Deformation and aging kinetics of model polymer systems

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Table of contents

1. Introduction ........................................................................................................................................... 3
2. Background .............................................................................................................................................. 4
  2.1. Mechanical behaviour of amorphous polymers ............................................................................ 4
    2.1.1. Intrinsic deformation ................................................................................................................ 4
    2.1.2. Deformation kinetics ................................................................................................................. 5
    2.1.3. Activation volume and time-to-failure ................................................................................... 5
  2.2. Thermal behaviour of polymers ....................................................................................................... 7
  2.3. Tacticity ........................................................................................................................................... 9
  2.4. Heterogeneity in amorphous polymers ........................................................................................... 10
3. Materials and methods .......................................................................................................................... 11
  3.1. Materials ......................................................................................................................................... 11
  3.2. Methods .......................................................................................................................................... 13
4. Discussion ............................................................................................................................................... 14
  4.1. Effect of tacticity on aging kinetics ............................................................................................... 14
    4.1.1. Introduction ............................................................................................................................. 14
    4.1.2. Experiment description .......................................................................................................... 14
    4.1.3. Results .................................................................................................................................... 15
  4.2. Deformation kinetics of polycarbonates ....................................................................................... 17
    4.2.1. Glass transition temperature .................................................................................................. 17
    4.2.2. Deformation kinetics ................................................................................................................. 17
  4.3. Interplay between deformation kinetics and aging ...................................................................... 20
    4.3.1. Material selection .................................................................................................................... 20
    4.3.2. Thermal analysis ....................................................................................................................... 20
    4.3.3. Mechanical analysis .................................................................................................................. 21
5. Conclusion ............................................................................................................................................. 22
6. References ............................................................................................................................................... 23
1. Introduction

In this study, the influence of features of the molecular architecture on physical aging and the deformation kinetics of amorphous polymers are investigated. Also a relation between the two phenomena is investigated. A schematic of the problem is given in figure 1.1.

Physical aging is a common feature of all polymeric materials. The rate and extent of this phenomenon depends on subtle details of the molecular structure and therefore differ from polymer to polymer. All polymers however, will age over time. While aging, polymers embrittle and this limits the number of applications. It would be very interesting to be able to control the aging process. However, it is still unclear which processes cause aging and what factors influence it.

To get a better understanding of the before mentioned, the influence of tacticity on aging is investigated. This is done by comparing the properties of atactic polystyrene (aPS) and syndiotactic polystyrene (sPS) after a number of different annealing times. By using the same base material, but with a different distribution of side groups, this comparison should clearly show if the tacticity of a polymer has an effect on aging.

The influence of molecular structure on deformation kinetics is investigated by measuring the deformation kinetics of a set of polycarbonate copolymers that differ by “small” details of the molecular structure. This could give some information on the influence of molecular structure on deformation kinetics. This data is then used to select three polymers with very different deformation kinetics. By analyzing these three materials a relationship between the deformation kinetics and the aging kinetics is sought.

figure 1.1 Schematic of problem
2. Background

2.1. Mechanical behaviour of amorphous polymers

2.1.1. Intrinsic deformation

The intrinsic deformation is a material's true stress-strain response during homogeneous deformation at a constant strain rate that can be obtained during a uniaxial compression test. In figure 2.1 a general representation of the intrinsic deformation of a polymer is depicted.

Initially, the relation between stress and strain is linear (a). For larger strain the relation becomes increasingly non-linear until the stress reaches a maximum called the yield stress (b). This marks the point at which the main polymer chains obtain segmental mobility, so they can start moving with deformation. This phenomenon is similar to the glass transition except for the fact that this time the mobility is stress induced and the glass transition is temperature induced. When the strain is increased even further, the stress drops. This effect is called strain softening (c). For even greater strain the stress starts to increase again. This last effect is called strain hardening (d). The intrinsic deformation is rate dependent and, as can be seen in figure 2.2, the yield stress increases with strain rate.

