

9 YIELD STRESS (GLASS PHASE)

9.1 DESCRIPTION

In a tensile tester a specimen of the polymer to be tested is stretched until it breaks. The test is usually done at room temperature. During this test the deformation of the specimen and the force used for the extension are measured. The speed of the deformation (or strain rate) is normally kept constant. An example of a stress-strain diagram thus obtained from PVC is shown in the figure. The actual stress in the specimen is calculated by dividing the measured force by the surface of the specimen.

At the start of the test, when the deformation is still small, the stress first rises fast until a maximum has been reached. This maximum is called the **yield stress**. On further deformation, the measured stress reduces some 10 to 20 % and then rises again.

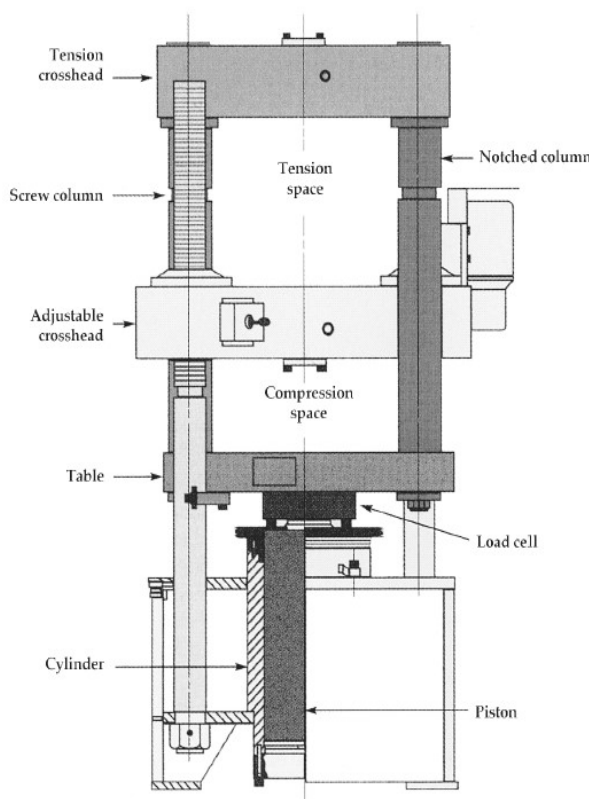


Figure 38: Tensile test equipment.

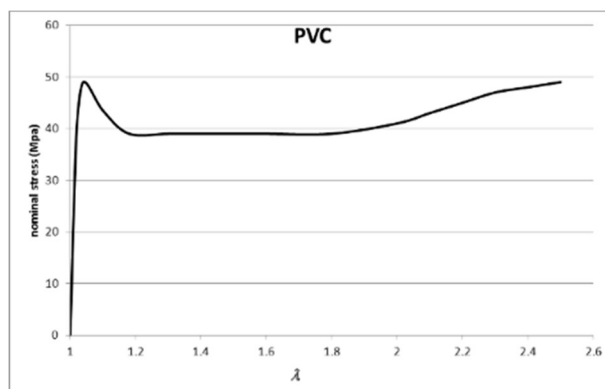


Figure 39: Nominal stress of PVC versus stretch ratio λ .

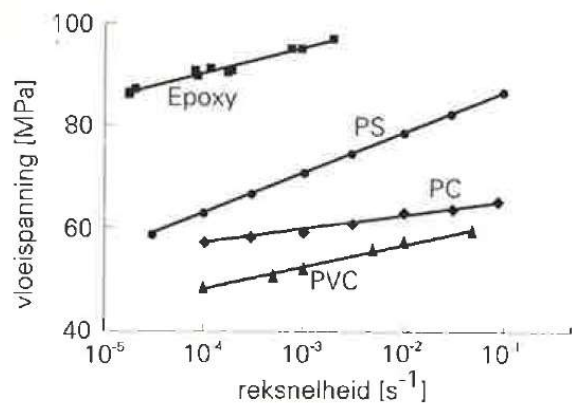


Figure 40: Relation yield stress and strain rate.

The yield stress gives an indication of the strength of the polymer. As long as the stress is below the yield stress then the polymer behaves like an elastic solid. Close to the yield stress however the polymer starts to deform plastically.

The tensile test can be done at different strain rates of the specimen. It is commonly observed that the yield stress increases logarithmically with the strain rate, as shown in Figure 40.

