

Viscoelasticity of polymers in glass, rubber and melt phase

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All about viscoelasticity in the solid and molten phase

1 WHAT IS VISCOELASTICITY?

Solids, fluids and gases. We are used to them in our day to day life. We breath the air, drink the water and eat the apple. We know that below 0 degrees Celsius water is frozen into ice. At room temperature water is a fluid and above 100 degrees Celsius it vaporizes. We live with the idea that matter is either a gas or a fluid or a solid.

Yet there are many materials that cannot be so easily classified. These materials can behave as a fluid but also as an elastic solid. That gives them properties that are stunning. We call these materials viscoelastic materials because, at the same time, they have both fluid (viscous) properties and elastic properties.

What is causing these viscoelastic properties? The answer is astonishing simple: any material that consists of long flexible fibre-like particles is in nature viscoelastic. Because of their shape the particles can temporarily connect to each other which causes the elastic properties. On the other hand, due to their flexibility, they will easily slide along each other which causes the fluid properties.



Figure 1: Spaghetti is a viscoelastic material.

Typical examples of viscoelastic materials are spaghetti, tobacco, a pile of worms moving through each other and (of course) polymers. Polymers are always viscoelastic because they consist out of long molecules which can be entangled with their neighbours.

2 ABOUT POLYMER MOLECULES

2.1 MANY REPEAT UNITS MAKE MACROMOLECULE

Polymer molecules are long chains built from many small identical repeat units, also called monomers. For example polyvinylchloride (PVC) consists of many vinylchloride ($-\text{CH}_2-\text{CHCl}-$) repeat units. And polyethylene (PE) consists of many ethylene ($-\text{CH}_2-\text{CH}_2-$) repeat units. The number of repeat units in a macromolecule can be very large: up to 10000 or more.

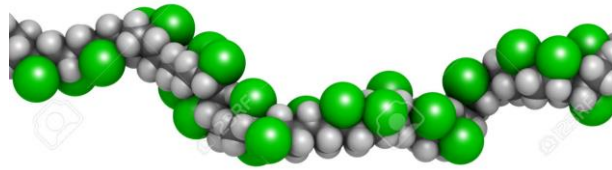


Figure 2: Model of PVC macromolecule (www.shutterstock.com).

2.2 CONFORMERS AND CONFORMATION

Each repeat unit has one or more bonds that allow rotation. Such bonds are called **conformers**. They make it possible that the shape (**conformation**) of the repeat unit changes and thus also the shape (conformation) of the polymer molecule.

Suppose that a repeat unit has three conformers and that each conformer has two stable directions. Such a repeat unit would be able to take $2^3 = 8$ different shapes or conformations. A macromolecule made of N such repeat units would be able to have 2^{3N} different conformations.

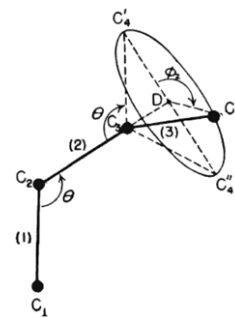


Figure 3: Restriction in possible conformations due to fixed valence angle.

2.3 KUHN SEGMENT

Each repeat unit is hindered in its freedom by neighbouring repeat units and valence angles. Their possibility to change their direction is limited. It takes several repeat units in a row to be able to randomly take any direction. Such a group of repeat units is called a **Kuhn segment**. The number of repeat units in a Kuhn segment is a fixed number for each polymer. It is called the **characteristic ratio** C_∞ . Some examples of this ratio and the size of the Kuhn segments are shown in the table below.

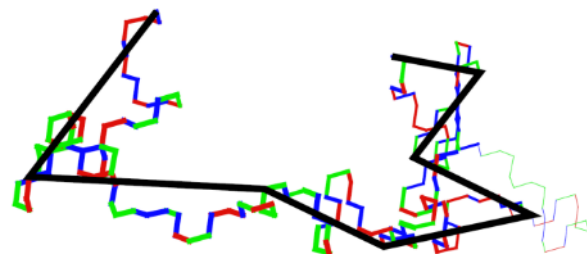


Figure 4: Schematic representation of the macromolecule (coloured lines) and the Kuhn segments (black lines)..

Characteristic ratio and Kuhn length for several polymers.							
	PB	PP	PE	PVC	PMMA	PS	PC
C_∞	5.5	6.0	8.3	6.8	8.2	9.5	1.3
$l_k (\text{\AA})$	10	11	15	26	15	18	2.9

Let us assume that a polymer molecule contains N repeat units. Then the number of Kuhn segments in the macromolecule N_k can be calculated from:

Equation 1

$$N_K = \frac{N}{C_\infty}$$

2.4 SHAPE AND SIZE OF MACROMOLECULE

Macromolecules are never fully stretched. Each Kuhn segment can randomly take any direction in space. The shape of the macromolecule in space therefor follows a random path (random coil conformation).

Statistics now predict for the random coil conformation that the square of the average end to end distance of such a chain ($\langle r_0^2 \rangle$) consisting out of N_K chain segments with bond length l_K will be:

Equation 2

$$\langle r_0^2 \rangle = l_K^2 N_K$$

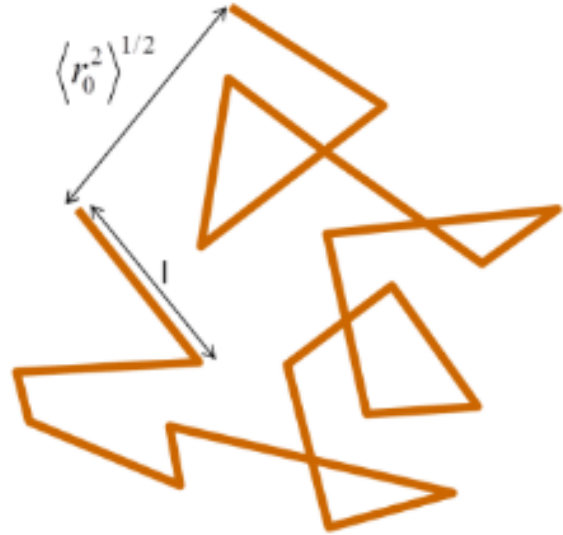


Figure 5: Schematic view of a freely jointed chain.

2.5 ENTANGLEMENTS AND BLOBS

The macromolecule is surrounded by many other macromolecules in the plastic. They will therefore all interfere with each other. Each macromolecule will be entangled with several other macromolecules. At each entanglement, the possible movements of the Kuhn segments will be seriously limited.

In between two entanglements the Kuhn segments will follow a random path. This part of the macromolecule is called a blob. If there are on average N_e Kuhn segments in a blob, then the average radius of the blobs r_{blob} will be:

Equation 3

$$\langle r_{blob}^2 \rangle = l_K^2 N_e$$

Our macromolecule contains N_K/N_e blobs. Also the blobs will follow a random path in space.

Therefore the start to end distance $\langle r_0^2 \rangle$ of the macromolecule will be:

Equation 4

$$\langle r_0^2 \rangle = \langle r_{blob}^2 \rangle \frac{N_K}{N_e} = l_K^2 N_K$$

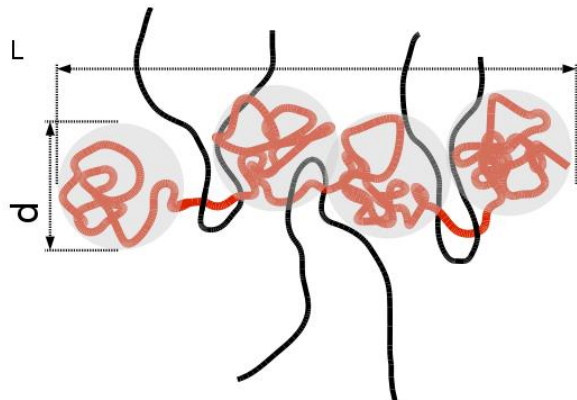


Figure 6: Macromolecule with entanglements. Blobs are formed between the entanglements.

All about viscoelasticity in the solid and molten phase

This is the same size as that of a macromolecule without any blobs. Therefore, the size of the macromolecule is independent of the number of entanglements (or blobs) present. The total number of blobs in the macromolecule will be:

Equation 5

$$N_{blob} = \frac{N_K}{N_e}$$

3 POLYMER STRUCTURE

3.1 DISORDERED STRUCTURE

A polymeric material is build-up from many randomly coiled polymer molecules that are extensively entangled with each other. This results in a kind of network that connects all polymer molecules with each other (Figure 7.).

Because of these entanglements the interaction between the molecules is very strong. Each individual molecule will intersect with many other molecules. The polymer structure can best be visualized with, for example, a pile of worms or a pan with spaghetti.

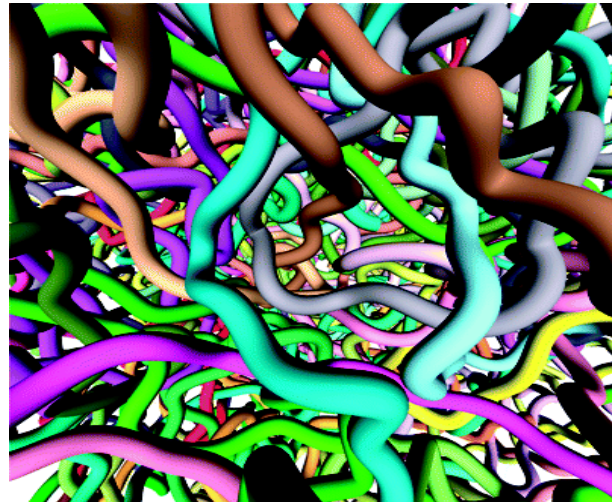


Figure 7: In a polymer the long molecules are all entangled with each other (scitation.aip.org).

3.2 ENTANGLEMENTS AND NETWORK DENSITY

All polymer molecules are connected with each other by means of physical entanglements or chemical crosslinks. An entanglement can be viewed as a connection between two molecules caused by a kink or knot, as shown in Figure 8.

In the glass phase the macromolecules have limited mobility. They can slightly change their conformation by rotating chain segments, but they cannot move into another position. Therefore the number of entanglements in the glass phase is constant and equal to the entanglement density at the glass – rubber transition.

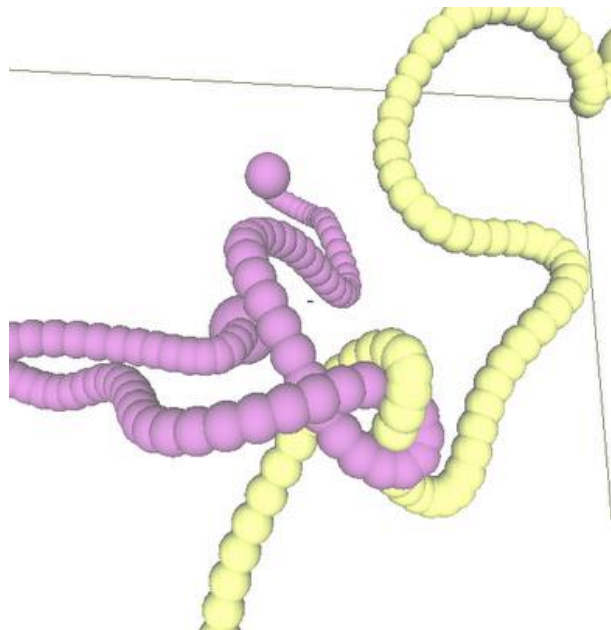


Figure 8: Physical entanglement between two neighbouring polymer molecules (go-entangle.blogspot.ca).

In the melt phase such an entanglement has a finite lifetime: the molecules can disentangle from each other by simply moving into another position (reptation). This happens at higher temperatures. Polymers that show this kind of bindings are called thermoplastics.

The network density or entanglement density is defined as the number of entanglements per unit volume (m^3). Typical values for the entanglement density range from $3 \times 10^{25} \text{ m}^{-3}$ for PS to $3,9 \times 10^{26} \text{ m}^{-3}$ for PC. Some values of the network density are shown in Table 1.

Table 1: Network density for some polymers	
Polymer name	Network density (m^{-3})
PVC	$1,00 \times 10^{26}$
PC	$3,90 \times 10^{26}$
PS	$3,00 \times 10^{25}$
PMMA	$8,00 \times 10^{25}$
PE100	$2,80 \times 10^{26}$
PE80	$2,80 \times 10^{26}$

The network density ν_c is directly related to the number of entangled Kuhn segments N_e via:

Equation 6

$$\nu_c = \frac{\rho}{m_K N_e}$$

3.2.1 Influence of entanglements on mechanical properties

The number of entanglements per volume (the entanglement density or the network density ν_e) has a pronounced influence on the mechanical properties of the glass phase, the rubber phase and the melt phase. Polymers with a high entanglement density are tougher than polymers with a low entanglement density. This is for example reflected in a strongly reduced growth of cracks in polymers with a high network density. Such polymers show an increased resistance against environmental stress cracking.

In the glass phase the entanglement density influences the strain hardening modulus of the polymer during the tensile test and the long-term ductile and brittle failure of the polymer. With increasing entanglement density, the strain hardening modulus increases linearly and the long-term failure times increase exponentially. This is illustrated in Figure 11 and Figure 12.

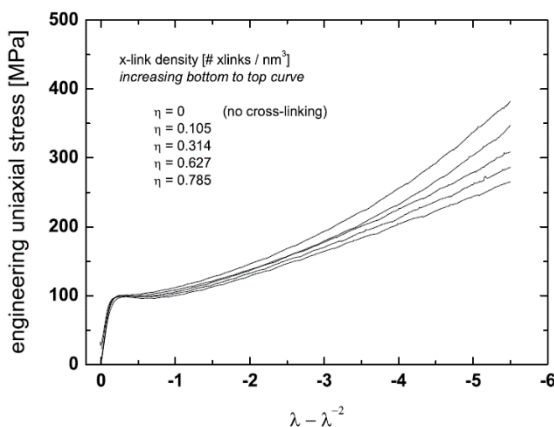


Figure 9: Tensile test results of PMMA with different network densities.

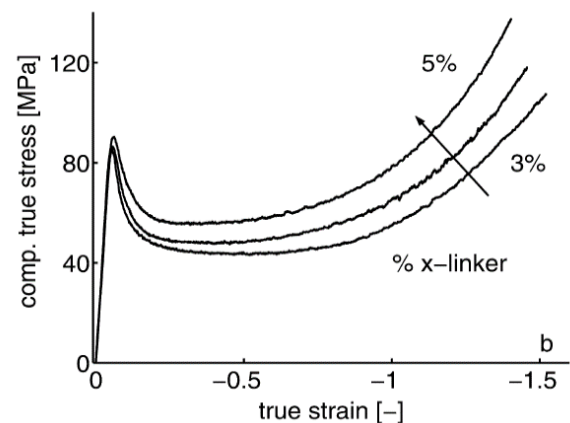


Figure 10: Tensile test results of PS with different network densities.

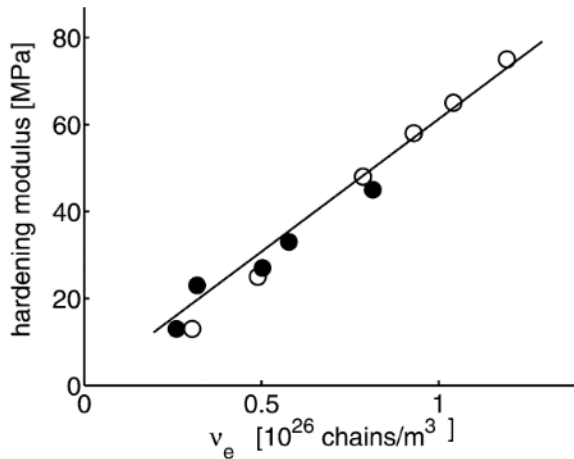


Figure 11: Strain hardening modulus versus network density for several PS / PPO blends and cross-linked PS.

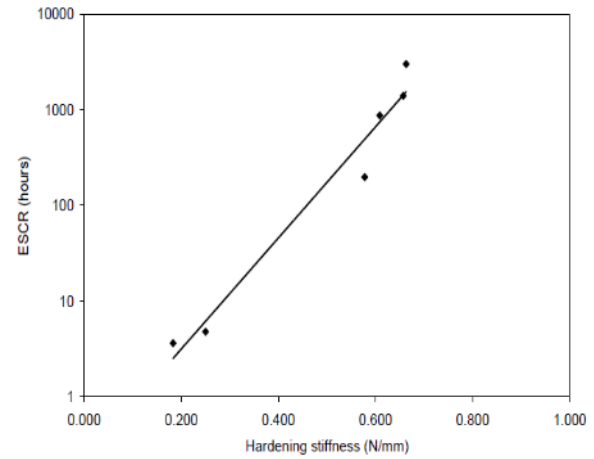


Figure 12: Environmental stress crack resistance versus strain hardening modulus for several HDPE types.

In the rubber and the melt phase the network density is directly related to the rubber shear modulus. From the rubber elasticity theory, it follows that the shear modulus in the rubber phase is linearly dependant on the network density and the temperature:

Equation 7

$$G_{rub} = \nu_c kT$$

That would imply that the shear modulus would slowly increase with temperature above the glass transition temperature T_g . For chemically cross-linked polymers that is indeed the case but not for simply entangled polymers. Those polymers usually show a decrease of the rubber shear modulus with increasing temperature. An example is given in Figure 13 that shows the dynamic modulus of PS-PPO blends. The rubber modulus decreases with temperature.

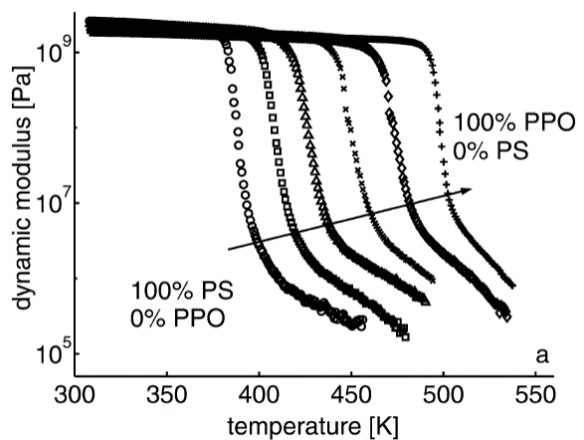


Figure 13: Dynamic modulus of PS-PPO blends. The rubber modulus decreases exponentially with temperature.

The network in these polymers is built by entanglements that act as temporary physical cross-links. Upon increasing the temperature, the free volume between the molecules will increase and this will gradually remove many of the adjacent and hooked entanglements in the polymer.

3.3 FREE VOLUME FRACTION

Because of their unordered structure the molecules do not fit perfectly together. This creates some empty space between the molecules that is called free volume. This free volume takes up about 5 to 10 % of the total volume of a polymer structure. With increasing temperatures, the free volume increases and with reducing temperatures the free volume reduces.

The level of free volume is very important for the mobility of the polymer molecules. At high temperatures, where the free volume is relatively large, the mobility of the molecules will be very high. They can move around in the polymer structure. It is like a room in which only a few people are present: they can wander around without seriously hindering their neighbours.

At low temperatures however the free volume is low. Now the molecules are so close together that they hinder each other in their movements. Just consider the same room but now densely packed with people: with enough people pressed in the room it may even be impossible for them to move their arms or legs.

The free space or the free volume is the difference between the volume of the 100 % amorphous structure and the volume of the 100 % crystalline structure. In Figure 14 a simple diagram is shown of the crystalline and the amorphous volume around the glass transition temperature T_G . The crystalline volume continuously increases with temperature with a volume expansion coefficient α_0 . The amorphous phase always has a higher volume and its volumetric expansion coefficient suddenly increases from α_G to α_R above the glass transition temperature T_G due to the segmental rotations. Below the glass transition temperature, the expansion coefficient of the crystalline state is approximately the same as that of the amorphous state ($\alpha_c \approx \alpha_a$).

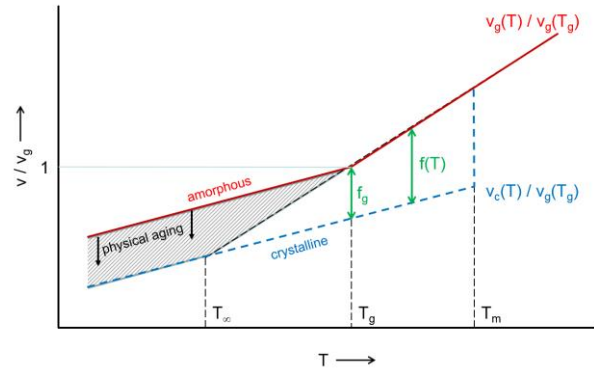


Figure 14: Schematic diagram of crystalline volume and amorphous volume. The difference is the free volume.

For the physical processes the free volume fraction, which is the ratio of the free volume ($v_a - v_c$) and the total volume (v_a), is more important. It is defined as:

Equation 8

$$\psi_{free} = \frac{v_a - v_c}{v_a} = \frac{(\alpha_a - \alpha_c)(T - T_\infty)}{1 + \alpha_a(T - T_\infty)} \approx (\alpha_a - \alpha_c)(T - T_\infty)$$

Equation 8 is only valid for $T > T_\infty$. The free volume fraction (ψ_{free}) is calculated relative to the Kauzmann temperature T_∞ . This is the (virtual) temperature where the rubber phase would have the same relative volume as the crystalline phase and the free volume would be zero (see Figure 14). The free volume fraction near the glass transition temperature is usually about 0.025 to 0.0050 for most polymers.

