8 STRESS RELAXATION

In chapter 6 we have learned how a deformation of the polymer causes stress in the polymer. We have also learned in chapter 4 that the polymer molecules are mobile: the Kuhn segments of the macromolecule rotate and the entire molecules reptate. Due to this mobility any stress will reduce with time. This is called stress relaxation.

8.1 STRESS RELAXATION IN THE GLASS PHASE

In the glass phase the polymer molecules are not very mobile. Rotation of the Kuhn segments is possible, but at a very low frequency. At the glass transition temperature the rotation time is 1 second. At lower temperatures one single rotation may need a time as much as a million seconds or more.

Yet it is these rotations that cause the stress to disappear. Let us visualize the polymer molecule with its Kuhn segments as a folding ruler. The rotating parts of the ruler are the Kuhn segments.

Now let us suppose that the hinges between the rotating parts of the folding ruler are rusty; it is difficult to rotate them. If we would deform the ruler a little bit then the parts of the folding ruler would first bend a little, as shown in Figure 38 at the left-hand side.

However, after some time one or more of the hinges will give way and some parts of the folding ruler will rotate. This will effectively reduce the bending of the parts and will thus reduce the stress. This is shown in the picture above at the right-hand side. The stress is relaxing due to the rotation of the parts.

In the same way the stress in a polymer in the glass phase (the glass stress) will relax due to the rotation of the Kuhn segments. Once a sufficient amount of Kuhn segments have rotated all bending will have disappeared. The stress has then completely disappeared. The relaxation time of stresses in the glass phase is identical with the Kuhn segment rotation time.

\[ \theta_{\text{gla}} = \theta_{\text{rot}} \]

The typical time for this stress reduction (the glass relaxation time) is equal to the time that the Kuhn segments need for making one rotation. At the glass transition temperature, where the Kuhn segments need 1 second for a rotation, the relaxation time is always 1 second. At a temperature far below the glass transition temperature the relaxation time may increase to many millions of seconds.
The change of the glass stress with time due to relaxation can be mathematically described by means of a differential equation. If there is no other influence on the glass stress than the glass relaxation process then the change of stress with time looks as follows: 

\[ \text{change of glass stress per unit of time} = - \frac{\text{glass stress}}{\text{glass relaxation time}} \]

The differential equation above describes a situation where glass stress can only disappear due to relaxation. The level of the stress will gradually reduce to zero with time. This is a very special situation. More common is that a polymer is continuously deformed. In such a case the “change of the glass stress per unit time” consists of two parts:

1. An increase of the stress due to the deformation
2. A decrease of the stress due to the relaxation: “glass stress / glass relaxation time”

The differential equation now looks like:

\[ \text{change of glass stress per unit of time} = + \frac{\text{change of glass stress due to deformation per unit of time}}{\text{glass stress}} / \text{glass relaxation time} \]

In mathematical representation:

**Equation 48**

\[
\frac{d\sigma_{\text{gla}}}{dt} = \frac{d\sigma_{\text{gla}}}{d\varepsilon_{\text{ben}}} \frac{d\varepsilon_{\text{ben}}}{dt} \frac{\sigma_{\text{gla}}}{\theta_{\text{rot}}} 
\]

The term \( \frac{d\sigma_{\text{gla}}}{d\varepsilon_{\text{ben}}} \) relates the change in glass stress to the change in deformation by bending. In case of small strain during uniaxial elongation it is the glass Young’s modulus \( (Y_{\text{gla}}) \). In case of shear it is the glass shear modulus \( (G_{\text{gla}} = Y_{\text{gla}}/3) \).

In some cases the modulus \( \frac{d\sigma_{\text{gla}}}{d\varepsilon_{\text{ben}}} \) is constant (independent of the strain). That happens, for example when the strains are small. Then the glass stress is directly related to the deformation by bending:

**Equation 49**

\[ \sigma_{\text{gla}} = \frac{d\sigma_{\text{gla}}}{d\varepsilon_{\text{ben}}} \varepsilon_{\text{ben}} \]

By combining Equation 48 and Equation 49 we find a simple differential equation for the momentary deformation by rotation:

**Equation 50**

\[
\frac{d\varepsilon_{\text{ben}}}{dt} = \frac{d\varepsilon_{\text{ben}}}{dt} \frac{\varepsilon_{\text{ben}}}{\theta_{\text{rot}}} 
\]

It is important to realize that the initial deformation by bending is converted into deformation by rotation. The total deformation remains constant:
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Equation 51

\[ \varepsilon_{ben} + \varepsilon_{rot} = \text{constant} \rightarrow d\varepsilon_{rot} = -d\varepsilon_{ben} \]

Due to the Kuhn segment rotation the initial glass stress is converted into a much lower rubber stress. The total deformation does not change.

