

## 12 STRESS RELAXATION AFTER A STEP-DEFORMATION

### 12.1 THE RELAXATION PROCESS

When a plastic body is suddenly deformed then a stress will be created inside the body. The deformation is kept constant. First the stress will be relatively high, but it will continuously reduce with time. The speed of the stress reduction is fast in the beginning and slows down later, as shown in Figure 53.

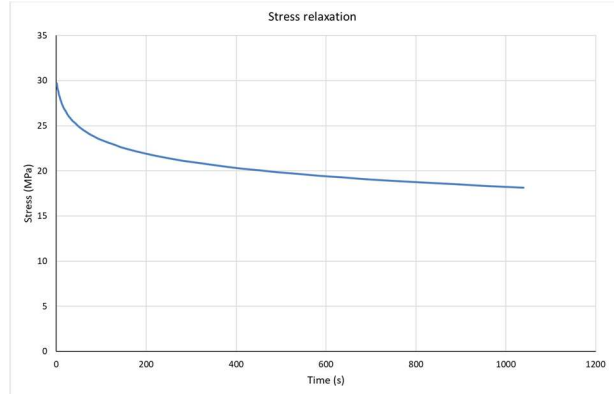


Figure 53: Reduction of the stress after a stepwise deformation.

The reduction of stress with time is called **stress relaxation**. It occurs both in the glass phase and in the rubber phase.

In the glass phase the stress relaxation is caused by rotation of chain segments (Kuhn segments). The fast decay in the beginning is due to the high stress that reduces the segmental rotation time.

In the rubber phase the stress relaxation is caused by reptation of the deformed polymer molecules into new positions. The fast decay in the beginning is again due to the high stress that reduces the reptation time.

### 12.2 MATHEMATICAL ANALYSIS OF STRESS RELAXATION AFTER STEP DEFORMATION

The viscoelastic relations are:

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

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

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

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

Boundary conditions:

- At time  $t = 0$  a shear deformation  $\gamma_0$  is applied.
- Since the deformation is kept constant the shear rate is zero:

$$\frac{d\gamma}{dt} = 0$$

- For the glass shear stress and the rubber shear stress we have:

$$\sigma_{gla} = G_{gla} \gamma_{ben}, \quad \sigma_{rub} = G_{rub} \gamma_{rot} \quad \text{and} \quad \sigma = \sigma_{gla} + \sigma_{rub}$$

The viscoelastic relations become:

Equation 92

$$\frac{d\gamma_{ben}}{dt} = -\frac{\gamma_{ben}}{\theta_{rot}} \quad \text{and} \quad \frac{d\gamma_{rot}}{dt} = \frac{\gamma_{ben}}{\theta_{rot}} - \frac{\gamma_{rot}}{\theta_{rep}}$$

All about viscoelasticity in the solid and molten phase

The step deformation experiment can be done below the glass transition temperature and above the glass transition temperature. We will discuss both situations.

### 12.2.1 Below glass transition temperature

Below the glass transition the reptation relaxation time  $\theta_{rep}$  is infinitely high. The viscoelastic relations become:

Equation 93

$$\frac{d\gamma_{ben}}{dt} = -\frac{\gamma_{ben}}{\theta_{rot}} \quad \text{and} \quad \frac{d\gamma_{rot}}{dt} = \frac{\gamma_{ben}}{\theta_{rot}} = -\frac{d\gamma_{ben}}{dt}$$

According to these equations the deformation by bending reduces with time and is fully converted into deformation by rotation. So, the deformation by rotation increases with time.

Usually the stresses involved are high enough to influence the rotation relaxation time  $\theta_{rot}$ . In that case the differential equations can only be solved numerically. An example of such a numerical solution for PVC at 30 C with an initial stress of 30 MPa is shown in Figure 54.

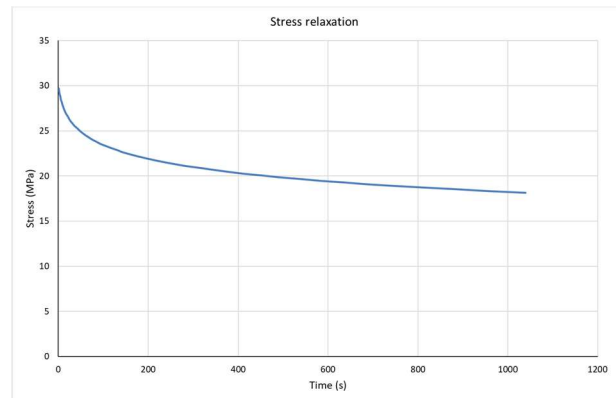


Figure 54: Stress relaxation of PVC at 30 C with an initial stress of 30 MPa.

In case that the stresses are very small ( $\sigma_{gla} \ll kT/V_{rot}$ ) then the relaxation time is not influenced by the stress. Now the differential equations can be solved analytically. The result is:

Equation 94

$$\gamma_{ben} = \gamma_0 \exp\left(-\frac{t}{\theta_{rot}}\right)$$

$$\gamma_{rot} = \gamma_0 \left[1 - \exp\left(-\frac{t}{\theta_{rot}}\right)\right]$$

$$\sigma = G_{gla}\gamma_0 \exp\left(-\frac{t}{\theta_{rot}}\right) + G_{rub}\gamma_0 \left[1 - \exp\left(-\frac{t}{\theta_{rot}}\right)\right]$$

### 12.2.2 Above glass transition temperature

Above the glass transition temperature the rotation relaxation time is very small and the deformation by bending can be neglected. The viscoelastic relations now become:

Equation 95

$$\frac{d\gamma_{rot}}{dt} = -\frac{\gamma_{rot}}{\theta_{rep}}$$

## All about viscoelasticity in the solid and molten phase

Now deformation by bending is immediately converted into deformation by rotation and the deformation by rotation is lost due to reptation. In case that the rubber stress is high enough to influence the reptation relaxation time then this differential equation can only be solved numerically. In case that the stress is small enough ( $\sigma_{rub} \ll kT/V_{rep}$ ) then the relaxation time is not influenced by the rubber stress. The analytical solution is then:

*Equation 96*

$$\gamma_{rot} = \gamma_0 \exp\left(-\frac{t}{\theta_{rep}}\right)$$
$$\sigma = G_{rub} \gamma_0 \exp\left(-\frac{t}{\theta_{rep}}\right)$$