4 DEFORMATION OPTIONS OF POLYMER MOLECULES

Polymer molecules can be regarded as chains from flexible segments (Kuhn segments) that are entangled with each other. They have three ways to deform: bending of the chain segments, rotation of the chain segments and reptation of the entire molecule.

4.1 BENDING OF CHAIN SEGMENTS

The chain segments (Kuhn segments) in a polymer molecule will bend a little bit when a load is applied. This results in a small deformation of the polymer molecule. The polymer feels stiff and its elasticity modulus is high.

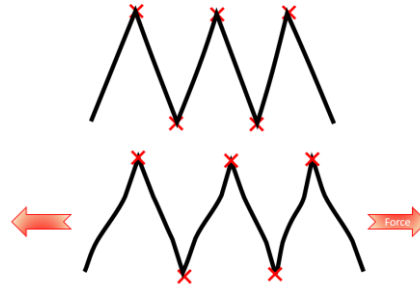


Figure 15: Bending of chain segments results in a small deformation. The relative position of the molecules does not change.

4.2 ROTATION OF CHAIN SEGMENTS

Due to the thermal vibrations of the atoms the chain segments (Kuhn segments) in a polymer molecule can rotate in any direction. This allows the molecule to change its shape under load. The rotations of the chain segments make a polymer flexible. The polymer feels elastic and its elasticity modulus is low.



Figure 16: Rotation of chain segments results in a large deformation. The relative position of the molecules does not change.

The time needed for these rotations, the **rotation time**, is strongly temperature dependent. At low temperatures the rotation time is long and at high temperatures the rotation time is short. At a sufficiently high temperature the Kuhn segments have a rotation time of, for example, 0.001 second. Now the polymer molecules easily change their shape under a force. The polymer is flexible now. On the other hand, at low temperature the rotation time can be as high as 1 million seconds. The polymer behaves as a rigid (stiff) solid now.

We humans experience the polymer as flexible when the rotation time is less than 1 second. The polymer feels as a rubbery substance. We experience the polymer as stiff when the rotation frequency is much higher than 1 second. The polymer now feels as a rigid glassy substance. The temperature at which the rotation time is 1 second is the glass transition temperature.



Figure 17: Below the glass temperature a polymer can be deformed but will not forget its original shape.

Rotation of the chain segments allow for large deformations in the polymer molecule. However, the position of each molecule relative to others does not change. Due to this, a polymer deformed by a force will regain its original shape when heated close to the glass transition temperature.

4.3 REPTATION OF POLYMER MOLECULES

Due to the wriggling motions of all the rotation Kuhn segments the entire polymer molecule may shift its position a little bit. The surrounding molecules will limit this shift to a displacement along the axis of the molecule. Other displacements are not possible. The polymer molecule moves as a snake along its axis through the other molecules. This way of motion is called **reptation**.

Compared to rotation the reptation is a relatively slow process. Due to the random nature of the rotations that counteract each other a single shift over the length of one Kuhn segment may take very many rotations.

After some time, the polymer molecule will have reptated over its entire length. It has moved into an entirely new position compared to the surrounding molecules. The time that this process takes is called the

reptation time. At times longer than the reptation time the polymer behaves as a fluid because the position of the molecules changes continuously. Contrary to the rotation of the Kuhn segments the reptation makes the polymer to forget its original shape.

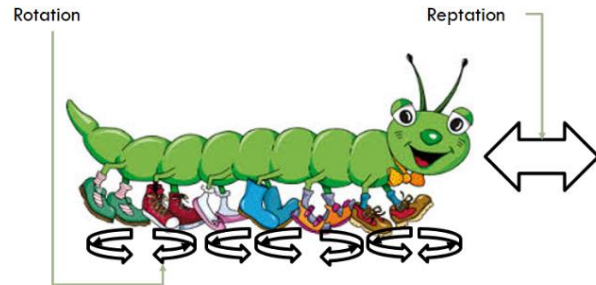


Figure 18: Reptation is caused by the random rotation of the Kuhn segments.

We humans experience a polymer as a fluid when the reptation time is less than 1 second. In case that the reptation time is higher than 1 second then we experience the polymer as a rubber. The temperature at which the reptation time is 1 second is the **rubber-melt transition temperature**.

4.4 KUHN SEGMENT ROTATION TIME

4.4.1 Rotation above the glass transition temperature

Segments of the polymer molecules rotate at a certain frequency causing the molecules to reptate through each other. The rotations in the polymer molecules occur at a time dictated by thermal activation. The energy barrier E_{rot} that must be passed is dependent on temperature:

Equation 9

$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{E_{rot}(T)}{kT}\right)$$

In Equation 9 $\theta_{rot,0}$ is the rotation time at infinitely high temperatures and will be of the order of magnitude of 10^{-13} s.

Just like any other material polymer molecules also tend to rearrange themselves into crystalline structures when the temperature is sufficiently low. Due to their disordered nature however, polymer molecules will have difficulties in forming such crystalline structures, if they can at all. Some polymers like polyethylene are at best partially crystalline below the melting temperature; many polymers show no crystallinity at all.

Yet all polymers, whether they are partially crystalline or not, do experience an attractive potential U to crystallize. This causes clusters of polymer segments that move simultaneously. Such clusters are

called cooperatively rearranging regions (CRR's). The nett result is that segmental rotation of one molecule is copied by neighbouring molecules into a cooperative action. In this way, local crystalline structures are formed on a sub-molecular scale.

Upon further cooling the volume continues to decrease as if the material is still a liquid. However, the level of cooperativity continues to increase. More and more polymer segments are coupled into larger groups that act together in the same way. The effective activation energy (E_{rot}) for such co-ordinated movements increases linearly with the number of cooperating segments (z_0).

Equation 10

$$E_{rot} = z_0 E_0$$

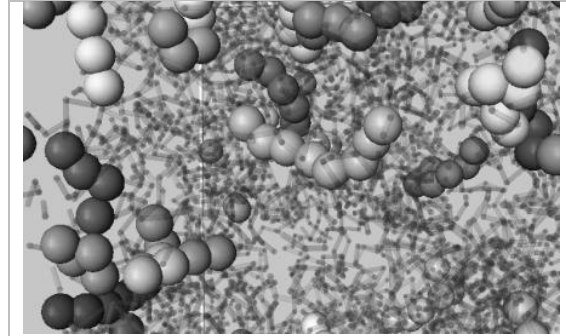


Figure 19: Graphical illustration of CRR's in the polymer.

E_0 can be regarded as the energy barrier for rotation of a single repeat unit. A Kuhn segment consists of c_∞ repeat units. Therefore the minimum activation energy for the rotation of a Kuhn segment is $c_\infty E_0$. Also the minimum level of the number of cooperating segments z in a CRR will be c_∞ .

The fraction of polymer segments p_β which have a thermal energy higher than the attractive potential is given by:

Equation 11

$$p_\beta = \exp\left(-\frac{U}{kT}\right)$$

This polymer fraction is relatively flexible because their mobility is not hindered (not cooperative). We call this fraction the β -phase and this phase can also be considered as a melt. The other fraction consists of cooperatively moving polymer segments that are strongly hindering each other. We call this fraction the α -phase. This phase can be considered as being formed from crystallites on a sub-molecular scale.

At the crystalline melting temperature T_m the probability for a segment to leave the CRR is just as large as the probability to enter the CRR: $p_\beta = 1/2$. We then find for the attractive potential U :

Equation 12

$$p_\beta = \exp\left(-\frac{U}{kT_m}\right) = \frac{1}{2} \Rightarrow U = kT_m \ln(2)$$

We then find for the fraction of the β -phase:

Equation 13

$$p_\beta = 2^{-T_m/T}$$

The CRR's in the α -phase are separated from each other by the flexible β -phase with a thickness of at least one segment. The α -phase and the β -phase, at a temperature above the glass transition temperature, are in a dynamic equilibrium with each other. Depending on the local thermal energy segments in the β -phase can change into the α -phase and vice versa.

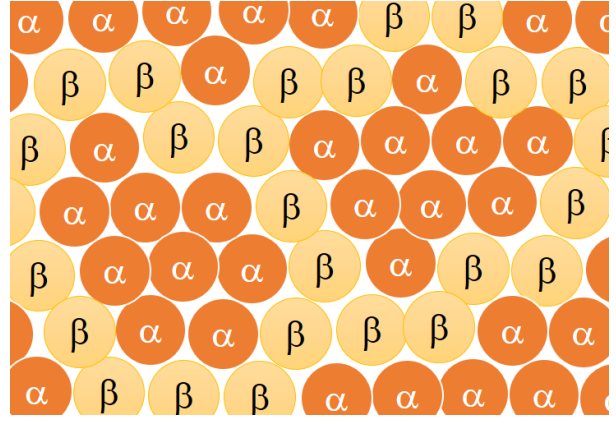


Figure 20: Schematic representation of the α -phase and the β -phase. The CRR's in the α -phase are separated by a one segment thick layer of β -phase.

The number of cooperating segments in a CRR is estimated by means of volume considerations. Let us assume that the shape of the CRR's is approximately spherical and that each CRR is surrounded by a layer of the β -phase with a thickness of half a segment. If the volume of one segment is V_0 then we can write for the volume of the α -phase V_α and the β -phase V_β :

Equation 14

$$V_\alpha = z_0 V_0 \text{ and } V_\beta = \frac{3}{2} z_0^{2/3} V_0$$

The fraction of polymer segments p_β in the β -phase is equal to the volume fraction of the β -phase:

Equation 15

$$p_\beta = \frac{V_\beta}{V_\alpha + V_\beta} = \frac{1}{\frac{2}{3} z_0^{1/3} + 1}$$

It then follows for the number of segments in a CRR:

Equation 16

$$z_0 = \left(\frac{3 - 3p_\beta}{2p_\beta} \right)^3 \text{ with } p_\beta = 2^{-T_m/T}$$

This equation only holds for $z_0 \geq 2$ (or $p_\beta \leq 0.54$) because a CRR must have at least two coupled segments.

The rotation time is now described with:

Equation 17

$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{z_0 E_0}{kT}\right) \text{ with } z_0 = \left(\frac{3 - 3p_\beta}{2p_\beta} \right)^3 \text{ and } p_\beta = 2^{-T_m/T}$$

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The value of E_0 can be calculated from the glass transition temperature. At T_g the rotation time is, by definition, 1 s. It then follows for E_0 using Equation 17:

Equation 18

$$E_0 = - \frac{kT_g \ln(\theta_{rot,0})}{z_0(T_g)}$$

A graphical representation of Equation 17 is shown in Figure 21 for PVC with $\theta_{rot,0} = 10^{-13}$ s, $T_m = 513$ K and $T_g = 358$ K. E_0 was determined to be 8.9×10^{-21} J.

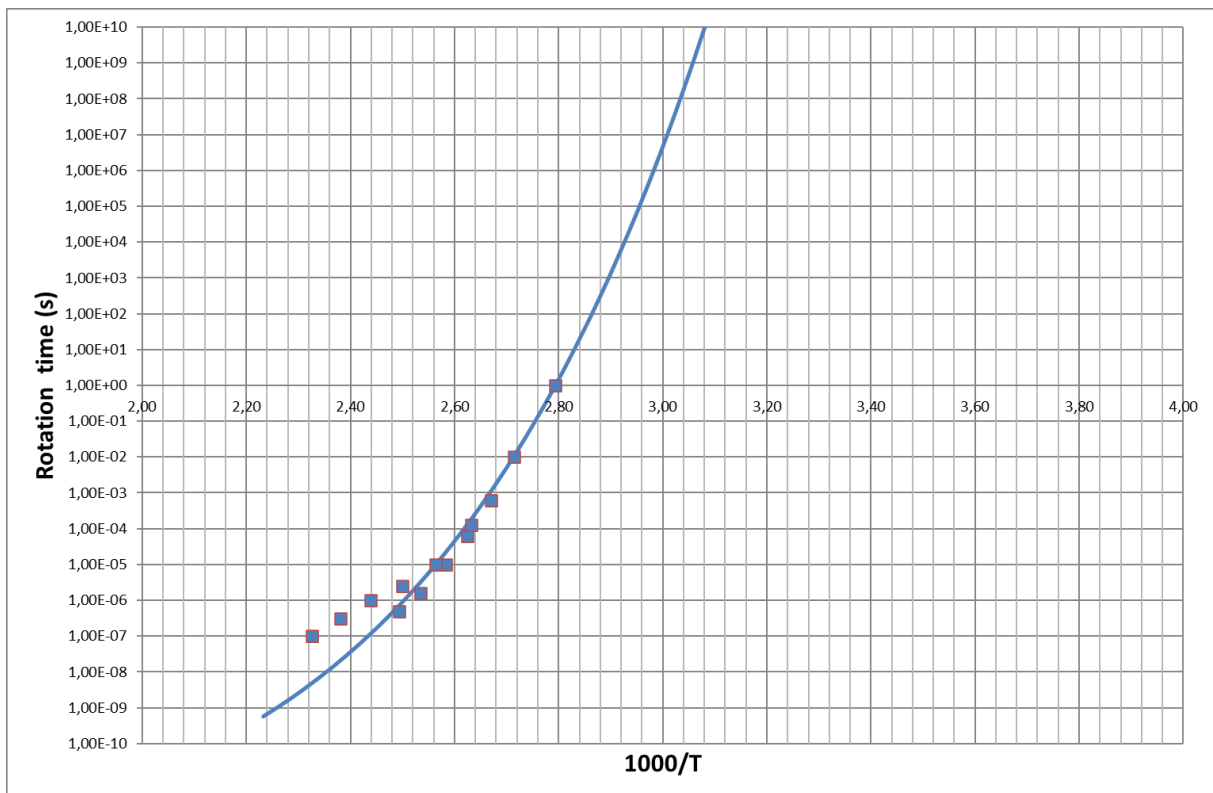


Figure 21: Segmental rotation times for PVC. Dots measured data. Line calculated according to Equation 17 with $\theta_{rot,0} = 10^{-13}$ s, $T_m = 513$ K and $T_g = 358$ K. E_0 was determined to be 8.9×10^{-21} J.

4.5 CHAIN REPTATION TIME

4.5.1 General

Chain reptation, the axial movement of the polymer molecules, requires the combined motion of many chain segments. That means that reptation is virtually impossible at temperatures below the glass transition temperature. Also, in a limited region above the glass transition temperature where the frequency of the segment rotation is above 1 s^{-1} reptation is still difficult.

In the melt phase the polymer molecules are flexible: their chain segments can make many rotations in a short time. The macromolecules are also able to slide into other positions by means of reptation. This allows for large plastic deformations of the material: it is a fluid with elastic properties.

4.5.2 Sliding of macromolecules through tubes

Due to all surrounding macromolecules, it is impossible for a single polymer molecule to move freely in any direction. The macromolecule must “slide” along its own axis, in a kind of a tube formed by the other molecules. Driven by thermal energy each polymer chain can diffuse via a snake-like motion known as reptation. The macromolecule makes forward and backward jumps in a random way. The movement is to be considered as a one-dimensional random walk.

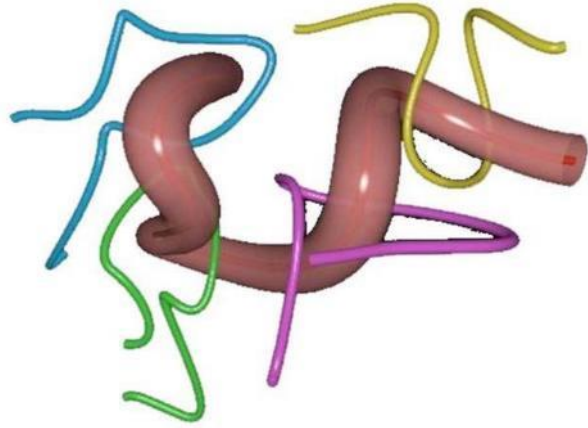


Figure 22: Polymer chain diffuses through tube.

4.5.3 Reptation time

The diffusion of the macromolecule through the matrix is caused by the uncorrelated displacements of the Kuhn pairs. Suppose that we have a fictive molecule that consists of 1 Kuhn segment. It will make steps with a size l_k randomly backwards and forwards (+ and -) during θ_{rot} seconds. Another molecule that consists of 2 Kuhn segments has 4 different step configurations (++ , +- , -+ and --). Only 2 of these configurations will result in a displacement with size b . A single step forwards or backwards will therefore take $2 \theta_{rot}$ seconds. A macromolecule with N_k Kuhn segments will reptate randomly backwards and forwards with step size l_k during a time of $N_k \theta_{rot}$ seconds.

The reptation time is the time needed for the macromolecule to diffuse over N_k Kuhn segments:

Equation 19

$$\theta_{rep} = N_k^2 N_k \theta_{rot} = N_k^3 \theta_{rot}$$

According to Equation 19 the reptation time strongly increases with temperature and it is proportional to the third power of the number of Kuhn segments in the macromolecule (N_k) or the molecular weight (m_w). Investigations have shown that the reptation time increases even faster: it increases with the molecular weight to the power 3.5:

Equation 20

$$\theta_{rep} = N_k^{3.5} \theta_{rot}$$

The reptation time is thus directly proportional to the rotation time. All temperature dependant effects of the rotation time will be duplicated in the reptation time:

Equation 21

$$\theta_{rot} = N_k^{3.5} \theta_{rot,0} \exp\left(\frac{z_0 E_0}{kT}\right) \text{ with } z_0 = \left(\frac{3 - 3p_\beta}{2p_\beta}\right)^3 \text{ and } p_\beta = 2^{-T_m/T}$$

5 GLASS, RUBBER AND MELT PHASE

We distinguish three different phases in the polymer: the glass phase, the rubber phase and the melt phase. On top of this the polymer can be partially crystalline and partially amorphous.

5.1 GLASS PHASE

At low enough temperatures the rotation time of the Kuhn segments is far more than 1 second. The macromolecules are rigid now. The polymer is difficult to deform: any load will hardly change the shape of the polymer molecules. The chain segments can only bend a little bit. An applied force will only result in a small deformation of the plastic. When a polymer is in this condition then it is said to be in the **glass phase**.

Many plastic products like pipes, toys, cutlery, etcetera, need to be able to take up some load when used. That means that these products are made of plastics that are in the glass phase at room temperature.

Although it may take a long time, rotation of the Kuhn segments is still possible: we only must wait long enough. Suppose that on average it takes 1 million seconds for a Kuhn segment to rotate. If we would now apply a force on the plastic for a time longer than 1 million seconds, then the Kuhn segments do have sufficient time to rotate and the plastic will start to deform. This deformation of course happens very slowly and it is called creep of the polymer.



Figure 23: Plastic pipes made from PVC in the glass phase.

The resulting elasticity-modulus or Yong's modulus will be high because it is mainly determined by bending of chain segments. This is illustrated in Figure 24 that shows the storage modulus, the loss modulus and the ratio loss – storage modulus ($\tan(\delta)$) for PVC as measured by means of DMA.

Upon increasing the temperature, the thermal energy becomes large enough to make rotations of the chain ends and side groups possible on a human time scale (1 s). For PVC this happens at a temperature of about -50 °C. However, the polymer molecules are so close together that nearby macromolecules strongly hinder the segmental rotation. There is not enough free volume present in between the macromolecules. Only at the chain ends enough free volume is present to enable the end segments of the macromolecules to rotate. This is shown by the

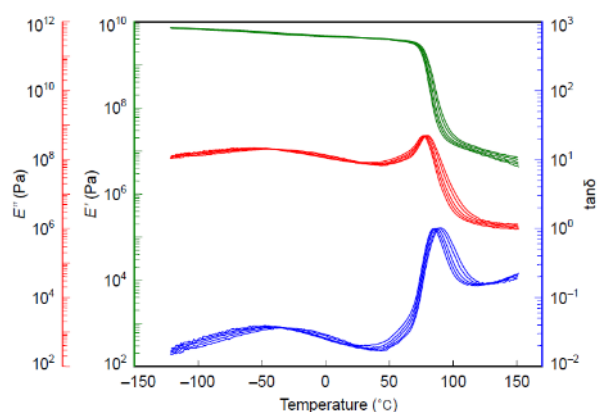


Figure 24: Storage modulus (E'), loss modulus (E'') and $\tan(\delta)$ as measured by dynamic mechanical analysis.

rather weak peak at -50 C in the loss modulus and the $\text{tg}(\delta)$ curve in Figure 7. The macromolecules are still immobile in this region because the major part of the chain segments is not able to rotate.

5.1.1 Glass transition temperature

By further increasing of the temperature the thermal energy becomes high enough to create locally some free volume around the chain segments. This will allow the chain segments of the macromolecules to start rotating more quickly. At the glass transition temperature there is enough thermal energy available for all chain segments to rotate within a time of about 1 s. The macromolecules change into flexible chains. The stiffness of the polymer now reduces strongly (about 100 to 1000 times). For PVC this happens at a temperature of about 85 C as shown in Figure 24. For a material like HDPE this happens at a temperature of -130 C.

