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Exploring the elongation properties of a linear polystyrene melt

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Abstract

The rheological behavior of polymers melts plays a crucial role in the industrial world, allowing manufacturers to fine-tune and design their products with specific properties. While our understanding of linear rheology is quite well-developed, with models available to predict the linear viscoelastic properties of polymers with different chemistries and molecular architectures, our knowledge of non-linear elongation properties remains limited.

In particular, understanding the impact of temperature and strain rate on these properties is essential for optimizing industrial processes that involve high strain (rate) conditions. Therefore, this study aims to investigate the non-linear elongation properties of polymers, focusing on a commercial polystyrene sample, chosen as it is a linear polymer.

The rheological analysis is conducted using a rotational ARES system to assess the linear viscoelastic properties, and a filament stretching VADER system to evaluate non-linear elongation properties. Additionally, mechanical tensile tests are performed on an Instron system, at elevated temperatures, to provide a better understanding of the polymer's elongation properties.

A direct comparison between the results obtained from the two non-linear characterization methods cannot directly be established, due to variations in experimental conditions, such as in true strain rate. However, each method has offered valuable insights into the elongation properties of the commercial polystyrene. As a perspective, this study also helped designing a new experimental protocol to bridge rheological and mechanical properties.

Contents

1 Introduction

1.1 Rheology

Rheology is the science of material deformation and flow. Understanding rheological properties is vital for optimizing manufacturing processes and the properties of finished objects. Rheology can be found in many areas of science, including food, packaging, cosmetics, and pharmaceuticals. This project explores the rheological behavior of polymers. Polymers exhibit complex viscoelastic properties when subjected to external stresses. Understanding their viscoelastic properties can help to optimize manufacturing processes.
Rheology is highly sensitive to small changes in polymer structure. This makes it ideal for characterizing polymers, which require a good control of their viscosity to obtain good processability. The control of viscosity is necessary to obtain a good processability of polymer. Rheology is therefore a highly appropriate tool for managing processes and the quality of finished objects [1] [2].

There are many industrial processes, including injection molding, film blowing and extrusion. Elongational viscosity is very important in processes involving free surface deformations because the material is stretched very quickly [2]. In processes such as blow molding, it is important to control viscosity, which changes how the material flows. This viscosity varies enormously with the temperature at which the polymer is heated. Viscosity also depends on the average molar mass and polydispersity of the polymer, which also has a large influence on its ability to stretch. Moreover, temperature has an impact on the material's adhesion to the mold wall. It is therefore a compromise between different parameters and characteristics that must be perfectly mastered, which is where rheology comes into its own for industry [3].

1.2 Polystyrene

In this project, the material used throughout is polystyrene. Polystyrene is a polymer that is rigid, translucent, and solid. The base monomer of polystyrene is styrene, which is a liquid hydrocarbon. Polystyrene has many interesting properties that determine its final application. This polymer accounts for 7% of global plastic demand, making it the fifth most popular plastic in the world, with a global market of 11 million tonnes in 2022. It is why the polystyrene is interesting to study [4] [5].

Polystyrene can be found in many industrial sectors. It is mainly used in packaging, household appliances, building and construction, and electronics products. But it is also useful in the

automotive and medical sectors.
In food service, polystyrene insulates better and keeps food fresher for longer. It is used to protect the consumer products against damage and spoilage. It is also widely used in construction in the form of expanded polystyrene (EPS), a light, rigid foam that improves thermal insulation and is highly resistant to impact. However, this form of polystyrene is not the most widespread. The polystyrene market is 60% dominated by high-impact polystyrene (HIPS). This type of polystyrene is highly versatile, with high impact resistance, and is easy to thermoform and print. It can be found in applications such as parts for audiovisual equipment, household appliances, printed circuits and the automotive sector [5] [6].

The polystyrene used in this project is a linear polydisperse polystyrene. It is a polymer in which the monomers are linked in a long chain without branching or complex structures such as stars.

1.3 Objectives

The aim of this master's thesis is to explore and understand the elongation properties of linear polystyrene samples, which are very important in processing. The second objective of this work is to explore the possibility to bridge the rheological and mechanical properties of a sample. These two fields are usually studied separately. However, being able to understand the viscoelastic response of a polymer, from its molten state down to its glass transition temperature or even lower, would be very helpful to control its processing properties.

The first part of this work is to understand and study the rheological properties in the linear regime of deformation. Once the linear mode is studied, the research continued in non-linear elongation. Polystyrene is analyzed using two different material characterization techniques. The first is a rheological technique involving elongation with a constant Hencky strain rate. While the second is a mechanical technique involving a standard tensile test with a constant engineering strain rate. For both methods, the aim is to understand the influence of temperature and strain rate in elongation. The final objective, after analyzing the results and understanding the elongation behavior of the polymer, is to try to make a comparison between these two types of techniques. These steps will help to advance the study of polymers under non-linear elongation.

2 Theoretical background

In the framework of this master's thesis, the viscoelastic properties of a polydisperse linear polystyrene (PS) sample are studied. To this end, our experimental investigation is mainly based on rheology (in the linear and nonlinear regime) as well as mechanical (tensile) tests. The basics of these techniques are reported here.

2.1 Linear Rheology

Rheological measurements in the linear regime allow relating the stress applied to a viscoelastic sample to its deformation, or vice versa, while keeping the deformation small enough in order to preserve the structure of the sample. A stress relaxation test consists in applying a constant shear strain γ to the material, and measuring the stress $\sigma(t)$ required to maintain the strain constant. The relaxation modulus $G(t)$ is defined as $\sigma(t)/\gamma$.

The viscoelastic behavior is a combination of elastic and viscous responses. The elastic response reflects the storage modulus, the energy of the system being restored when the applied stress disappears. The viscous response is represented by the loss modulus, which reflects the energy dissipated by the system. Viscosity, or η, is defined as the ratio between a stress and a strain rate applied to the material [7].

Characterization is generally performed using a small amplitude oscillatory shear experiment (SAOS). A sinusoidal deformation is applied with an amplitude γ_0 that remains in the linear domain and a frequency ω. In the linear regime, the corresponding stress that needs to be applied in order to obtain the sinusoidal deformation is also sinusoidal, but shifted by a phase angle δ with a value between 0° and 90°, representing respectively a purely elastic response and a purely viscous response respectively [8].

The strain and stress applied can be written as

$$\gamma(t) = \gamma_0 \; sin(\omega t) \tag{1}$$

$$\sigma(t) = \gamma_0 \; sin(\omega t + \delta) \tag{2}$$

Equation 2 can be re-written in two terms, the first being in phase with the deformation, and the

second one being in phase with the rate of the deformation:

$$\sigma(t) = \gamma_0(G'(\omega)sin(\omega t) + G''(\omega)cos(\omega t)) \tag{3}$$

The latter equation clearly shows that G' accounts for the elastic response of the sample, while G'' describes its viscous part.

The Boltzmann Superposition Principle links storage modulus (G'), loss modulus (G''), viscosity (η) and relaxation modulus ($G(t)$). This principle of linear viscoelasticity states that the stress in the material is the sum of the stress contributions from all the strains that have been applied until time t. It can be applied since all deformations are linear and independent of each other. Therefore:

$$\sigma(t) = \gamma_0\ \omega\ cos(\omega t) \int_0^\infty G(s)\ cos(\omega s)\ ds + \gamma_0\ \omega\ sin(\omega t) \int_0^\infty G(s)\ sin(\omega s)\ ds \tag{4}$$

From Equation 4, it appears that G' and G" are the Fourier Transform of $G(t)$.

$$G'(\omega) = \omega \int_0^\infty G(s)\ sin(\omega s)\ ds \tag{5}$$

$$G''(\omega) = \omega \int_0^\infty G(s)\ cos(\omega s)\ ds \tag{6}$$

The phase angle, mentioned earlier, links storage and loss modulus together. It is the angle formed between these two components in the complex plane.

$$tan(\delta) = \frac{G''}{G'} \tag{7}$$

In the complex plane, the complex dynamic modulus is found, which is a common notation to describe the dynamic modulus and also links storage and loss modulus [7].

$$G^*(\omega) = G' + i\ G'' \tag{8}$$

2.2 Time Temperature Superposition Principle

Viscosity can vary by several orders of magnitude in just a few tens of degrees. Depending on the analysis temperature, it can take from a few nanoseconds, or even picoseconds for some materials, to weeks to reach the terminal flow regime of a polymer and be able to determine its viscosity. The aim of the Time Temperature Superposition Principle is to bring all temperatures down to a reference temperature. Measurement at a certain temperature and frequency corresponds to a higher temperature and a lower time, or conversely to a lower temperature and a longer time. This makes it possible to select the right temperatures and frequencies to obtain the widest possible frequency range.

Each different temperature curve undergoes therefore a horizontal shift over its frequency range. This shift factor is denoted a_T. The shift of these values at a given reference temperature gives a master curve. The expression used to find the shift factor for each temperature is the Williams-Landel-Ferry (WLF) equation.

$$log(a_T) = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)} \tag{9}$$

Where T_r is the reference temperature and C_1, C_2 are constants dependent on the reference temperature [7].

Sometimes a vertical shift factor is used, which takes into account the compensation between temperature and material density. This vertical shift factor is defined as [8]:

$$b_T = \frac{\rho_{ref} T_{ref}}{\rho T} \tag{10}$$

When the TTS is performed, it is interesting to look at the $\tan(\delta)$ curve to see if the horizontal shift of the data is correct, since vertical shifts are suppressed in this curve.

2.3 Non-linear Rheology

While the linear regime is very well understood, the non-linear behavior of polymers is still a subject of debate and discussion in the field of rheology. That is why it is important to explore this regime, which is still misunderstood.

Non-linear elongational rheology is the behavior of a material when subjected to large extensional deformation, which leads to the stretching of the chains. Compared to the linear regime, large deformations are of interest, as they better reflect the sample deformation during its processing.