Aging affects the intrinsic mechanical behaviour increasing yield stress and leaving strain hardening unchanged, see figure 2.3. As a result of the increased softening, the material embrittles over time.
2.1.2. Deformation kinetics

Unlike, for instance, metals and ceramics, the mechanical behaviour of polymers is strain rate dependent. This makes it possible to construct a graph of the yield stress versus the strain rate. A general representation of such a graph, called deformation kinetics, is given in figure 2.4 for three generic polymers and a metal. Note that the x-axis is logarithmically scaled.

2.1.3. Activation volume and time-to-failure

When the observation time-scale is sufficiently long, amorphous polymers behave like fluids also below T_g. Therefore, when loaded, they will fail eventually. The time to failure depends on the applied stress as can be seen in figure 2.5.

An unusual reading of figure 2.4 can be used to define a failure criterion: when loaded with a constant stress \( \sigma \), the material deforms plastically at a constant rate \( \dot{\varepsilon}^p \). Plastic deformation accumulates (}
\[ \varepsilon_{pl}(\sigma, t) = \int_0^t \varepsilon^*(\sigma) \, dt' = \varepsilon^*(\sigma) \cdot t \] and when it exceeds a critical value \( \varepsilon_{pl} = \varepsilon_{cr} \), the material fails. The life-time of the material or time to failure is defined by the critical condition:

\[ \varepsilon^*(\sigma) \cdot t_i = \varepsilon_{cr} \Rightarrow t_i = \frac{\varepsilon_{cr}}{\varepsilon^*(\sigma)} \quad (2.1) \]

The flow behaviour below Tg can be described with the Eyring’s equations [5].

\[ \dot{\varepsilon}(\sigma, T) = \dot{\varepsilon}_0^* (T) \cdot \sinh \left( \frac{\sigma \cdot \nu}{k \cdot T} \right) \quad (2.2) \]

With

\[ \dot{\varepsilon}_0^* = \dot{\varepsilon}_0 \cdot \exp \left( \frac{\Delta U}{R \cdot T} \right) \quad (2.3) \]

where \( \dot{\varepsilon}_0^* \) a reference strain rate at an arbitrary temperature, \( \sigma \) the applied stress, \( \nu \) the activation volume, \( k \) Boltzmann’s constant, \( T \) the absolute temperature, \( \dot{\varepsilon}_0 \) the absolute reference strain rate, \( \Delta U \) the activation energy and \( R \) the gas constant.

From this, one can conclude that the activation volume \( \nu \) is an important parameter in determining the time-to-failure. This parameter can easily be calculated using the deformation kinetics of a material [1]. Assume the slope of the deformation kinetics in MPA/decade is \( \phi \), the activation volume can then be calculated using

\[ \nu = \ln(10) \cdot \frac{kT}{\phi} \quad (2.4) \]

figure 2.5 General representation of time-to-failure vs. applied stress
2.2. Thermal behaviour of polymers

The thermal behaviour of polymers can be studied with a technique called Differential Scanning Calorimetry (DSC). In figure 2.6 the general thermal response of a crystallizable polymer is depicted as a function of the temperature. In this picture three characteristic features of the curve are indicated.

Starting from low temperature, the first feature observed is the glass transition resembling a step-wise change of the heat capacity. The midpoint of this shift is the glass transition temperature (T_g). The next feature represents the crystallization of the polymer. As this is an exothermic process the peak is positive, meaning that less heat has to flow to the sample in order to maintain a constant heating rate. The last feature shows the melting of the polymer as a negative peak as this is an endothermic process where the lattice is broken down.

DSC can be used to study aging as well. One feature that is not present in the curve of figure 2.6 is the enthalpy overshoot that is observed in aged polymers heated across T_g, see figure 2.7. The area of the peak increases for longer annealing times [2]. The size of this peak is therefore a measure for the “age” of the material.
figure 2.7 Enthalpy overshoot
2.3. Tacticity

Many polymers, for instance vinyl polymers which consist of an extended alkane chain backbone with substituents attached to this base chain, can exhibit different tacticity or stereo regularity. Tacticity is the spatial positioning of the side group with respect to the side groups of the adjacent repeating units. These side groups can either be located at the same side of the backbone, on alternating sides or randomly on either of the sides as shown for polystyrene (PS) in figure 2.8 a to c. When the side groups are consistently on the same side of the molecule the material is called isotactic, when they alternate syndiotactic and when they are randomly distributed atactic.

