14 PHYSICAL AGING

14.1 INTRODUCTION

When a product is made from a polymer usually the polymer is first heated until it is molten (the fluid phase), then brought into the correct shape and then cooled down until it is solid again (the glass phase). In the glass phase however, the mobility of the large polymer molecules is too slow to fully conform to the rapidly changing temperature

There is not enough time for the molecules to move into the correct position or shape that corresponds to the current temperature. As a result of this, the polymer molecules “freeze” into far from optimal positions. The volume of the polymer is too high directly after cooling. Excess volume exists between the polymer molecules. The molecules will move closer together later onwards.

In due time the molecules will move themselves into more favourable positions. This causes the volume of the polymer to decrease. The time scale of this process is determined by the segmental rotation time of the Kuhn segments. The reduction of volume will further reduce the mobility of the polymer molecules. As a result, the process of moving into more favourable positions slows down even more. It is a self-retarding process.

In due time the polymer structure becomes more compacted, which will influence important properties like tensile strength and flexibility. This process of properties changing with time is called “physical aging”.

Physical aging is not limited to polymers only. Many materials in day-to-day practice show aging effects. A famous example is sand. When sand is first poured into a hole then it can be stirred easily. Its surface is too soft to build anything on top of it. The sand grains need to be compacted first. This will happen in time due to small vibrations, but it can be accelerated by using a compactor.

Figure 59: A compactor densifies the sand.

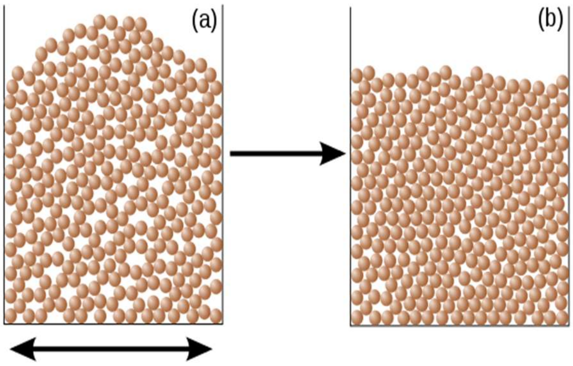

Figure 60: The effect of time or compaction on the structure of sand.

Aging of polymers is a slow and self-retarding process. It may take many years before a final equilibrium is reached. That causes several properties of the polymer to change slowly:

- The polymer becomes denser. The volume of a product made from the polymer will reduce somewhat.

- The tensile strength of the polymer increases. That means that a product made from the polymer becomes stronger with time. Slow deformation of the product under continuous load will become less.
- The stiffness of the polymer increases. It becomes more difficult to bend or deform the plastic product.
- The polymer becomes more brittle. That means that a product made from the polymer may break more easily when it falls.
- The fatigue strength reduces. A product made from the polymer under fluctuating load will have a shorter lifetime.

Aging of polymers can have rather dramatic effects on our life. For example, a water supply pipe in town that suddenly fails after a couple of years of service time. Due to the increasing brittleness, rapid crack growth may occur suddenly releasing many cubic meters of water into the street.

Figure 61: Aging can cause a polymer pipe for water supply to suddenly break.

Another, less dramatic result of aging is the plastic hanging basket with an expansive plant that suddenly breaks and falls to the floor.

14.2 DEVIATION FROM EQUILIBRIUM STATE

At temperatures above the glass transition temperature T_G the Kuhn segment rotation time is much less than 1 second. An equilibrium between the α and β-phase will be established almost immediately. However, below the glass transition temperature the rotation time of the Kuhn segments increases to very high levels. Any change in the conformation of the structure will need a time equal to this rotation time.

Figure 62: A plastic hanging basket may suddenly break and fall to the floor after aging.

During cooling of the polymer from above to below the glass transition temperature the structure of the polymer “freezes” now that the glass transition temperature has been passed. As a result, the structure of the polymer directly after cooling to below the glass transition temperature, deviates from the structure it should have at the actual temperature. A deviation from the equilibrium state has been created.

