10 VISCOSITY (MELT PHASE)

10.1 DEFINITION OF VISCOSITY

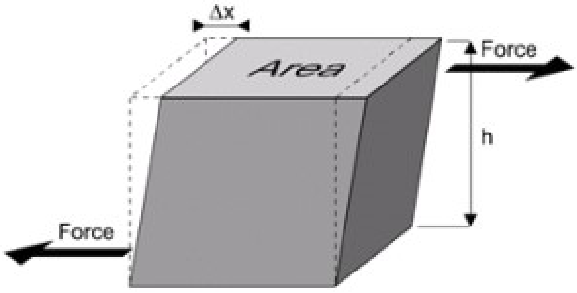

Figure 44: Cube deformed by a shear stress.

Consider a cube made from an elastic material, having ribs with length h. The cube is glued to a table. If we would apply a force to the top of the cube parallel to the surface of the table then the top of the cube will be displaced over a distance Δx, as shown in Figure 44. This kind of deformation is called **shear deformation**. Its value is the deformation divided by the height Δx/h. The force acting on the cube divided by the area of the cube (F/h^2) is called the **shear stress**.

The ratio between the shear stress and the shear deformation is called the **shear modulus**. It can be calculated from:
[shear modulus] = [shear stress] / [shear deformation] or *[shear stress] = [shear modulus] * [shear deformation]*

Now suppose that the cube is made from a fluid like water or molten polymer. If a shear stress would be applied to this cube, then the top of the cube would continuously move in the direction of the stress with a certain velocity as long as the force exists. This continuous deformation is called shear rate and it is defined as the velocity of the top v divided by the height h: v/h.

The ratio between the shear stress and the shear rate is called the **viscosity**. It can be calculated from:
[viscosity] = [shear stress] / [shear rate] or *[shear stress] = [viscosity] * [shear rate]*
In mathematical form:

Equation 70

$$\eta = \tau \Big/ \frac{d\gamma}{dt} \quad \text{or} \quad \tau = \eta \frac{d\gamma}{dt}$$

The viscosity is an important material property of a fluid. With the aid of the viscosity the shear stress can be calculated when the fluid is sheared. Eventually this gives us the possibility to calculate the required pressure to move a fluid through a channel.

10.2 HOW TO CALCULATE THE VISCOSITY FROM THE DIFFERENTIAL EQUATION

In chapter 8 we have shown the general outline of the differential equation for the rubber and melt phase:
[change of rubber stress per unit of time] = + [change of rubber stress due to deformation per unit time] – [rubber stress] / [rubber relaxation time]

This differential equation can be used for the calculation of the viscosity from the material properties. The rubber stress is the same as the shear stress. We assume that after some time of

shearing the shear stress has become constant. We have a dynamic equilibrium. That means that the change of stress has become zero:
0 = + [change of rubber stress due to deformation per unit time] – [shear stress] / [rubber relaxation time]

The change of rubber stress per unit time is the shear modulus times the shear rate:
*[change of rubber stress due to deformation per unit time]= [shear modulus] * [shear rate]*

By combining these two equations we get:
*0 = [shear modulus] * [shear rate]] - [shear stress] /* [relaxation *time]*

This can be rewritten into:
*[shear stress] = [shear modulus] * [relaxation time] * [shear rate]*

Remember that the viscosity has been defined as:
[viscosity] = [shear stress] / [shear rate]

Which gives us the following result for the viscosity:
*[viscosity] = [shear modulus] * [relaxation time]*

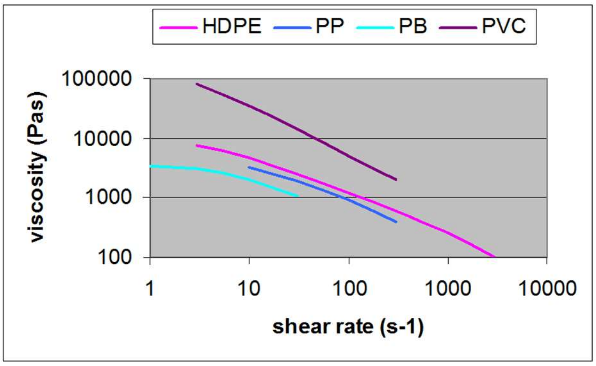

Figure 45: The viscosity of a polymer reduces with increasing shear rate or shear stress.