8.2 Stress Relaxation in the Rubber and Melt Phase

In the rubber phase the time that the Kuhn segments need to rotate is much less than 1 second. That implies that any glass stress will disappear almost immediately to zero. Glass stress is not relevant in the rubber phase.

The quickly rotating Kuhn segments will deform the macromolecules in a random shape. It is called the random coil configuration and that is the natural shape of the macromolecules. If we would now apply a deformation to the polymer then the random coil configuration is disturbed. The shape of the macromolecules changes from a sphere into an ellipsoid. The macromolecules will react on this deformation by creating a stress that tends to bring their shape back to that of a sphere. This stress is called the rubber stress.

We can visualize this rubber stress by means of a rotating jumping rope. Due to the rotating rope the ends of the rope are pulled together. And the faster that the rope rotates the more force on the rope ends is created. In the same way the rubber stress increases with temperature!

In the rubber phase the macro molecules can slowly change their position due to reptation. This gives the macromolecules the possibility to reshape themselves into their wished random coil configuration. Thus, the rubber stress will disappear in time. The time scale on which this happens is simply the reptation time. Therefor the rubber relaxation time is equal to the reptation time.

Equation 52

\[ \theta_{rub} = \theta_{rcp} \]

The change of the rubber stress with time due to relaxation can be mathematically described by means of a differential equation that is very similar with the one for the glass stress. If there is no other influence on the rubber stress than the rubber relaxation process then the change of stress with time looks as follows:

\[ \text{[change of rubber stress per unit of time]} = - \frac{[\text{rubber stress}]}{[\text{rubber relaxation time}]} \]

The differential equation above describes a situation where rubber stress can only disappear due to relaxation. The level of the stress will gradually reduce to zero with time. This is a very special situation. More common is that a polymer is continuously deformed. In such a case the “change of the rubber stress per unit time” consists of two parts:
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1. An increase of the stress due to the deformation
2. A decrease of the stress due to the relaxation: “rubber stress / rubber relaxation time”

\[ \text{[change of rubber stress per unit of time]} = + \text{[change of rubber stress due to deformation per unit time]} - \frac{\text{rubber stress}}{\text{rubber relaxation time}} \]

In mathematical representation:

**Equation 53**

\[
\frac{d\sigma_{\text{rub}}}{dt} = \frac{d\sigma_{\text{rub}}}{d\varepsilon_{\text{ben}}} \frac{d\varepsilon_{\text{ben}}}{d\varepsilon_{\text{rot}}} \frac{\sigma_{\text{gla}}}{\theta_{\text{rot}}} - \frac{\sigma_{\text{rub}}}{\theta_{\text{rep}}} \]

The term \( \frac{d\sigma_{\text{gla}}}{d\varepsilon_{\text{ben}}} \) relates the change in rubber stress to the change in deformation by rotation. In case of small strain during uniaxial elongation it is the rubber Young’s modulus \( (Y_{\text{gla}}) \). In case of shear it is the rubber shear modulus \( (G_{\text{gla}} = \frac{Y_{\text{gla}}}{3}) \).

The term \( \left(\frac{d\varepsilon_{\text{ben}}}{d\sigma_{\text{gla}}}\right)\left(\frac{\sigma_{\text{gla}}}{\theta_{\text{rot}}}\right) \) is the change of the rubber deformation \( (d\varepsilon_{\text{rot}}/dt) \) due to the rotation of the Kuhn segments (glass stress relaxation). Deformation by bending is converted into deformation by rotation.