14.3 SLOW, SELF-RETARDING RETURN TO THE EQUILIBRIUM STATE

At the start of reaching the temperature T, the actual time dependant size of the co-operative rearranging regions (CRR's) will have the same level as they would have at the glass transition temperature: $z_0(T_G)$. The CRR's that form the α-phase will slowly grow at the cost of the β-phase. Eventually, after a long time, the size of the CRR's will reach the equilibrium level $z_0(T)$. In the meantime, the volume of the polymer will decrease slowly as the α-phase occupies less volume then the β-phase.

The structure of the polymer structure will have to conform to the new situation. The time scale for this process is the Kuhn segment rotation time θ_{rot}. However, the Kuhn segment rotation time will increase strongly upon the growing CRR's since the activation energy for segment rotation increases proportional with their size ($E_{rot} = E_0 z$). This will slow down the process to reach the equilibrium continuously.

14.4 PHYSICAL PROPERTIES CHANGE WITH TIME

A map of the rotation times, corrected for the aging process of an amorphous polymer after being quenched through the glass transition temperature is shown in Figure 63 below. The frequency map has become time dependant for temperatures below the glass transition temperature.

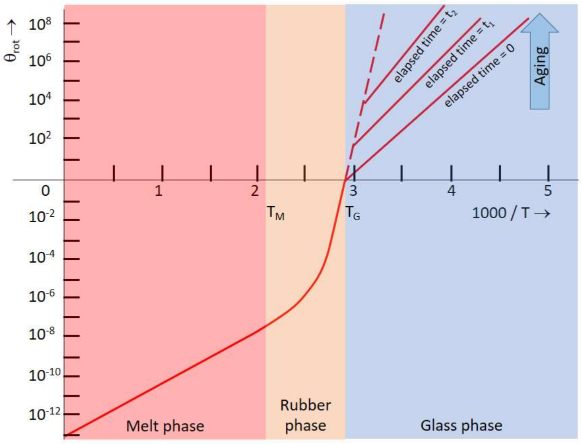

Figure 63: Frequency map of rotation times in an amorphous polymer.

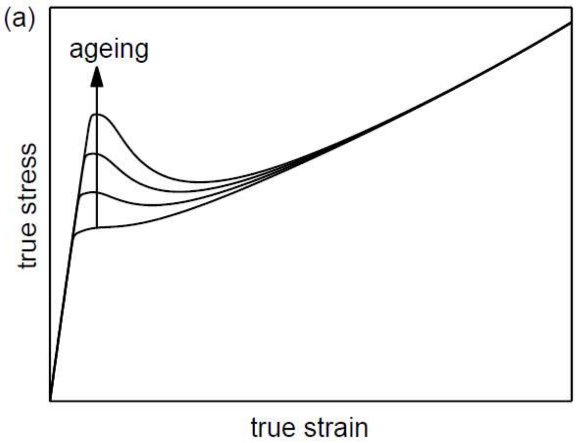

Figure 64: The effect of aging on the yield strength of a polymer.

*Below the glass transition temperature physical properties of the polymer that depend on the rotation time of the Kuhn elements will continuously change in time. In many cases equilibrium may never be reached on human time scale. Examples of such properties are the stiffness, the yield strength and the impact strength (*Figure 64*).*

Due to physical aging the chain mobility reduces in time. The stiffness and the yield strength of the polymer will increase. The creep of the polymer under prolonged load will reduce.

An example for PS and PC is shown in Figure 65. Due to aging the yield stress of both polymers increases logarithmically with the elapsed time.