By using a differential equation in a dynamic equilibrium, we have proven that the viscosity of a fluid is simply the shear modulus time the relaxation time. Since the relaxation time of a polymer strongly reduces with the applied stress it follows that the viscosity of a polymer will also decrease with increasing shear stress or shear rate. This is a commonly observed phenomenon with polymers as shown in Figure 45.

10.3 MATHEMATICAL DERIVATION OF VISCOSITY VERSUS SHEAR STRESS AND SHEAR RATE

The viscoelastic relations are:

$$\frac{d\sigma_{gla}}{dt} = \frac{d\sigma_{gla}}{d\varepsilon_{ben}}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}} \text{ with } \theta_{rot} = \theta_{rot,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rot}\sigma_{gla}}{kT}\Big/\sinh\left(\frac{V_{rot}\sigma_{gla}}{kT}\right)$$

$$\frac{d\sigma_{rub}}{dt} = \frac{d\sigma_{rub}}{d\varepsilon_{rot}}\frac{d\varepsilon_{ben}}{d\sigma_{gla}}\frac{\sigma_{gla}}{\theta_{rot}} - \frac{\sigma_{rub}}{\theta_{rep}} \text{ with } \theta_{rep} = \theta_{rep,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rep}\sigma_{rub}}{kT}\Big/\sinh\left(\frac{V_{rep}\sigma_{rub}}{kT}\right)$$

$$\sigma = \sigma_{gla} + \sigma_{rub}$$

$$\varepsilon = \varepsilon_{ben} + \varepsilon_{rot}$$

Boundary conditions:

- The polymer is under a constant rate of deformation (dε/dt) and the stresses do not change anymore:

  $\frac{d\sigma_{gla}}{dt} = 0$ and $\frac{d\sigma_{rub}}{dt} = 0$

The viscoelastic relation for the glass stress then becomes:

Equation 71

$$\frac{d\sigma_{gla}}{d\varepsilon_{ben}}\frac{d\varepsilon}{dt}-\frac{\sigma_{gla}}{\theta_{rot}}=0$$

$$\frac{d\sigma_{rub}}{d\varepsilon_{rot}}\frac{d\varepsilon_{ben}}{d\sigma_{gla}}\frac{\sigma_{gla}}{\theta_{rot}}-\frac{\sigma_{rub}}{\theta_{rep}}=0$$

From which follows:

Equation 72

$$\sigma_{gla}=\theta_{rot}\frac{d\sigma_{gla}}{d\varepsilon_{ben}}\frac{d\varepsilon}{dt}$$

$$\sigma_{rub}=\theta_{rep}\frac{d\sigma_{rub}}{d\varepsilon_{rot}}\frac{d\varepsilon}{dt}$$

For the total stress created by the deformation rate we find:

Equation 73

$$\sigma=\sigma_{gla}+\sigma_{rub}=\theta_{rot}\frac{d\sigma_{gla}}{d\varepsilon_{ben}}\frac{d\varepsilon}{dt}+\theta_{rep}\frac{d\sigma_{rub}}{d\varepsilon_{rot}}\frac{d\varepsilon}{dt}$$

We consider the case that the deformation of the polymer is a shear deformation, usually denoted by γ:

Equation 74

$$\sigma_{gla}=G_{gla}\gamma_{ben}\ ,\ \sigma_{rub}=G_{rub}\gamma_{rot}\ \text{and}\ \frac{d\varepsilon}{dt}=\frac{d\gamma}{dt}$$

