the element surface that was perpendicular to that direction is designated T_{qq} or T_{11} . Similarly, T_{zz} or T_{22} acts normal to the horizontal surfaces and T_{rr} or T_{33} acts normal to the surfaces perpendicular to the cylinder's radius

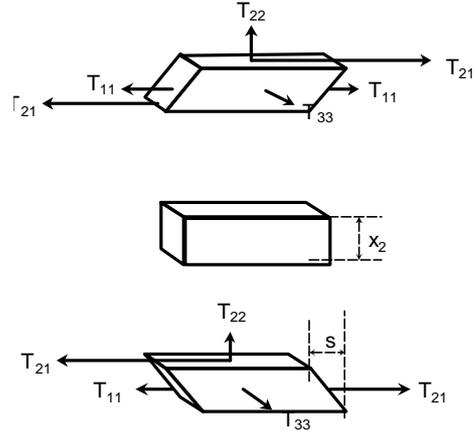
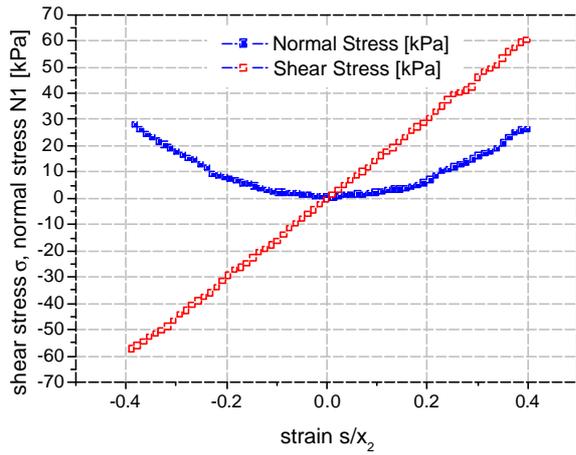


Figure 3. a) Shear and normal stresses versus shear strain for a silicone rubber sample subject to simple shear shown schematically. The data points indicate the normal stress difference, necessary to keep the block at constant thickness X_2 , while the squares are the shear stress data (from Macosko, 1994). The lines are for an ideal rubber with $G = 163 \text{ kPa}$

If the same rubber is twisted between a small angle cone and a disk in a cone/plate rheometer, the shear and normal stresses can be simply and directly related to the torque and normal forces:

$$T_{21} = \frac{M}{pR^3} \quad (1)$$

$$T_{11} - T_{22} = N_1 = \frac{2F}{pR^2} \quad (2)$$

Figure 3 shows shear stress and normal stress data for silicone rubber vs. shear strain. Strain is directly related to the twist angle:

$$g = \frac{Rq}{R \sin a} \cong \frac{Rq}{Ra} \quad \text{for small } a \quad (3)$$

where a is the angle of the cone. Note that a normal stress difference generates the force F . This is due to the curvature of the sample as in twisting the rubber rod.

Ideal rubber obeys Hooke's law in shear, i.e. the shear stress is proportional to the strain

$$T_{21} = Gg \quad (4)$$

where G is the shear modulus. Figure 3 shows that shear stress is linear with strain over a wide range and $G = 163 \text{ kPa}$. If Hooke's law is extended to large strains (neo-Hookean) it

predicts the normal stress:

$$T_{11} - T_{22} = N_1 = Gg^2 \quad (5)$$

In figure 3 these relations fit the data well. Note the quadratic shape of $T_{11} - T_{22}$ and that when the strain is reversed it stays positive. Since there