9.2 WHAT MAKES A POLYMER YIELD?

In the glass phase the Kuhn segment rotation time is very long. When a small stress is applied the polymer chains can only bend a little. This gives the polymer a stiff behaviour.

However, things change when the stress becomes high enough. We have seen in chapter 7 that the stress strongly reduces the rotation time of the Kuhn segments. When the stress has reached the yield stress the rotation time has reduced to a few seconds. That is low enough to make the plastic deform on a human time scale. It now behaves rubbery.

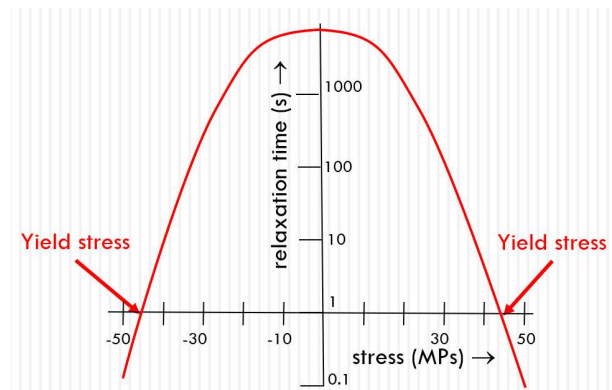


Figure 41: Near the yield stress the segment rotation time is 1 second.

9.3 HOW TO CALCULATE THE YIELD STRESS FROM THE DIFFERENTIAL EQUATION

In chapter 8 we have shown the general outline of the differential equation for the glass phase:
 $[change\ of\ glass\ stress\ per\ unit\ of\ time] = + [change\ of\ glass\ stress\ due\ to\ deformation\ per\ unit\ of\ time] - [glass\ stress] / [glass\ relaxation\ time]$

This differential equation can be used for the calculation of the yield stress from the material properties. At the moment of yield the stress does not change anymore. It is constant and equal to the yield stress. That means that the change of glass stress per unit of time is zero. Now the differential equation looks as follows:

$$0 = + [change\ of\ glass\ stress\ due\ to\ deformation\ per\ unit\ of\ time] - [yield\ stress] / [glass\ relaxation\ time]$$

In case of small deformations, which is the case before yielding, the stress is proportional to the deformation. The proportionality factor is the Young's modulus:

$$[glass\ stress] = [Young's\ modulus] * [deformation]$$

It then follows that the change of glass stress per unit of time is equal to the Young's modulus times the deformation speed:

$$[change\ of\ glass\ stress\ due\ to\ deformation\ per\ unit\ of\ time] = [Young's\ modulus] * [deformation\ speed]$$

We can rewrite this equation to determine the glass stress under those particular circumstances:

$$[yield\ stress] = [Young's\ modulus] * [glass\ relaxation\ time] * [deformation\ speed]$$

The yield stress is now found by applying the actual material properties into the equation above.

9.4 MATHEMATICAL DERIVATION OF THE YIELD STRESS

The viscoelastic relations are:

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

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

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

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

Boundary conditions:

- The tensile test is usually done with a polymer in the glass phase. The rubber stress is much smaller than the glass stress and can be neglected:

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

- For the description of the viscoelastic behaviour we will therefore use the viscoelastic relation for the glass stress only:

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

- The tensile test is a typical example of uniaxial deformation. The relation between glass stress and deformation is therefore described by Equation 34:

$$\sigma_{gla} = G(\exp(2\varepsilon_{ben}) - \exp(-\varepsilon_{ben}))$$

- The material yields at relatively low strains (0.1 to 0.2) and that results in a simple relation between stress and strain:

$$\sigma_{gla} = 3G\varepsilon_{ben}$$

- At the moment of yield the stress (σ_y) is constant and therefore its derivative with time is zero:

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

The viscoelastic equations now simplify to:

Equation 65

$$\frac{d\sigma_{gla}}{dt} = 3G \frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}} = 0 \quad \text{or} \quad \sigma_{gla} = \sigma_y = 3G\theta_{rot} \frac{d\varepsilon}{dt}$$

Now combining Equation 65 with the equation for the relaxation time in the glass phase using $\sigma_{gla} = \sigma_y$ results in the following equation for the yield stress:

Equation 66

$$\sigma_y = \frac{kT}{V_{rot}} \sinh^{-1}\left(\frac{3G_{gla} V_{rot}}{kT} \exp\left(\frac{E_{rot}}{kT}\right) \theta_{rot,0} \frac{d\varepsilon}{dt}\right)$$