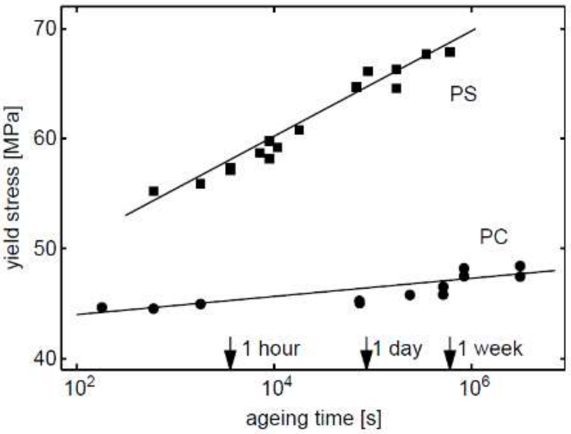

Figure 65: Increase of yield stress after rejuvenation of PS and PC.

14.5 MATHEMATICAL DESCRIPTION OF PHYSICAL AGING

As long as there is some mobility in the macromolecules present physical aging will continue to slowly change the mechanical properties of the amorphous polymer. Physical aging will stop when all mobility has ceased to exist.

During the aging process the CRR's will slowly grow. This growth involves a reduction of the fraction of β-phase and an increase of the fraction of the α-phase. Parts of the CRR's must be freed and redistributed. In the glass phase time span of the aging process of the polymer is equal to the Kuhn segment rotation time of the polymer molecules:

Equation 108

$$\theta_{aging} = \theta_{rot}$$

The current size of the CRR's at time t is z(t) and the final equilibrium size for temperature T is $z_\infty(T)$. We may then write for the change of the size of the CRR's in time:

Equation 109

$$\frac{dz}{dt} = \frac{z_\infty - z}{\theta_{rot}} \text{ with } \theta_{rot} = \theta_0 exp\left(\frac{E_0 z}{kT}\right)$$

During the aging process the actual size of the CRR's z is smaller than the equilibrium size z_∞. Thus, the size of the CRR's will increase with a relaxation time θ_{rot}. This causes the relaxation time to increase, which reduces the speed of the growth of the CRR's even more. These events continue for ever at always reducing speeds. It is a self-retarding process.

It follows for the change of the relaxation time with elapsed time:

Equation 110

$$\frac{d\theta_{rot}}{dt} = \frac{d\theta_{rot}}{dE_{rot}}\frac{dE_{rot}}{dz}\frac{dz}{dt} = \frac{E_0}{kT}(z_\infty - z)$$

Which results in the following differential equation for the relaxation time during aging:

Equation 111

$$\frac{d\theta_{rot}}{dt} = ln\left(\frac{\theta_\infty}{\theta_{rot}}\right)$$

The final relaxation time θ_∞ is described in chapter 4. *Mobility of polymer molecules*:

Equation 112

$$\theta_\infty = \theta_0 exp\left(\frac{E_0 z_\infty}{kT}\right) \ and \ z_\infty = \left(\frac{3-3p_\beta}{2p_\beta}\right)^3 \ with \ p_\beta = 2^{-T_m/T}$$

Equation 110 can only be solved numerically. Usually, the aging process is started by cooling the polymer from above to below the glass transition temperature. Therefor the initial size of the CRR's (z_{ini}) will be the size they have at the glass transition temperature (T_G):

$$z_{ini} = \left(\frac{3-3p_{ini}}{2p_{ini}}\right)^3 \ with \ p_{ini} = 2^{-T_m/T_G}$$

The result of the numerical solution for PVC is shown in Figure 66 below. The parameters for PVC used are: $\theta_{rot,0} = 10^{-13}$ s, $T_m = 513$ K, $T_G = 358$ K and $E_0 = 8.9 \times 10^{-21}$ J.