By combining Equation 73 with Equation 74 we find for the relation between the stress and the strain rate:

Equation 75

$$\sigma=\left(G_{gla}\theta_{rot}+G_{rub}\theta_{rep}\right)\frac{d\gamma}{dt}$$

The shear viscosity η_s of a polymer is defined as:

Equation 76

$$\sigma=\eta_s\frac{d\gamma}{dt}$$

It then follows for the shear viscosity of a polymer:

Equation 77

$$\eta_s = G_{gla}\theta_{rot} + G_{rub}\theta_{rep}$$

Shear viscosity is usually determined in the rubber phase. In that case the product $G_{rub}\theta_{rep}$ is much higher than $G_{gla}\theta_{rot}$ (G_{rub} is 1000 times lower than G_{gla} but θ_{rep} is 10^6 to 10^8 time higher than θ_{rot}). Therefor the shear viscosity of a rubber is simply the product of the shear modulus and the rubber relaxation time:

Equation 78

$$\eta_s = G_{rub}\theta_{rep}$$

Equation 78 combined with the equation for the reptation relaxation time gives us:

Equation 79

$$\eta_s = G_{rub}\theta_{rep,0}\, exp\left(\frac{E_{rot}}{kT}\right)\frac{\frac{V_{rep}\sigma_{rub}}{kT}}{sinh\left(\frac{V_{rep}\sigma_{rub}}{kT}\right)} = \eta_{s,0}\frac{\frac{V_{rep}\sigma_{rub}}{kT}}{sinh\left(\frac{V_{rep}\sigma_{rub}}{kT}\right)}$$

In Equation 79 we have defined the zero-stress (or zero-shear) viscosity $\eta_{s,0}$ as:

