13 Recovery of a deformed plastic body

13.1 The recovery process

Given a sufficiently high stress any polymer will deform, even if the temperature is far below the glass transition temperature. A good example is yielding of the polymer at the yield stress.

Once the stress is removed after yielding the polymer seems to remain deformed. In reality, the polymer will very slowly return to its original dimensions that it had before the deformation. This is called **recovery**.

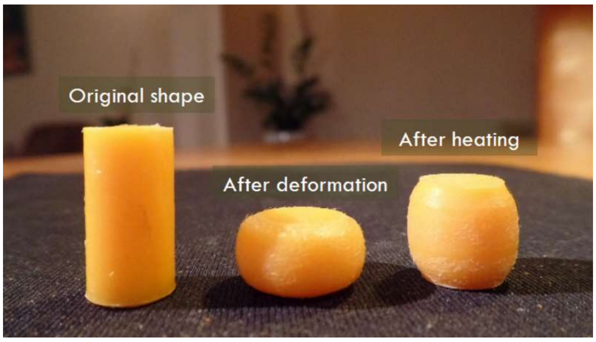

Figure 55: Below the glass temperature a polymer can be deformed but will not forget its original shape.

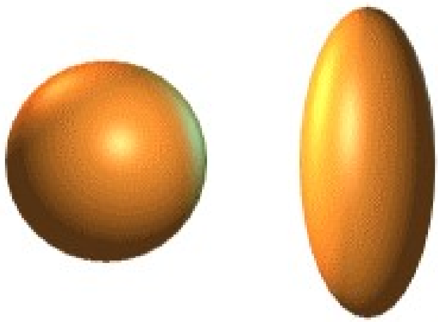

Figure 56: Yielding causes the spherical molecules to be deformed into an ellipsoid shape.

Due to the yielding all polymer molecules are deformed from a spherical into an ellipsoid shape. This induces a rubber stress in the molecules. The rubber stress will cause Kuhn segments in the molecules to rotate in such a way that the spherical shape returns in due time.

At temperatures around the glass transition temperature recovery lasts a few hours. It is a slow process. The time for recovery will increase very rapidly at lower temperatures. At a sufficiently low temperature recovery is not observable on human time scale.

13.2 Mathematical analysis of recovery after shear deformation

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 applied deformation is a shear deformation. For the glass shear stress and the rubber shear stress we have:
  $\sigma_{gla} = G_{gla}\gamma_{ben}$ and $\sigma_{rub} = G_{rub}\gamma_{rot}$
  $\frac{d\sigma_{gla}}{d\gamma_{ben}} = G_{gla}$ and $\frac{d\sigma_{rub}}{d\gamma_{rot}} = G_{rub}$
- The recovery is done below the glass transition temperature. We can then safely assume that the reptation relaxation time θ_{rep} is infinitely high.
- During the recovery process the glass stress and the rubber stress balance each other and the total stress σ is zero:
  $\sigma_{rub} = -\sigma_{gla}$ and $\frac{d\sigma_{rub}}{dt} = -\frac{d\sigma_{gla}}{dt}$

The viscoelastic relations now become:

Equation 97

$$\frac{d\gamma}{dt} = \frac{G_{gla} - G_{rub}}{G_{gla}} \frac{\gamma_{ben}}{\theta_{rot}}$$

Since $\sigma_{rub} = -\sigma_{gla}$ and $\gamma = \gamma_{ben} + \gamma_{rot}$ it follows that:

Equation 98

$$\gamma_{ben} = -\frac{G_{rub}}{G_{gla} - G_{rub}}\gamma$$

Finally, by combining Equation 97 and Equation 98 we obtain a very simple differential equation for the recovery of a deformed product:

Equation 99

$$\frac{d\gamma}{dt} = -\frac{G_{rub}}{G_{gla}} \frac{\gamma}{\theta_{rot}}$$

Figure 57 shows the numerical solution of Equation 99 for PVC at 85 C after an initial deformation of 300 %.

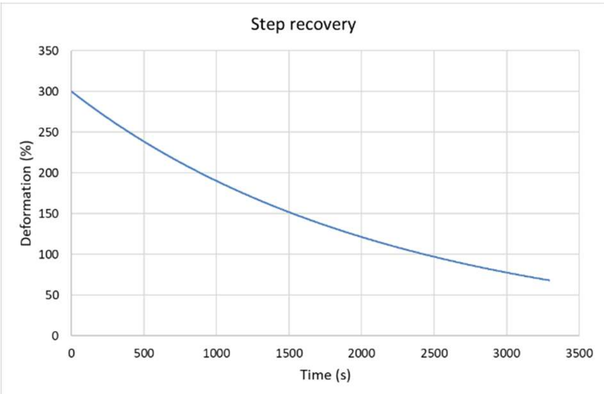

Figure 57: Recovery of PVC at 85 C after an initial deformation of 300 %.

The rubber stress that balances the glass stress is usually relatively low. That means that the rotation relaxation time is not influenced by the stress. In that case the differential Equation 99 can be solved mathematically. If the deformation at the start of the recovery process is γ_0 then the solution of this differential equation is:

Equation 100

$$\gamma = \gamma_0 \exp\left(-\frac{G_{rub}}{G_{gla}\theta_{rot}} t \right)$$

The recovery process happens on a time scale that is (G_{gla}/G_{rub}) ≈ 1000 times longer than the rotation relaxation time. That means that even at the glass transition temperature, where the rotation relaxation time is 1 second, the recovery takes at least 1000 seconds or more. It is a very slow process.