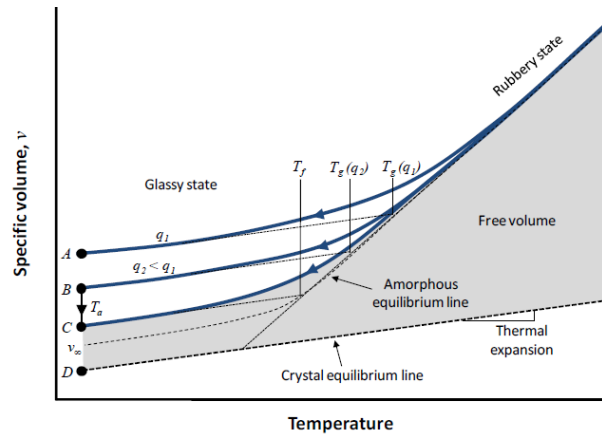


Figure 25: Diagram of specific volume versus temperature. At the glass transition temperature T_g the expansion coefficient suddenly increases.

5.2 RUBBER PHASE

With increasing temperatures, the rotation time of the Kuhn segments will decrease. The temperature at which the rotation time is 1 second is the glass-rubber transition temperature. Above this temperature the rotation time is less than 1 second. In this condition the polymer molecules will easily deform under an applied load due to the rotating Kuhn segments. The polymer is now in the **rubber phase**. It is a flexible material.

Plastics that are in the rubber phase at room temperature is used for flexible products like automotive tires and rubber bands.

In the rubber phase reptation of the macromolecules can be neglected. It would simply take a too long time before that happens. For reptation over some distance many millions of Kuhn segment rotations are needed. The deformation of the plastic is entirely due to **molecular deformation**.



Figure 26: Elastic band made from a polymer in the rubber phase.

The degree of freedom of the macromolecules has increased, which is reflected in a suddenly higher thermal expansion and a higher heat capacity of the polymer above the glass transition temperature. The average free volume around the macromolecule increases now, thus reducing the activation energy needed for segmental rotation.

The rubber phase is defined as the region where the rotation time is less than 1 s but reptation is still difficult. Reptation times are much higher than 1 s. The material behaves like an elastic solid with a

low stiffness. In the rubber phase, large deformations of the polymer are possible, caused by alignment of the rotating Kuhn segments.

Upon increasing temperatures, the chain segments continue rotating at increasing speeds. More free volume is created around the macromolecules due to the thermal expansion. It becomes possible for the macromolecules to slide forwards and backwards along their own axis (like a snake wriggling through a pile of other snakes). Due to reptation, macromolecules can move into other positions. This **molecular displacement** makes the polymer to behave as a kind of a fluid with strong elastic properties.

The reptation of the macromolecules into new positions enables the polymer to relax imposed stresses. As the deformed polymer molecules move into new locations the molecular deformation (and thus the stress) disappears. The time needed to significantly reduce a stress in the rubber (the **rubber relaxation time**) is there for the identical to the **reptation time** of the polymer.

We define the onset of the melt phase as the temperature at which stresses relax on a human time scale. This means a reptation time in the order of 1 s.

5.3 MELT PHASE

Since the rotation time of the Kuhn segments keeps on decreasing with increasing temperature the time for the molecules to reptate into a new position will decrease. At temperatures where the reptation time is 1 second or less the macromolecules easily move into new positions. The polymer will forget its shape after a short time due to molecular displacement. The polymer has changed from a rubber into a liquid.

The melt phase is typically used to give the polymer its final shape for use. For example, pipes are made by extrusion of polymer melt, plastic toys are made by injection moulding and bottles are made by blow moulding the melt.

The properties of the polymer now have changed from that of a rubber into that of a melt. The melt phase is defined as the temperature region where the reptation time is less than 1 s. The macromolecules can reptate on a human time scale, causing stresses to be released in less than a second. The stress relaxation times have reduced to less than a second.

Polymers normally have a high viscosity in the melt phase: in the order of magnitude of 10^4 Pas or more. Some elastic properties are still present; they are reflected for example in die swell during processing.

5.4 GLASS-RUBBER AND RUBBER-MELT TRANSITION TEMPERATURE

In Table 2 the chain segment rotation times and the polymer reptation times have been summarized. At the glass – rubber transition temperature the rotation time is 1 second and at the rubber – melt transition temperature the reptation time is 1 second.

Table 2: Rotation and reptation times in the different phases of the polymer		
	Rotation time	Reptation time
Glass phase	$> 1 \text{ s}$	$\gg 1 \text{ s}$
Glass – rubber transition temperature	1 s	
Rubber phase	$< 1 \text{ s}$	$> 1 \text{ s}$
Rubber – melt transition temperature		1 s
Melt phase	$\ll 1 \text{ s}$	$< 1 \text{ s}$

5.5 AMORPHOUS AND CRYSTALLINE POLYMERS

Due to their nature polymer molecules like to have a random shape. Combined with other macromolecules they form a disordered structure (amorphous). However, some polymers are able to arrange their macromolecules with some regularity with neighbouring macromolecules. The regular structures now formed are called crystalline regions.

In a crystalline region the macromolecules are more closely packed than in an amorphous region. The free volume is less which causes the macromolecules to be strongly hindered in their movements. They are less mobile in a crystalline region. When macromolecules are arranged in a crystalline structure, they form a rigid and strong plastic, even when the amorphous part of the polymer would be in the rubber phase.

Polymers are usually classified into amorphous polymers and crystalline polymers. Amorphous polymers have a fraction of crystalline material that is usually less than 10 %. Crystalline polymers have a crystalline fraction that is larger than 50 %. Typical examples of amorphous polymers are polycarbonate (PC), polystyrene (PS) and polyvinylchloride (PVC). Typical examples of crystalline polymers are polyethylene (PE) and polyethylene terephthalate (PET).

At a high enough temperature the crystalline region will melt. This is the crystalline melting point. The crystalline melting point is always higher than the glass-rubber transition temperature.

In case of a crystalline polymer like HDPE a crystalline phase will be present both in the glass phase and in the rubber phase. In the glass phase the stiffness of the amorphous part will be so high that the influence of the crystalline phase can be neglected. This is not the case in the rubber phase however.

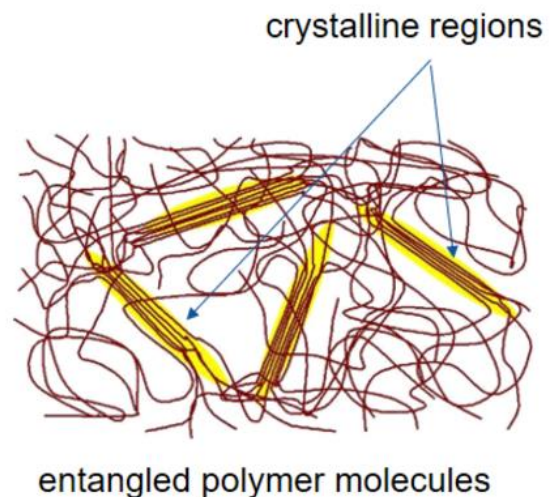


Figure 27: Regular crystalline regions in an amorphous matrix.

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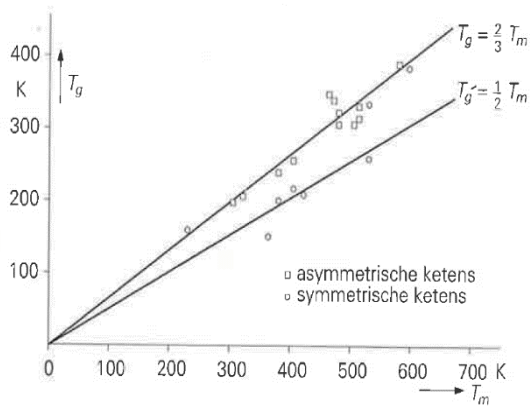


Figure 28: Glass transition temperature and crystalline melting point of several polymers.

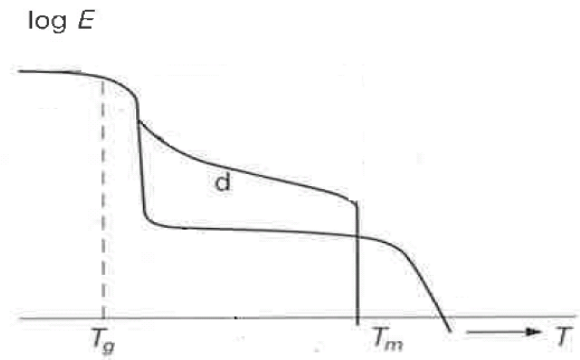


Figure 29: The crystalline phase (d) effectively increases the stiffness of the polymer.

In all polymers the crystalline melting temperature is higher than the glass transition temperature. This is indicated in Figure 28. That implies that in a crystalline polymer the crystalline phase will always modify the properties of the rubber phase.

The crystalline regions (spherulites) will slow down the rotation of the polymer segments, at least in or near by the lamellae. This will increase the stiffness of the rubber phase very much, as indicated in Figure 29. Large deformations of the polymer are only possible by ripping the polymer chains out of the crystalline regions (see Figure 30).

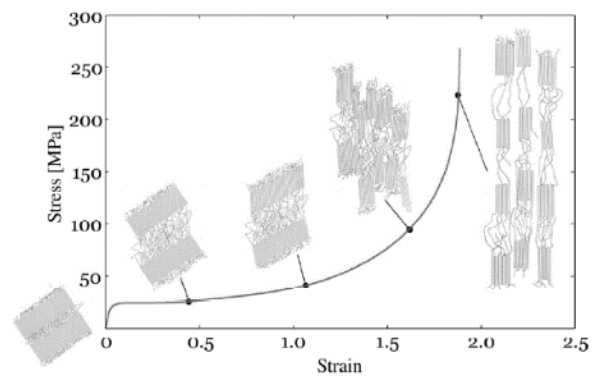


Figure 30: Deformation of a crystalline polymer. The polymer chains are ripped out of the crystals.

In crystalline polymers the level of crystals formed below the melting point is so high that chain reptation becomes directly seriously hindered. Below the crystalline melting point reptation suffers from an extra energy barrier to pass: the melting energy. The reptation frequency will suddenly drop several orders of magnitude, causing the reptation to cease. The rubber phase is now extended from the glass transition temperature up to the crystalline melting temperature.

Table 3: Rotation and reptation times in the amorphous and crystalline phases of the polymer			
	Crystalline material?	Rotation time	Reptation time
Glass phase	Amorphous region	$> 1 \text{ s}$	$>> 1 \text{ s}$
Glass phase	Crystalline region	∞	∞
Rubber phase	Amorphous region	$< 1 \text{ s}$	$>> 1 \text{ s}$
Rubber phase	Crystalline region	$>> 1 \text{ s}$	∞
Melt phase		$<< 1 \text{ s}$	$< 1 \text{ s}$

5.6 CRYSTALLINE TO FLUID PHASE TRANSITION IN SHORT

In a crystalline material the atoms or molecules have arranged themselves in a very regular way. They attract each other by means of their intermolecular forces. Each molecule is “captured” by the other neighbouring molecules. This is called the crystalline phase.

Next to the regular crystalline structure molecules can also have a disordered structure in which they can move around. This is called the fluid phase. In the fluid phase the molecules have an increased thermal energy due to the increased disorder (entropy ΔS) which gives them more degrees of freedom. Due to the increased disorder, each molecule occupies more volume and therefore the density of the fluid will be less than that of the crystal.

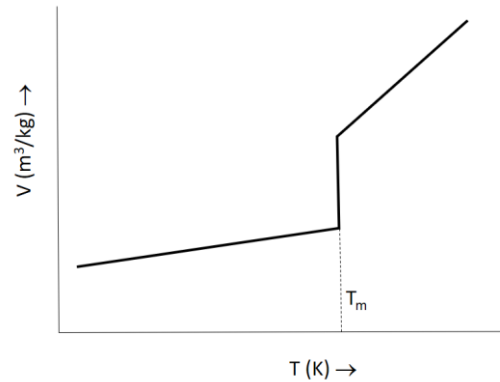


Figure 31: Volume temperature diagram of a crystalline material.

Figure 31 shows a schematic diagram of the specific volume versus the temperature of a crystalline material. Below the melting point T_m the volume increases due to thermal expansion with temperature up to the melting point. At the melting point the phase changes from crystalline to fluid and the volume suddenly increases. Above the melting point the thermal expansion has increased due to the increased disorder of the material.

To free one of the molecules from the crystal structure into the fluid a certain amount of energy will be needed. This is the heat of melting (ΔU). And when a molecule moves from the fluid back into the crystal this heat of melting will be released again.

There is always an exchange of molecules between the crystalline phase and the fluid phase. At the melting temperature (T_m) the number of molecules that leave the crystalline phase equal the number of molecules that leave the fluid phase. Below the melting temperature more molecules enter the crystalline phase than those that leave the crystalline phase. Everything becomes solid. Above the melting temperature there are more molecules that leave the crystalline phase than those that enter the crystalline phase. Everything becomes fluid.

The melting temperature depends on the heat of melting (ΔU) and the change of thermal energy of the molecules when the leave or enter the crystalline phase. This change of thermal energy is simply the change of disorder (configurational entropy ΔS_c) times the temperature (T). At the melting temperature (T_m) the heat of melting equals the change of thermal energy of the molecule. It then follows that:

Equation 22

$$\Delta U = T_m \Delta S_c \text{ or } T_m = \frac{\Delta U}{\Delta S_c}$$

6 STRESS AND DEFORMATION

6.1 SMALL AND LARGE DEFORMATIONS

When a force is applied to a body then that body will be deformed. This is true for any material, including polymers. Figure 32 shows a rod that is deformed by a compression force (left) and by a tensile force (right). The original not deformed rod is shown in the middle.

We define the deformation or strain (ε) as the change of length of the body (Δl) divided by the original length of the body (l_0):

Equation 23

$$\varepsilon = \frac{\Delta l}{l_0}$$

Example: When a body with a length of 100 mm is stretched by 2 mm then the strain is $2 / 100 = 0.02$.

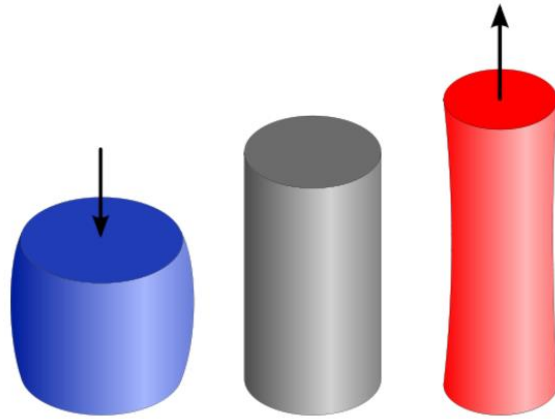


Figure 32: A body subjected to a force will be deformed (commons.wikimedia.org).

Instead of the force (F) it is common to use stress instead (σ), which is the force per unit area (A) in the body:

Equation 24

$$\sigma = \frac{F}{A}$$

Example: A force of 100 N on a body with a surface of $1000 \text{ cm}^2 (= 0.1 \text{ m}^2)$ will cause a stress of $100 / 0.1 = 1000 \text{ N/m}^2$, which is the same as 1000 Pa.

In case of a small deformation the stress is proportional to the deformation. This fact is known as Hooke's law. It says that the stress (σ) is equal to the deformation (ε) times the Young's modulus (Y):

Equation 25

$$\sigma = Y\varepsilon$$

The Young's modulus is a material property. Example: Steel has an modulus of 210,000 MPa ($1 \text{ MPa} = 10^6 \text{ N/m}^2$). In order to create a strain of 0.02 in the bar a stress equal to $210,000 \times 0.02 = 4,200 \text{ MPa}$ is needed.

With this set of equations the stresses and strains in many situations are well described as long as the strain is small: not more than something like 0.03. When a body is deformed more than a few percent than Hooke's law is not valid anymore.

Most polymers can be deformed much more than a few percent, especially when they are in the rubber phase. Think of a rubber band that can be stretched five to ten times before it breaks.

Therefore, we need another way to describe the relation between stress and deformation in polymers. It is common to specify the deformation of the polymer by the stretch ratio (λ), which is the new length (l) divided by the original length (l_0):

Equation 26

$$\lambda = \frac{l}{l_0}$$

Example: A body has an original length of 10 cm. If the body is stretched to a length of 15 cm then the stretch ratio is $15 / 10 = 1.5$. If that same body would have been compressed to 5 cm then the stretch ratio is $5 / 10 = 0.5$.

In case of large deformations, where Hooke's law is not valid, the relation between stress and stretch ratio is as follows:

Equation 27

$$\sigma = G \left(\lambda^2 - \frac{1}{\lambda} \right)$$

In this equation, G is the shear modulus of the body. Like the Young's modulus it is a material property. Usually the shear modulus is about 1/3 of the Young's modulus ($G = Y/3$).

Example: Rubber has a shear modulus of about 10 MPa. If the rubber is stretched 2 times then the stress in the rubber will be $10 \times (2^2 - \frac{1}{2}) = 35$ MPa. In case of undeformed rubber the stretch ratio is 1 and the stress will be $10 \times (1 - 1) = 0$ MPa.

6.2 NEO-HOOKEAN MODEL FOR LARGE DEFORMATIONS

For describing the behaviour of a rubber we will use the “**Neo-Hookean model**”. This model is an extension of Hooke's law for the case of large deformations. The model of neo-Hookean solid is usable for plastics and rubber-like substances. Since deformations (strains) and resulting true stresses are dependent on the direction, tensor notation will be used in this chapter.

The stress tensor σ is related to the shear modulus G of the polymer, the deformation gradient tensor $\mathbf{F}$ and the pressure p as follows:

Equation 28

$$\sigma = G \mathbf{F} \mathbf{F}^T - p \mathbf{F} \mathbf{F}^{-1} \text{ (or written in index notation: } \sigma_{ij} = G \sum_{k=1}^3 F_{ik} F_{jk} - p \sum_{k=1}^3 F_{ik} F_{kj}^{-1} \text{)}$$

σ is the stress tensor that describes the normal stresses and the shear stresses in the polymer:

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Equation 29

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \text{ with } \sigma_{ij} = \sigma_{ji}$$

The indices 1, 2 and 3 refer to the axis in a 3-dimensional space. For example, 1 could be the x-axis, 2 the y-axis and 3 the z-axis. The first index defines the plane on which the force is acting: 1 means the plane perpendicular to the x-axis, 2 the plane perpendicular to the y-axis and 3 the plane perpendicular to the z-axis. The second index defines the direction of the force: 1 in the direction of the x-axis, etc. σ_{11} , σ_{22} and σ_{33} are the normal stresses; σ_{12} , σ_{13} and σ_{23} are the shear stresses.

The deformation gradient tensor $\mathbf{F}$ describes all shear and strain deformations in the rubber material. It is the ratio between the deformed state (x) and the undeformed state (X):

Equation 30

$$F_{ij} = \frac{\partial x_i}{\partial X_j}$$

In the case of a simple shear $\gamma = \gamma_{12}$ on plane 1 in axis direction 2 $\mathbf{F}$ becomes: $\mathbf{F} = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	In the case of uniaxial extension $\lambda = \lambda_{11} = L_{\text{new}} / L_{\text{old}}$ on plane 1 in axis direction 1 $\mathbf{F}$ becomes: $\mathbf{F} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{bmatrix}$
--	---

$\mathbf{F}^T$ is the transposed deformation tensor. This tensor is simply generated by exchanging the rows for the columns ($F_{ij} \leftrightarrow F_{ji}$).

In case of a simple shear: $\mathbf{F}^T = \begin{bmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	In case of uniaxial extension: $\mathbf{F}^T = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{bmatrix}$
---	--

$\mathbf{F}^{-1}$ is the inverse of the deformation tensor. By definition: $\mathbf{F}\mathbf{F}^{-1} = \mathbf{I}$, where $\mathbf{I}$ is the unit tensor with $I_{ij} = 1$ for $i=j$ and $I_{ij} = 0$ for $i \neq j$.

In case of a simple shear: $\mathbf{F}^{-1} = \begin{bmatrix} 1 & -\gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	In case of uniaxial extension: $\mathbf{F}^{-1} = \begin{bmatrix} 1/\lambda & 0 & 0 \\ 0 & \sqrt{\lambda} & 0 \\ 0 & 0 & \sqrt{\lambda} \end{bmatrix}$
---	---

6.3 EXAMPLE: SIMPLE SHEAR IN RUBBER

Let us consider the case that a rubber is only sheared on plane 1 in the axis direction 2 by an amount of γ . Now Equation 28 becomes:

Equation 31

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \left(G \begin{bmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} - p \begin{bmatrix} 1 & -\gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \right) =$$

$$\begin{bmatrix} G - p + G\gamma^2 & p\gamma + (G - p)\gamma & 0 \\ G\gamma & G - p & 0 \\ 0 & 0 & G - p \end{bmatrix}$$

Since the strain tensor is symmetric ($\sigma_{ij} = \sigma_{ji}$) it follows that $p = G$ and we now find for the stress tensor:

Equation 32

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} = \begin{bmatrix} G\gamma^2 & G\gamma & 0 \\ G\gamma & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

σ_{12} is the shear stress τ . It increases linearly with the shear deformation γ . This is just like the well-known relation for shear strain and shear stress in an elastic solid according to Hooke's law for small deformations.

σ_{11} is the normal stress that is induced in the rubber due to the shear deformation. It is also often referred to as the first normal stress difference ($\sigma_{11} - \sigma_{22}$). The normal stress increases quadratically with the shear deformation γ .

