

Polymerization Technology – Laboratory

Viscometry/Rheometry

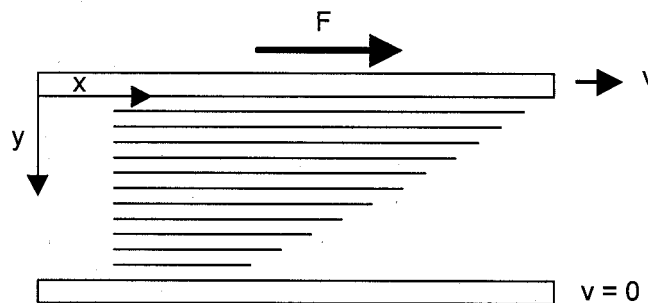
Tasks

1. Determination of the flow behaviour of polyvinylalcohol in water
2. Observation of a crosslinking reaction of polyvinylalcohol

Theory

The most important values to describe the flow behaviour of any substance are the *viscosity*, the *shear rate* and the *shear stress*.

The meanings of them can be explained easily with the following figure. The substance, which is able to flow, is located between two parallel plates of the same area A .



Now a force in x -direction is applied to the upper plate. It moves with the velocity v . The lower plate is fixed. In our model the substance shall consist of separate and very thin layers parallel to the plates. These layers will move with different velocities, because the outer layers are as fast as the plates. The upper most layer moves with $v = v$ (at the moving plate) and the lowest layer moves with $v = 0$. The layers in between have a velocity ranging from 0 to v . The velocity gradient dv/dy describes the change of velocity between the layers in y -direction. Newton's law of viscosity predicts that this velocity gradient is proportional to the force (in x -direction) per area F/A applied the upper plate. The constant factor between the gradient and the force per area is called *viscosity*:

$$\frac{F}{A} = \eta \frac{dv}{dy} \quad (1)$$

Now we define $\xi = dx/dy$ to be the *strain*, that is applied to the substance. With $dv = dx/dt$ follows:

$$dv/dy = d\xi/dt = \dot{\xi} \quad (2)$$

The change of the strain with time $d\varepsilon/dt = \dot{\varepsilon}$ is called shear rate. It is identical to the velocity gradient in the substance. The quotient F/A is called *shear stress* t

$$t = h\dot{\varepsilon} \quad (3)$$

In liquids the Newtonian behaviour shear rate and shear stress are proportional and therefore viscosity h is constant over the whole range of the applied shear rate or stress.

If h is not constant but a function of the shear rate, we call the behavior of a substance to be *pseudo plastic* (viscosity decreases with increasing shear rate) or *dilatant* (viscosity increases with increasing shear rate). But in most cases a plateau of constant viscosity at very low shear rates can be observed. In this region the sample behaves like an Newtonian fluid and the viscosity at those very low shear rates is called *zero viscosity*:

$$\lim_{\dot{\varepsilon} \rightarrow 0} h = h_0 \quad (4)$$

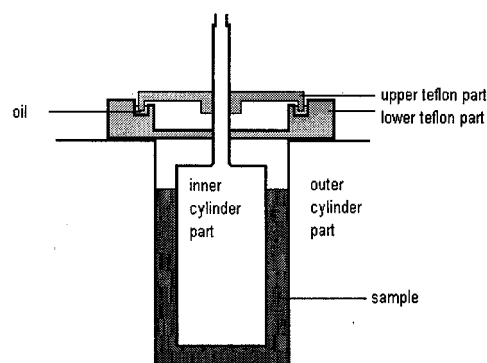
The flow behavior of pseudo plastic substances can be described with the Oswald De Waele equation:

$$\dot{\varepsilon} = Kt^n \quad (5)$$

Gelation

If a polymer is crosslinked, macromolecules form bigger macromolecules and viscosity increases. The gel point is reached, if one three dimensional macromolecule fills out the whole reaction volume. The process of increasing viscosity will be observed with the rheometer.

Measuring principle



measuring system

The measuring system consists of a solid inner cylinder, which is rotating, and a hollow outer cylinder. The substance is filled in the gap between them.

r is the distance from the rotating axis and ω is the angular velocity. The velocity of a liquid layer in the distance r is $v = r\omega$. The velocity gradient over the gap is:

$$\frac{dv}{dr} = r \frac{d\omega}{dr} \quad (6)$$

The inner cylinder has approximately the same radius r (small gap) and the height l . On its area $A = 2\pi rl$ acts the force F (see equation 1):

$$F = \eta A \frac{dv}{dr} = 2\pi h l r^2 \frac{d\omega}{dr} \quad (7)$$

The torque T at the inner cylinder is given by the product between force and radius:

$$T = F \cdot r = 2\pi h l r^3 \frac{d\omega}{dr} \quad (8)$$

This equation can be integrated with following integration limits: The radius of the outer cylinder is R and its angular velocity is zero: $\omega = 0$ at $r = R$. The radius of the inner cylinder is $f \cdot R$ ($f < 1$) with $\omega = \omega$ at $r = f \cdot R$.

$$\int_{fR}^R \frac{dr}{r^3} = \frac{2\pi h l}{T} \int_{\omega}^0 d\omega \quad \Rightarrow \quad \frac{1}{R^2} \left(\frac{1-f^2}{f^2} \right) = -\frac{4\pi h l}{T} \omega \quad (9)$$

Thus we obtain a relation between the torque T at the inner cylinder and its angular velocity ω :

$$T = 4\pi h l R^2 \frac{f^2}{f^2 - 1} \cdot \omega \quad (10)$$

The viscosity can be determined from equation (10) directly, because the geometrical data R , f and l of the measuring system are known. The shear rate is determined from the angular velocity, while the shear stress is determined from the torque by internal calculation with constants that are specific for the applied measuring system.

The CS10 rheometer, that is used here, controls the applied torque at the inner cylinder and measures the angular velocity of it.

Experimental

1. A solution of polyvinylalcohol (10 wt% in water) is filled into the measuring system. The flow behavior is measured at different temperatures (25/30/35/40/45 °C) by variation of the shear stress.
2. The crosslinking reaction of polyvinylalcohol is observed at room temperature. Glutardialdehyde is used as cross-linking agent (8 mol% in relation to vinylalcohol monomer).

Analysis

1. Plot the data of methylcellulose in x/y graphs for each temperature: τ/h , $\dot{\epsilon}/h$ (log/log plots) and $\tau/\dot{\epsilon}$ (linear plot).
2. Determine the different zero viscosities for each temperature and plot them in dependence on the temperature.
3. Fit the 25°C data with the Oswald De Waele equation.
4. For the crosslinking reaction: *analysis method will be given to you by the assistant.*

Literature

Macosco, C.W., *Rheology*, p.109ff, VCH Verlag (1994)