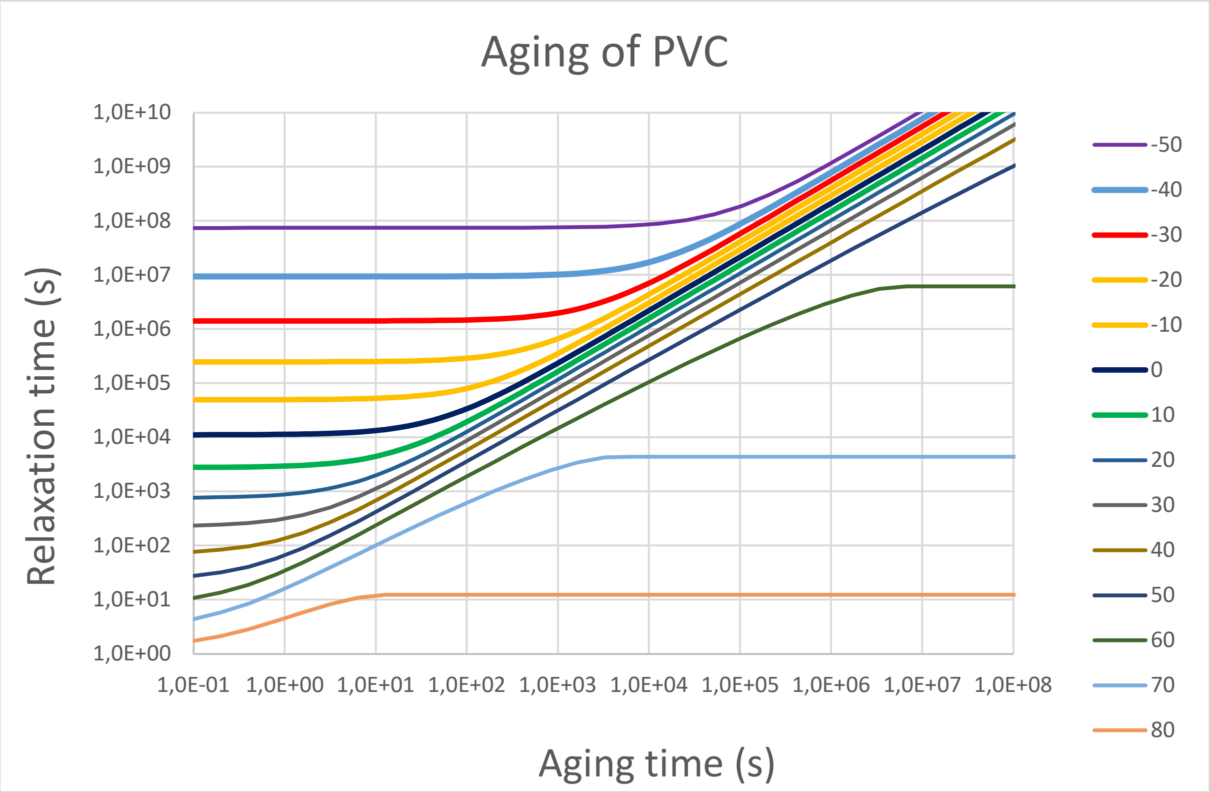

Figure 66: Plot of the relaxation time as a function of the aging time and temperature. $\theta_{rot,0} = 10^{-13}$ *s,* $T_m = 513$ *K,* $T_g = 358$ *K and* $E_0 = 8.9 \times 10^{-21}$ *J.*

Aging starts when the elapsed time is about 1 to 10 % of the initial relaxation time. For PVC at a temperature of -50 C aging starts after an elapsed time of about 10^6 seconds, which is about 10 days.

From that time onwards the relaxation time increases linearly with the elapsed time until equilibrium has been reached. This is usually after a very long time.

Aging stops when the size of the CRR's has become equal to the equilibrium size, as specified in Equation 112. In practice this will only happen close to the glass transition temperature. At lower temperatures the time needed to reach equilibrium is usually much longer than the service lifetime of the polymer products as indicated in the graph. For example, at a temperature of 50 C the time needed to reach equilibrium is already 10^{11} s, which is about 3000 years!

In the aging region the relaxation time increases linearly with the elapsed time (θ_{rot} is about 10 to 100 times the elapsed time). In the aging region the relaxation time is also dependant on the temperature. However, this temperature dependency is much less than outside the aging region as shown in Figure 66. For a change in temperature from 0 C to 70 C the relaxation time in the aging region reduces only 100 times.