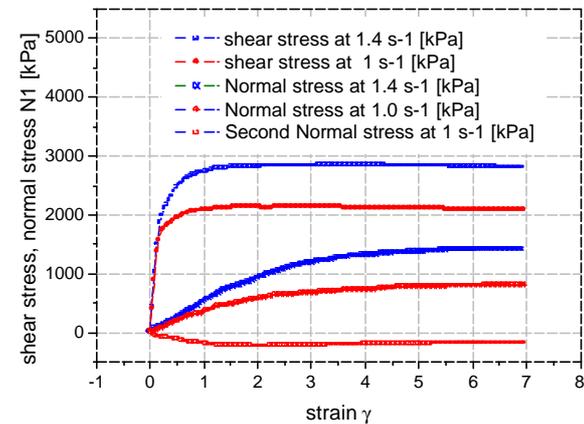


Figure 4. Shear stress and normal stress differences for a polystyrene melt (at 220°C) vs. shear strain after the start up of steady shearing). The dotted lines are the predictions for an ideal rubber, eq. 4-6. Data taken on ARES with force rebalance transducer. T_{12} and N_1 were measured with cone and plate, eq. 1 and 2. N_2 was determined by subtracting cone and plate normal stress data from parallel plate results on the same material.

are up to three components of the normal stress there can be another independent normal stress difference:

$$T_{22} - T_{33} = N_2 \quad (6)$$

For an ideal rubber $N_2=0$. For real rubbers and polymeric liquids N_2 is typically significantly smaller than N_1 and of opposite sign. This is shown in Figure 4.

Polymeric liquids behave much like rubber at short times. Figure 4 illustrates shear and normal stresses for a polymer melt. At small strains the response looks like that for rubber. The shear stress can be fit to eq. 4 and N_1 to eq. 5. At high strains the stresses decrease and eventually reach a steady value. These steady state values increase with the shear rate as shown in Figure 4.

At low shear rates the shear stress increases linearly with the shear rate and the normal stresses stress with the shear rate squared. In order to study the shear rate effects the data are reduced with the shear rate. Thus, the shear stress coefficient or *viscosity* and the first and second normal stress coefficients are defined as:

$$\frac{T_{21}}{\dot{\mathbf{g}}} = \mathbf{h} \quad \frac{N_1}{\dot{\mathbf{g}}^2} = \Psi_1 \quad \frac{N_2}{\dot{\mathbf{g}}^2} = \Psi_2 \quad (7) \quad (8) \quad (9)$$

WHAT CAUSES NORMAL STRESSES?

Figure 4 shows that typical polymer melts behave like cross-linked rubber at short times and high strain rates. This is because the chains in typical polymer melts are highly entangled and the entanglements form a temporary network. At large strain the entanglement network comes apart. At higher shear rates the stresses can go through a maximum as the chains disentangle. Eventually equilibrium between entangling (due to Brownian motion) and disentangling (due to the shearing) is reached, generating steady stresses (see Figure 4). At lower shear rates the steady state stresses decrease because there is more time for entanglement. As the shear rate goes to zero, so do the stresses as expected for a true liquid. Note also in Figure 4 that the second

normal stress, N_2 , is not zero but $N_2 = -0.25 N_1$. This is typical for polymeric liquids.

This same behavior illustrated in Figure 4 qualitatively occurs for dilute polymer solutions because even a single polymer coil will deform due to the flow (See Figure 6a). Brownian motion tries to randomize the chain bringing it back to an un-deformed coil which creates tension, T_{11} , along the streamlines. Tiny rod-like particles will also orient in shear flows. Brownian motion tries to randomize this orientation. As with the random coil this generates tension along stream-lines, which can generate shear normal stresses which will increase with the degree of orientation. Emulsion droplets deform due to flow and interfacial tension tries to restore them to a spherical shape also generating normal stresses. Of course, stresses for these dilute systems are typically much smaller than those for entangled polymers

For polymer melts normal stresses are very sensitive to molecular weight and molecular weight distribution. For entangled melts the low shear rate shear viscosity depends strongly on the average molecular weight

$$\begin{array}{ll} \mathbf{h}_o \sim M_w^{3.4} & \text{unentangled } M_w \ll M_{entangle} \\ \mathbf{h}_o \sim M_w & \text{entangled } M_w > M_{entangle} \end{array} \quad (10)$$

$$\lim_{\dot{\mathbf{g}} \rightarrow 0} \frac{N_1}{\dot{\mathbf{g}}^2} = \Psi_{1,0} \approx M_w M_z^2 \quad (11)$$

Thus, we might expect normal stresses to be very useful in polymer characterization. However, at small shear rates the first normal stress is just twice the elastic or storage modulus measured in sinusoidal shearing.