6.4 EXAMPLE: UNIAXIAL EXTENSIONAL STRESS

Let us now consider a rubber of which plane 1 is stretched into the 1-direction. The stretch ratio $\lambda = L_{\text{new}} / L_{\text{old}}$. Now Equation 28 becomes:

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Equation 33

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{bmatrix} \left(G \begin{bmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{bmatrix} - p \begin{bmatrix} 1/\lambda & 0 & 0 \\ 0 & \sqrt{\lambda} & 0 \\ 0 & 0 & \sqrt{\lambda} \end{bmatrix} \right)$$

$$= \begin{bmatrix} G\lambda^2 - p & 0 & 0 \\ 0 & \frac{G}{\lambda} - p & 0 \\ 0 & 0 & \frac{G}{\lambda} - p \end{bmatrix}$$

Under uniaxial extension the stress in the 11-direction is σ and the stress in all other directions is 0. It then follows that $p = G/\lambda$ and we find for the stress tensor:

Equation 34

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} = \begin{bmatrix} G\left(\lambda^2 - \frac{1}{\lambda}\right) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The stretch ratio λ can also be expressed in strain ε as $\lambda = e^\varepsilon$, which results in:

Equation 35

$$\sigma = G(e^{2\varepsilon} - e^{-\varepsilon})$$

For small values of the strain ($\varepsilon \ll 1$) it then follows that $\sigma = 3G\varepsilon$ and for incompressible materials the Young's modulus $Y = 3G$. So for small deformations we find Hooke's law again:

Equation 36

$$\sigma = Y\varepsilon \quad (\text{for } \varepsilon \ll 1)$$

7 INFLUENCE OF STRESS ON ROTATION AND REPTATION TIME

As discussed before polymer molecules have two ways of moving: the chain segments (Kuhn segments) can rotate and the entire molecule can slide along its own axis (reptate).

We have learned that both the Kuhn segment rotation time and the reptation time are strongly temperature dependant. Temperature is in fact the same as motion of the atoms and molecules. Increasing temperatures thus give increasing mobility of atoms and molecules and thus shorter relaxation times.

A very important phenomenon that we have so far not discussed is the fact that both the rotation time and the reptation time are also strongly dependant on the stress present.

7.1 INFLUENCE OF STRESS ON KUHN SEGMENT ROTATION TIME

The rotations of the Kuhn segments will normally be forwards and backwards in a random way in the absence of a stress. When a stress is present however, rotation in one direction may increase the stress and rotation in the other direction may reduce the stress.

Rotations that reduce the stress are favoured: the stress helps the Kuhn segment to rotate. The rotations that reduce the stress will therefor speed up. The time needed for rotations that reduce the stress will strongly decrease. This causes the glass stress relaxation time to decrease strongly too.

For rotations that increase the stress the situation is opposite: the stress will counteract these rotations. The rotations that increase the stress will therefor slow down. The time needed for such rotations will increase strongly. Their contribution to the glass stress relaxation time will diminish. On average, any stress will cause the glass stress relaxation time to reduce strongly.

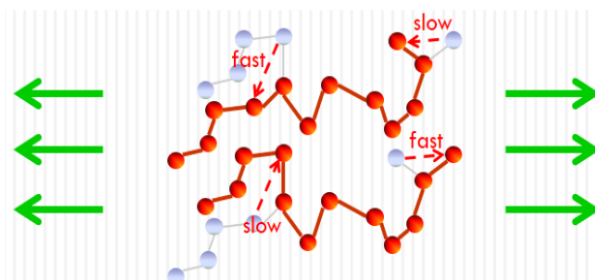


Figure 33: Rotations that reduce the stress will be favoured.

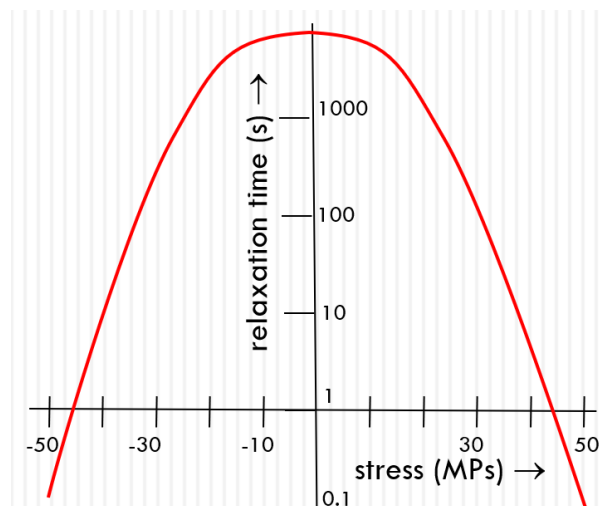


Figure 34: The average relaxation time strongly reduces with increasing stress.

As an example, a sketch of its influence is shown in Figure 34. The horizontal axis shows the stress and the vertical axis shows the relaxation time. When the stress is zero the relaxation time is maximal at a level (in this example) of about 1000 seconds. Positive tensile stresses or negative compression stresses will strongly reduce the relaxation time. At a stress level of about 20 MPa the relaxation time is already 1000 times less.

7.1.1 Equations for the glass stress relaxation time

When the polymer is deformed then elastic energy is stored in the macromolecules. The macromolecules will try to reduce the stored energy by means of rotation of their chain segments. In this way, the stored elastic energy will be lost into energy needed for rotating the chain and is effectively dissipated into heat.

The rotations can happen into any direction. Rotations that cause a deformation opposite to the imposed deformation will experience an increased energy barrier; their rotation time will be increased. Rotations that cause a deformation in the direction of the imposed deformation will experience a reduced energy barrier; their rotation time will be reduced. The energy per blob that is dissipated by the plastic deformation is Δu_{plas} . This energy is used to help a Kuhn pair rotate in each blob. The energy barrier to overcome for this rotation will be changed by the same amount. The rotation time then becomes:

Equation 37

$$\theta_{rot}(\Delta u_{plas}) = \theta_{rot,0} \exp\left(\frac{E_{rot} + \Delta u_{plas}}{kT}\right)$$

Since the Kuhn pair rotations cause plastic deformations in random directions they will experience variations in the energy barrier between $-\Delta u_{plas}$ and $+\Delta u_{plas}$. Some rotation times will increase; others will reduce. The effective rotation time will be the inverse of the average number of rotations per second:

Equation 38

$$\theta_{rot} = \left[\frac{1}{\theta_{av}} \right]^{-1} = \left[\frac{1}{2\Delta u_{plas}} \int_{-\Delta u_{plas}}^{\Delta u_{plas}} \frac{d\Delta u_{plas}}{\theta_{rot}(\Delta u_{plas})} \right]^{-1} = \theta_{rot,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{\Delta u_{plas}}{kT} \bigg/ \sinh\left(\frac{\Delta u_{plas}}{kT}\right)$$

The energy that is consumed during plastic deformation of the polymer is used to make a Kuhn pair rotate in all blobs of the polymer. During plastic deformation the stress σ_{gla} remains more or less constant. Therefore, the energy consumed during plastic deformation for each blob will be:

Equation 39

$$\Delta u_{plas} = \frac{1}{v_c} \int_0^{\epsilon} \sigma_{gla} d\epsilon \approx \frac{\Delta \epsilon}{v_c} \sigma_{gla} = V_{rot} \sigma_{gla}$$

The rotation time then becomes:

Equation 40

$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{V_{rot} \sigma_{gla}}{kT} \bigg/ \sinh\left(\frac{V_{rot} \sigma_{gla}}{kT}\right)$$

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From Equation 40 we can conclude that the relaxation time with which the glass stress reduces is strongly influenced by temperature and stress. Increasing stresses and increasing temperatures cause the relaxation time for rotation to reduce.

V_{rot} is defined as the activation volume for rotation and is given by:

Equation 41

$$V_{rot} = \frac{\Delta \varepsilon}{v_c}$$

In the equation above v_c is the entanglement density of the polymer. It is directly related to the number of entangled Kuhn segments N_e , the mass of a Kuhn segment m_K and the density of the polymer ρ :

Equation 42

$$v_c = \frac{\rho}{m_K N_e}$$

The average number of Kuhn segments present in one blob (the number of entangled Kuhn segments) is N_e . Since the size of one blob is $b\sqrt{N_e}$ and the change of length due to Kuhn pair rotation is $2b$ the induced strain in the blob $\Delta \varepsilon$ will be:

Equation 43

$$\Delta \varepsilon = \frac{2}{\sqrt{N_e}}$$

We now find for the activation volume for Kuhn pair rotation:

Equation 44

$$V_{rot} = \frac{2m_K \sqrt{N_e}}{\rho} \text{ or } V_{rot} = \sqrt{\frac{4m_K}{\rho v_c}}$$

7.2 INFLUENCE OF STRESS ON REPTATION TIME

In the rubber phase the Kuhn segments can freely rotate thus giving the macromolecules a large flexibility. They are easy to deform. Any deformation imposed to the polymer induces a rubber stress in the material.

In the rubber phase reptation of the macromolecules is possible. Without stress they will move along their own axis randomly forwards and backwards if the stress is zero. This will change when stress is present however.

The deformation of the polymer also has deformed the individual macromolecules. Their normal spherical shape has been changed in, for example, an ellipsoid. If now the macromolecules reptate a step into a new position, then the average deformation of the molecule changes:

1. The change may result in a reduction of the deformation of the macromolecule. Due to this the stress locally in the macromolecule will reduce.
2. The change may result in an increase of the deformation of the macromolecule. Due to this the stress locally in the macromolecule will increase.

Reptation in a direction that reduces the stress is favoured because then the stress “helps” the molecule to move into that position. It is as if it moves with the wind in the back. Therefore, the time for the macromolecule to reptate into this direction will reduce considerably.

In the same way the time to reptate into a position that increases the stress will be counteracted. Now it is like the molecule is moving against the wind. The time needed to move into those positions will strongly increase. These reptations will not contribute anymore to the total relaxation because they stop to happen at higher stresses.

Thus, the average relaxation time of all deformed polymer molecules will strongly decrease while under stress. The stress simply helps the molecules to move into new positions where their deformation becomes zero. The nett result is a rubber relaxation time that is maximal at zero stress and which reduces strongly with either compression or tensile stresses. Just like the relaxation time of the glass stress does.

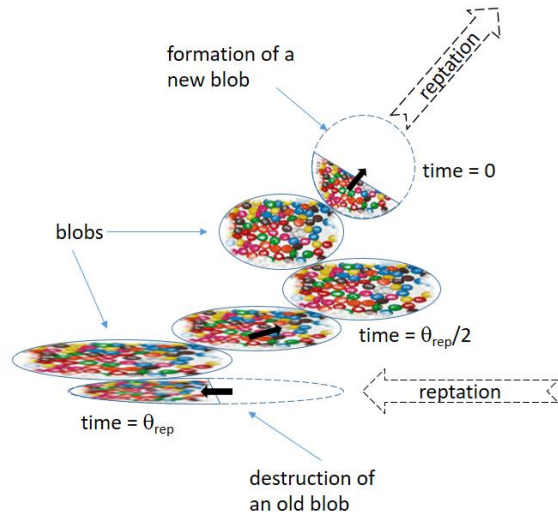


Figure 35: Reptation causes the deformation of the macromolecule to be reduced.

The Kuhn elements inside a blob are supposed to be able to rotate freely. Restrictions for reptation are caused by the entanglements in between the blobs. For reptation it is necessary that a Kuhn element passes the entanglement. We assume that this can only happen during a rotation of that Kuhn element. The elastic energy that is stored in the other Kuhn elements in the blob will help the Kuhn element at the blob to pass.

7.2.1 Equations for the rubber stress relaxation time

The reptation time is directly related to the rotation time and the size of the macromolecule as shown in chapter 4. That implies that the stress will influence the reptation time in the same way as the rotation time:

Equation 45

$$\theta_{rep} = N_K^{3.5} \theta_{rot,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{V_{rep} \sigma}{kT} \left/ \sinh\left(\frac{V_{rep} \sigma}{kT}\right) \right.$$

Since rotation of the Kuhn segments is the driving force for reptation the activation energy for reptation is the same as the activation energy for rotation. The activation volume for reptation will be larger however than the activation energy for rotation. This is because the stored elastic energy in all blobs in the polymer stimulates the reptation of the polymer. It means that:

Equation 46

$$V_{rep} = N_{blob} V_{rot}$$

The only important stress in the rubber and melt phase will be the rubber stress σ_{rub} . The glass stress σ_{gla} will have relaxed to zero. We can then write the equation for the reptation time also as:

Equation 47

$$\theta_{rep} = N_K^{3.5} \theta_{rot,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{N_e V_{rot} \sigma_{rub}}{kT} / \sinh\left(\frac{N_e V_{rot} \sigma_{rub}}{kT}\right) = \theta_{rep,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{V_{rep} \sigma_{rub}}{kT} / \sinh\left(\frac{V_{rep} \sigma_{rub}}{kT}\right)$$

7.3 IMPLICATIONS

We have seen that the time with which stress disappears in time (relaxation) is strongly dependant on the actual level of the stress. This has certain implications for the behaviour of the polymers when stress is applied. We will shortly discuss three examples:

1. **Multiple relaxation times.** A polymer bar is suddenly deformed and this deformation is kept constant. Initially the stress is high. Due to the high stress the relaxation time will be short. In time the stress reduces and this causes the relaxation time to increase. This continues until the stress is close to zero after a long time and the relaxation time will be down to the level dictated by the temperature. This means that initially the stress will reduce rather quickly in time but this speed of reduction reduces after longer times. In fact, a spectrum of relaxation times rule this process.
2. **Yield stress.** A polymer in the glass phase has a certain yield stress. Below the yield stress the deformation of the polymer is relatively small and recoverable. At the yield stress the polymer will suddenly start to deform plastically until it breaks. The reached deformation at break can be up to 500 % or more. This behaviour is due to the influence of the stress on the relaxation time. At low stress the relaxation time for Kuhn segment rotation in the glass phase will be very high: in the order of a couple of years or more. When the stress is increased the relaxation time for rotation will reduce strongly. Eventually a stress will be reached where the relaxation time for Kuhn segment rotation is in the order of a few seconds. At that moment the Kuhn segments will start to rotate quickly and the polymer will deform enormously with the applied stress. This is the yield stress.
3. **Viscosity.** It is a well-known phenomenon that the viscosity of a polymer reduces with the shear rate. This is caused by the higher shear stress at higher shear rates. The increased stress reduces the rubber relaxation time (reptation time) which will reduce the viscosity.

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.

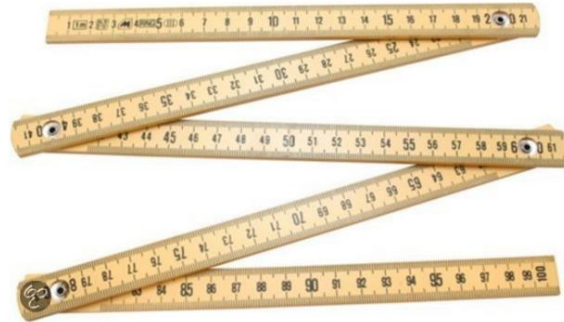


Figure 36: A macromolecule in the glass phase can be visualized as a folding ruler.

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 37 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 has rotated all bending will have disappeared. The stress has then reduced considerably. The glass stress, due to bending of the chain segments, has been replaced by the rubber stress which is due to the rotation of the Kuhn segments. The relaxation time of stresses in the glass phase is identical with the Kuhn segment rotation time.

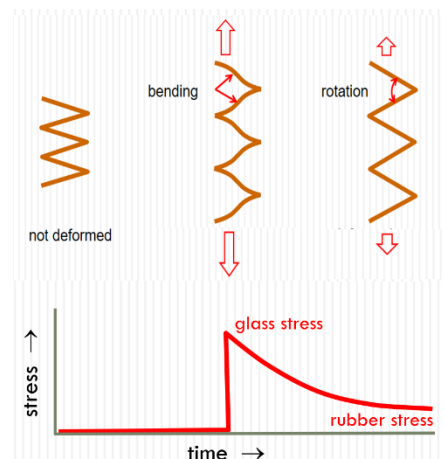


Figure 37: A deformation causes the Kuhn elements to bend. This creates the glass stress. Due to rotation the bending disappears and the stress reduces.

Equation 48

$$\theta_{gla} = \theta_{rot}$$

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:

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

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:

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

In mathematical representation:

Equation 49

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

The term $d\sigma_{gla}/d\varepsilon_{ben}$ 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_{gla}). In case of shear it is the glass shear modulus ($G_{gla} = Y_{gla}/3$).

In some cases the modulus $d\sigma_{gla}/d\varepsilon_{ben}$ 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 50

$$\sigma_{gla} = \frac{d\sigma_{gla}}{d\varepsilon_{ben}} \varepsilon_{ben}$$

By combining Equation 49 and Equation 50 we find a simple differential equation for the momentary deformation by rotation:

Equation 51

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

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

Equation 52

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

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**.

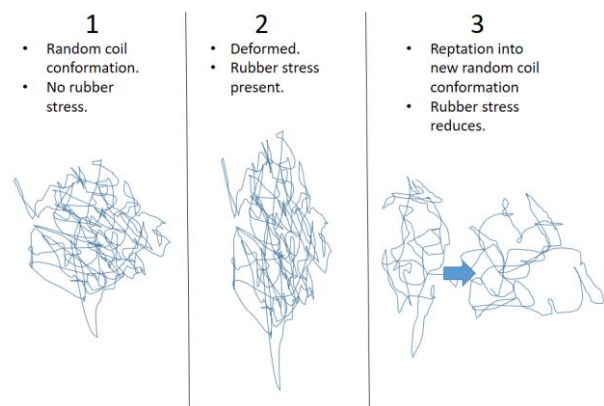


Figure 38: A deformation in the rubber or melt phase reduces by reptation.

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. Therefore the rubber relaxation time is equal to the reptation time.

Equation 53

$$\theta_{rub} = \theta_{rep}$$

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:

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

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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:

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”

[change of rubber stress per unit of time] = + [change of rubber stress due to deformation per unit time] – [rubber stress] / [rubber relaxation time]

In mathematical representation:

Equation 54

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

The term $d\sigma_{gla}/d\varepsilon_{ben}$ 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_{gla}). In case of shear it is the rubber shear modulus ($G_{gla} = Y_{gla}/3$).

The term $(d\varepsilon_{ben}/d\sigma_{gla})(\sigma_{gla}/\theta_{rot})$ is the change of the rubber deformation ($d\varepsilon_{rot}/dt$) 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 $d\sigma_{rub}/d\varepsilon_{rot}$ 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 55

$$\sigma_{rub} = \frac{d\sigma_{rub}}{d\varepsilon_{rot}} \varepsilon_{rot}$$

By combining Equation 54 and Equation 55 we find a simple differential equation for the momentary deformation by rotation:

Equation 56

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

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 53 then gives:

Equation 57

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

Combining Equation 54 and Equation 57 results in a simplified differential equation for the rubber and melt phase:

Equation 58

$$\frac{d\sigma_{rub}}{dt} = \frac{d\sigma_{rub}}{d\varepsilon_{rot}} \frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}}$$

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 (ε_{ben}) and glass stress (σ_{gla}) in the glass phase and deformation by rotation (ε_{rot}) of chain segments and rubber stress (σ_{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 59

$$\begin{aligned}\varepsilon &= \varepsilon_{ben} + \varepsilon_{rot} \\ \sigma &= \sigma_{gla} + \sigma_{rub}\end{aligned}$$

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 (σ_{gla}) and one for the rubber stress due to random rotation of the Kuhn segments (σ_{rub}).

Glass stress:

Equation 60

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

Rubber stress:

Equation 61

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

Total stress:

Equation 62

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

Total deformation:

Equation 63

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

In case that the moduli $d\sigma_{gla}/d\varepsilon_{ben}$ and $d\sigma_{rub}/d\varepsilon_{rot}$ are independent of strain then Equation 60 and Equation 61 can also be represented as differential equations for the deformation by bending and the deformation by rotation:

Equation 64

Deformation by bending:

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

Equation 65

Deformation by rotation:

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

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

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stress to increase. The relaxation time for this process is determined by the time that the Kuhn segments need to rotate (θ_{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.

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.

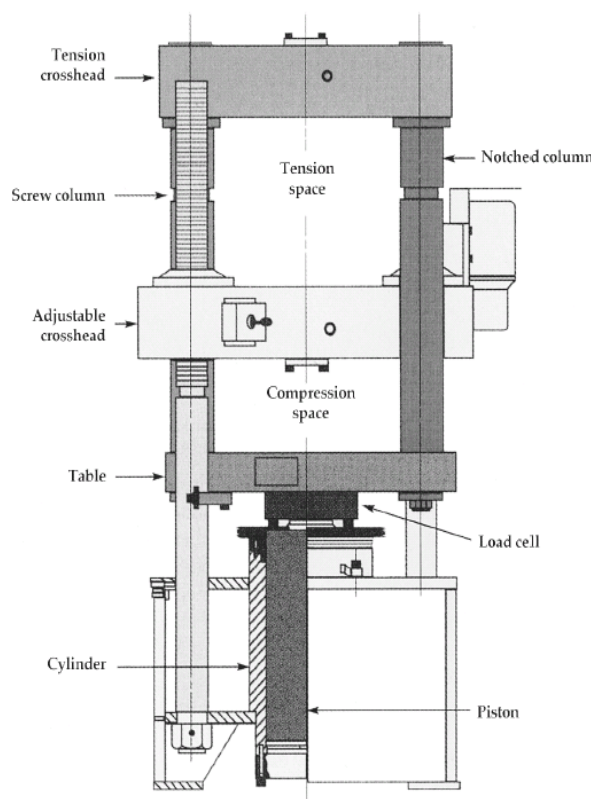


Figure 39: Tensile test equipment.