Tacticity can hugely influence the mechanical properties of a material [3]. The ability to crystallize for instance is dependent on the tacticity since for crystallization the side groups have to be regularly distributed. For PS for example, this means that the atactic variant cannot crystallize due to the random stereoregularity of the side groups.

![Molecular structure of polystyrene with different tacticity](image)

figure 2.8 Molecular structure of polystyrene with different tacticity
2.4. Heterogeneity in amorphous polymers

When a polymer is quickly cooled below $T_g$, the material will not be in thermo dynamical equilibrium as depicted in figure 2.9. Because of the high cooling rate, the mobility of the molecules is too small to assemble with a denser packing and, at the same time, comply with the decreasing thermal expansion coefficient [1]. The molecules are, so to say, frozen-in before being able to move closer to each other. Therefore the material will have a specific volume larger than the equilibrium value.

Amorphous polymers lack tri-dimensional long-range order. However, it is still possible to encounter small domains where molecules are closer to each other. These static density fluctuations or *heterogeneities* are the result of a natural tendency towards the thermodynamic equilibrium. The situation is schematically shown in figure 2.10. The nature of the heterogeneities is not yet clarified. Nevertheless, their fingerprint is readily observed, for instance, in scattering experiments. Eventually, the densification process leads to thermodynamic equilibrium (figure 2.9).

Since densification is caused by structure formation in the amorphous polymer, the structure of the molecules could probably influence the phenomenon. For instance, it is known that chain regularity influences a materials’ possibility to crystallize. If these heterogeneities are, in fact, a result of structure formation at micro scale then this too could be dependent on the regularity of the base chain and its side groups.
3. Materials and methods

3.1. Materials

To investigate the influence of tacticity on aging, we have investigated syndiotactic and atactic polystyrene, sPS and aPS respectively (Shell N5000 and Dow Questra 101). Both materials were compression moulded at 280°C and cooled either by dropping them into ice water of \(\sim 5^\circ C\) or between water cooled plates.

The materials used to study the deformation kinetics in polycarbonates are given with their respective structural formula in table 3.1. The supplier as well as the temperature at which they were compression moulded are also listed in the same table. Unlike PS, PC absorbs water. To rule out effects due to moisture absorbed, the material was dried in vacuum before sample preparation.

The last material used in this study is poly-L-lactide IVI 4.2 (PLLA), provided by Purac Biochem (Gorinchem, The Netherlands). The bulk material was kept in a freezer to avoid degradation due to the absorption of moisture. After the material had thawed, it was put in a vacuum chamber to dry for at least two days. Compression moulding took place at a mould temperature of 200°C after which the material was cooled between water cooled plates.
<table>
<thead>
<tr>
<th>Name and providing company</th>
<th>Mould temperature [°C]</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
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<td><img src="image1" alt="Structural formula" /></td>
</tr>
<tr>
<td>TMPC (Bayer)</td>
<td>240</td>
<td><img src="image2" alt="Structural formula" /></td>
</tr>
<tr>
<td>Bisphenol AP (SABIC)</td>
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<tr>
<td>DMBPC (SABIC)</td>
<td>200</td>
<td><img src="image4" alt="Structural formula" /></td>
</tr>
<tr>
<td>Thiodiphenol (SABIC)</td>
<td>240</td>
<td><img src="image5" alt="Structural formula" /></td>
</tr>
<tr>
<td>30%mol BP (SABIC)</td>
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<tr>
<td>12%mol SA (SABIC)</td>
<td>180</td>
<td><img src="image7" alt="Structural formula" /></td>
</tr>
<tr>
<td>Isosorbide (SABIC)</td>
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<td><img src="image8" alt="Structural formula" /></td>
</tr>
<tr>
<td>Tert. butyl HQ (SABIC)</td>
<td>190</td>
<td><img src="image9" alt="Structural formula" /></td>
</tr>
</tbody>
</table>
3.2. Methods