2.3.1 Extensional flow

Extensional rheology involves pulling a sample in a purely extensional manner, without any shear deformation. In the context of this master's thesis, the uniaxial extension is the reference, but there are two other types of extensional deformation, namely biaxial extension and planar extension. The sample is subjected to homogeneous extension with a constant Hencky strain rate in one direction.
In the case of elongation, the term deformation is inevitable. For the deformation in extension, engineering strain or Cauchy strain (ϵ_e) is used for small deformations. While for large deformations, the true strain or Hencky strain (ϵ_t) is used. So in non-linear elongation, the discussion focused on the true strain rate.

$$\epsilon_e = \frac{\Delta L}{L_0} \tag{11}$$

$$\epsilon_t = ln(1 + \frac{\Delta L}{L_0}) = ln(\frac{L(t)}{L_0}) \tag{12}$$

Where L_0 is the initial length of the sample and L(t) is the length at a certain time t. But the true strain can be expressed differently for an incompressible fluid [9] [10].

This expression can be expressed as a function of the diameter, which is useful for elongation experiments since the strain rate is calculated as a function of diameter at a certain time.

$$\epsilon_t = -2ln(\frac{D(t)}{D_0}) \tag{13}$$

With D(t), the diameter at time t and D_0 the initial diameter of the sample [9].

2.3.2 Non-linear Elongation

For a monodisperse polymer, the linear response of the polymer is characterized by a smooth evolution to a plateau with zero viscosity. This linear response is called the linear viscoelastic region (LVE). The linear viscoelastic envelope in elongation is proportional to the linear viscoelastic envelope measured in shear, and the proportionality factor is called the Trouton ratio. Trouton established that a ratio of 3 exists between uniaxial extensional viscosity and shear viscosity [9].

$$\eta_E = 3\eta \tag{14}$$

On Figure 1, in addition to the linear response in black, curves for different extensional strain rates are present. One observes that the curves deviate from the linear envelope, showing a larger extensional stress growth coefficient $\eta_E^+(t)$. Usually, a transient strain hardening is observed when the chains are deformed fast enough to be stretched. On the right figure, the steady-state elongational viscosities are plotted against the strain rate, showing the constant zero-rate regime which is then followed by a decrease, hence extensional thinning. Although the majority of work carried out on this subject shows thinning, in some cases extensional thickening can happen.

Polydispersity makes the elongation behavior of polymers even more complex. It has been shown that adding long chains to a monodisperse linear polymer leads to thickening instead of the thinning effect. This phenomenon can be explained by the fact that long chains stretch more easily and make a greater contribution to hardening. Short chains, on the other hand, relax more rapidly and do not stretch. This in turn reduces the height of the linear envelope and the zero-elongation viscosity [8].

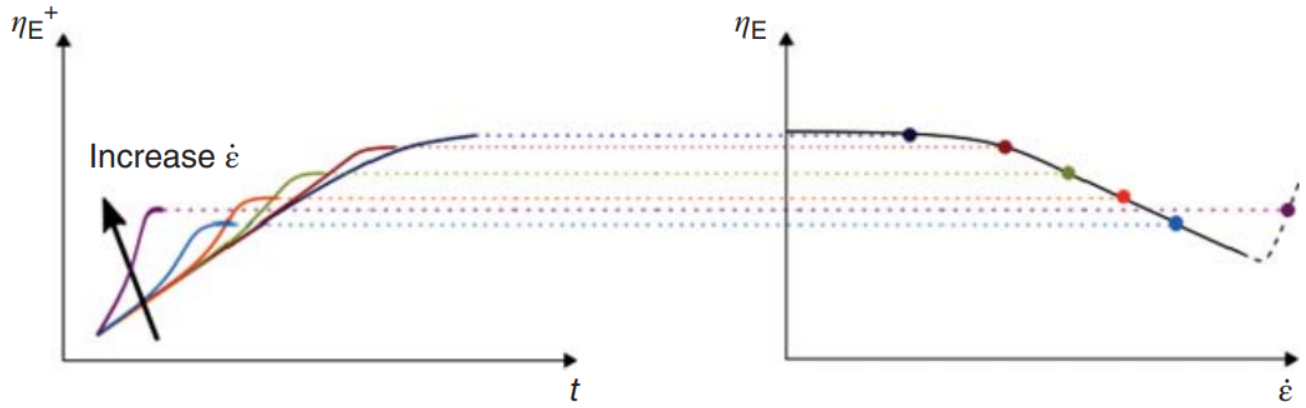

Figure 1: Left : Extensional stress growth coefficient as a function of time in uniaxial extension for different extensional rates. Right : The obtained steady-state uniaxial extensional viscosities from the left graph are plotted against extensional rate [8].

Polymer chains react differently depending on the strain rate applied to the sample. At very low strain rates, the chains have no trouble maintaining structural equilibrium. The steady-state extensional viscosity will then tend towards its linear value, *i.e.* three times the zero-shear viscosity, so it is still in the linear regime. With higher strain rates, the system enters the non-linear regime, the chains are strongly stretched in one direction, giving rise to extensional thinning [11].

It is possible to characterize the stretching and alignment of chains in elongation with the Weissenberg number, which quantifies the orientation and stretch of chains. This dimensionless number depends on relaxation time and extension rate. When this value is less than 1, the polymer is in the linear mode. It can therefore determine whether the imposed strain rate is sufficient to be in the non-linear mode when W_i is greater than 1 [12].

$$W_i = \dot{\epsilon}\tau_{rel} \tag{15}$$

Where W_i is the Weissenberg number, $\dot{\epsilon}$ is the strain rate and τ_{rel} is the polymer relaxation time, which is of the order of the Rouse time.

2.4 Tensile Test

The tensile test is a destructive mechanical process which provides information on the physical parameters of our material, such as the yield strength, Young's modulus and ductility. It provides information on force as a function of strain during traction. The experiment runs until the material breaks, or the machine reaches its limit if working with viscous materials [13]. There are different stages in a stress-strain curve which can be obtained and which give information about the mechanical properties of our material and how it reacts to deformation.

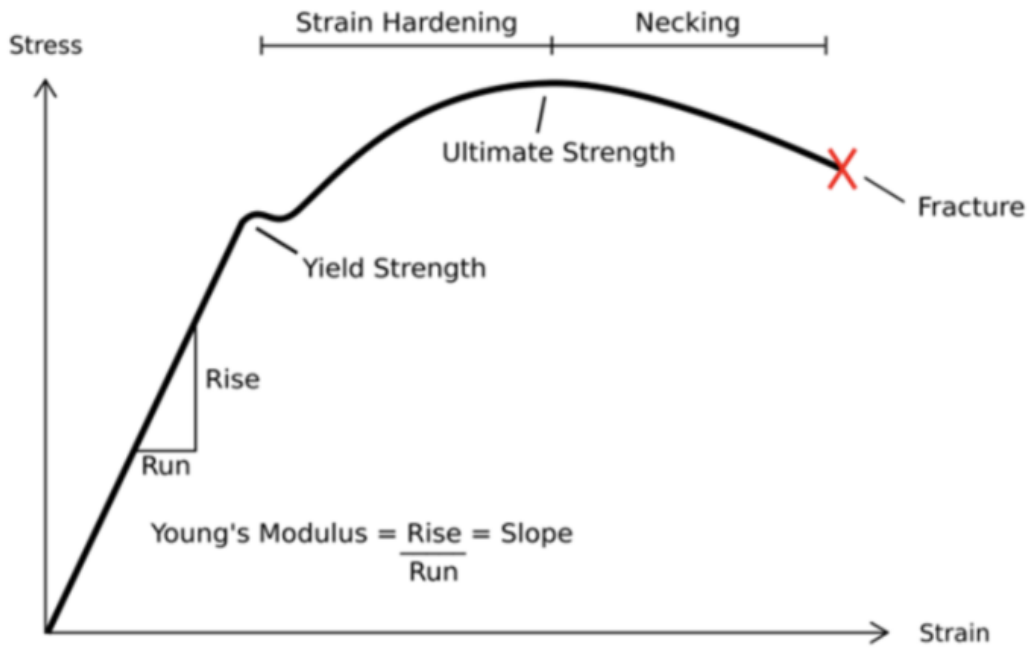

Figure 2: Stress–strain typical curve of a low-carbon steel [14].

It is important to understand the different parts of the stress-strain curve. The Figure 2 is divided into two main parts: the elastic part, until the yield strength is reached, and the plastic part, which lasts until material fracture.

At the beginning of the curve, the Young's modulus is obtained, and represented by the slope of the first part of the curve. When the yield strength is reached, the material enters the plastic region. Deformations in this zone are permanent. The strain hardening phenomenon occurs before reaching ultimate strength, which is the maximum stress the material can withstand before failure. After this maximum, the necking phenomenon occurs, with all deformations localized in a small

region of the sample. This rapidly reduces the diameter of the sample in this zone, leading to material fracture [15].

This typical graph of a tensile test is found in metals, and is a good first example for understanding stress-strain curves. For polymers, however, the behavior can be quite different, and temperature plays a very important role. An example is provided in Figure 3.

At very low temperatures (curve a), depending on the polymer chosen, the material acts like an elastic system, with so-called brittle fracture. At higher temperatures, the yield point appears on the curve, giving rise to a plastic domain with irreversible deformation. A ductile fracture is also present in this case, due to the presence of plasticity.
Curve c shows the appearance of necking and a phenomenon known as strain softening, which will be detailed after.
Finally, as shown by the curve d, at even higher temperatures ($T > T_g$), the curve flattens out more and more, with the polymer acting like a rubber [16].