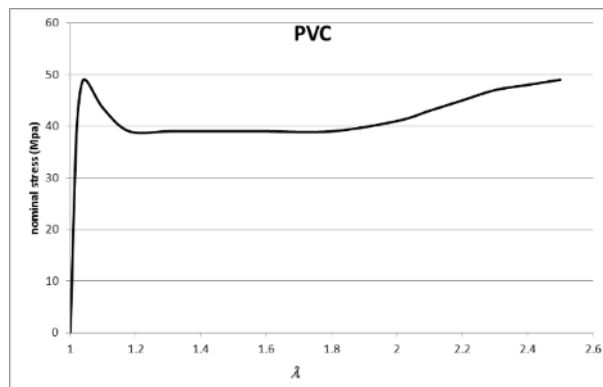


Figure 40: Nominal stress of PVC versus stretch ratio λ .

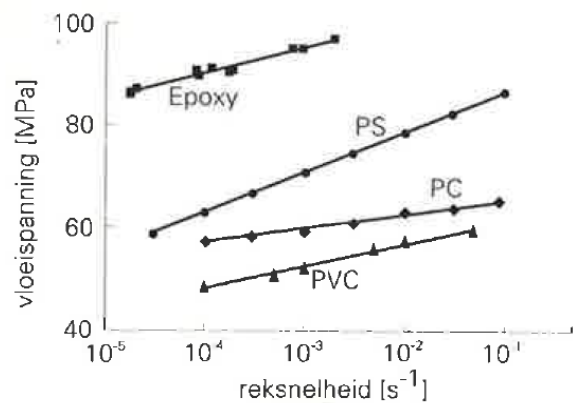


Figure 41: Relation yield stress and strain rate.

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 41.

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.

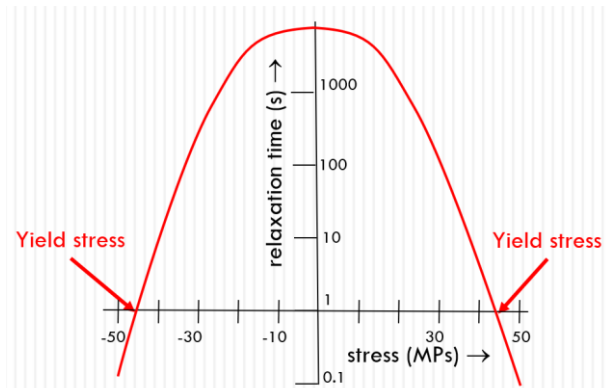


Figure 42: Near the yield stress the segment rotation time is 1 second.

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:

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

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

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

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

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 therefor 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 35:

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

- 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 66

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

Now combining Equation 66 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 67

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

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

Equation 68

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

And Equation 67 can be simplified to:

Equation 69

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

From Equation 69 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.

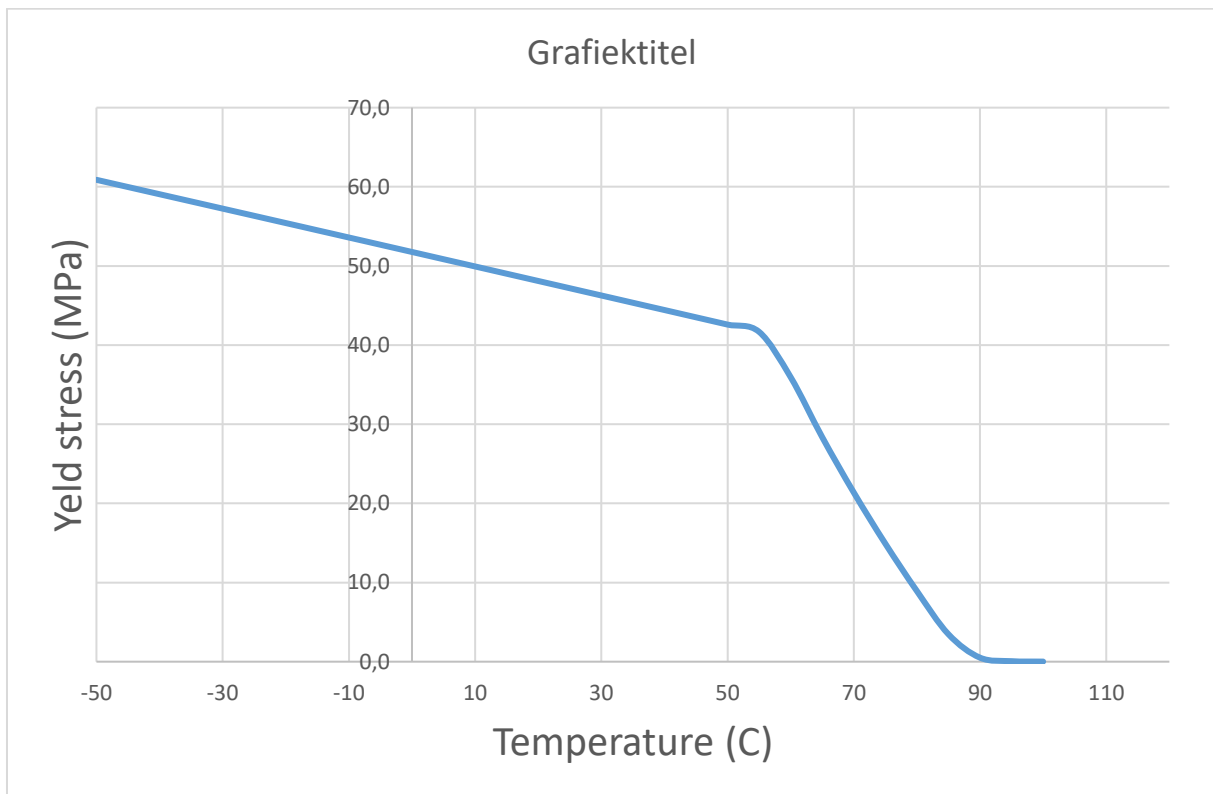


Figure 43: Yield stress of PVC as calculated with the aid of Equation 69.

10 VISCOSITY (MELT PHASE)

10.1 DEFINITION OF VISCOSITY

Consider a cube made from an elastic material, having ribs with length h . The cube is glued to a table. If we would apply a force to the top of the cube parallel to the surface of the table then the top of the cube will be displaced over a distance Δx , as shown in Figure 44. This kind of deformation is called **shear deformation**. Its value is the deformation divided by the height $\Delta x/h$. The force acting on the cube divided by the area of the cube (F/h^2) is called the **shear stress**.

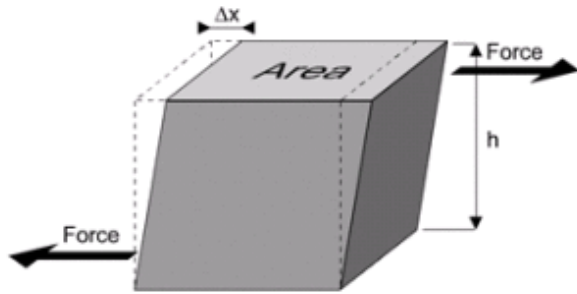


Figure 44: Cube deformed by a shear stress.

The ratio between the shear stress and the shear deformation is called the **shear modulus**. It can be calculated from:

$$[\text{shear modulus}] = [\text{shear stress}] / [\text{shear deformation}] \quad \text{or} \quad [\text{shear stress}] = [\text{shear modulus}] * [\text{shear deformation}]$$

Now suppose that the cube is made from a fluid like water or molten polymer. If a shear stress would be applied to this cube, then the top of the cube would continuously move in the direction of the stress with a certain velocity as long as the force exists. This continuous deformation is called shear rate and it is defined as the velocity of the top v divided by the height h : v/h .

The ratio between the shear stress and the shear rate is called the **viscosity**. It can be calculated from:

$$[\text{viscosity}] = [\text{shear stress}] / [\text{shear rate}] \quad \text{or} \quad [\text{shear stress}] = [\text{viscosity}] * [\text{shear rate}]$$

In mathematical form:

Equation 70

$$\eta = \tau / \frac{d\gamma}{dt} \quad \text{or} \quad \tau = \eta \frac{d\gamma}{dt}$$

The viscosity is an important material property of a fluid. With the aid of the viscosity the shear stress can be calculated when the fluid is sheared. Eventually this gives us the possibility to calculate the required pressure to move a fluid through a channel.

10.2 HOW TO CALCULATE THE VISCOSITY FROM THE DIFFERENTIAL EQUATION

In chapter 8 we have shown the general outline of the differential equation for the rubber and melt phase:

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

This differential equation can be used for the calculation of the viscosity from the material properties. The rubber stress is the same as the shear stress. We assume that after some time of

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shearing the shear stress has become constant. We have a dynamic equilibrium. That means that the change of stress has become zero:

$$0 = + [\text{change of rubber stress due to deformation per unit time}] - [\text{shear stress}] / [\text{rubber relaxation time}]$$

The change of rubber stress per unit time is the shear modulus times the shear rate:

$$[\text{change of rubber stress due to deformation per unit time}] = [\text{shear modulus}] * [\text{shear rate}]$$

By combining these two equations we get:

$$0 = [\text{shear modulus}] * [\text{shear rate}] - [\text{shear stress}] / [\text{relaxation time}]$$

This can be rewritten into:

$$[\text{shear stress}] = [\text{shear modulus}] * [\text{relaxation time}] * [\text{shear rate}]$$

Remember that the viscosity has been defined as:

$$[\text{viscosity}] = [\text{shear stress}] / [\text{shear rate}]$$

Which gives us the following result for the viscosity:

$$[\text{viscosity}] = [\text{shear modulus}] * [\text{relaxation time}]$$

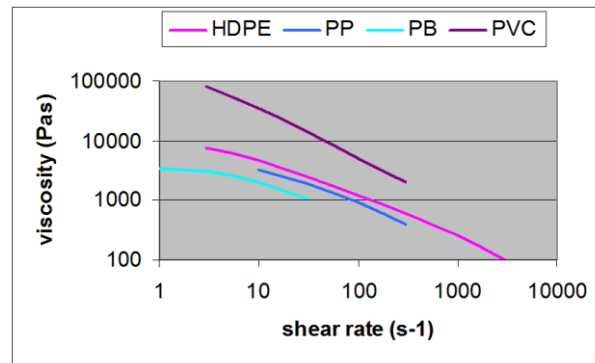


Figure 45: The viscosity of a polymer reduces with increasing shear rate or shear stress.

By using a differential equation in a dynamic equilibrium, we have proven that the viscosity of a fluid is simply the shear modulus time the relaxation time. Since the relaxation time of a polymer strongly reduces with the applied stress it follows that the viscosity of a polymer will also decrease with increasing shear stress or shear rate. This is a commonly observed phenomenon with polymers as shown in Figure 45.

10.3 MATHEMATICAL DERIVATION OF VISCOSITY VERSUS SHEAR STRESS AND SHEAR RATE

The viscoelastic relations are:

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

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

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

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

Boundary conditions:

- The polymer is under a constant rate of deformation ($d\varepsilon/dt$) and the stresses do not change anymore:

$$\frac{d\sigma_{gla}}{dt} = 0 \quad \text{and} \quad \frac{d\sigma_{rub}}{dt} = 0$$

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The viscoelastic relation for the glass stress then becomes:

Equation 71

$$\frac{d\sigma_{gla}}{d\varepsilon_{ben}} \frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}} = 0$$

$$\frac{d\sigma_{rub}}{d\varepsilon_{rot}} \frac{d\varepsilon_{ben}}{d\sigma_{gla}} \frac{\sigma_{gla}}{\theta_{rot}} - \frac{\sigma_{rub}}{\theta_{rep}} = 0$$

From which follows:

Equation 72

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

$$\sigma_{rub} = \theta_{rep} \frac{d\sigma_{rub}}{d\varepsilon_{rot}} \frac{d\varepsilon}{dt}$$

For the total stress created by the deformation rate we find:

Equation 73

$$\sigma = \sigma_{gla} + \sigma_{rub} = \theta_{rot} \frac{d\sigma_{gla}}{d\varepsilon_{ben}} \frac{d\varepsilon}{dt} + \theta_{rep} \frac{d\sigma_{rub}}{d\varepsilon_{rot}} \frac{d\varepsilon}{dt}$$

We consider the case that the deformation of the polymer is a shear deformation, usually denoted by γ :

Equation 74

$$\sigma_{gla} = G_{gla} \gamma_{ben} , \sigma_{rub} = G_{rub} \gamma_{rot} \text{ and } \frac{d\varepsilon}{dt} = \frac{d\gamma}{dt}$$

By combining Equation 73 with Equation 74 we find for the relation between the stress and the strain rate:

Equation 75

$$\sigma = (G_{gla} \theta_{rot} + G_{rub} \theta_{rep}) \frac{d\gamma}{dt}$$

The shear viscosity η_s of a polymer is defined as:

Equation 76

$$\sigma = \eta_s \frac{d\gamma}{dt}$$

It then follows for the shear viscosity of a polymer:

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Equation 77

$$\eta_s = G_{gla} \theta_{rot} + G_{rub} \theta_{rep}$$

Shear viscosity is usually determined in the rubber phase. In that case the product $G_{rub} \theta_{rep}$ is much higher than $G_{gla} \theta_{rot}$ (G_{rub} is 1000 times lower than G_{gla} but θ_{rep} is 10^6 to 10^8 time higher than θ_{rot}). Therefore the shear viscosity of a rubber is simply the product of the shear modulus and the rubber relaxation time:

Equation 78

$$\eta_s = G_{rub} \theta_{rep}$$

Equation 78 combined with the equation for the reptation relaxation time gives us:

Equation 79

$$\eta_s = G_{rub} \theta_{rep,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{\frac{V_{rep} \sigma_{rub}}{kT}}{\sinh\left(\frac{V_{rep} \sigma_{rub}}{kT}\right)} = \eta_{s,0} \frac{\frac{V_{rep} \sigma_{rub}}{kT}}{\sinh\left(\frac{V_{rep} \sigma_{rub}}{kT}\right)}$$

In Equation 79 we have defined the zero-stress (or zero-shear) viscosity $\eta_{s,0}$ as:

Equation 80

$$\eta_{s,0} = G_{rub} \theta_{rep,0} \exp\left(\frac{E_{rot}}{kT}\right)$$

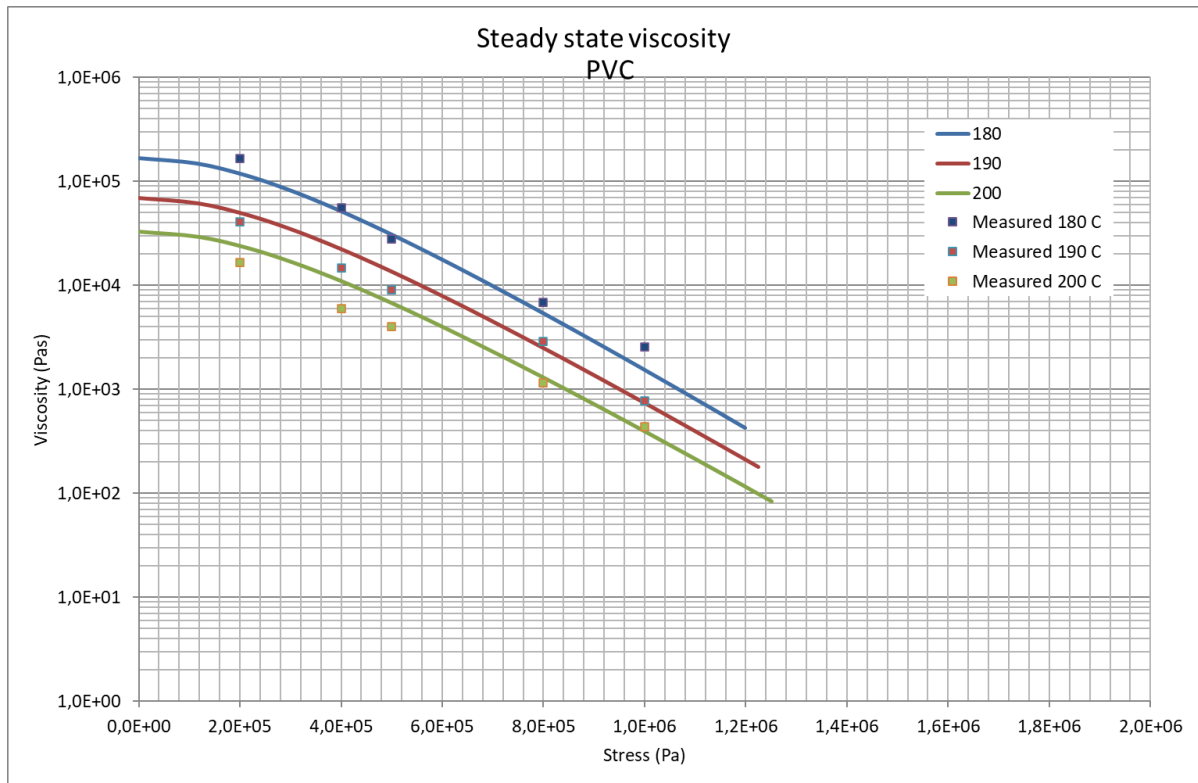


Figure 46: Shear viscosity of PVC K67 versus shear stress.

In Figure 46 the viscosity of PVC at 180 to 200 C has been calculated with the aid of and Equation 79 with the physical constants of PVC. The viscosity data are logarithmically plotted versus the shear stress. Note that at higher stresses the viscosity η_s decrease approximately exponentially with the shear stress σ_{rub} .

Note that in the model described above the viscosity is described as a function of the stress. From a physical perspective this is natural because it is the stress that the polymer molecules experience. Increasing stress will reduce the viscosity because the relaxation time of the rubber stress reduces.

In practice the viscosity is however often represented as a function of the shear rate. The equation that describes the shear rate dependence of the viscosity can be derived from Equation 79:

Equation 81

$$\eta_s = \frac{kT}{V_{rep}} \frac{1}{\frac{d\gamma}{dt}} \ln \left[\left(\eta_{s,0} \frac{V_{rep}}{kT} \frac{d\gamma}{dt} \right) + \sqrt{1 + \left(\eta_{s,0} \frac{V_{rep}}{kT} \frac{d\gamma}{dt} \right)^2} \right]$$

Equation 81 describes the viscosity as a function of the shear rate. It has been plotted for PVC at 180 to 200 C in Figure 47.

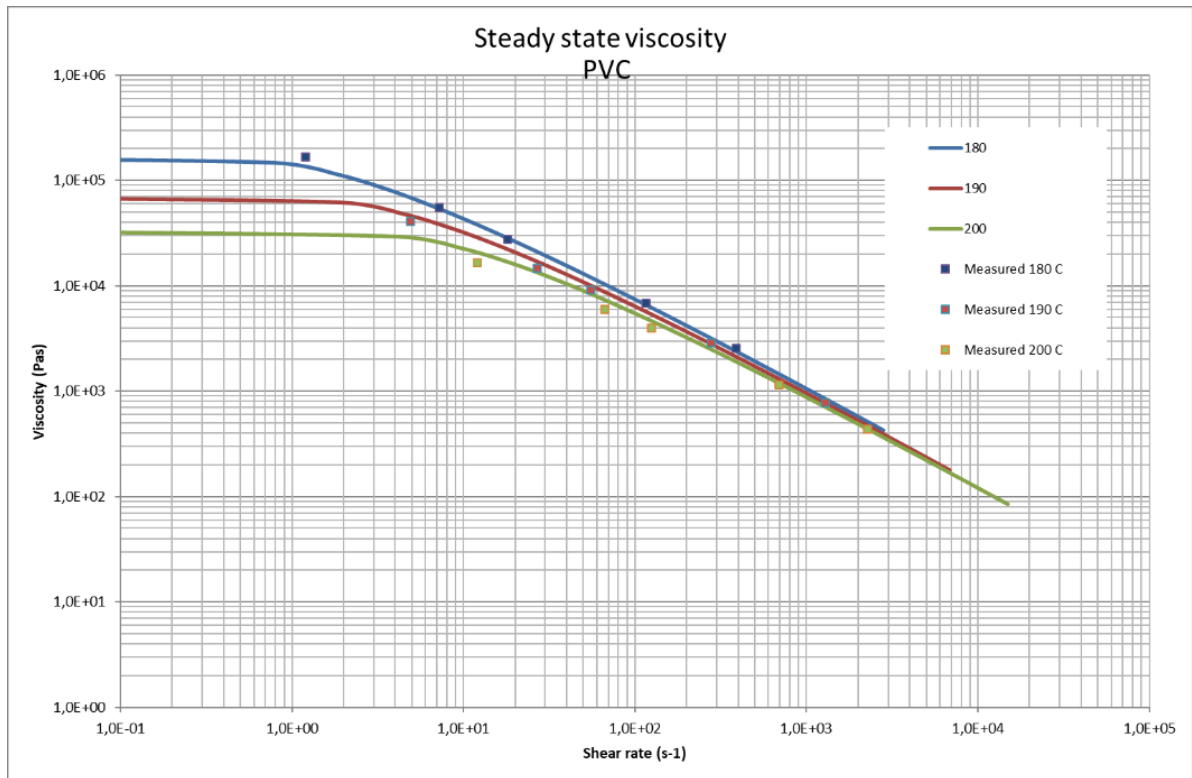


Figure 47: Shear viscosity of PVC K67 versus shear rate. At shear rates below 1 s^{-1} the behaviour is Newtonian, above 10 s^{-1} the behaviour is non-Newtonian.