Both tensile and compression tests are performed on a Zwick tensile tester. For tensile testing tensile bars of 1x2x18.5 mm are used. These are made by compression moulding 1 mm thick plates of 30x60 mm and punching the tensile bars out. Compression tests are done on samples with a diameter of 4.5 mm or 6 mm and a ratio between the diameter and the height of approximately 1, to avoid buckling and to attain homogeneous deformation. Friction between the sample and compression plates is reduced by spraying the compression plates with PTFE lubricant and by applying a thin film of PTFE tape to both ends of the sample.

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC823e equipped with a FRS5 sensor.

WAXD was performed on a Rigaku diffractometer in Bragg-Brentano configuration.
4. Discussion

4.1. Effect of tacticity on aging kinetics

4.1.1. Introduction

The effect of tacticity on aging kinetics is studied by measuring the differences between aPS and sPS. These are the same materials except for the tacticity, so this eliminates any other factors that might influence the aging results. Because of this difference in tacticity however, one of the materials, sPS, can crystallize and the other one, aPS, cannot. To be able to really compare the results both materials should be amorphous. This is only possible for sPS if the material is cooled very rapidly at a cooling rate of about 200°C/s [7]. This rate can only be achieved for very thin films. As seen in figure 4.1, the absence of sharp peaks in the WAXD pattern indicates that there are no crystalline structures in the sample quenched in ice water (\(\dot{T} = 200^\circ\text{C/s}\)), unlike the sample which is cooled between water cooled plates (\(\dot{T} = 100^\circ\text{C/min}\)).

![WAXD of sPS for two different cooling rates](image)

4.1.2. Experiment description

To demonstrate aging in polymers, we normally look at the increase in yield stress and strain softening by mechanically testing the material. However, amorphous PS is brittle; therefore, we would need to prepare samples for compression tests. For aPS these samples are easy to make since the material cannot crystallize. For sPS, instead, a very high cooling rate is needed, and this is cannot be achieved in...
(thick) compression samples. This makes an alternative way of analysing the aging kinetics necessary. As mentioned before, one can study aging by looking at the thermal behaviour in DSC. Since it is possible to make thin films of amorphous sPS it is no problem to make samples for thermal analysis. The samples are made by compression moulding a thin film of 200 μm and dropping it into ice water to avoid crystallization. Even though aPS cannot crystallize, the samples are prepared in the same way, to give both materials the same thermal history before testing. The test is done by heating the sample to 80°C on the DSC equipment and keeping it at that temperature for different annealing times. Afterwards the material is cooled to room temperature and is then heated to 300°C at a rate of 10°C/min.

4.1.3. Results

By calculating the area under the peak of the enthalpy overshoot a measure of the amount of aging is obtained. The results are given in figure 4.2a. From these results one can conclude that sPS shows more aging after the same annealing time at the same temperature. However, this conclusion neglects the difference in \( T_g \) between aPS and sPS that can be seen in figure 4.3. In fact, the glass transition temperature of aPS is 5°C higher than that of sPS (96°C vs. 101°C), which is probably a result of a different molecular weight. Because of this, the materials are not annealed at the same distance from \( T_g \) and will therefore not have the same chain mobility. When both materials are annealed at the same distance from \( T_g \) they behave very similarly as can be seen in figure 4.2b. An extra annealing time of 30 hours has been added, because the difference should be more distinct for longer annealing time. There seems to be almost no difference between aPS and sPS however.