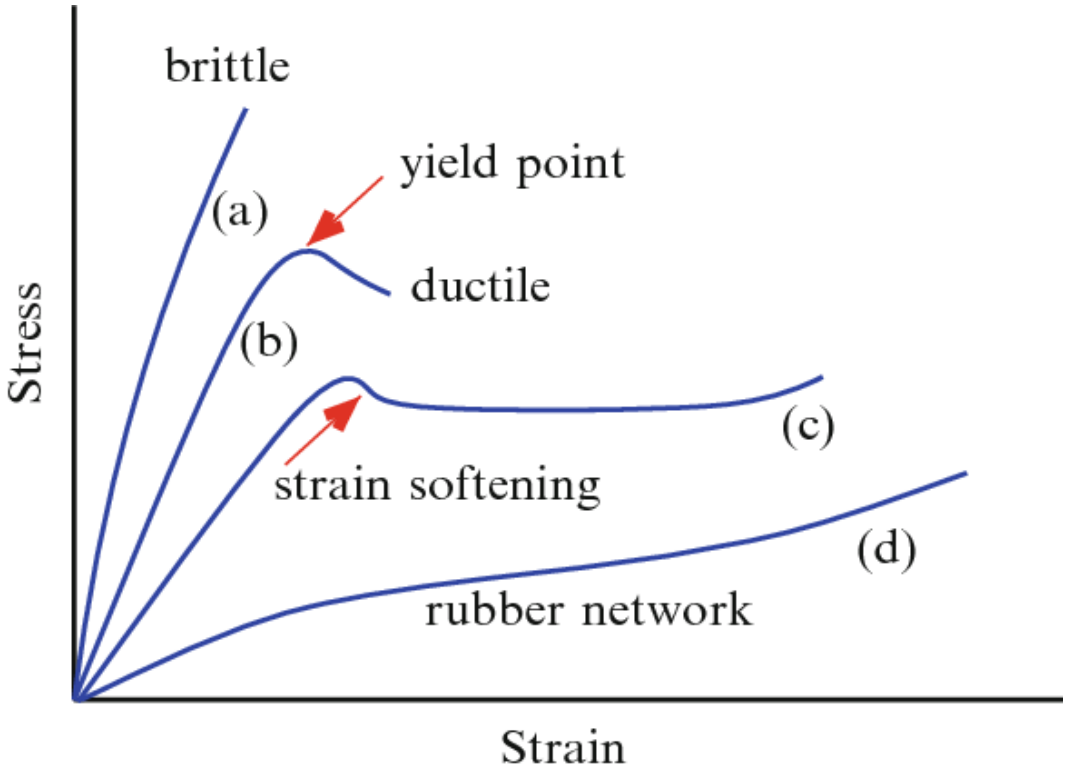

Figure 3: A typical stress-strain curves of polymer tested at different temperatures: curves (a)-(c) represent polymers with a temperature below, T_g with increasing temperature from (a) to (c). The curve (d) corresponds to the rubber state with temperature above T_g [16].

It is also worth talking about strain hardening and strain softening in tensile testing. In this example, the temperature is still below T_g, and Figure 4 shows two different types of behavior in the plastic region. The first is strain softening, which is highly dependent on the polymer's thermo-mechanical history and represents a deterioration in material strength as strain increases. The polymer then goes through a strain hardening phase that lasts until fracture. This phenomenon is mainly determined by the response of the chain network, the chains are stretched so fast that they do not have time to disentangle, so they block each other, creating this strain hardening. Parameters like the density of entanglements plays an important role in this case [17].

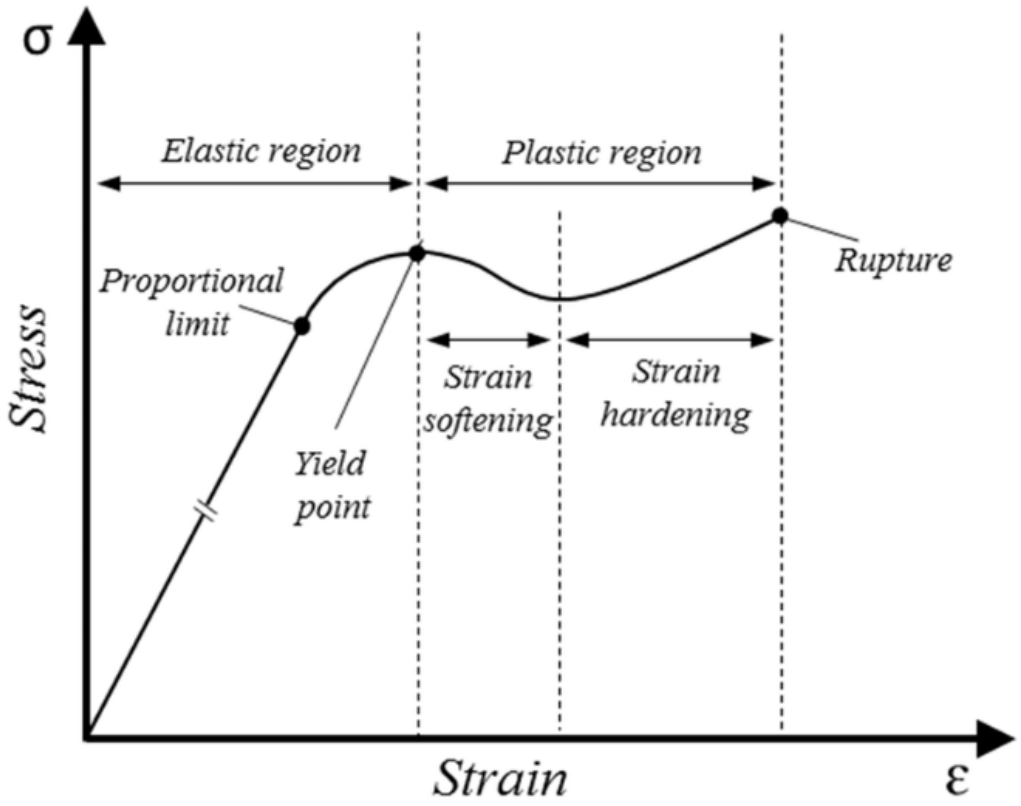

Figure 4: Typical stress-strain graph of a polymer [18].

The ratio of softening to hardening is of great importance in the behavior of failure. When strain softening is high compared to hardening, there is extreme localization of stresses in one region of the sample. Whereas with strong strain hardening, deformation is more stable and there is stable neck growth.

It has been mentioned that certain physical and chemical parameters influence the softening and hardening behavior of the material. Aging increases yield strength and thus lead to greater strain softening. While the chemical composition and chains present have an effect on strain hardening. For example, in Figure 5, PS has a low entanglement density and high molecular weight compared with PC. As a result, PC has a much greater strain hardening than PS [17].

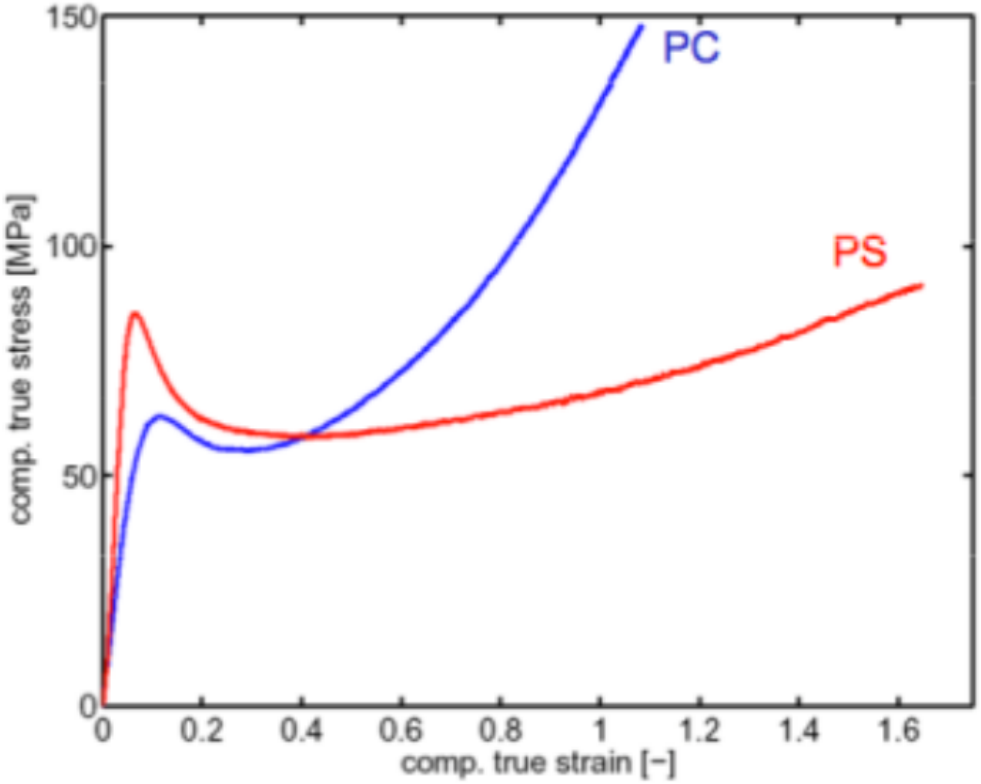

Figure 5: Behavior of polycarbonate PC and polystyrene PS [17].

2.5 Method of comparison between elongation rheology and tensile test results

When conducting a review of the scientific literature, numerous papers can be found discussing the mechanical properties of linear polymers below their glass transition temperature, as well as many others that explore the rheological properties of polymers in their molten state (*i.e.*, above the glass transition temperature). Despite the abundance of research in these two significant fields, a comprehensive understanding of the link between them remains elusive.

It is important to note that the models predicting mechanical properties differ significantly from those for viscoelastic properties and are based on different assumptions. In our current study, one of our primary objectives is to begin bridging the gap between these two fields. We aim to develop and articulate our reasoning for establishing connections between standard mechanical tensile testing and rheological analyses.

The comparison of the results provided by both techniques could be done by using a constant engineering strain rate or using a constant true strain rate. Although, it seems that a constant true strain rate is a better approach, efforts are still underway to achieve this goal. Therefore, in this study, we present only the comparison of the results from rheological analyses with those obtained from mechanical tensile tests using a constant engineering strain rate.

The rheological technique is performed with the Versatile Accurate Deformation Extensional Rheometer (VADER 1000), while the mechanical technique is performed with the Instron. Both methods are described in detail in Section 3.7 and Section 3.8.

2.5.1 VADER method

For measurements based on the VADER rheometer, a constant true strain rate is imposed on the sample, from this experiment, the viscosity versus time is obtained. Whereas in the tensile machine, what is imposed is a constant engineering strain rate. What is quickly noticed when using the VADER is that the tensile speed increases with time. Indeed, since it is calculated in relation to the filament diameter, in order to maintain a constant true strain rate, the speed must be increased as the cross-section is reduced. Whereas in the tensile test, the tensile speed remains constant throughout the experiment.