10.4 THE POWER LAW MODEL

10.4.1 Low shear rates

At low shear rates the viscosity of the polymer is independent of the shear rate. The polymer melt behaves **Newtonian**. According to Equation 81 for small shear rates the viscosity becomes equal to the zero-shear viscosity:

Equation 82

$$\eta_s = \eta_{s,0}$$

This equation is only valid for low enough shear rates:

$$\frac{d\gamma}{dt} \ll \frac{kT}{V_{rep}\eta_{s,0}}$$

10.4.2 High shear rates

At high shear rates ($d\gamma/dt \gg kT/V_{rep}\eta_{s,0}$) the viscosity approximates to be a power of the shear rate. The polymer melt behaves **non-Newtonian**. In this region Equation 81 reduces to:

Equation 83

$$\eta_s = \frac{kT}{V_{rep}} \frac{1}{\frac{d\gamma}{dt}} \ln \left[2 \left(\eta_{s,0} \frac{V_{rep}}{kT} \frac{d\gamma}{dt} \right) \right]$$

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In a log viscosity – log shear rate plot as Figure 47 such a dependence shows up to be an almost straight line, the slope of it being between -0.5 and -1.0. This feature is used to make a simple description of the viscosity versus shear rate. It is called the **power law**:

Equation 84

$$\frac{\eta_s}{\eta_*} = \left(\frac{d\gamma}{dt} \right)^{n-1}$$

In this equation n is called the **power law index**. η_* is the viscosity at a shear rate of 1 s^{-1} . From Equation 81 the value of n can be derived by using $n - 1 = d\ln(\eta_s)/d\ln(d\gamma/dt)$:

Equation 85

$$n = \frac{kT}{V_{rep}\eta_{s,0} \frac{d\gamma}{dt}}$$

For high enough shear rates, the viscosity becomes inversely proportional to the shear rate because the power law index n tends to 0.

Note that especially at the higher shear rates the viscosities of the different temperatures seem to coincide. When operating at constant shear rate with increasing temperatures the stress will reduce. This increases the relaxation time and counteracts for a part the viscosity reduction due to temperature increase.

11 BEHAVIOUR OF POLYMERS UNDER CYCLIC LOAD

11.1 TEST UNDER CYCLIC LOAD

A common way to investigate the behaviour of polymers is to subject them to a small cyclic deformation while measuring the resulting stress. With a cyclic deformation we mean a kind of push and pull action that is done (for example) once every second. A graphical representation of such a cyclic deformation is shown in Figure 48. The shape of the deformation with time is called sinusoidal.

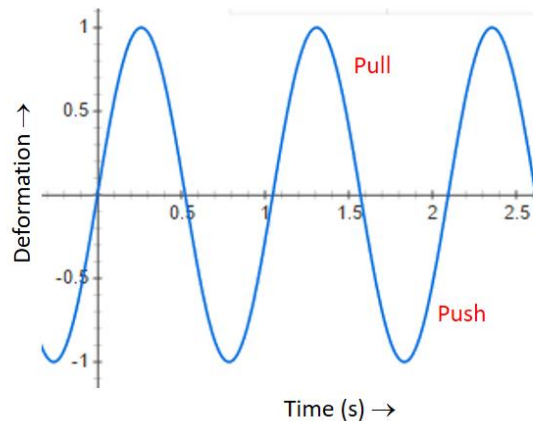


Figure 48: Cyclic deformation.

The cyclic deformation test can be done at varying temperatures and then it gives us information about the temperatures where phase transitions occur and about the stiffness in the glass phase and rubber phase. We will discuss this test in more detail in this chapter.

The cyclic deformation test can also be performed at a constant temperature for a prolonged time for fatigue testing. The applied deformation is chosen in such a way that the resulting stress is below the yield stress. The test is continued until the specimen breaks. This gives us information about the sensitivity of a polymer for brittle failure. Details about this test will be discussed in another chapter.

11.2 DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical analysis (DMA) is a technique used to study and characterize materials. A sinusoidal deformation is applied and the stress in the material is measured. The temperature of the sample or the cycle time of the deformation can be varied. Often a cycle time of about 1 second is chosen.

DMA allows a quick comparison of material properties between two materials. The technique can be used to determine the linear viscoelastic region of viscoelastic materials.



Figure 49: Dynamic mechanical analysis (DMA) instrumentation (en.wikipedia.org).

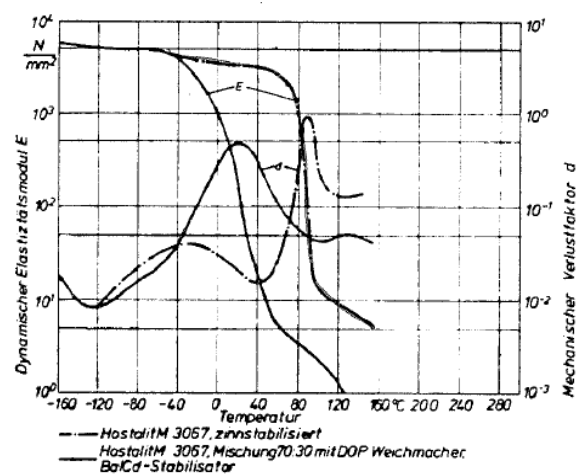


Figure 50: DMA of uPVC and plasticized PVC.

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In the glass phase, where the polymer is rigid, the stress will follow the applied strain per Hook's law. The ratio of stress and strain is the same as the glass elasticity modulus. The deformation applied to the polymer results in deformation by bending of the chain parts of the molecules.

At the glass transition temperature the rotation time of the Kuhn segments is 1 second. That means that during a cycle of 1 second the stress relaxes from the glass stress to the rubber stress. The nett result is that the time of maximum stress starts to deviate from the time of maximum deformation. The stress-time curve is now shifted from the strain-time curve, as shown in Figure 51.

In the rubber phase the Kuhn segment rotation time is much less than 1 second. The deformation applied to the polymer results in an immediate deformation by rotation of the Kuhn segments. The stress follows the applied strain without any shift. The ratio between stress and strain in the rubber phase is the rubber elasticity modulus.

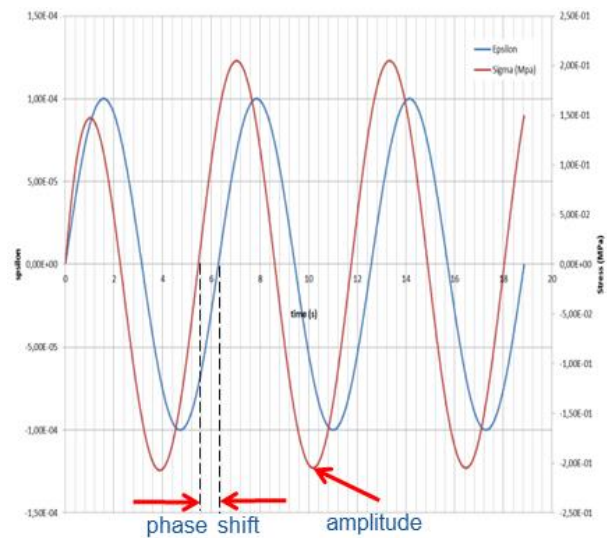


Figure 51: Deformation (blue) and resulting stress (red) during DMA. The amplitude of the stress and the phase shift give information about the storage and the loss modulus.

In the melt phase the reptation time is less than 1 second. During a 1 second cycle of the test the rubber stress relaxes due to reptation of the molecules. As near the glass transition temperature this leads to a shift in time between stress and strain. The minimum and maximum stresses are now found at the moment that the deformation speed is maximum, which means zero deformation. The stress is zero when the deformation speed is zero, which means at minimum or maximum deformation.

The ratio between stress and deformation and the time shift enables us to calculate a storage modulus and a loss modulus. The storage modulus gives information about the elastic behaviour of the polymer; the loss modulus gives information about the viscous behaviour of the polymer.

For a perfectly elastic solid, the resulting strain and the stress will be in phase. For a purely viscous fluid, there will be a half a cycle time delay of stress with respect to strain. Viscoelastic polymers have the characteristics in between where some time shift will occur during DMA tests. A typical DMA curve is shown in Figure 52.

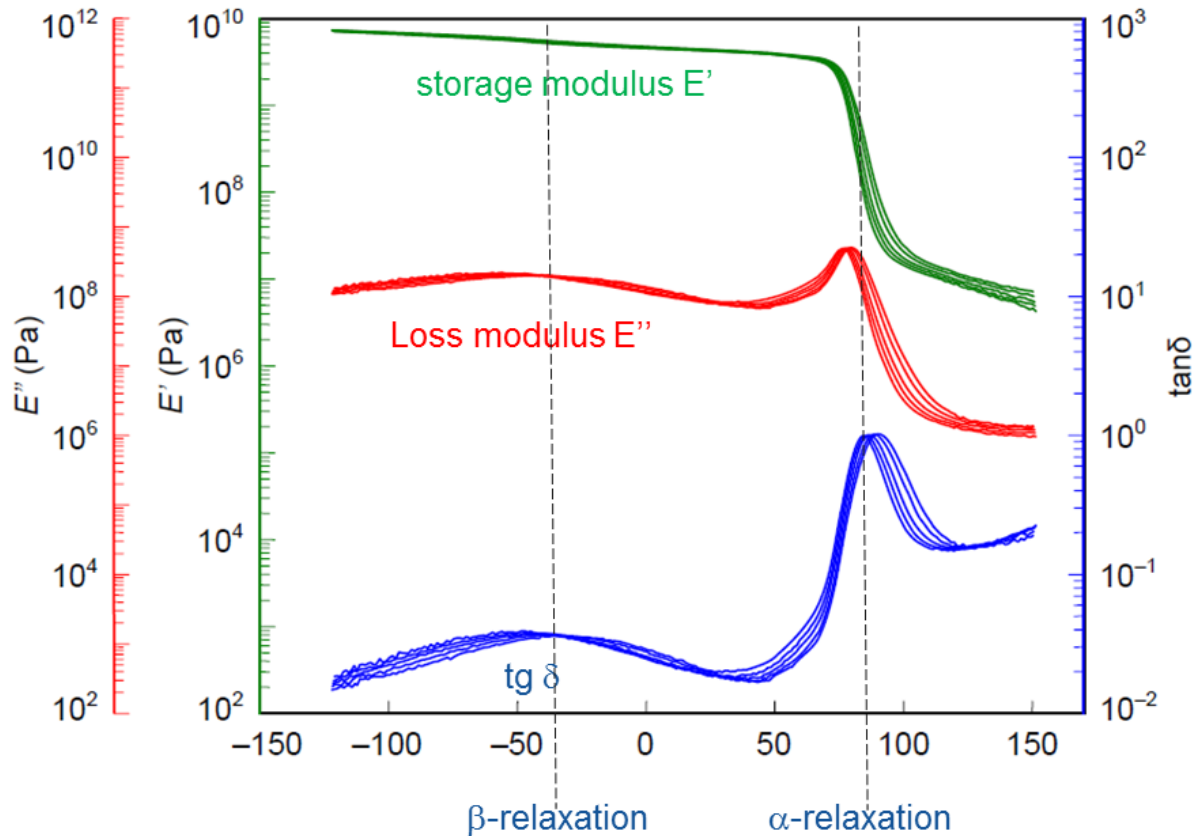


Figure 52: Example of DMA curve. Green = storage modulus, red = loss modulus, blue = tangent of loss angle ($\tan \delta$). At the glass transition point T_g the storage modulus suddenly reduces and the loss modulus peaks.

Starting from high temperature and reducing to 0 K a number of transitions will be found. They are labelled per the Greek alphabet:

1. First transition is called alpha-transition. This is usually the glass transition temperature in case of amorphous polymers or the crystalline melting point in case of crystalline polymers.
2. Second is called beta-transition. This transition is usually attributed to the first occurrence of chain rotation in case of amorphous polymers.
3. Third is called gamma-transition.
4. Etcetera.

11.3 STORAGE MODULUS AND LOSS MODULUS

For the with time varying strain $\varepsilon(t)$ and stress $\sigma(t)$ we can write:

Equation 86

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t)$$

Equation 87

$$\sigma(t) = E_d(\omega) \varepsilon_0 \sin(\omega t + \delta)$$

Where:

ω = frequency of strain oscillation (rad/s)

t = time (s)

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δ = loss angle

E_d = dynamic modulus

The storage modulus measures the stored energy, representing the elastic portion, and the loss modulus measures the energy dissipated as heat, representing the viscous portion. The tensile storage and loss moduli are defined as follows:

Equation 88

$$\sigma(t) = E_d(\omega)\varepsilon_0 \sin(\omega t + \delta) = \varepsilon_0 [E_d \cos(\delta) \sin(\omega t) + E_d \sin(\delta) \cos(\omega t)] = \varepsilon_0 [E' \sin(\omega t) + E'' \cos(\omega t)]$$

We can now define the storage modulus E' as:

Equation 89

$$E' = E_d \cos(\delta)$$

And the loss modulus E'' as:

Equation 90

$$E'' = E_d \sin(\delta)$$

From this it follows that:

Equation 91

$$\tan(\delta) = \frac{E''}{E'} \text{ and } E_d = \sqrt{E'^2 + E''^2}$$

The amount of energy per volume W lost during one cycle is given by:

Equation 92

$$W = \int_0^{2\pi/\omega} \sigma d\varepsilon = \int_0^{2\pi/\omega} \varepsilon_0 [E' \sin(\omega t) + E'' \cos(\omega t)] d\varepsilon_0 \sin(\omega t) = \pi \varepsilon_0^2 E''$$

So the dissipated energy is linear proportional to the loss modulus, which explains the name of this modulus.

11.4 MATHEMATICAL ANALYSIS OF RESPONSE TO CYCLIC DEFORMATION

The viscoelastic relations are:

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

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

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

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

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Boundary conditions:

- The applied deformation ε is uniaxial and varies sinusoidal with a small amplitude:

$$\sigma_{gla} = 3G_{gla}\varepsilon_{ben} \text{ and } \sigma_{rub} = 3G_{rub}\varepsilon_{rot}$$

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t) \text{ and } \frac{d\varepsilon}{dt} = \omega\varepsilon_0 \cos(\omega t)$$

- During the test the stresses are so small that they do not reduce the rotation time or the reptation time. That means that θ_{rot} and θ_{rep} are only temperature dependent:

$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{E_{rot}}{kT}\right) \text{ and } \theta_{rep} = \theta_{rep,0} \exp\left(\frac{E_{rep}}{kT}\right)$$

Under these conditions the viscoelastic relations reduce to:

Equation 93

$$\frac{d\varepsilon_{ben}}{dt} = \omega\varepsilon_0 \cos(\omega t) - \frac{\varepsilon_{ben}}{\theta_{rot}}$$

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

The differential equations can be solved analytically and result in:

Equation 94

$$\varepsilon_{ben}(t) = \frac{\omega\theta_{rot}\varepsilon_0}{\omega^2\theta_{rot}^2 + 1} (\omega\theta_{rot} \sin \omega t + \cos \omega t)$$

$$\varepsilon_{rot}(t) = \frac{\omega\theta_{rep}\varepsilon_0}{(\omega^2\theta_{rot}^2 + 1)(\omega^2\theta_{rep}^2 + 1)} \left[\omega(\theta_{rot} + \theta_{rep}) \sin \omega t + (1 - \omega^2\theta_{rot}\theta_{rep}) \cos \omega t \right]$$

It then follows for the resulting stress:

Equation 95

$$\begin{aligned} \sigma(t) = 3G_{gla}\varepsilon_{ben}(t) + 3G_{rub}\varepsilon_{rot}(t) = & \left(3G_{gla}\varepsilon_0 \frac{\omega^2\theta_{rot}^2}{\omega^2\theta_{rot}^2 + 1} + 3G_{rub}\varepsilon_0 \frac{\omega^2\theta_{rep}(\theta_{rot} + \theta_{rep})}{(\omega^2\theta_{rot}^2 + 1)(\omega^2\theta_{rep}^2 + 1)} \right) \sin \omega t + \\ & \left(3G_{gla}\varepsilon_0 \frac{\omega\theta_{rot}}{\omega^2\theta_{rot}^2 + 1} + 3G_{rub}\varepsilon_0 \frac{\omega\theta_{rep}(1 - \omega^2\theta_{rot}\theta_{rep})}{(\omega^2\theta_{rot}^2 + 1)(\omega^2\theta_{rep}^2 + 1)} \right) \cos \omega t \end{aligned}$$

With the aid of Equation 94 to Equation 95 we now find for the storage modulus E' , the loss modulus E'' and the loss angle δ :

Equation 96

$$E' = 3G_{gla} \frac{\omega^2\theta_{rot}^2}{\omega^2\theta_{rot}^2 + 1} + 3G_{rub} \frac{\omega^2\theta_{rep}(\theta_{rot} + \theta_{rep})}{(\omega^2\theta_{rot}^2 + 1)(\omega^2\theta_{rep}^2 + 1)}$$

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Equation 97

$$E'' = 3G_{gla} \frac{\omega\theta_{rot}}{\omega^2\theta_{rot}^2 + 1} + 3G_{rub} \frac{\omega\theta_{rep}(1 - \omega^2\theta_{rot}\theta_{rep})}{(\omega^2\theta_{rot}^2 + 1)(\omega^2\theta_{rep}^2 + 1)}$$

Equation 98

$$\tan\delta = \frac{E''}{E'} = \left(\frac{G_{gla}\omega^2\theta_{rot}^2}{\omega^2\theta_{rot}^2 + 1} + \frac{G_{rub}\omega^2\theta_{rep}(\theta_{rot} + \theta_{rep})}{(\omega^2\theta_{rot}^2 + 1)(\omega^2\theta_{rep}^2 + 1)} \right) \left/ \left(\frac{G_{gla}\omega\theta_{rot}}{\omega^2\theta_{rot}^2 + 1} + \frac{G_{rub}\omega\theta_{rep}(1 - \omega^2\theta_{rot}\theta_{rep})}{(\omega^2\theta_{rot}^2 + 1)(\omega^2\theta_{rep}^2 + 1)} \right) \right.$$

A plot of Equation 96 to Equation 98 for the storage modulus, the loss modulus and the tangent of the loss angle is shown in Figure 53 below. These results have been calculated with the physical constants for the viscoelasticity of PVC. The plot clearly shows the glass to rubber transition of PVC at about 85 C and the rubber to melt transition near 180 C.

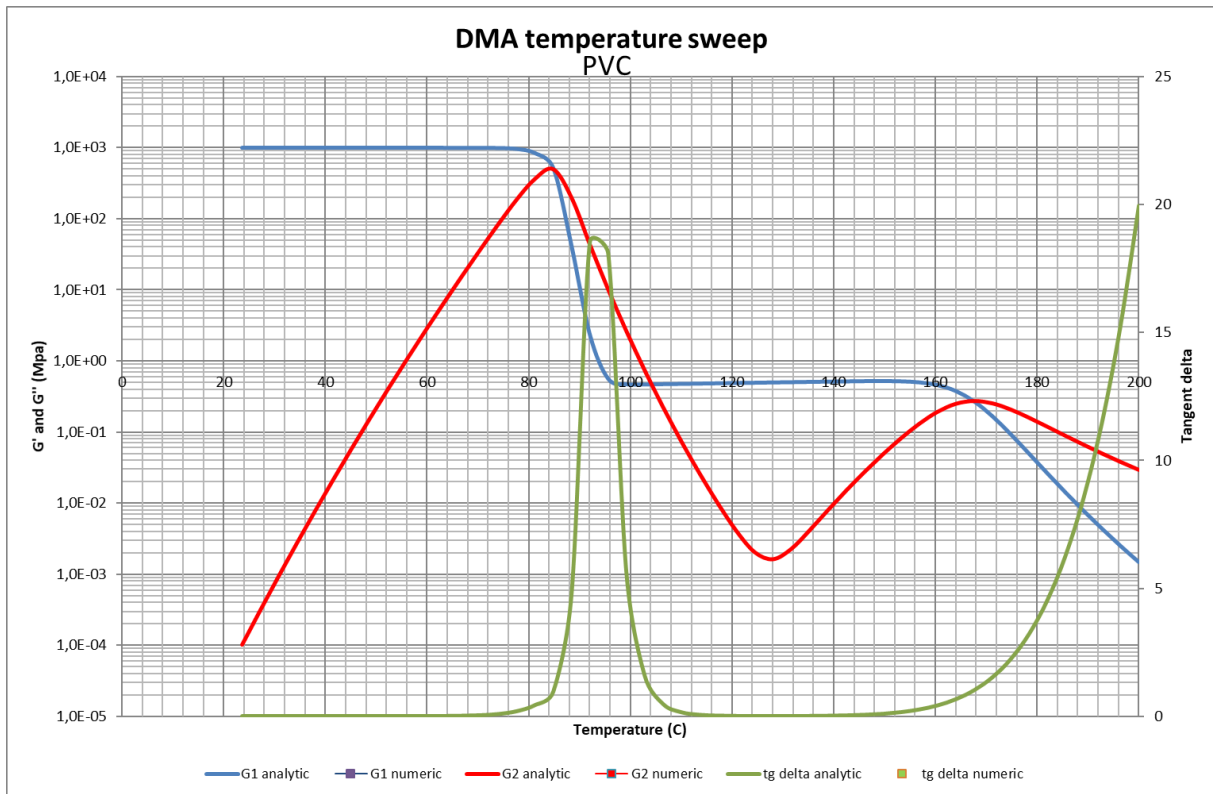


Figure 53: Storage modulus (blue), loss modulus (red) and tangent delta (green) for PVC K67. Calculated with Equation 96 to Equation 98 using $E_{rot} = 1.85 \times 10^{-19}$ J, $V_{rot} = 1.5 \times 10^{-27}$ m³, $G_{gla} = 10^9$ Pa, $\theta_0 = 10^{-13}$ s and $\omega = 1$ s⁻¹. The rubber modulus is calculated with the data of chapter 3.