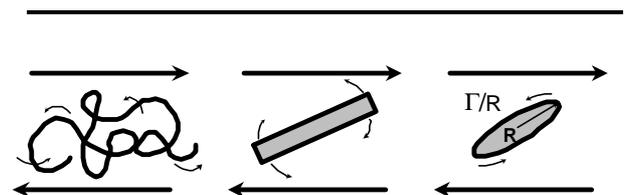


Figure 6: Normal stresses arise in shear flow of a) polymer coils and b) rod-like particles due to Brownian motion and in c) liquid drops due to interfacial tension, G

$$\lim_{\dot{g} \rightarrow 0} N_1 = \lim_{w \rightarrow 0} 2G' \quad (12)$$

In Figure 5 the dynamic data are compared to the steady shear viscosity and normal stress. The correlation holds over a wide range of shear rate and frequency. At higher rates or frequencies, the dynamic and steady results deviate.

Measuring the dynamic moduli only perturbs polymer chains around their equilibrium configuration. Normal stress measurements involve large strains as do most processing operations. Thus shear normal stress can be sensitive to micro-structural changes caused by process flows such as large scale disentangling of chains, deformation of drops or phase change due to shear. Data on normal stress development with shearing, like Figure 4, is very valuable to build and test constitutive equations. These equations then in turn can be used to model process flows. But even without a full model of the process, useful correlation with normal stress data can be made of drops or phase change due to shear. Normal stresses are very sensitive and can easily be masked by instrument affects. As such, normal stress measurements need to be done carefully. Refer to the product brief “Measuring normal forces” for more information.

REFERENCES

1. Macosko, C. W. *Rheology: Principles, Measurement and Applications,*; VCH Publishers: New York, 1994.
2. Rheometric Scientific Applications Brief, *Measuring normal forces*
3. Weissenberg, K. *Nature*, 1947, 159, 310.

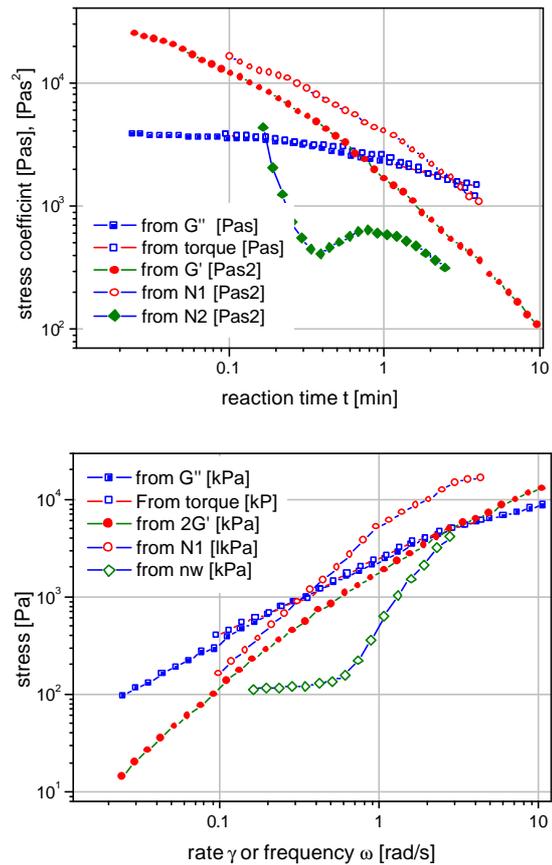


Figure 5: a) Steady state shear, first normal stress difference and second normal stress difference for a polyethylene melt. Also shown are the dynamic moduli from sinusoidal oscillations vs. oscillation frequency. b) The same data are re-plotted as viscosity, first normal stress coefficient and second normal stress coefficient. But the first normal stress coefficient is even more sensitive and also depends on higher averages of molecular weight .