It was first thought to add an extensometer to the tensile machine device to enable real-time calculation of the deformation undergone by the sample, and then to calculate the speed that should be applied to keep the true strain rate constant. However, it was not possible to add such a device to the machine because of the oven present. Alternatives to the extensometer were therefore thought of, such as adding two marker dots on the sample to calculate transverse deformation. But working with polymers above the glass transition temperature, the marker dots would have diffused in the material and possible material flow would have made the method too approximate.

2.5.2 Instron method with constant engineering strain rate

Since it was not possible to calculate transverse deformation directly, it was decided to create a velocity profile evolving over time towards a possible curve obtained with the VADER. To accomplish this, the time-dependent evolution of the diagonal of the cross-section of the sample used for the tensile test was calculated. The cross-section is the rectangular part in the middle of the dogbone (Shape of the sample for the tensile test). It can be seen that, at constant speed, the length of the diagonal decreases sharply at the beginning, sketching the $1/x$ curve as shown on Figure 6.

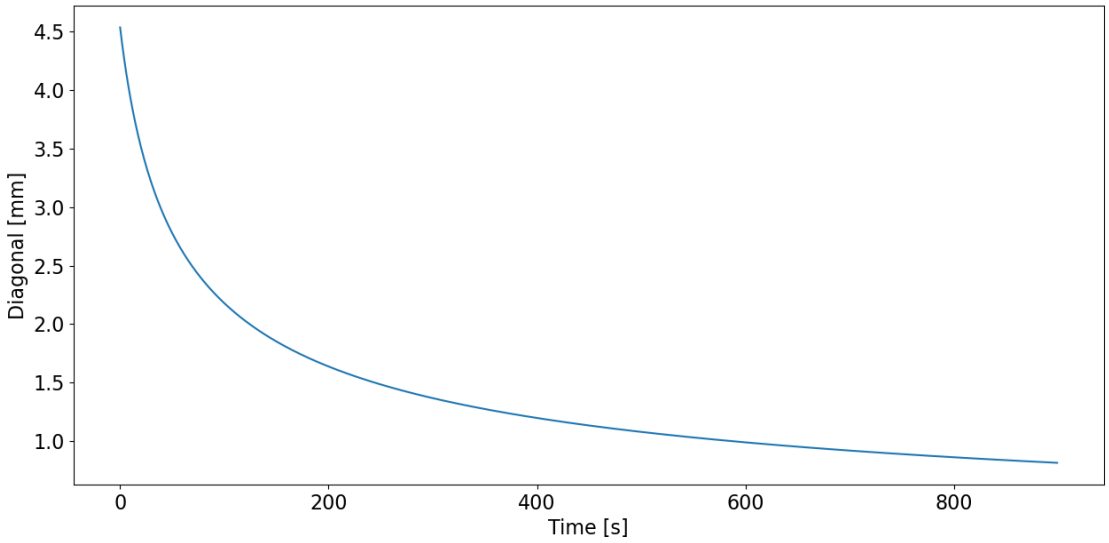

Figure 6: Evolution of the diagonal of the cross-section of the sample used for the tensile test in time at a traction speed of 50 mm/min.

From the evolution of the calculated diagonal, the true strain rate applied to the sample during the tensile test can be found. As shown in Figure 7, a comparison can be made with the constant true strain rate of the VADER. It can be seen, for example, that for times above 200 seconds, a true strain rate of 0.003 s^{-1} tends to the curve obtained in the Instron for a tensile speed of 50 mm/min. Unfortunately, it is not possible to just compare the end of the two curves, since in rheology, the history of the material is very important [19]. The deformations undergone prior to 200 seconds are important to be able to compare the two techniques correctly.

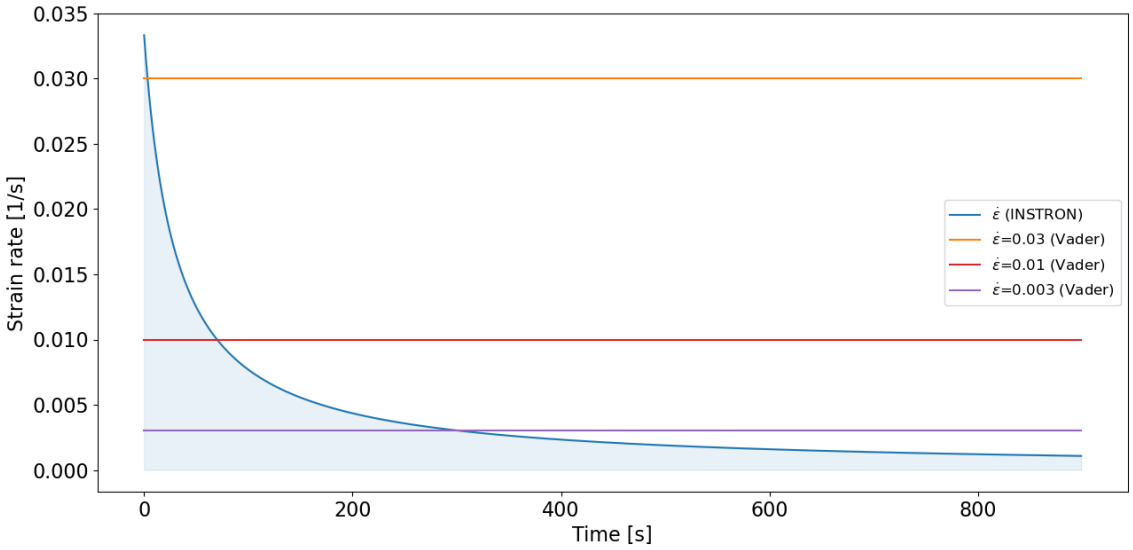

Figure 7: Comparison of the true strain rate in the VADER to the true strain rate for a tensile speed of 50 mm/min in the Instron.

The velocity profile can therefore be created by adjusting the traction speed when the true strain rate value falls below a certain limit. In this case, to approximate a true strain rate of 0.01 s^{-1} in the VADER, a minimum true strain rate of 0.008 s^{-1} is chosen. A new velocity value is then recalculated to stay close to 0.01 s^{-1} while remaining below 0.012 s^{-1} and above 0.08 s^{-1}. So 0.08 s^{-1} and 0.012 s^{-1} are the minimum and maximum bounds of the true strain rate imposed on the tensile test, and the tensile speed is then calculated to stay between these bounds throughout the experiment. The velocity profile that can be imposed with the Instron based on this method is illustrated in the Figure 8.

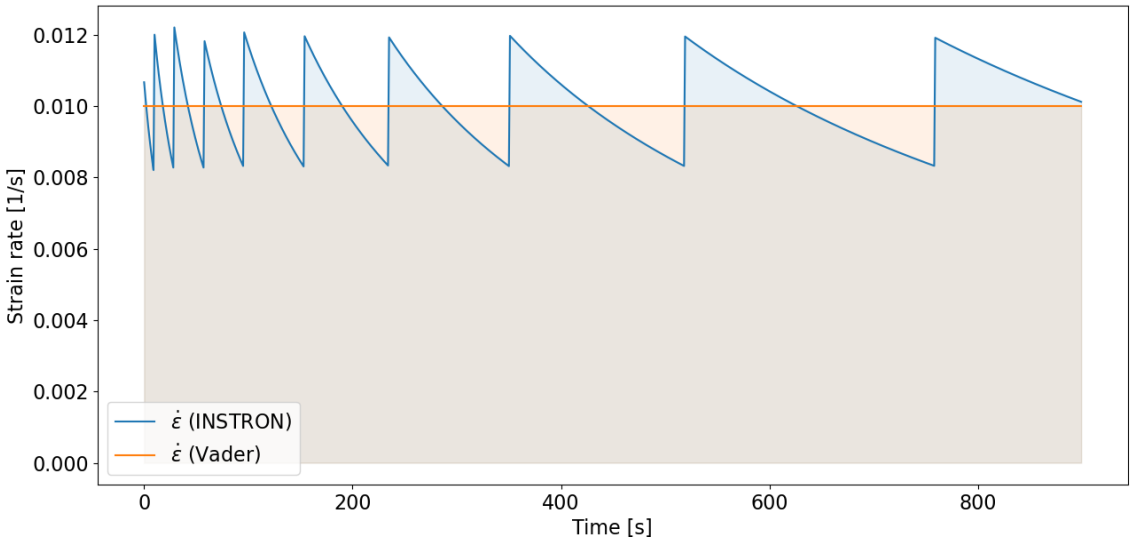

Figure 8: Comparison of the true strain rate in the VADER to a possible true strain rate in the Instron when doing a velocity profile.

2.5.3 Attempt at using a true strain rate with Instron

Ideally, another method should be used, which would be to directly implement a function that would change the speed at each time step, thus obtaining a true strain rate very close to the one of the VADER. Therefore, a function needs to be found where the Instron's true strain rate is close to that of the VADER over time. As can be seen in the Figure 9, the slope of the true strain rate decreases with time in the Instron due to the constant velocity. Hence, by imposing a velocity that changes as a function of time, it should be possible to approximate the VADER curve to be able to compare results.

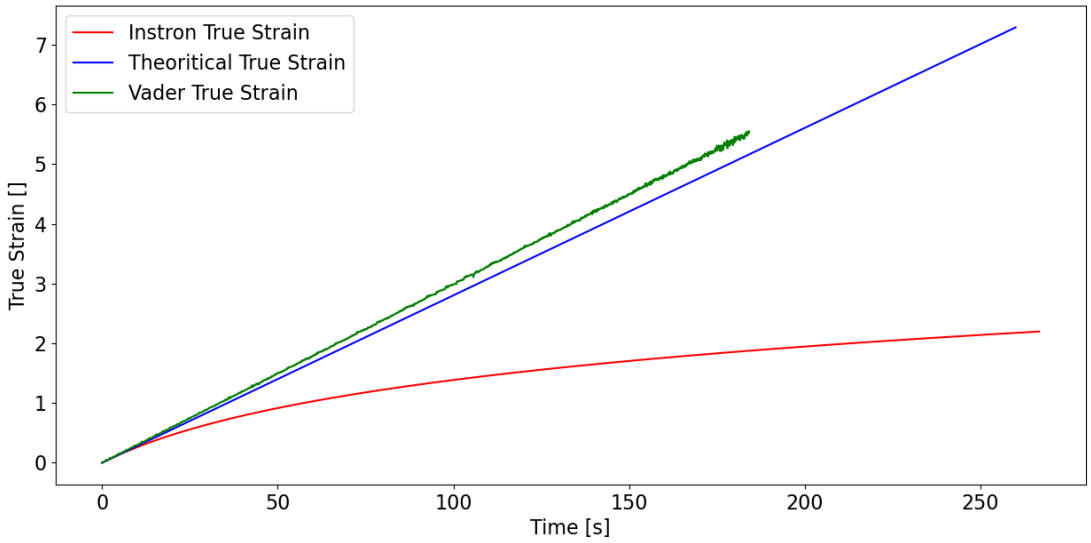

Figure 9: Comparison of the true strain in VADER and Instron.