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 54.

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

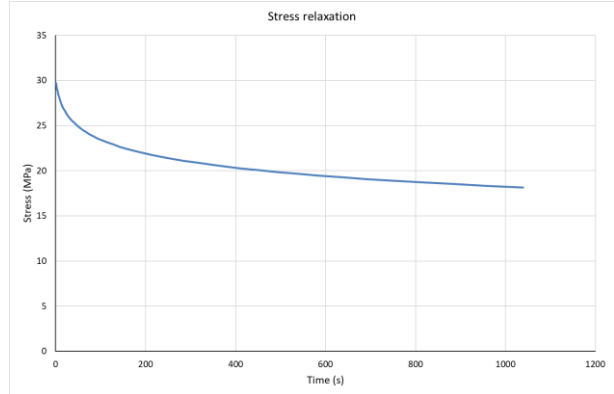


Figure 54: Reduction of the stress after a stepwise deformation.

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:

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

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

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

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

Boundary conditions:

- At time $t = 0$ a shear deformation γ_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:

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

The viscoelastic relations become:

Equation 99

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

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 θ_{rep} is infinitely high. The viscoelastic relations become:

Equation 100

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

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 θ_{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 55.

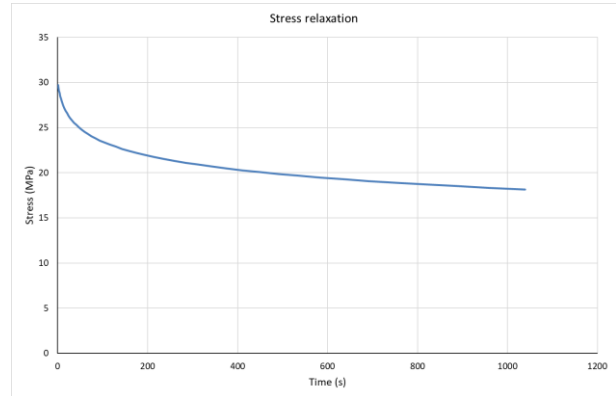


Figure 55: Stress relaxation of PVC at 30 C with an initial stress of 30 MPa.

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 101

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

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 102

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

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 103

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

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**.

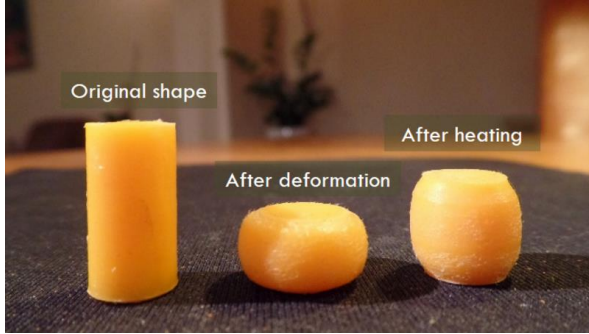


Figure 56: Below the glass temperature a polymer can be deformed but will not forget its original shape.

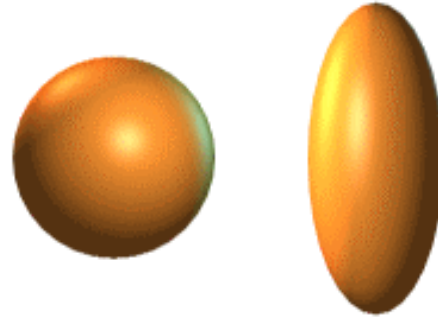


Figure 57: Yielding causes the spherical molecules to be deformed into an ellipsoid shape.

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:

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

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

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

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

All about viscoelasticity in the solid and molten phase

Boundary conditions:

- The applied deformation is a shear deformation. For the glass shear stress and the rubber shear stress we have:

$$\sigma_{gla} = G_{gla} \gamma_{ben} \text{ and } \sigma_{rub} = G_{rub} \gamma_{rot}$$

$$\frac{d\sigma_{gla}}{d\gamma_{ben}} = G_{gla} \text{ and } \frac{d\sigma_{rub}}{d\gamma_{rot}} = G_{rub}$$

- 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:

$$\sigma_{rub} = -\sigma_{gla} \text{ and } \frac{d\sigma_{rub}}{dt} = -\frac{d\sigma_{gla}}{dt}$$

The viscoelastic relations now become:

Equation 104

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

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

Equation 105

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

Finally, by combining Equation 104 and Equation 105 we obtain a very simple differential equation for the recovery of a deformed product:

Equation 106

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

Figure 58 shows the numerical solution of Equation 106 for PVC at 85 C after an initial deformation of 300 %.

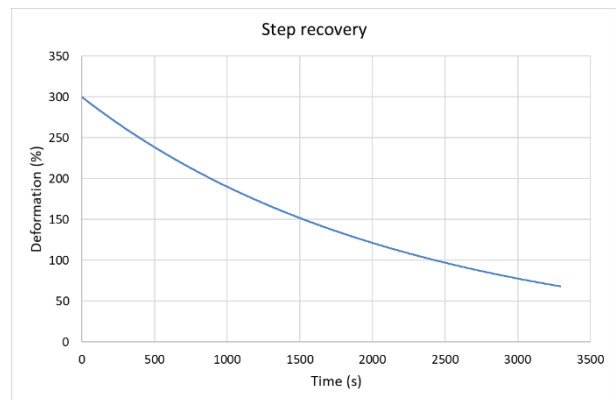


Figure 58: Recovery of PVC at 85 C after an initial deformation of 300 %.

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 106 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:

All about viscoelasticity in the solid and molten phase

Equation 107

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

The recovery process happens on a time scale that is $(G_{gla}/G_{rub}) \approx 1000$ 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.

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.

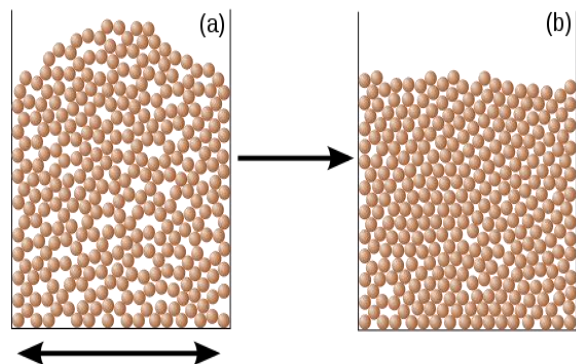


Figure 60: The effect of time or compaction on the structure of sand.

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.

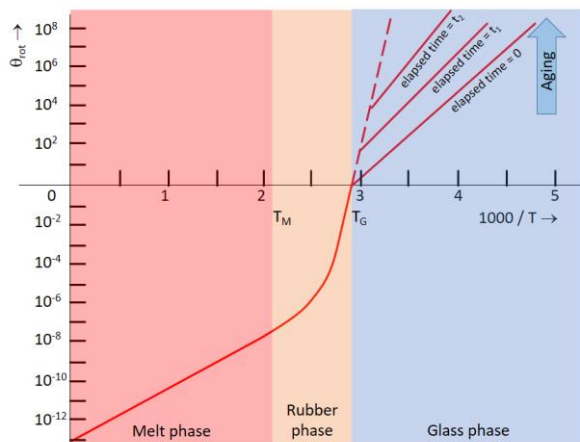


Figure 63: Frequency map of rotation times in an amorphous polymer.

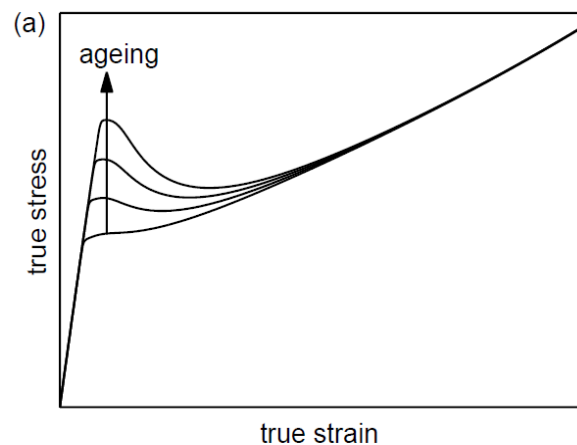


Figure 64: The effect of aging on the yield strength of a polymer.

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.

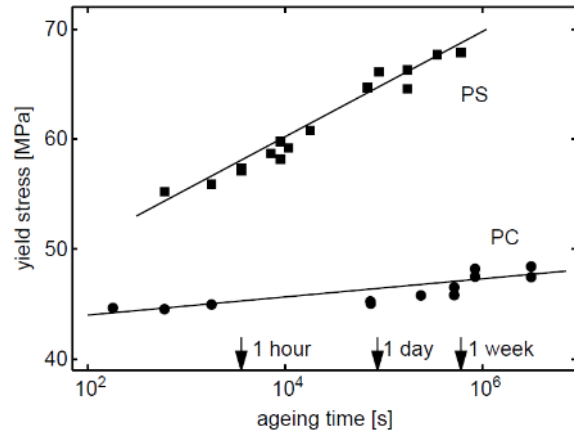


Figure 65: Increase of yield stress after rejuvenation of PS and PC.

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

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

All about viscoelasticity in the solid and molten phase

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

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

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. Therefore the initial size of the CRR's (z_{ini}) will be the size they have at the glass transition temperature (T_G):

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

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.

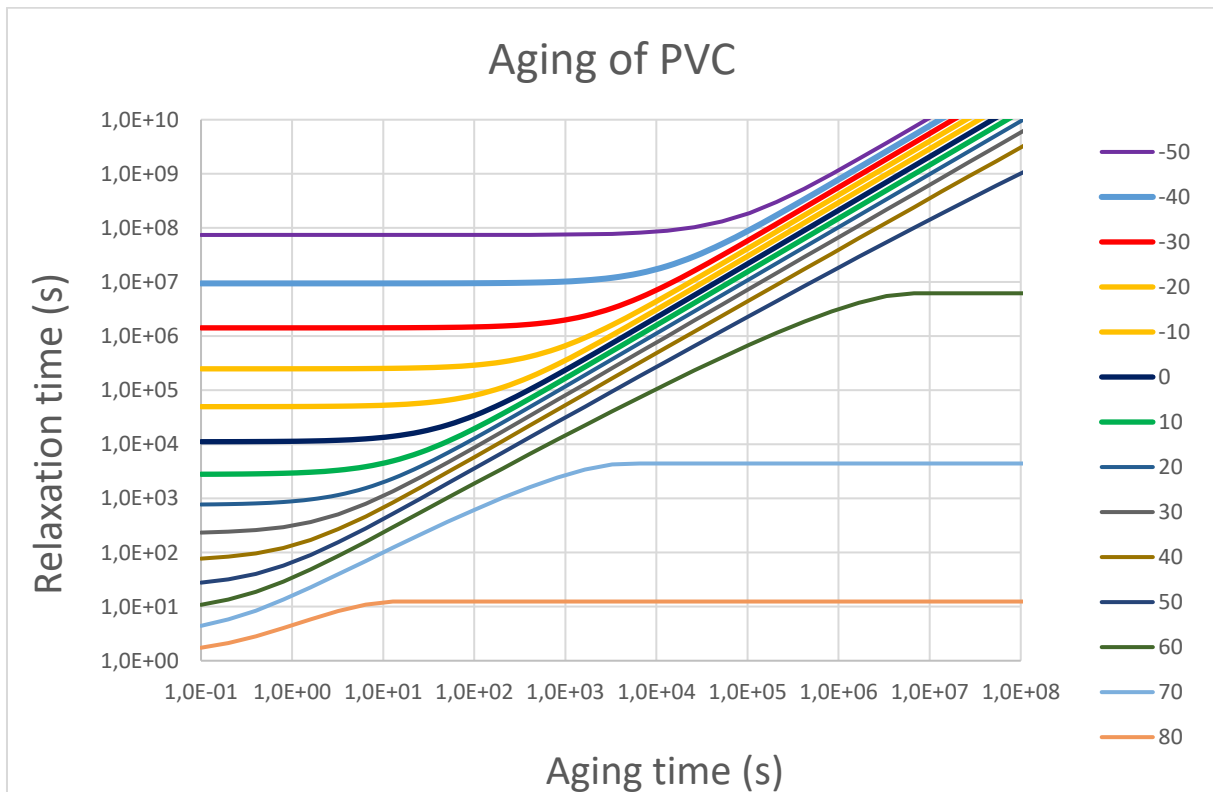


Figure 66: Plot of the relaxation time as a function of the aging time and temperature. $\theta_{rot,0} = 10^{-13}$ s, $T_m = 513$ K, $T_g = 358$ K and $E_0 = 8.9 \times 10^{-21}$ J.

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 $E_{rot} = kT \ln(\theta_{rot}/\theta_0)$. By using the relaxation times from Figure 66 we obtain the changing activation energy for segmental rotation for PVC at several temperatures:

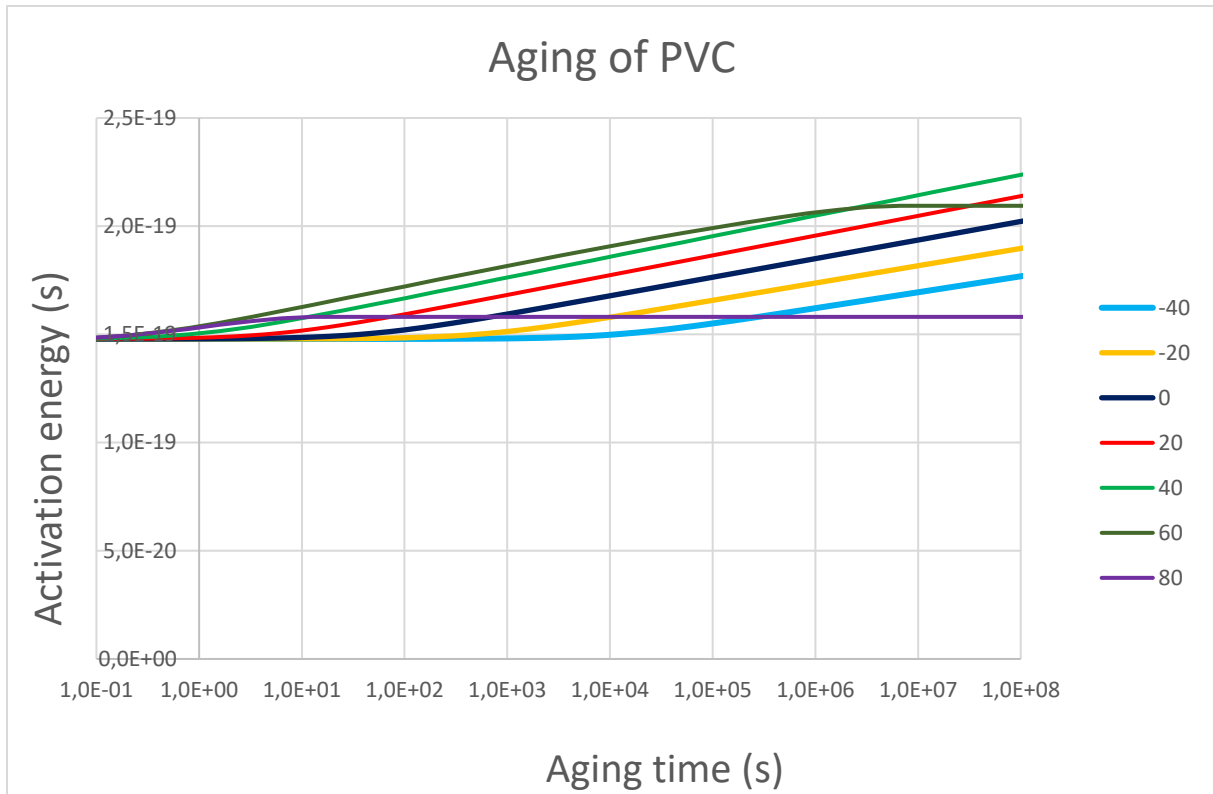


Figure 67: Activation energy for Kuhn segment rotation versus the aging time. Data calculated from Figure 66 with $E_{rot} = kT \ln(\theta_{rot}/\theta_0)$.

At short times the activation energy of PVC is 1.5×10^{-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 in 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).

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*.

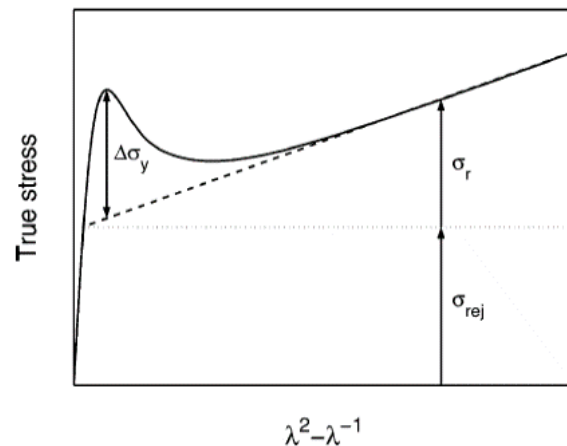


Figure 68: Stress - strain diagram obtained from a compression test. The drop of the stress after the yield point is caused by mechanical rejuvenation.

15 CREEP OF POLYMERS



Figure 69: A glacier slowly creeps into the sea.

Most materials under continuous load will slowly deform. Typical examples are metals, window glass, plastics, ice and rock. Ancient glass windows in churches have deformed under gravity in such an way that at the bottom the glass has become thicker than at the top. The ice of the glaciers slowly flows downwards and the basalt rocks in a mountain become plastically deformed by gravity forces. So plastics is just one group of the very many materials that show slow deformation once subjected to a force for a prolonged time. The common name for this slow deformation under load is **creep**.

15.1 DESCRIPTION OF THE CREEP PROCESS

When a load is put on a body made from a polymer it will be deformed. This deformation is time dependant, as shown in Figure 70 and consists of two parts:

1. An elastic deformation that occurs immediately after applying the load.
2. A plastic deformation that grows in time for the duration of the load.

After removing the load, the elastic deformation will disappear immediately. The plastic deformation, however, will take a long time to disappear. Under practical circumstances time will be too short to remove all plastic deformation. Some plastic deformation will be left in the product.

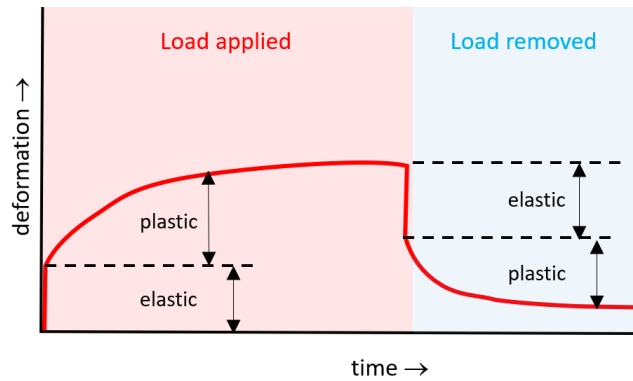


Figure 70: The deformation of a polymer body changes in time.

The load on the body has changed the shape of the polymer molecules by rotation of the chain segments. A part of this deformation will be recovered after some time. This is due to the rubber stress that is induced in the body due to the deformation. This rubber stress forces the polymer molecules back into their original shapes. This recovery process will take a long time however, because the rubber stress is relatively low (see chapter 13 Recovery of a deformed plastic body).

15.2 CREEP OR PLASTIC FLOW?

The speed with which the dimensions of the polymer body under load change (the strain rate) is strongly dependant on the height of the load (stress) and on the temperature of the body. Increasing loads and increasing temperatures will increase the speed of this process.

1. Under low stresses, it may take hours or days before some noticeable dimension changes can be observed. This slow process of changing dimensions is called **creep**.
2. Under high stresses, noticeable dimension changes can be seen already after seconds or minutes. This fast process of changing dimensions is called **plastic flow**.

Although the names are different, the underlying process is the same. In both cases the polymer molecules are deformed due to the rotation of the chain segments under load. The main difference between the two is the speed of the process.

Figure 71 shows a schematic representation of the deformation of a product under stress changing with time. This is called a **creep curve**. In this example three different creep curves are shown for three different stresses (σ_1 is the lowest and σ_3 is the highest stress on the body).

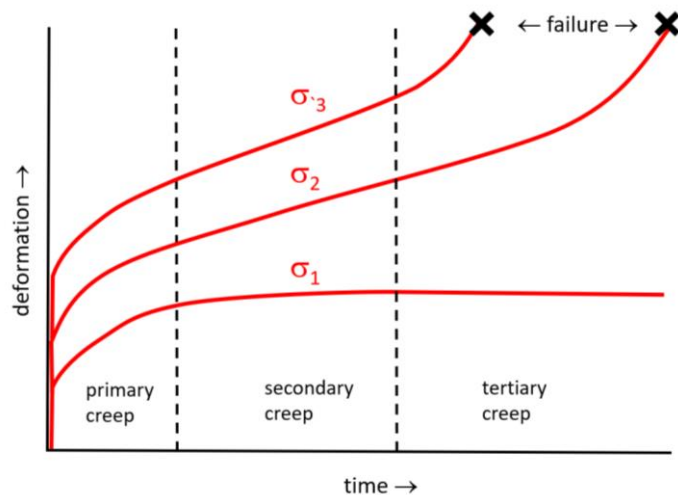


Figure 71: The deformation of a polymer body changes in time.