If the argument in the inverse hyperbolic sine function is much larger than 1 we get:

Equation 67

$$\sinh^{-1}(x) = \ln(x + \sqrt{x^2 + 1}) \approx \ln(2x) \quad \text{for } x \gg 1$$

And Equation 66 can be simplified to:

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Equation 68

$$\sigma_y = \frac{E_{rot}}{V_{rot}} + \frac{kT}{V_{rot}} \ln\left(\frac{6G_{gla}V_{rot}}{kT}\right) + \frac{kT}{V_{rot}} \ln\left(\theta_{rot,0} \frac{d\varepsilon}{dt}\right)$$

From Equation 68 we learn that the yield stress during the tensile test increases with the logarithm of the strain rate ε , which is commonly observed in practice. For PVC the yield stress has been calculated using $E_{rot} = 2.2 \times 10^{-19}$ J (after 1 year of aging at 20 C), $V_{rot} = 2.2 \times 10^{-27}$ m³, $G_{gla} = 10^9$ Pa, $\theta_0 = 10^{-13}$ s and $d\varepsilon/dt = 1.67 \times 10^{-3}$ s⁻¹.

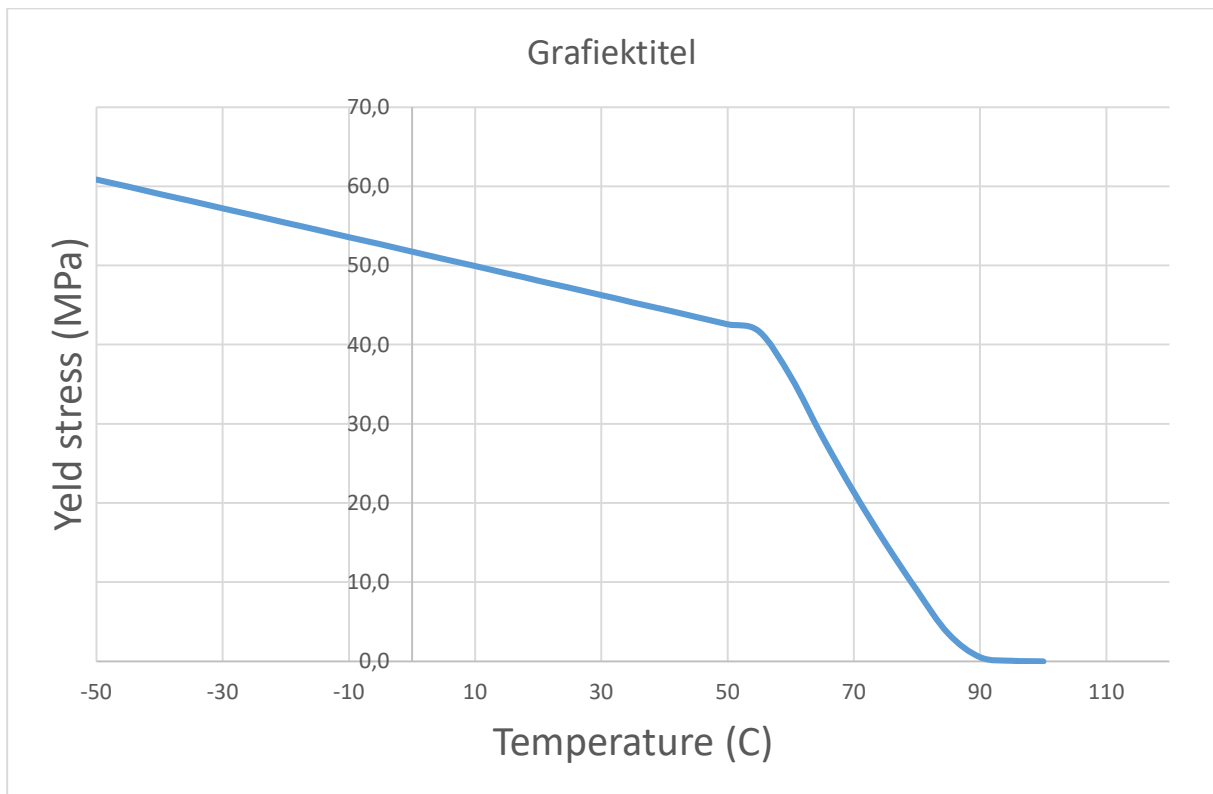


Figure 42: Yield stress of PVC as calculated with the aid of Equation 68.