The function directly implemented in Instron software:

$$v = \frac{"Length"}{"Time"}\ exp(X\ [m/m/s]\ "Time") \tag{16}$$

In this function, "Length" is the initial length of the sample, "Time" is the variable corresponding to the current time of the experiment and v is the machine's traction speed. X is the true strain rate ($\dot{\epsilon}$) chosen to impose, a value is therefore chosen in place of the letter X in the software. The expression [m/m/s] is inserted in this equation because the software required the exponential to be dimensionless, it corresponds to the units of X.

This function is derived from these equations to obtain the machine's traction speed:

$$v = \frac{L(t)}{t} \tag{17}$$

with L(t) the length of the sample at a certain time and t the variable "Time". L(t) can be re-expressed as a function of the true strain rate.

$$L(t) = L_0\ exp(\dot{\epsilon}\ t) \tag{18}$$

With L_0 the "Length" variable and $\dot{\epsilon}$ the imposed true strain rate, which has been illustrated by an X.

When this function was implemented in the software, it was found that the traction speed did not change over time. It was finally concluded that the "Time" variable did not change over time and therefore remained frozen at its initial value of zero. In order to resolve this problem, which originated from Instron's software, discussions are held with the manufacturer to enable further results to be obtained.

Assumptions for a true strain rate

This method remains an approximation of a theoretical model, and assumptions have been made throughout to arrive at this final method. These assumptions are based on the VADER conditions for obtaining results with a constant true strain rate.

For a true strain rate, the sample diameter has to decrease homogeneously over time.
In VADER, the diameter decrease is measured in real time to adjust the rate correctly, whereas in tensile test, an attempt is made to approximate the rate.
It is also important to maintain a homogeneous temperature gradient throughout the oven, as the traction machine's oven is much larger, the temperature differences can quickly occur, and they are not negligible [20].

3 Materials and methods

3.1 Material characteristic

The polymer used for the experiments is a polystyrene (PS1160). It is an amorphous polymer with a high heat resistance, which has been produced by TotalEnergies. TotalEnergies has a wide range of polystyrene products. This sample is available to us in large quantities in the laboratory and has been chosen for this study. [21].

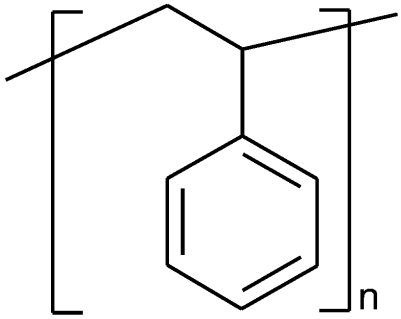

Figure 10: Chemical Structure of Polystyrene [22].

3.2 Sample Preparation

3.2.1 Advanced Rheometric Expansion System (ARES)

Polystyrene disks are extracted from a polystyrene plate. The sample taken is an 8 mm-diameter disc, the same size as the ARES plates. The plate is created using a press heated to high temperature.

Procedure:

1. Heat to 170°C, higher temperatures would risk material degradation.
2. 3 pressure cycles are performed to remove any air bubbles that may be present, the 3 cycles lasting 8 minutes each with a pressure of 5 tons.

Note : The time is set at 8 min, since too little time would prevent the polystyrene pellets from melting properly. Too long time, on the other hand, could lead to material degradation.

3.2.2 Versatile Accurate Deformation Extensional Rheometer (VADER 1000)

For the VADER experiments, 6 mm-diameter disks were first produced, compressed in a mold heated to 165°C and connected to a vacuum pump. A schema of the home-made mold is shown on Figure 11. Unfortunately, when the sample was subjected to high temperature in the VADER, the disk flowed as if the pellets contained in the disk were trying to separate from each other. This is probably due to the fact that the polystyrene chains were still under stress when the mold was cooled down. Consequently, upon heating, the chains further relax, leading to an elastic recoil of the sample. This defect in the discs did not lead to conclusive results in the experiments.

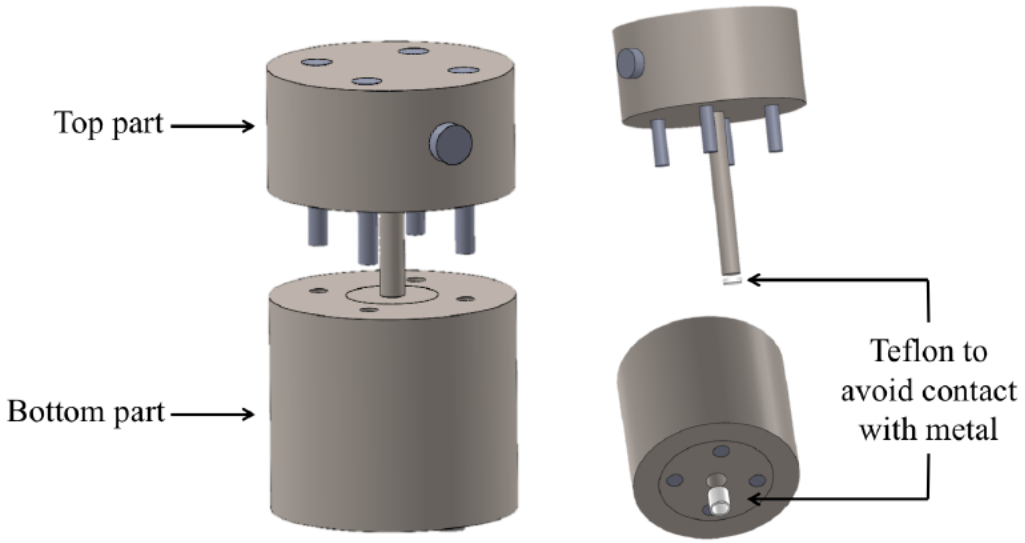

Figure 11: Home-built mold to prepare PS samples [9].

To overcome this problem, it has been thought to heat at higher temperatures or for longer time to allow the chains to reach a state of equilibrium during cooling, but no procedure has been conclusive.
In order to obtain results, a simple pellet was introduced into the machine. This simplified procedure meant that less polystyrene was used, but good adhesion to the plates was achieved, and so reproducible results were obtained.

3.2.3 Tensile machine (Instron)

For a tensile test, the reference specimen is a dogbone, the dimensions of the central part are 25 mm long, 4 mm wide and 2.14 mm thick. These samples are produced using the HAAKE MiniJet

Pro Piston Injection Molding System.

Procedure:

1. Load pellets into a cylinder heated at 200°C.
2. Allow pellets to melt for 10 min.
3. Manually press the pellets and refill with pellets, then wait 5 min. This step is repeated until the cylinder is full.
4. The cylinder is then installed in the machine and a pressure is applied to inject the polystyrene into the mold, which is heated at 80°C.
5. Once injected, the mold is plunged directly into a bucket of water at room temperature.

Note: A lubricant is applied to the mold to facilitate removal of the sample after cooling. This lubricant is a Kluber lubrication uh1 96-402.

Defects may be noted, such as bubbles, excess lubricant or burnt lubricant, these defects are shown on Figure 12 and Figure 13. Bubbles may be present if the pellets are not heated and pressed sufficiently into the cylinder before handling. Burnt lubricant, on the other hand, is caused by the lubricant having been in the mold for too long before handling. These types of samples are of course not used for the tensile experiments.

Figure 12: Burnt lubricant samples.

Figure 13: Samples with bubbles.

3.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry is used to determine the glass transition temperature of the polystyrene used. To carry out this experiment, a Toledo AG204 Delta Range is used. The sample is heated and cooled at a rate of 10°C/min to give the best possible view of the phase transitions. The experiments are also carried out under an inert gas, nitrogen. Nitrogen is supplied at a rate of 5 ml/min for the duration of the experiment. The initial polystyrene mass is 7.06 mg.

Procedure:

1. Set and maintain the temperature at 25°C for 2 minutes.
2. Heat to a temperature of 150°C at a rate of 10°C/min.
3. Maintain the temperature of 150°C for 2 minutes.
4. Cool down to a temperature of 25°C at a rate of 10°C/min.
5. Maintain the temperature of 25°C for 2 minutes.
6. Reheat to a temperature of 150°C at a rate of 10°C/min.

3.4 Gel Permeation Chromatography (GPC)

The Gel Permeation Chromatography (GPC) is a method used to determine the molar mass distribution of the sample. The experiment is performed on a Waters GPC instrument with dimethyl formamide (DMF) as an eluent.

This method gives the value of the number-average molar mass M_n, the weight-average molar mass M_w and the polydispersity of the sample.

Procedure:
The diluted solution of polystyrene in DMF is injected into the GPC columns with a flow rate of 1 mL/min. The total volume of solution injected is 0.1 mL. The columns are maintained at a temperature of 35°C.

3.5 Thermogravimetric Analysis (TGA)

The Thermogravimetric Analysis is a method in which physical and chemical phenomena are detected, such as phase transitions, adsorption, absorption, etc. The variation of a sample's mass over time is examined as a function of temperature.

Procedure:
For the purposes of this master's thesis, the temperature is maintained at 200°C for 3h to see if polystyrene degradation occurs at this temperature.

3.6 Rheometry Experiment

The experiments are performed with an Advanced Rheometric Expansion System (ARES) using two circular parallel plates. The diameter of the top plate is 8 mm and 25 mm for the bottom plate.