Equation 80

$$\eta_{s,0} = G_{rub}\theta_{rep,0}\, exp\left(\frac{E_{rot}}{kT}\right)$$

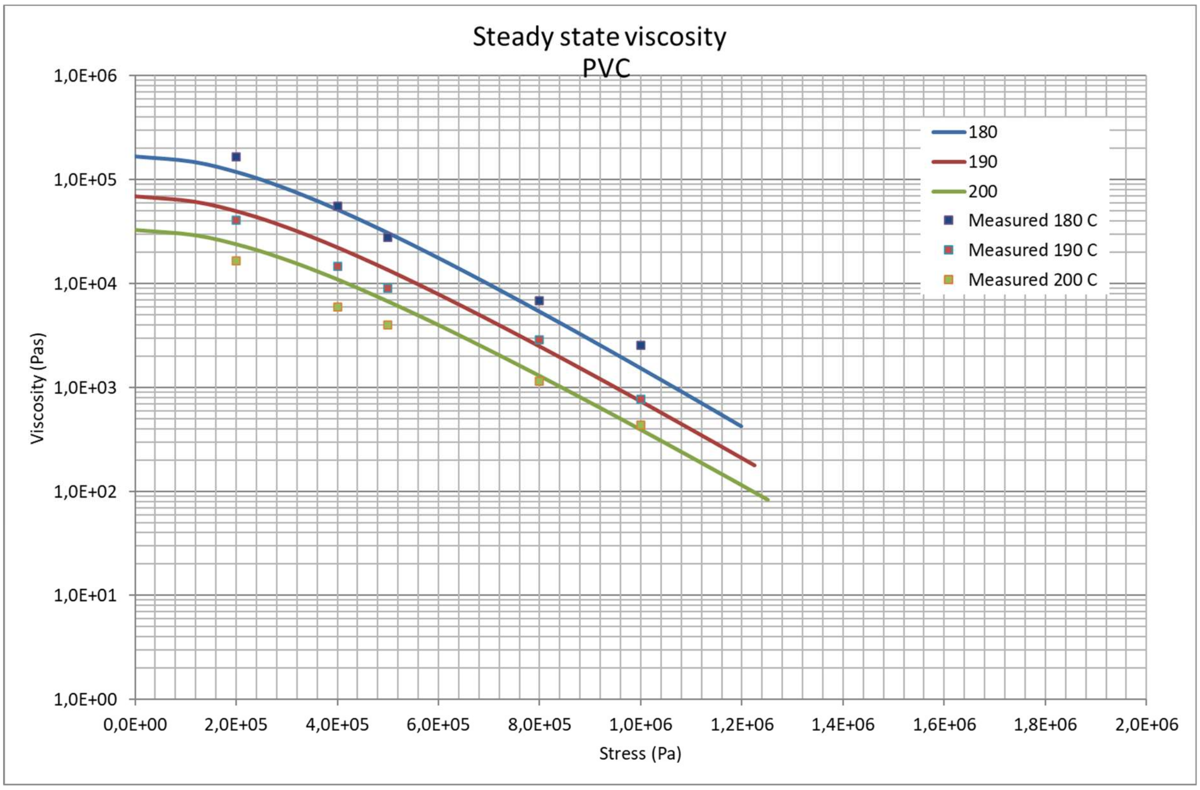

Figure 46: Shear viscosity of PVC K67 versus shear stress.

In Figure 46 the viscosity of PVC at 180 to 200 C has been calculated with the aid of and Equation 79 with the physical constants of PVC. The viscosity data are logarithmically plotted versus the shear stress. Note that at higher stresses the viscosity η_s decrease approximately exponentially with the shear stress σ_{rub}.

Note that in the model described above the viscosity is described as a function of the stress. From a physical perspective this is natural because it is the stress that the polymer molecules experience. Increasing stress will reduce the viscosity because the relaxation time of the rubber stress reduces.

In practice the viscosity is however often represented as a function of the shear rate. The equation that describes the shear rate dependence of the viscosity can be derived from Equation 79:

Equation 81

$$\eta_s = \frac{kT}{V_{rep}} \frac{1}{\frac{d\gamma}{dt}} ln\left[\left(\eta_{s,0} \frac{V_{rep}}{kT} \frac{d\gamma}{dt}\right) + \sqrt{1 + \left(\eta_{s,0} \frac{V_{rep}}{kT} \frac{d\gamma}{dt}\right)^2}\right]$$

Equation 81 describes the viscosity as a function of the shear rate. It has been plotted for PVC at 180 to 200 C in Figure 47.

