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 have to 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 22: 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 23 that shows the storage modulus, the loss modules and the ratio loss – storage modulus (tg(δ)) 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
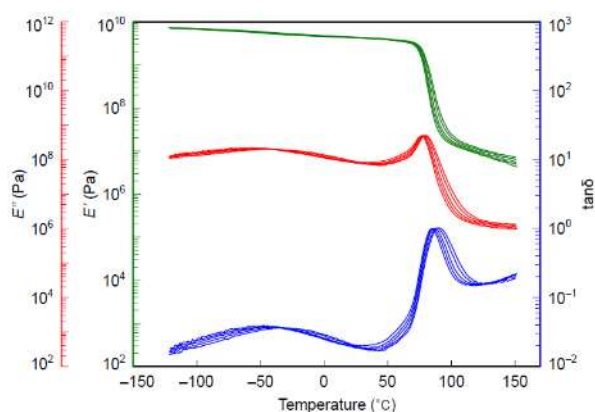

Figure 23: Storage modulus (E'), loss modulus (E") and tg(δ) as measured by dynamic mechanical analysis.

rather weak peak at -50 C in the loss modulus and the tg(δ) 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 enough thermal energy is 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 23. For a material like HDPE this happens at a temperature of -130 C.
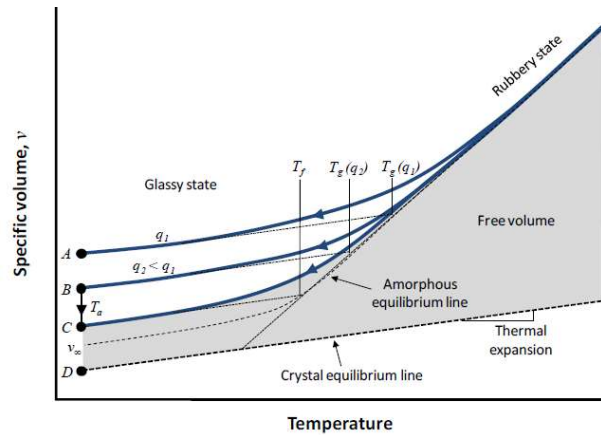

Figure 24: Diagram of specific volume versus temperature. At the glass transition temperature T_g the expansion coefficient suddenly increases.

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.

Figure 25: 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 and 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 makes the polymer to behave as a kind of a fluid with strong viscoelastic properties.

The reptation of the macromolecules into new positions enables the polymer to relax imposed stresses. The time needed to significantly reduce a stress (the **rubber relaxation time**) of the rubber is the same as 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. The 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. It 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 s	>> 1 s
Glass – rubber transition temperature	1 s	
Rubber phase	< 1 s	> 1 s
Rubber – melt transition temperature		1 s
Melt phase	<< 1 s	< 1 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 and this 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.

Figure 26: Regular crystalline regions in an amorphous matrix.

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.
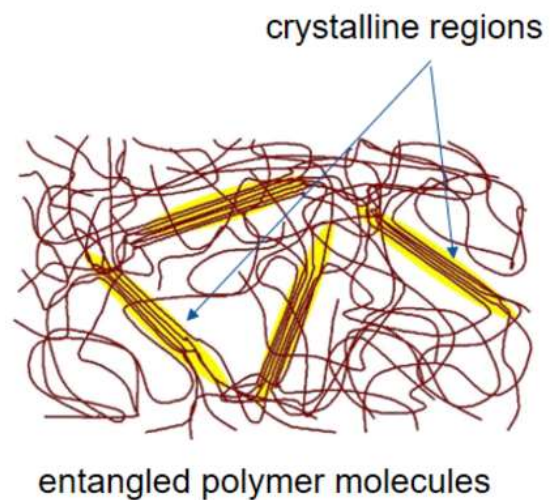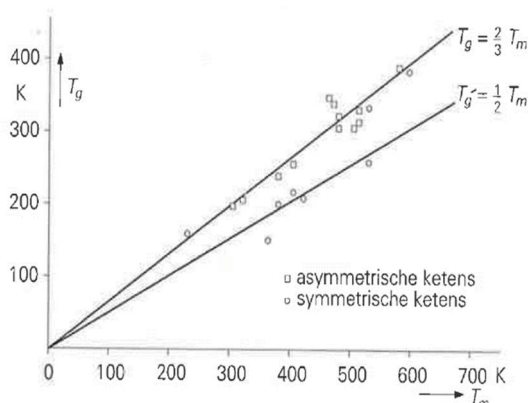

Figure 27: Glass transition temperature and crystalline melting point of several polymers.
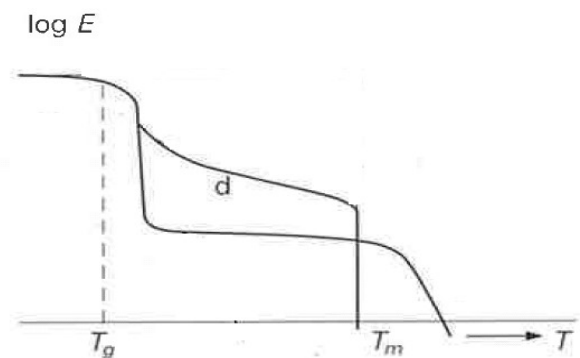
Figure 28: The crystalline phase (d) effectively increases the stiffness of the polymer.

All about viscoelasticity in the solid and molten phase

In all polymers the crystalline melting temperature is higher than the glass transition temperature. This is indicated in Figure 27. 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 28. Large deformations of the polymer are only possible by ripping the polymer chains out of the crystalline regions (see Figure 29).
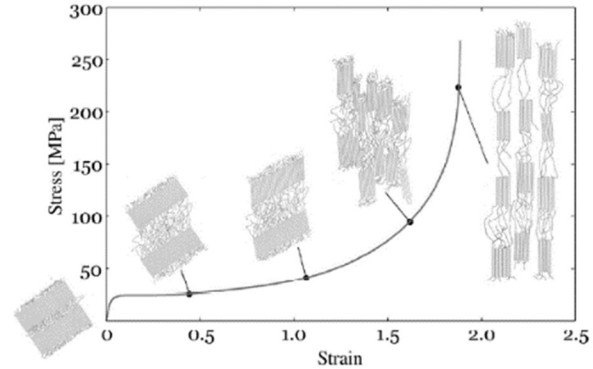

Figure 29: Deformation of a crystalline polymer. The polymer chains are ripped out of the crystals.

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		Rotation time	Reptation time
	Crystalline material?	Rotation time	Reptation time
Glass phase	Amorphous region	> 1 s	>> 1 s
Glass phase	Crystalline region	∞	∞
Rubber phase	Amorphous region	< 1 s	>> 1 s
Rubber phase	Crystalline region	>> 1 s	∞
Melt phase		<< 1 s	< 1 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.
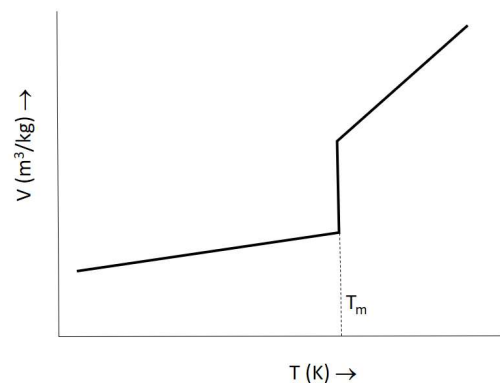

Figure 30: Volume temperature diagram of a crystalline material.

All about viscoelasticity in the solid and molten phase

Figure 30 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 21

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