The outcome of the second experiment suggests that aPS and sPS age with the same kinetics. This is not sufficient to confirm or rule out the influence of molecular regularity on the formation of heterogeneities. It only suggests that aging is caused by structures smaller than the typical length scale of regular (syndiotactic) sequences in sPS.
figure 4.3 Difference in Tg between aPS and sPS
4.2. Deformation kinetics of polycarbonates

4.2.1. Glass transition temperature

To find the influence of molecular structure on deformation kinetics a number of PCs have been analyzed. First of all the glass transition temperature is determined with DSC. The results are given in figure 4.4 below. It is not simple to establish a relationship between the molecular structure of the polymers and T\textsubscript{g} without performing detailed simulations on the properties of the molecular structure. In this project however, the value of T\textsubscript{g} is instrumental as it used to find an estimate for the mould temperature, since beforehand there was very little information on the different polycarbonates.

![figure 4.4 T\textsubscript{g} for different polycarbonates](image)

4.2.2. Deformation kinetics

To determine the deformation kinetics either tensile bars or compression samples are made depending on the properties of the specific PC. 30%mol BP, 12%mol SA, Bisphenol AP and BPA behave ductile are tested in tension. Thiodiphenol, however, is a brittle material and is tested in compression. TMPC and Isosorbide, on the other hand, are so brittle that it is impossible to produce compression samples and so they cannot be tested. The DMBPC provided by SABIC is also too brittle to prepare samples. The deformation kinetics of DMBPC is therefore determined using a different grade of the same material, presumably with a higher molecular weight. This is possible because the deformation kinetics is not
affected by the molecular weight [6]. The last material, tert. butyl HQ, can in some cases be tested in
tension, but the results are largely dependent on small cracks in the tensile bar. If some cracks are
present in the tensile bar from cutting these can ruin the measurement as depicted in figure 4.5. In this
figure it is clear that the yield point is not always reached, even for very low strain rates, as a result of
small cracks in the side walls of the tensile bar. To eliminate this problem tert. butyl HQ is also tested in
compression.

![Figure 4.5 Crack growth vs. yielding](image)

The deformation kinetics of the materials are found by determining the yield stress for five different
strain rates (\( \varepsilon = 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} \) and \( 10^{-5} \)). A line of the form \( a \cdot \log_{10}(\varepsilon) + b \) is fitted to the measured
data. The results are given in figure 4.6. Note that the slope for bisphenol AP is only based on two points
and can thus only be regarded as an estimate. The slopes of the materials together with their structural
formula are given in table 4.2 in descending order.

![Figure 4.6 Deformation kinetics for different polycarbonates](image)
Two of the tested materials, tert. butyl HQ and DMBPC, have significantly higher slopes than the normal polycarbonate, BPA. On the other end of the spectrum 30%mol BP has a very low slope of only 1.7 MPa/decade. The link between molecular features and the observed slope is not obvious. For instance, there is no obvious correlation between $T_g$ and the slope. This means that the slope is not only dependent on the stiffness of the molecule, but is also influenced by other factors. This relation can be investigated in further studies.
4.3. Interplay between deformation kinetics and aging

4.3.1. Material selection

As it was discussed in paragraph 2.1, the ductile time-to-failure is closely related to the deformation kinetics. However, since aging increases yield stress, the time-to-failure is also related to aging. In this paragraph, the relation between deformation kinetics and aging kinetics is investigated for three materials with very different deformation kinetics, namely aPS, 30% BP and PLLA. The 30%mol BP shows a very low slope (1.7 MPa/decade) and is therefore selected. The next material used for this study is PLLA, since it has a very steep slope of 14 MPa/decade. The final material is aPS, which has a slope of 8 MPa/decade. The aging kinetics of these three materials will be tested by looking at both their thermal and mechanical behaviour after different annealing times.

4.3.2. Thermal analysis

First, we look at the thermal response of the materials for different annealing times varying from 30 minutes to 30 hours. In paragraph 4.1, it was already discussed that the annealing should take place at a constant distance from \( T_g \). For this reason, all materials are annealed at 19°C below \( T_g \), which means 139°C for 30%mol BP, 85°C for aPS and 42°C for PLLA. The results are obtained in the same way as before, by calculating the size of the enthalpy overshoot. The results are given in figure 4.8.