In some cases the modulus \( \frac{d\sigma_{\text{rub}}}{d\varepsilon_{\text{rot}}} \) is constant (independent of the strain). That happens, for example when the strains are small. Then the rubber stress is directly related to the deformation by rotation:

**Equation 54**

\[
\sigma_{\text{rub}} = \frac{d\sigma_{\text{rub}}}{d\varepsilon_{\text{rot}}} \varepsilon_{\text{rot}} \]

By combining Equation 53 and Equation 54 we find a simple differential equation for the momentary deformation by rotation:

**Equation 55**

\[
\frac{d\varepsilon_{\text{rot}}}{dt} = \frac{\varepsilon_{\text{ben}}}{\theta_{\text{rot}}} - \frac{\varepsilon_{\text{rot}}}{\theta_{\text{rep}}} \]

At a temperature more than 10 to 20 degrees above the glass transition temperature the rotation relaxation time is very short. It then follows that the glass stress and the change of glass stress with time are always close to zero and Equation 52 then gives:

**Equation 56**

\[
\frac{\sigma_{\text{gla}}}{\theta_{\text{rot}}} = \frac{d\sigma_{\text{gla}}}{d\varepsilon_{\text{ben}}} \frac{d\varepsilon_{\text{ben}}}{dt} \]

Combining Equation 53 and Equation 56 results in a simplified differential equation for the rubber and melt phase:
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Equation 57

\[
\frac{d\sigma_{rub}}{dt} = \frac{d\sigma_{rub}}{d\epsilon_{rot}} \frac{d\epsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rub}}
\]

The polymer molecules are very flexible. Kuhn segment rotation is fast and the preferred conformation of the macromolecules is a random coil. Any deformation of the polymer in the rubber and melt phase will result in a deformation of the random coil. The stress connected to this deformation is the rubber stress.

Stress relaxation is now controlled by reptation. Due to reptation the initially deformed macromolecule leaves its position and creates a new random coil conformation at a nearby site. The rubber stress will disappear due to this process.

With increasing temperatures the reptation time reduces. At the rubber – melt transition temperature the reptation time is 1 second and the rubber relaxation time is 1 second too. Above this temperature the rubber stress will disappear so fast that it is not relevant anymore. The polymer is now in the melt phase.

We will show later how the differential equation above can be used to calculate the viscosity of the polymer.

8.3 Total Deformation and Total Stress

In the previous chapters we have discussed deformation by bending (\(\epsilon_{ben}\)) and glass stress (\(\sigma_{gla}\)) in the glass phase and deformation by rotation (\(\epsilon_{rot}\)) of chain segments and rubber stress (\(\sigma_{rub}\)) in the rubber phase. Both types of deformation and both types of stress always occur simultaneously. That means that the total deformation is the sum of deformation by bending and deformation by rotation and that the total stress is the sum of glass stress and rubber stress:

Equation 58

\[
\epsilon = \epsilon_{ben} + \epsilon_{rot}
\]

\[
\sigma = \sigma_{gla} + \sigma_{rub}
\]
8.4 SUMMARY

It has been shown that the viscoelastic behaviour of the glass, rubber and melt phase can be described with two coupled differential equations, one for the glass stress due to bending of the chain segments ($\sigma_{gla}$) and one for the rubber stress due to random rotation of the Kuhn segments ($\sigma_{rub}$).

**Glass stress:**

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

**Rubber stress:**

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

**Total stress:**

\[
\sigma = \sigma_{gla} + \sigma_{rub}
\]

**Total deformation:**

\[
\varepsilon = \varepsilon_{ben} + \varepsilon_{rot}
\]

In case that the moduli $d\sigma_{gla}/d\varepsilon_{ben}$ and $d\sigma_{rub}/d\varepsilon_{rot}$ are independent of strain then Equation 59 and Equation 60 can also be represented as differential equations for the deformation by bending and the deformation by rotation:

**Deformation by bending:**

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

**Deformation by rotation:**

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

Relaxation of the glass stress is caused by rotation of the Kuhn segments. This action causes deformation by bending of the chain segments to be converted into deformation by rotation of the Kuhn segments. The rotation of the Kuhn segments causes the glass stress to reduce and the rubber
stress to increase. The relaxation time for this process is determined by the time that the Kuhn segments need to rotate ($\theta_{\text{rot}}$). At the glass transition temperature this relaxation time is 1 second.

Relaxation of the rubber stress is caused by reptation of the polymer molecules into new positions. In this way the macromolecules will lose their deformation. Any stored elastic energy is converted into heat. This relaxation time is equal to the reptation time. At the rubber – melt transition temperature this relaxation time is 1 second.