14.6 ACTIVATION ENERGY FOR KUHN SEGMENT ROTATION AND PHYSICAL AGING

It has been explained that, after cooling the polymer down into the glass phase, the size of the CRR's slowly increases. This continues until the equilibrium size of the CRR's has been reached. The growing CRR's increase the activation energy for segmental rotation (E_{rot}). Due to this increasing activation energy many properties of the polymer change with time.

The aging process and the changing activation energy are one and the same thing. At any moment in time the activation energy for segmental rotation can be calculated from $E_{rot} = kTln(\theta_{rot}/\theta_0)$. By using the relaxation times from Figure 66 we obtain the changing activation energy for segmental rotation for PVC at several temperatures:

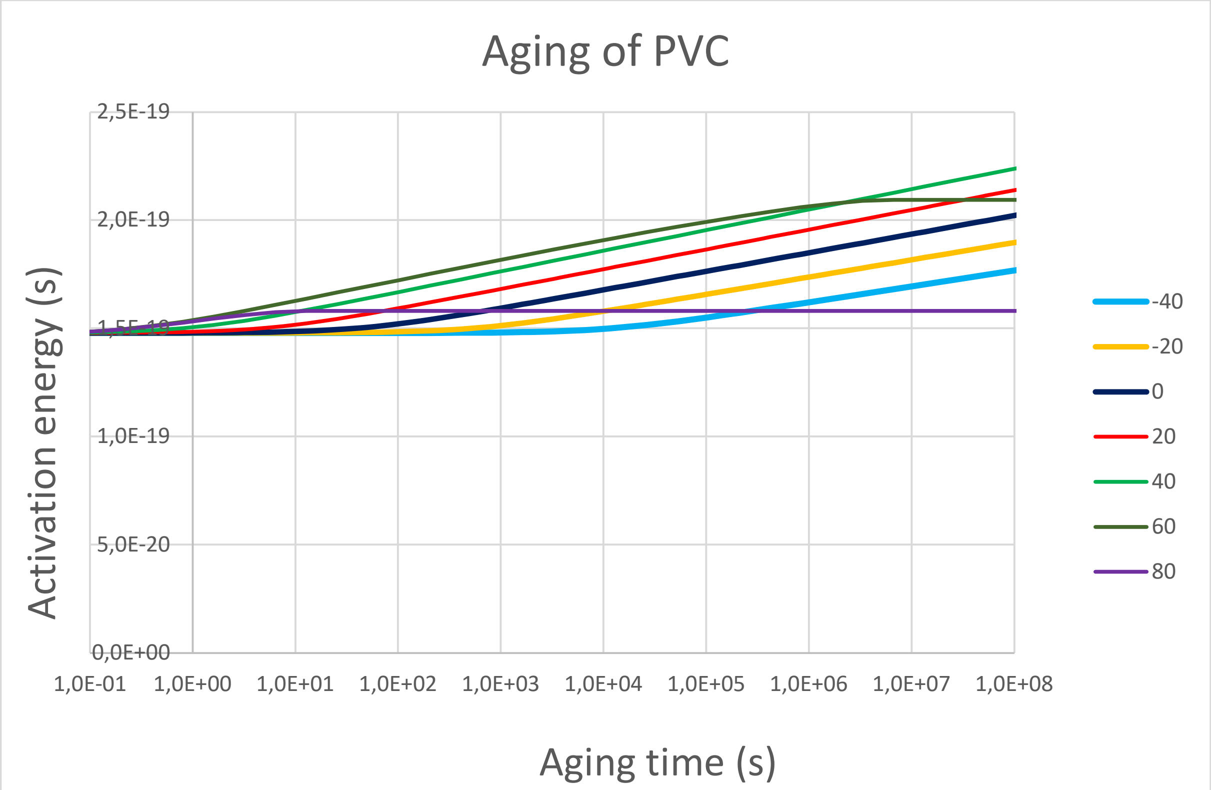

Figure 67: Activation energy for Kuhn segment rotation versus the aging time. Data calculated from Figure 66 with $E_{rot} = kTln(\theta_{rot}/\theta_0)$.