![Graph showing enthalpy overshoot for aPS, 30%mol BP and PLLA](image)

From the graph, it becomes clear that 30%mol BP ages slower than the other two materials. Interestingly, 30%mol BP has also the lowest slope in the deformation kinetics. Whereas, aPS and PLLA show a very similar aging kinetics despite the very different slopes (PLLA is almost twice as steep as aPS).
4.3.3. Mechanical analysis

Fortunately, in this case it is possible to also do some mechanical testing since test samples are producible for all three materials. Because 30\%mol BP is ductile, it is tested in tension whereas both aPS and PLLA are tested in compression due to their brittle nature.

PLLA is expected to age very fast already at room temperature. To prevent aging from taking place at room temperature, compression samples were milled directly after compression moulding and rapidly put in the oven at 42°C.

The results of the tests can be evaluated in two ways. We can look at the absolute values (figure 4.9), but it is also interesting to look at the change relative to the initial value (figure 4.10). Again, 30\%mol BP, shows very slow aging and the increase of yield stress is small compared with aPS and PLLA. The yield stress increased only 2 MPa after 30 hours which is equal to 3.5\% of its initial yield stress. Moreover, the increase seems to level off already after 30 hours of annealing.

Unlike in the thermal analysis however, this time there is a significant difference between PLLA and aPS. The slope of the yield stress versus the annealing time is higher for PLLA than for aPS. Especially in comparison to its original yield stress the slope of PLLA is almost three times as high as that of aPS. This clearly shows that the rate at which aging occurs is much higher in PLLA than in aPS. Whether or not PLLA also shows more aging, in the sense that the relative increase in yield stress will exceed the relative increase in yield stress for aPS for an infinite annealing time, is not sure. Eventually, the yield stress will reach a plateau level as already seems to be the case for 30\%mol BP after 30 hours. Even though the yield stress of PLLA increases much faster than that of aPS, there is no data on the maximum increase. A single test for aPS after 7 days of annealing suggests, however, that it keeps increasing for at least 7 days.

![Figure 4.9 Absolute yield stress versus annealing time](image1)

![Figure 4.10 Relative yield stress versus annealing time](image2)
5. Conclusion

It’s still unclear what the underlying cause of aging exactly is. Some light has been shed on a number of aspects however. First of all the influence of tacticity on aging kinetics was investigated. Based on the thermal analysis done on amorphous atactic polystyrene and syndiotactic polystyrene tacticity doesn’t seem to have an effect on aging. The study could be expanded by the use of micro indentation, so that the mechanical properties can also be compared. In this experiment it was also found that, in order to be able to compare the results, annealing should be performed at a constant distance from the glass transition temperature and not at a constant temperature.

To investigate if there is a relationship between molecular structure and deformation kinetics a number of polycarbonates was tested at multiple strain rates. When the logarithm of the strain rate is plotted versus the yield stress very different slopes are found. This suggests that subtle details of the molecular structure have large influence on the macroscopic mechanical behavior of the material.

To further investigate the effect of deformation kinetics three materials with very different slopes (30%mol BP, aPS and PLLA) were studied by looking at their thermal response as well as their mechanical response after different annealing times. The thermal analysis showed a big difference between 30%mol BP and the other materials. aPS And PLLA gave a very similar response however even though PLLA has a slope which is almost twice as high as that of aPS. From this experiment, at least, it is clear that 30%mol BP ages significantly slower. In order to see the difference, if any, between the other two materials mechanical testing was performed. This time PLLA seemed to age much faster than aPS, since the yield stress of PLLA went up much faster than that of aPS. Again 30%mol BP showed remarkably less aging than the others. In short, the results suggest that materials with a steep slope in the deformation kinetics tend to age faster than materials with a low slope, and mechanical testing is more sensitive towards aging than DSC.

The outcome of this second experiment clearly showed the limitations of DSC since that technique showed no difference between aPS and PLLA while there is a big difference between the two. The results obtained in the first experiment to study the influence of tacticity can therefore not be considered conclusive and a more extensive study is necessary to definitively determine the influence of tacticity on aging kinetics.
6. References