3.6.1 Sample loading

Firstly, the temperature is initialized to the highest value that will be used during the experiments. When the temperature is reached, the gap and force are set to 0. Once these steps are completed and the oven temperature is uniform, the sample can be placed on the bottom plate and the polystyrene allowed to relax for at least 15 minutes. It is also important to have a gaseous nitrogen flow to obtain an inert environment and avoid material degradation.

3.6.2 Dynamic Strain Sweep Test

The main idea behind this test is to study the behavior of the material under sinusoidal deformation at different amplitudes. It will be possible to determine the maximum strain that can be applied before the material enters the non-linear deformation domain. The deformation range is initially scanned from 0.1% to 100% at a high frequency of 100 rad/s. When entering the non-linear regime, a drop in the curve is detected as illustrated on Figure 14, so the experiment can be stopped, and the deformation limit is found. Figure 14 shows an example of the two regions governing the deformation of a viscoelastic material, as explained above.

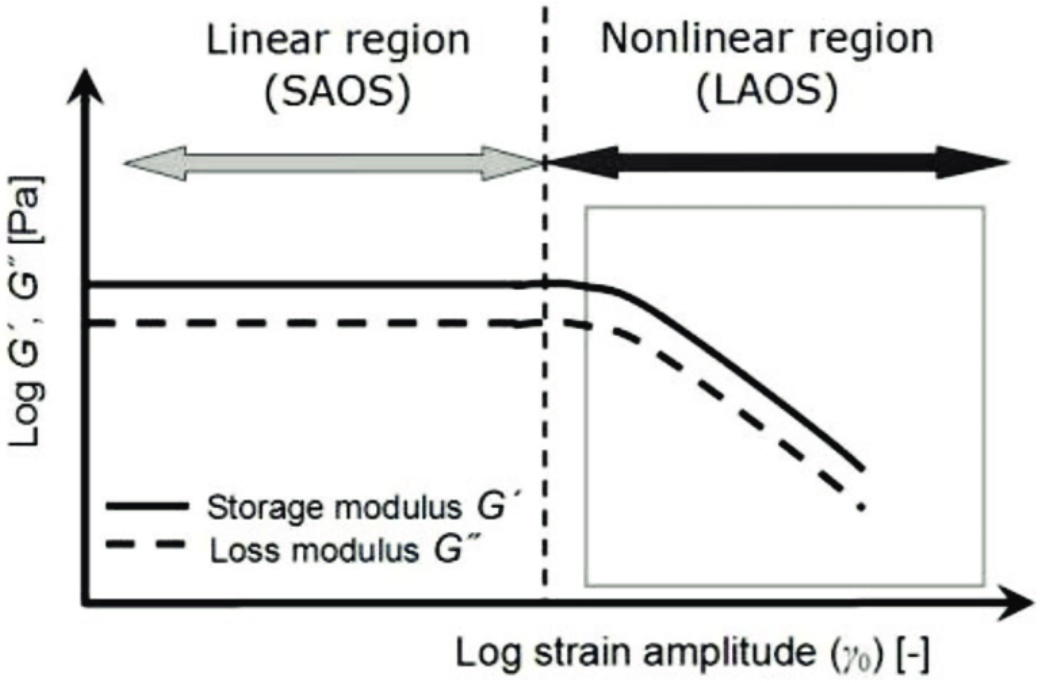

Figure 14: Theoretical Dynamic Strain Sweep Test [23].

Since temperature has an impact on polymer properties, the Dynamic Strain Sweep Test should be carried out at every temperature tested.

3.6.3 Dynamic Frequency Sweep Test

Once a deformation in the linear regime is selected, the next step is the Dynamic Frequency Sweep Test. The method used in this test is the small amplitude oscillatory shear experiment (SAOS). This method provides storage and loss modulus for each temperature. An oscillating shear strain is applied to the sample at each temperature. The oscillation frequency is decreased from a value of 100 rad/s down to 0.1 rad/s or 0.01 rad/s, depending on the range of the results required.

3.6.4 Gap Expansion

The first calibration is a calculation of the gap created between the two ARES plates when the temperature is varied. Since the plates are made of metal, thermal expansion plays a role in the actual gap between the two plates. These data are used to obtain the most accurate results possible for future experiments on this machine. This test is carried out starting at room temperature (25°C), then increasing by 15°C the first time, and then increasing by 10°C up to 200°C. Working

with polystyrene, it is preferable not to exceed 200°C to avoid degrading it, so the experiment stops at this temperature.

For information, Figure 15 shows that the gap difference increases linearly with temperature, reaching a difference of almost 0.5 mm. It would therefore be possible to predict the gap approximately if the experiments are performed at higher temperatures.

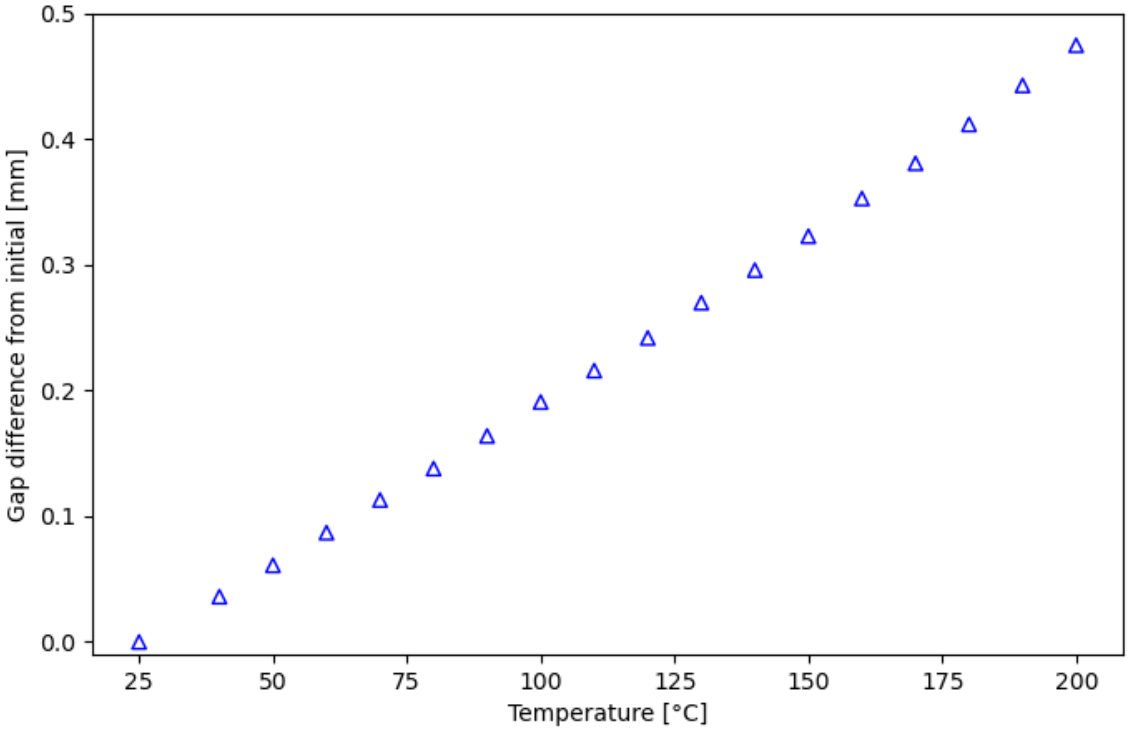

Figure 15: Variation of the gap between the two plates as a function of temperature.

3.6.5 Data Error Calibration

The observations in this section are made with the help of Alexandru Tudor Boborodea, who found discrepancies in some data obtained using the ARES. He found that a vertical shift appeared in some data, this shift ranging from 1.1 to 2. This deviation in results is well above the tolerated error of 10%. It was found that the results for polystyrene were not correct, and the curves obtained were too high compared with other results obtained by members of the research team or compared with the literature [24].

To check whether this error was due to the sample or the method, the ARES was used with a standard sample, which is P(DMS) (Polydimethylsiloxane). But the data obtained were still too high.

Continued testing P(DMS), it was found that the error could be related to the gap between the two plates, a smaller gap gives values closer to the theoretical data. This phenomenon is shown on the Figure 16 below.

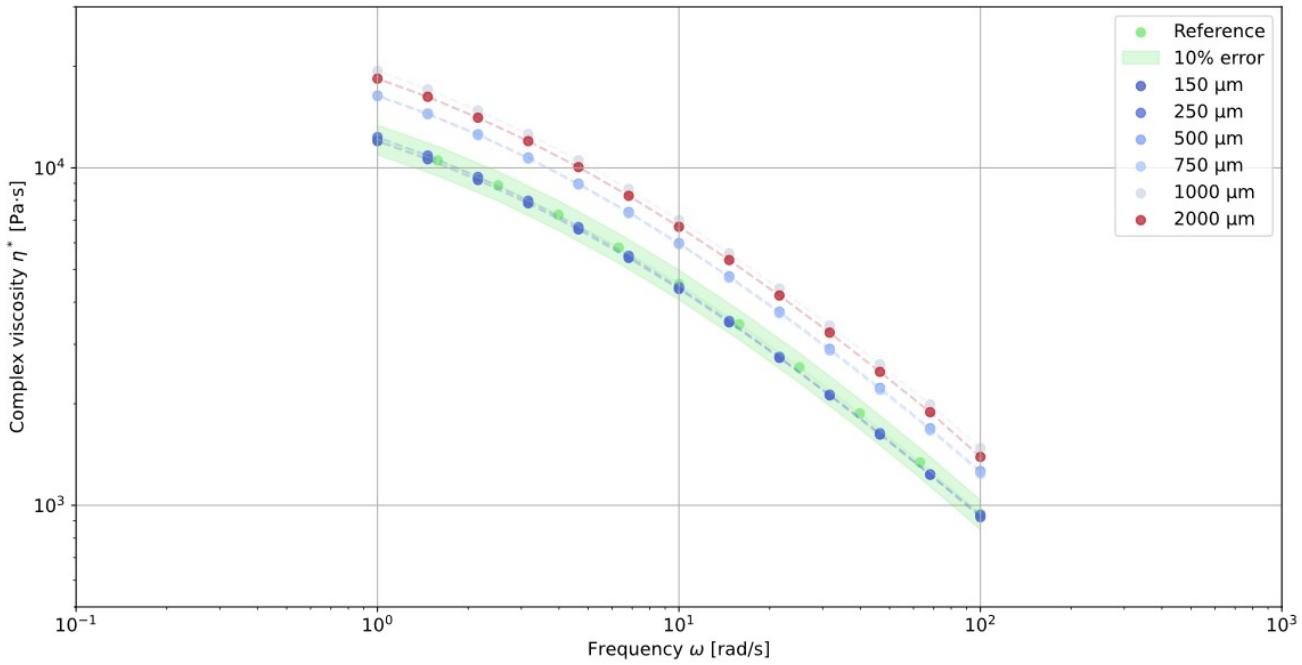

Figure 16: Complex viscosity for P(DMS) [standard] with an 8 mm vs. 25 mm plate diameters setup on ARES-1.