At short times the activation energy of PVC is 1.5 x 10^{-19} J, which is the activation energy at the glass transition temperature. After some time, the activation energy starts to increase logarithmically with time ($\theta_{rot} \sim ln(t)$). Other things of interest are:

- At a rather low temperature of -40 C the activation energy starts to increase after about 10^5 s (1 day). We can say that at this temperature aging starts to have effect on the material properties after about one day.
- At room temperature (20 C) the aging starts already after 10 seconds, continuing up to at least 10^8 seconds (3 years). Products made from PVC are rather flexible directly after production and become noticeably stiffer after one day.
- The largest effect of aging is found at a temperature some 30 C below the glass transition temperature.
- Close to the glass transition temperature (80 C) the effect of aging is limited because the response time of the molecules is short and equilibrium is quickly reached.

14.7 PHYSICAL AGING AND THE YIELD STRESS

In chapter 9 it has been proven that the yield stress of a polymer is, amongst other things, dependant on the activation energy for segmental rotation:

Equation 113

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

Since aging causes the activation energy to increase almost logarithmically with time this means also that aging causes the yield stress to increase logarithmically with time. This is illustrated in Figure 64 for PS and PC.

14.8 REMOVING PHYSICAL AGING

Physical aging can be undone it two ways:

1. By heating the plastic to above the glass transition temperature, followed by rapidly cooling down to room temperature. This process is called **thermal rejuvenation**
2. By mechanical deformation of the polymer to above its yield point at a temperature below the glass transition temperature. This process is called **mechanical rejuvenation**.

In both cases the size of the CRR's is reduced to that belonging to the glass transition temperature. The thermal rejuvenation simply results in a new equilibrium with smaller CRR's. The mechanical rejuvenation forces the chain segments to rotate which increases the free volume and reduces the size of the CRR's.

The rejuvenation will not last for a long time. After a couple of hours (or days, depending on the polymer) the physical aging will revert the effect of rejuvenation.

14.8.1 Effect of mechanical rejuvenation on the results of the tensile test

A well-known effect of physical aging and mechanical rejuvenation is observed during the tensile or compression test. Upon deformation of the polymer the stress will first increase until the yield point. The stress suddenly drops to a 10 to 20 % lower value, after which it starts to increase again (see Figure 68).

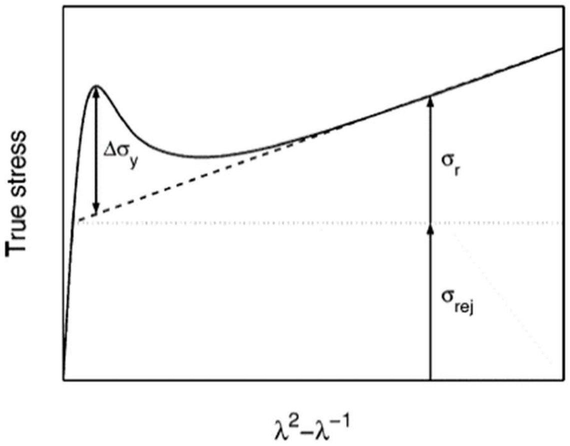

Figure 68: Stress - strain diagram obtained from a compression test. The drop of the stress after the yield point is caused by mechanical rejuvenation.

At the start of the compression test the deformation and the stress are small. The chain segments of the macromolecules will only bend a little. The activation energy for rotation is relatively high of the aged polymer. As soon as the stresses are high enough to force the chain segments to rotate the polymer starts to yield. At that moment the rotating chain segments push the neighbouring molecules aside thus breaking the CRR's into smaller pieces and reducing the activation energy for further rotations. This will cause the yield stress to decrease during further deformation. At larger deformations the macromolecules become oriented. This will cause the stress to increase again. This last effect is called *strain hardening*.