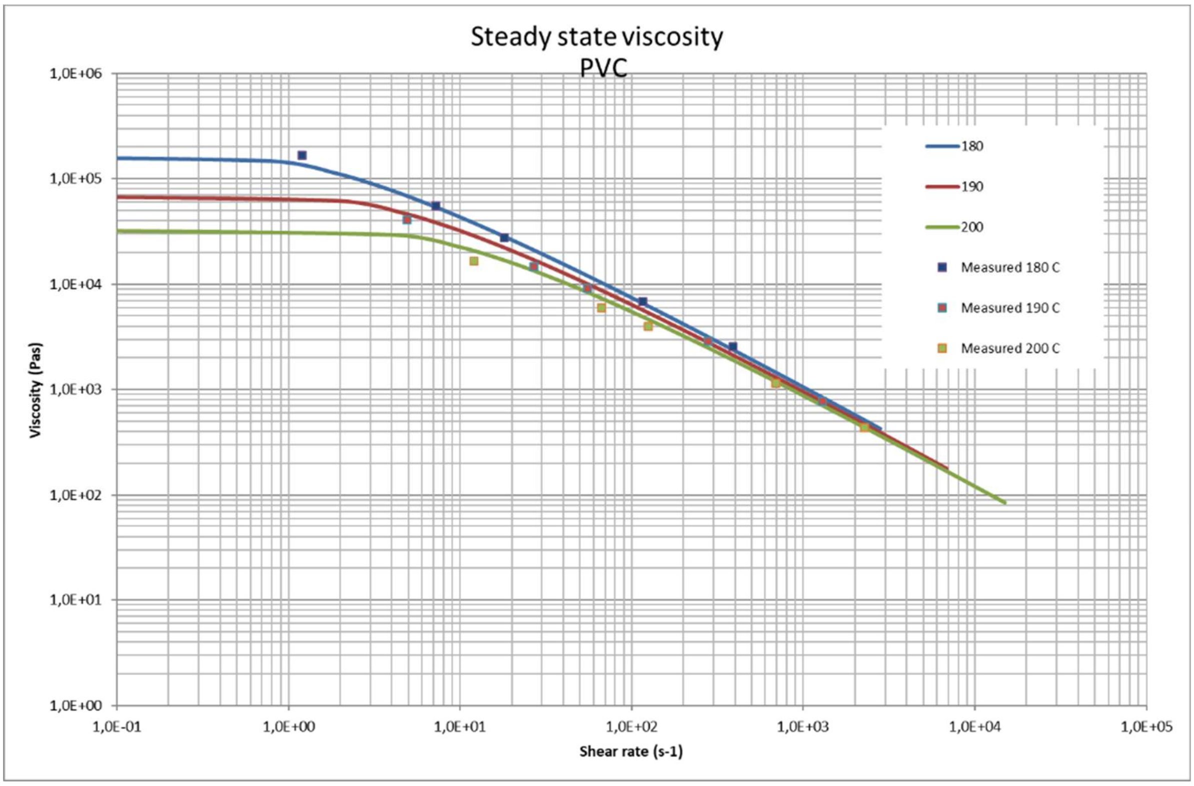

Figure 47: Shear viscosity of PVC K67 versus shear rate. At shear rates below 1 s^{-1} the behaviour is Newtonian, above 10 s^{-1} the behaviour is non-Newtonian.

10.4 THE POWER LAW MODEL

10.4.1 Low shear rates

At low shear rates the viscosity of the polymer is independent of the shear rate. The polymer melt behaves **Newtonian**. According to Equation 81 for small shear rates the viscosity becomes equal to the zero-shear viscosity:

Equation 82

$$\eta_s = \eta_{s,0}$$

This equation is only valid for low enough shear rates:

$$\frac{d\gamma}{dt} \ll \frac{kT}{V_{rep}\eta_{s,0}}$$

10.4.2 High shear rates

At high shear rates $\left(d\gamma/dt \gg kT/V_{rep}\eta_{s,0}\right)$ the viscosity approximates to be a power of the shear rate. The polymer melt behaves **non-Newtonian**. In this region Equation 81 reduces to:

Equation 83

$$\eta_s = \frac{kT}{V_{rep}} \frac{1}{\frac{d\gamma}{dt}} ln\left[2\left(\eta_{s,0}\frac{V_{rep}}{kT}\frac{d\gamma}{dt}\right)\right]$$

In a log viscosity – log shear rate plot as Figure 47 such a dependence shows up to be an almost straight line, the slope of it being between -0.5 and -1.0. This feature is used to make a simple description of the viscosity versus shear rate. It is called the **power law**:

Equation 84

$$\frac{\eta_s}{\eta_*} = \left(\frac{d\gamma}{dt}\right)^{n-1}$$

In this equation n is called the **power law index**. η_* is the viscosity at a shear rate of 1 s^{-1}. From Equation 81 the value of n can be derived by using $n - 1 = dln(\eta_s)/dln(d\gamma/dt)$:

Equation 85

$$n = \frac{kT}{V_{rep}\eta_{s,0}\frac{d\gamma}{dt}}$$

For high enough shear rates, the viscosity becomes inversely proportional to the shear rate because the power law index n tends to 0.

Note that especially at the higher shear rates the viscosities of the different temperatures seem to coincide. When operating at constant shear rate with increasing temperatures the stress will reduce. This increases the relaxation time and counteracts for a part the viscosity reduction due to temperature increase.