There is so an effect of the gap on the results obtained, but after some research, it is found that this effect is mainly due to the configuration of the plates used, which can be symmetrical or asymmetrical, with 8 mm and/or 25 mm plates. To get the wrong results from polystyrene, an asymmetrical configuration with the 8 mm plate above and the 25 mm plate below was used. This configuration was chosen to avoid polymer flow when working at very high temperatures. However, the sample did not flow as desired and took on a shape (A) (see on Figure 17) that was not optimal for the experiment. This shape does not allow torque to be distributed evenly in the sample, leading to errors in the results. This effect was reduced by decreasing the gap to get closer

to the desired shape (B) as shown in Figure 17.

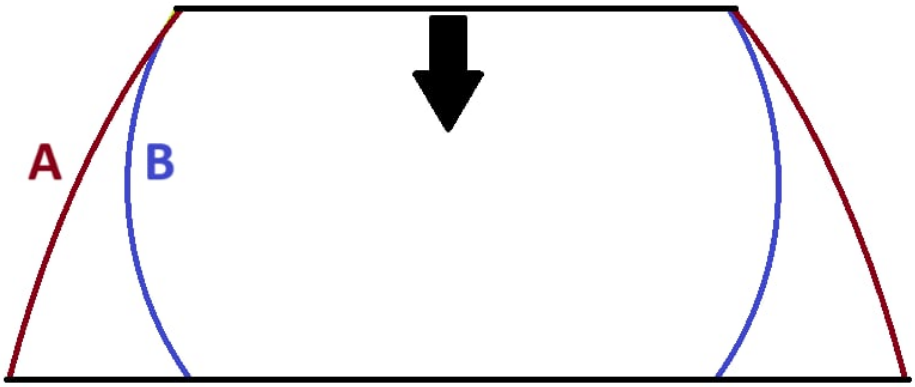

Figure 17: Schematic diagram of the shape of the polymer compressed between the two plates in the ARES. (A) is the shape obtained with asymmetrical plates and (B) is the desired shape obtained with symmetrical plates.

To obtain accurate and reliable results with ARES, a few recommendations are provided:

- A symmetrical-plate configuration (*i.e.*, identical diameters) should be used.
- When performing experiments at low temperatures, or temperatures close to the glass transition temperature of the material, 8 mm plates should be used to avoid large values for the measured torque.
- When performing experiments with low-viscosity polymers, or at temperatures much higher than the glass transition temperature of the material, 25 mm plates can be used to reduce the noise in the data.

The data obtained following these recommendations were in good agreement with the literature data.

3.7 Versatile Accurate Deformation Extensional Rheometer (VADER 1000)

The VADER 1000 is a rheometer for uniaxially stretching polymers. The machine is equipped with a laser that measures the smallest diameter at each time step, enabling to maintain a constant true strain rate. This technology of the instrument is called a feedback loop, which gives a better control of the true strain rate applied. This technology allows the filament to be stretched to high deformations, enabling the steady state of the materials to be reached. The equipment with a schema of the different components in the oven are shown on Figure 18 [9].

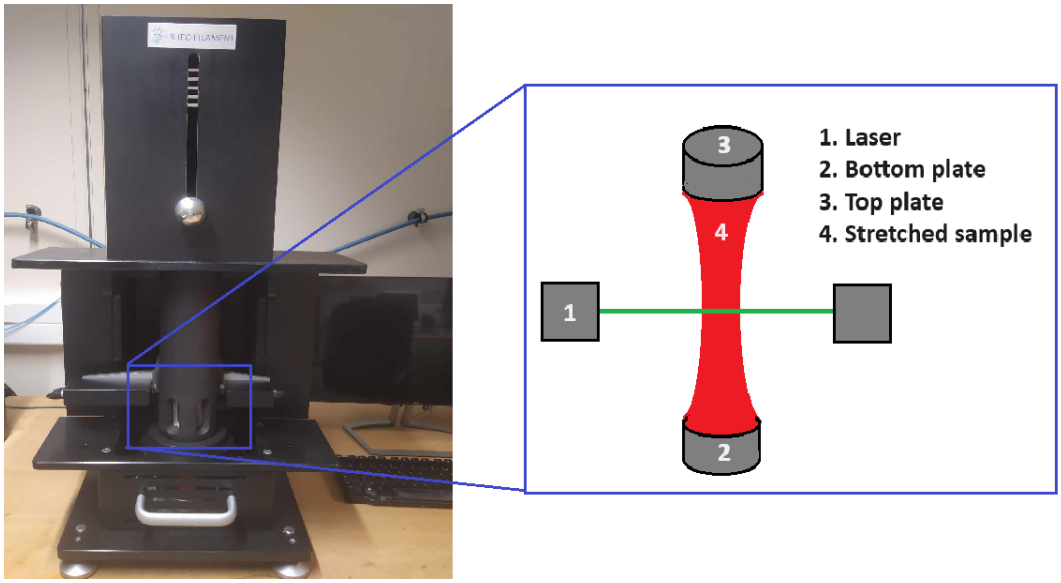

Figure 18: Picture of VADER 1000 with a schema of the sample inside the oven.

3.7.1 Sample loading

The sample is placed on the bottom plate, then the oven is closed to be heated to a temperature of 200°C. It is first heated to a high temperature to make the material flow, which in turn improves adhesion to the plates. Next, the sample is compressed by gently lowering the top plate. Compression continues until a "domed" shape is obtained on the sides of the plates. The temperature is then lowered to 170°C for pre-stretching, which results in a smaller radius to minimize the risk of lift-off during the experiment. The shape obtained after the pre-stretch is shown on Figure 18. In a second step, this also eliminates any local shear effect that might be present at the level of the plates. Finally, the temperature is lowered to the temperature of the experiment to launch the experiment.

Note: The higher the true strain rate, the smaller the initial diameter after pre-stretch to prevent filament detachment.

3.7.2 Elongation experiment

Once the desired temperature has been reached, the true strain rate is chosen for the experiment. Note that a true strain rate that is or may cause the sample to break during the experiment, whereas a true strain rate that is too low may cause the filament to flow downwards. For the purposes of this master's thesis, the strain rate is set between 0.003 and 0.1 s^{-1}. Once the value is chosen and the other parameters encoded, the experiment can start. The VADER has two limitations: the maximum elongation of the machine is 135 mm, and the laser cannot detect a filament with a minimum diameter of less than 0.1 mm.

3.8 Tensile machine (Instron)

Tensile tests are carried out using the Instron 6800 series benchtop model. This machine is equipped with an oven for heating samples to high temperatures. The drawback of this set-up is that the maximum possible deformation is reduced due to the height of the oven. The maximum deformation (while maintaining a safety distance) is 200 mm.

3.8.1 Sample loading

The oven is heated to the required temperature, followed by a 30 minutes wait to ensure, as much as possible, a uniform temperature distribution in the oven. For subsequent samples, a 10 minutes wait is sufficient, since the oven is warm. The tensile force of the jaws is first set to zero before introducing the dogbone into the machine. The sample is inserted in the middle of the two jaws and as perpendicular to them as possible to obtain the most longitudinal traction possible. A further 10 minutes wait is then allowed for the oven to return to the desired value and for the sample to heat up.

At high temperatures (above T_g), to ensure that the sample does not slip out of the jaws, after leaving the sample in the oven for 8 minutes, the jaws are tightened and another 2 minutes wait is done. However, there is too much variation in the results, which is probably due to the fact that the temperature is not sufficiently homogeneous.

Two different operating conditions were compared to see the impact on results. These conditions were tested at a temperature of 125°C and a tensile rate of 50 mm/min.

Protocol 1 : The basic protocol used, *i.e.,* waiting 8 minutes once the sample has been inserted, then tightening and waiting 2 more minutes before the experiment. In the first instance, the oven only rises to a temperature of 123°C.
Protocol 2 : Wait 8 minutes before tightening, and then wait for the oven temperature to rise to the desired temperature. In our case, 125°C. Note that it takes about 6 minutes to reach the desired temperature after the tightening.

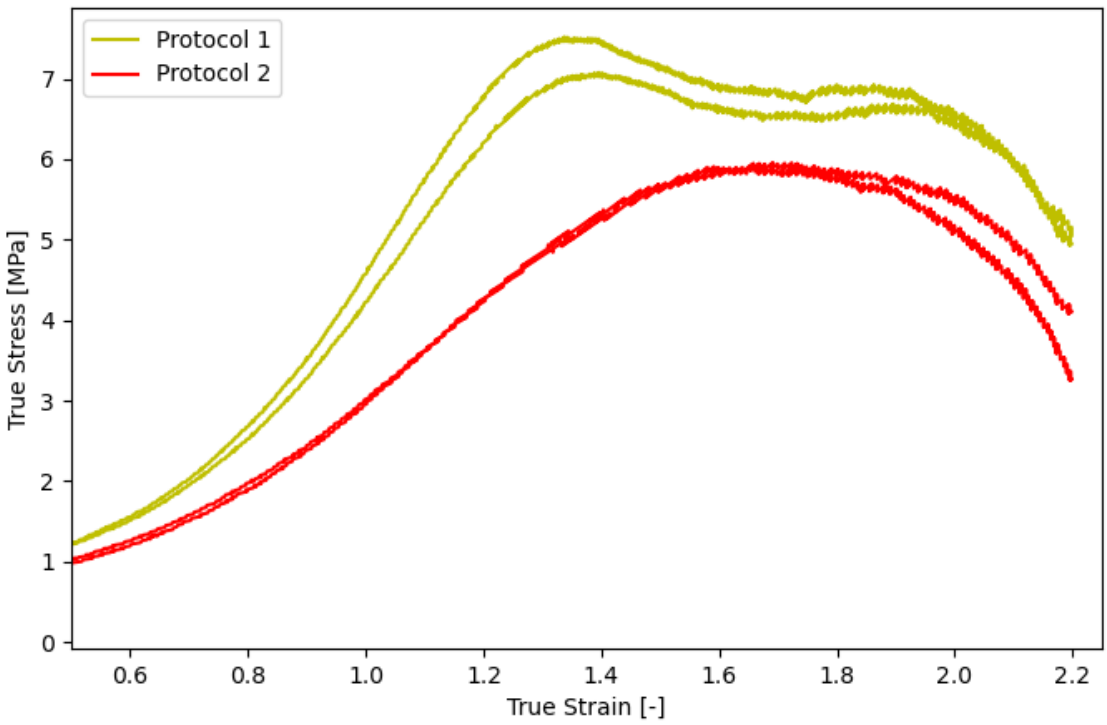

Figure 19: The two different protocols tested to see their impact on the results.