In case of the lowest stress the load (or stress) becomes balanced with the elastic rubber stress caused by deformation of the body. The dimensions of the body stop changing. In case of the two higher stresses such a balance is not obtained. Instead, the speed of the deformation increases until finally rupture of the body occurs.

Failure due to creep occurs as soon as the deformation exceeds a certain limit. This limit is the strain at which the polymer yields in a tensile test (see chapter 9).

Creep is an important mechanism for failure of plastic products under long-time load. An example of such a failure in a plastic pipe is shown in Figure 72.

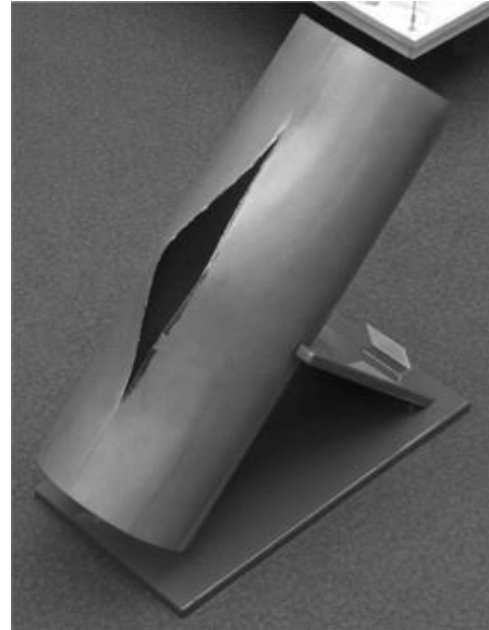


Figure 72: Failure of a plastic pipe due to creep rupture.

15.3 CREEP AND PHYSICAL AGING

The creep curve of a polymer can be roughly divided into three regions: the primary, the secondary and the tertiary region.

Initially:

Directly after applying the load the polymer deforms elastically. The stress – strain relation can be described by Hooke's law ($\sigma = E\varepsilon$). There is no creep yet: the segments of the macromolecules only bend under the applied stress.

Primary creep:

After some time, the chain segments of the macromolecule will rotate under influence of the stress. The conformation of the macromolecules changes. This is reflected in a continuous increase of the strain with time. Although the deformation of the body increases, the speed of the deformation reduces continuously.

The reduction of the speed of deformation is partly due to the increasing rubber stress that reduces the nett load. In case that the load on the body is small enough, the increasing rubber stress will eventually exceed the external load. The strain rate then reduces to zero and the body will stop deforming.

More important however, is the influence of **physical aging**. The creep process takes so much time that physical aging can reduce the mobility of the chain segments while creep is still ongoing. The rotation time of the chain segments increases linearly with the elapsed time during aging. Therefore physical aging reduces the speed of deformation during creep **inversely proportional with the elapsed time**.

Secondary creep:

Eventually the deformation of the polymer body is large enough to induce a beginning of **mechanical rejuvenation** in the plastic. Now the mobility of the chain segments increases. The speed of deformation (strain rate) stops reducing and becomes approximately constant.

Tertiary creep:

After prolonged time the strain in the polymer will reach a level that corresponds to the yield point in a tensile test. The plastic becomes fully rejuvenated. Now the chain segments of the polymer molecules will rotate easily under stress. The speed of deformation of the polymer suddenly increases, followed by a failure at higher strains.

15.4 MATHEMATICAL DESCRIPTION OF THE CREEP PROCESS

The viscoelastic relations are:

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

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

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

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

Boundary conditions:

- During the creep test the plastic is uniaxially deformed. The relation between glass stress and deformation is therefore described by Equation 35:

$$\sigma_{gla} = G(\exp(2\varepsilon_{ben}) - \exp(-\varepsilon_{ben}))$$
- The material yields and fails at relatively low strains (0.2 to 0.3) and that results in a simple relation between stress and strain:

$$\sigma_{gla} = 3G_{gla}\varepsilon_{ben} \text{ and } \sigma_{rub} = 3G_{rub}\varepsilon_{rot}$$
- The total stress on the plastic body is constant:

$$\sigma = \sigma_{gla} + \sigma_{rub} = \sigma_{load}$$
- The creep test is usually done below the glass transition temperature. Under these circumstances we assume the reptation time (θ_{rep}) to be infinite:

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

The viscoelastic equations now simplify to:

Equation 114

$$\frac{d\sigma_{gla}}{dt} = 3G_{gla} \frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

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

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

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

After some rewriting, we find for the strain rate during creep:

Equation 115

$$\frac{d\varepsilon}{dt} = \frac{\sigma_{load} - 3G_{rub}\varepsilon}{3G_{gla}\theta_{rot}}$$

The creep rate depends on the nett load and the chain segment rotation time, which is exponentially dependant on the nett load.

All about viscoelasticity in the solid and molten phase

If the load on the body is low enough then the increasing rubber stress ($3G_{rub}\epsilon$) will eventually balance the external load. The creep rate $d\epsilon/dt$ will become zero and the creep deformation will stop.

In most cases however, the creep rate will reduce because of the effects of physical aging. In chapter 14 we have seen that in the aging region the relaxation time increases linearly with the elapsed time (θ_{rot} is about 10 to 100 times the elapsed time).

Equation 116

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

We simplify this by inserting $\theta_{rot} = At$ into Equation 115:

Equation 117

$$\frac{d\epsilon}{dt} = \frac{\sigma_{load} - 3G_{rub}\epsilon}{3G_{gl}At}$$

According to Equation 117 the creep rate will reduce inversely proportional with the elapsed time as long as physical aging active. In Figure 73 examples of this behaviour in a plastic and in a metal alloy are shown.

This will only be valid in the primary region of creep. In the secondary and tertiary region the aging effect will be neutralized by mechanical rejuvenation.

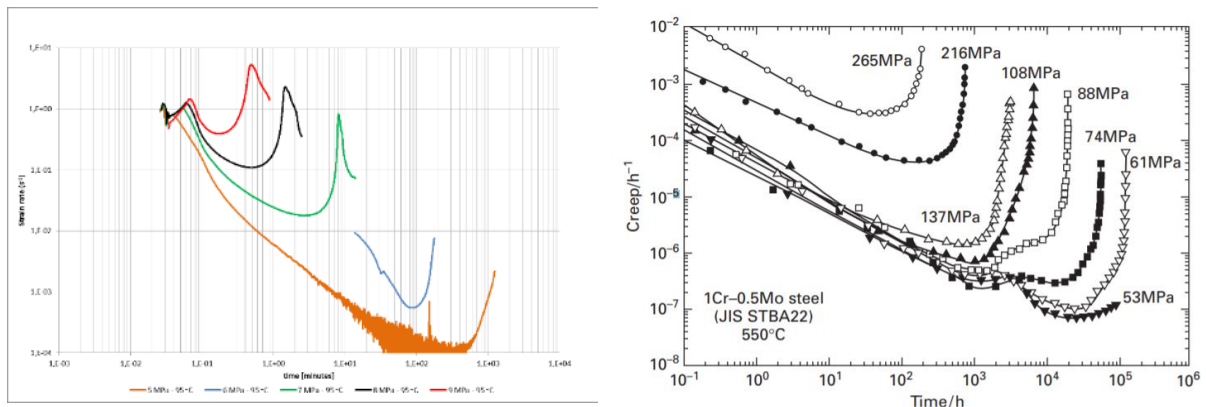


Figure 73: Creep rate versus time of a polymer and a metal alloy.

16 MECHANICAL ANALOGUE FOR STRESS IN POLYMERS

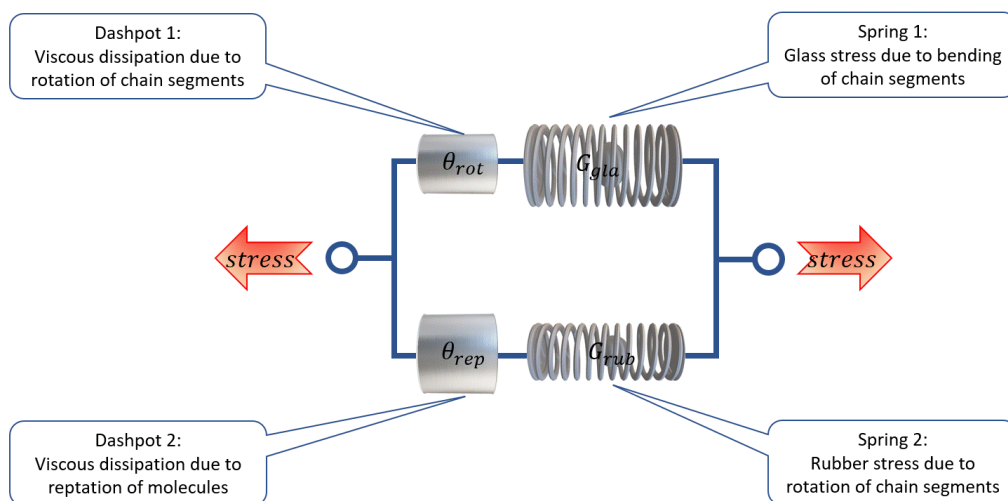
16.1 MODEL DESCRIPTION

Viscoelastic materials, like plastics, consist of long fiber-like particles. In case of plastics the fibers are formed by the macromolecules that are entangled with each other. Due to this structure, plastics can store elastic energy, at least temporarily.

Depending on the temperature these macromolecules can be stiff or flexible, causing the polymer to be in the **glass phase** or in the **rubber phase**. At even higher temperatures the macromolecules are able to move (reptate) into other positions. By then the plastic behaves like a fluid. It is in **the melt phase**.

In the previous chapters we have explained how the macroscopic behavior of the plastics (glass, rubber and melt phase, stress relaxation, creep, etcetera) are related to the molecular properties. This is good for a fundamental understanding of the physical properties of polymers. However, it may be difficult to extrapolate this knowledge into day-to-day practice for polymer products.

It is therefore common practice to visualize the plastic as a combination of springs and dashpots. The springs describe the elastic behavior of the plastic; the dashpots describe the viscous behavior of the plastic. Such a spring – dashpot representation of a polymer is shown in the figure below.



Spring 1 is a spring with a high stiffness. The spring modulus is the **glass modulus (G_{gla})**. It represents the glass stress in the polymer. Dashpot 1 will change its length after a relatively short time: the **segmental rotation time (θ_{rot})**. It represents the viscous dissipation due to rotation of the chain segments. Spring 2 is a spring with a low stiffness. The spring modulus is the **rubber modulus (G_{rub})**, which is about 1000 times less than the glass modulus. It represents the rubber stress in the polymer. Dashpot 2 will change its length after a relatively long time: the **reptation time (θ_{rep})**. It represents the viscous dissipation due to reptation of the macromolecules.

16.2 SOME EXAMPLES

16.2.1 Glass phase

Both the rotation time and the reptation time are large. Dashpots 1 and 2 are fully blocked. The stiffness of the system is that of the sum of both springs. The stiffness of spring 1, which represents the glass stress, is about 1000 times higher than that of spring 2. Therefore the glass stress is the most important stress in the glass phase.

16.2.2 Rubber phase

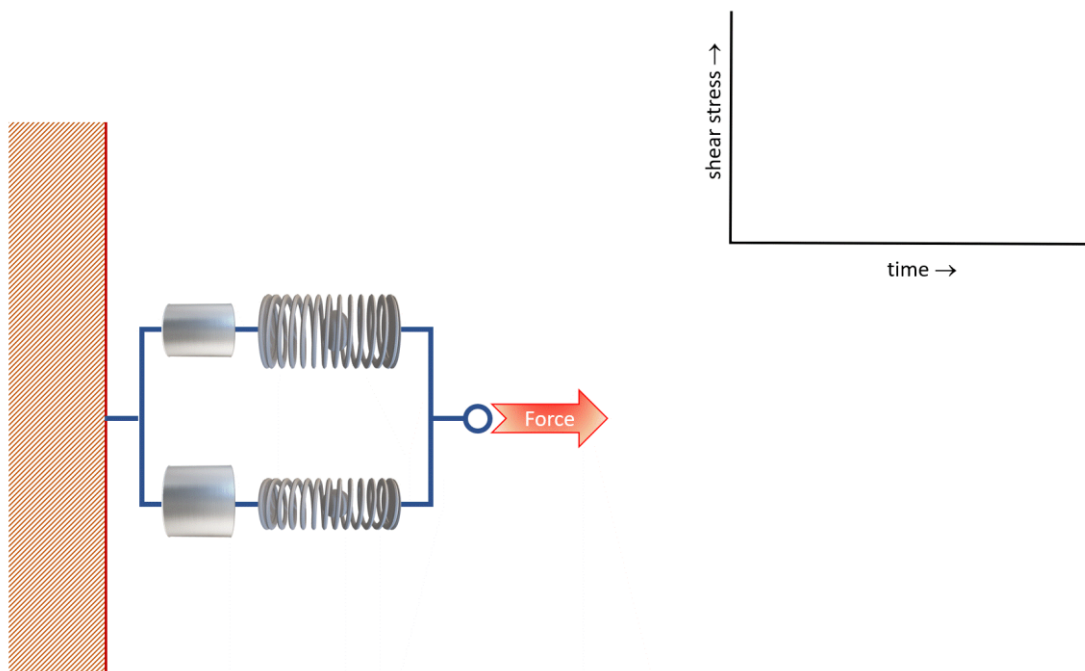
The rotation time is low (less than 1 second) but the reptation time is still large. Therefore dashpot 1 can move but dashpot 2 is still blocked. Spring 1, representing the glass stress becomes unloaded. Upon deformation the stress in the system will be represented by that of spring 2: the rubber stress.

16.2.3 Melt phase

Both the rotation time and the reptation time are low now. Both dashpot 1 and 2 can move. Any stress generated by deformation of the system (spring 1 and spring 2) will reduce in time due to the moving dashpots (**stress relaxation**). Since the segmental rotation time is much less than the reptation time, the stress of spring 1 will always be zero. The stress in the system is controlled by that of spring 2. The typical time with which the stress reduces is controlled by dashpot 2 (reptation time).

16.2.4 Viscous flow of melt

The speed of deformation of the plastic is high. Due to the high temperature in the plastic dashpots 1 and 2 are unblocked. Yet, dashpot 2 (reptation) still creates some resistance as long as the speed of deformation of the polymer (spring 2) exceeds that of dashpot 2. The rubber stress in the plastic will increase. The segmental rotation time (dashpot 1) is so low that the glass stress (spring 1) will remain zero.



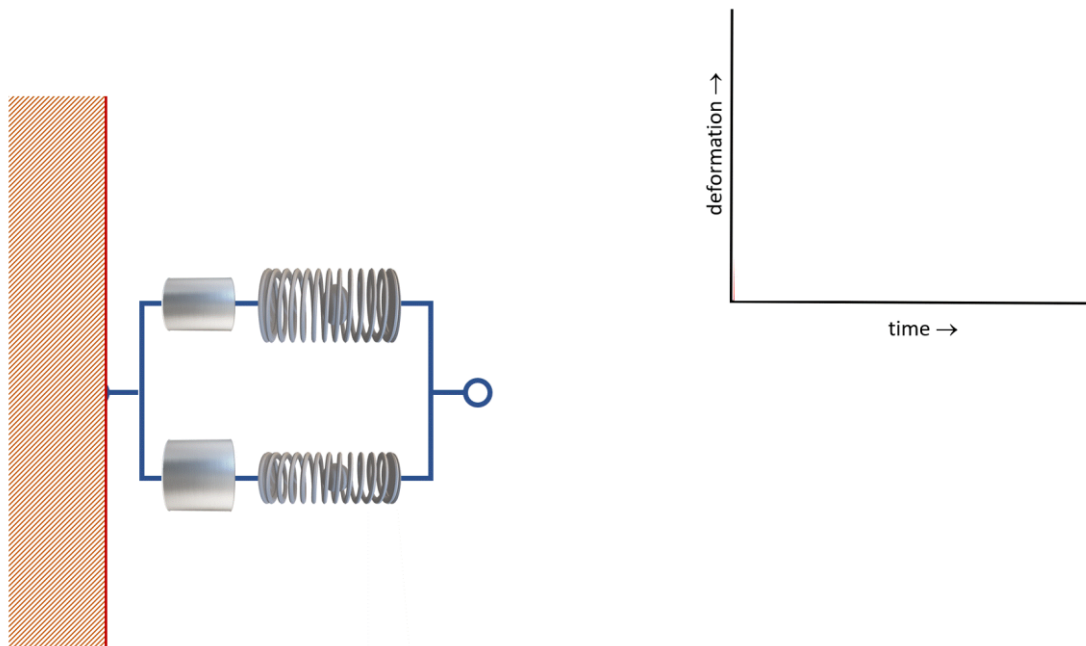
Upon ongoing deformation, the rubber stress (spring 2) will increase. Due to the increasing stress the reptation time (dashpot 2) reduces. It becomes increasingly difficult to create additional stress.

Eventually the speed of dashpot 2 will match the speed of deformation. The stress will now remain constant during deformation. The ratio between stress and speed of deformation is called viscosity.

16.2.5 Creep

Creep of the polymer is usually measured in the glass phase. A constant stress is applied to the product. Dashpots 1 and 2 are fully blocked on short time scale. Immediately after applying the stress spring 1 will be deformed. The initial deformation is elastic and fully recoverable.

The segmental rotation time (dashpot 1) is very long but not infinite. That means that dashpot 1 can very slowly move when waiting long enough. The deformation of the product now slowly increases which is called creep.



During the creep process spring 2, representing the rubber stress, is slowly extended while dashpot 2 (reptation) is fully blocked. Due to this the rubber stress in the product (spring 2) will slowly increase, counteracting the externally applied stress. This slows down the speed of the creep process.

On removing the stress spring 1 becomes undeformed immediately. The total deformation is partially undone. This part is called elastic recovery. The plastic is still deformed and the rubber stress present (spring 2) will slowly reduce the deformation by stimulating segmental rotation (dashpot 1). Due to the low level of the rubber stress a full recovery is impossible during the time span available.

16.2.6 Yield stress

The yield stress is usually important for the polymer in the glass phase. Both the rotation time and the reptation time are large. Dashpots 1 and 2 are fully blocked. The deformation of the product is continuously increased. Upon increasing the deformation, the stress in spring 1 increases (dashpot 1). The stress in spring 2 can be neglected. Due to the increasing stress the segmental rotation time will reduce. Once the segmental rotation time becomes less than 1 second the segments start to rotate and dashpot 1 starts moving. From this moment on spring 1 cannot create additional stress anymore. The stress remains constant and equals the yield stress.

16.3 MATHEMATICAL DESCRIPTION OF THE SPRING – DASHPOT MODEL

The mechanical model presented for polymers consist of two parallel spring – dashpot combinations:

1. A dashpot and spring for the glass phase. The stiffness of the spring corresponds to the glass modulus and the time response of the dashpot corresponds to segmental rotation.
2. A dashpot and spring for the rubber phase. The stiffness of the spring corresponds to the rubber modulus and the time response of the dashpot corresponds to reptation of the macromolecules.

The mathematical description of the stresses in this model is described by:

Equation 118

$$\begin{aligned}\frac{d\sigma_{gla}}{dt} &= G_{gla} \frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}} \\ \frac{d\sigma_{rub}}{dt} &= G_{rub} \frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}} \\ \sigma &= \sigma_{gla} + \sigma_{rub}\end{aligned}$$

These equations are almost identical to those of the original molecular model presented earlier:

Equation 119

$$\begin{aligned}\frac{d\sigma_{gla}}{dt} &= G_{gla} \frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}} \\ \frac{d\sigma_{rub}}{dt} &= \frac{G_{rub}}{G_{gla}} \frac{\sigma_{gla}}{\theta_{rot}} - \frac{\sigma_{rub}}{\theta_{rep}} \\ \sigma &= \sigma_{gla} + \sigma_{rub}\end{aligned}$$

In the original molecular model, the glass stress due to bending of chain segments is converted into rubber stress due to rotation of chain segments. So, deformation first creates glass stress which is then converted into rubber stress after some time. In the current mechanical model now discussed deformation creates both glass stress and rubber stress at the same time. This difference in the models creates the difference in the equations describing the stress.

In practice the results of the calculations with the equations for the molecular model en the mechanical model will be very close to each other. The reason for this is the fact that for all polymers the rubber modulus is about 1000 times less than the glass modulus. This reduces the error in the mechanical model to less than 0.1 %.

17 SOME PHYSICAL PROPERTIES OF POLYMERS

Pol. name	Mol. Weight (g/mol)	Mass repeat unit (g/mol)	Char. ratio	Netw. density (m ⁻³)	Density (kg/m ³)	Glass shear modulus (MPa)	Glass trans. temp. (C)	Cryst. melt. temp. (C)
PVC	140000	62,5	6,5	1.0x10 ²⁶	1380	1000	85	240
PC	21600	254,3	1,3	3.9X10 ²⁶	1220	700	147	357
PS		104,1	6,4	3.0x10 ²⁵	1050	1100	95	279
PMMA		100,1	8,2	8.0x10 ²⁵	1180	1100	110	302