It can be seen, for protocol 1, two peaks on the curves and that the curves are slightly higher. These two peaks are not consistent, since this would mean the appearance of two yield points, *i.e.* two elasticity inputs for our material. The appearance of this double peak is probably due to the fact that the oven continues to heat up by 2°C, since when the experiment is launched, the temperature is only 123°C. And it is well known that even a small temperature change in polymers heated just above their glass transition temperature can have a major impact on mechanical properties. Protocol 2 produces a much more theoretically consistent curve with a single peak, and both curves are reproducible.
The protocol that is retained for the results is protocol 2, which is to wait 8 minutes before tightening and then wait for the oven temperature to rise to the desired temperature.

3.8.2 Tensile test experiment

Once the sample is placed and the waiting time has elapsed, the experiment can start using the protocol created. The standard tensile test method is to impose a constant engineering strain rate

throughout the experiment. Before starting the experiment, the dimensions of the sample must be encoded in the system.

4 Results and Discussions

4.1 Differential Scanning Calorimetry (DSC)

A Differential Scanning Calorimetry is performed to determine the glass transition temperature of the polystyrene PS1160.

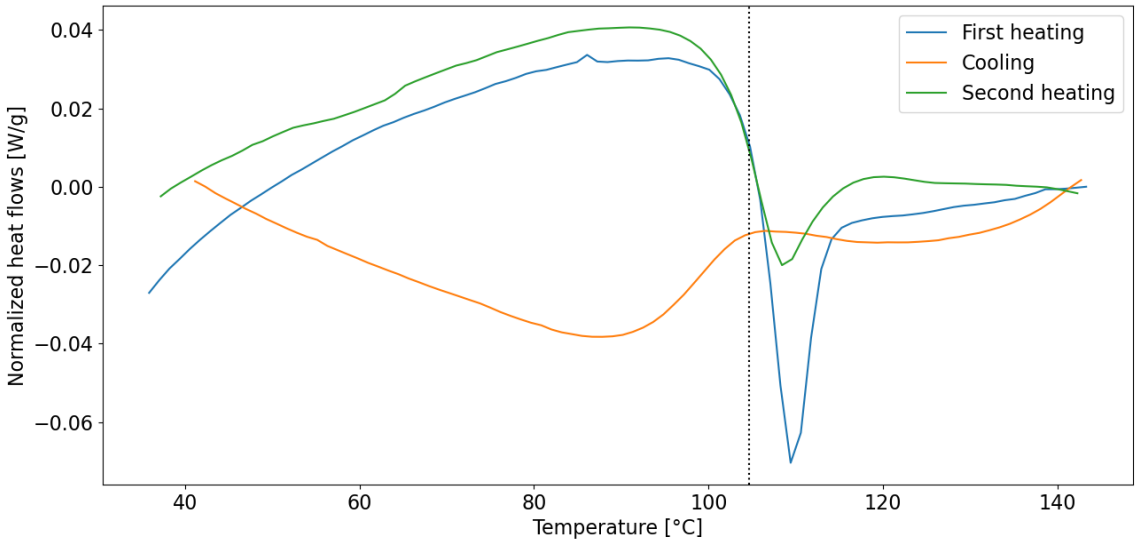

Figure 20: Normalized heat flow as a function of temperature.

The glass transition temperature of PS1160 is determined to be 104.6 ± 1°C.

4.2 Thermogravimetric Analysis (TGA)

The Thermogravimetric Analysis (TGA) measures changes in the sample weight of the polystyrene. By maintaining a temperature of 200°C for 3h, it is possible to detect material degradation, which may be useful for processing or for high-temperature experiments, since in the context of this master's thesis, it is necessary to work above the glass transition temperature.

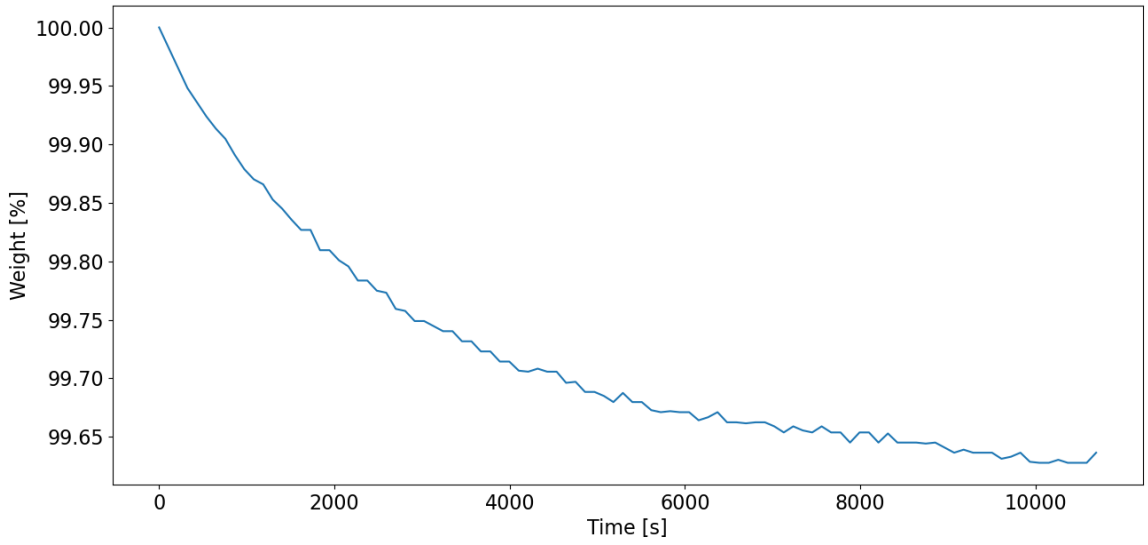

Figure 21: Degradation of the polystyrene at 200°C for 3h.

After 3h, the polystyrene mass decreased by around 0.35%. This is already a very small reduction, and the slope of the curve decreases over time, tending towards a final value. This decrease in mass is probably due to the presence of water in the atmosphere and on the sample.

Experiments and sample processing can therefore be carried out at temperatures of 200°C, minimal risk of degrading the polystyrene. Bearing in mind that the polystyrene will not be used at higher temperatures for more than 3 hours, there should not be degradation problems.

4.3 Gel Permeation Chromatography (GPC)

A Gel Permeation Chromatography analysis is done to determine the molar mass distribution of the polystyrene sample. This polystyrene has a polydispersity of 2.5, a number-average molar mass M_n of 81.45 kg/mol and a weight-average molar mass M_w of 200.2 kg/mol.

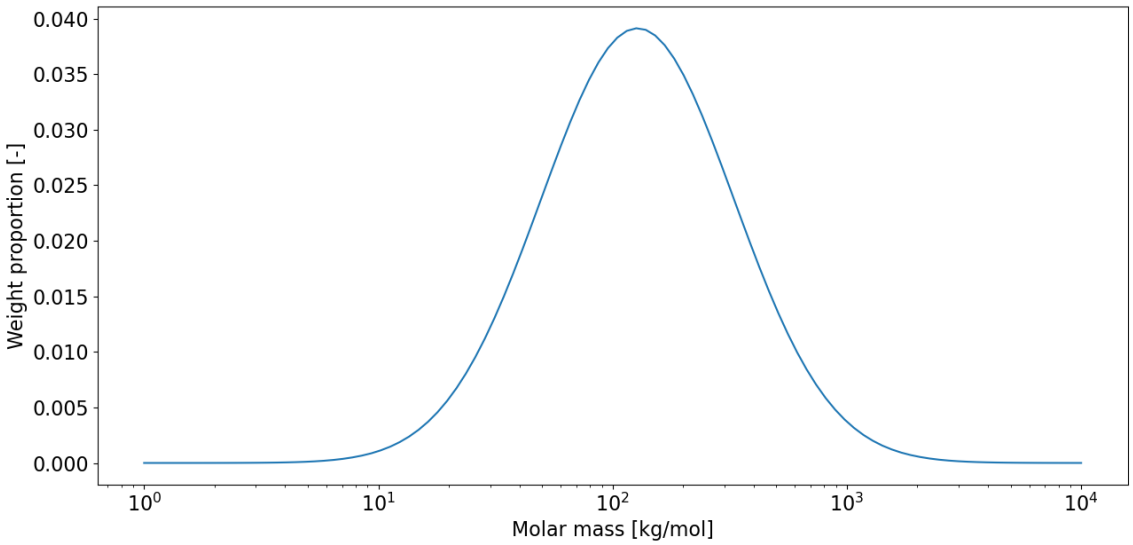

Figure 22: Molar mass distribution of PS1160.

As the polymer is polydisperse, it is interesting to plot the molar mass distribution using GPC data. The molar mass distribution is shown on Figure 22.

4.4 Rheometry Experiment

4.4.1 Experimental Data

The linear viscoelastic properties of polystyrene must first be determined to understand the material's behavior above its glass transition temperature. Several experiments ranging from 120°C to 190°C with an interval of 10°C are carried out. The data obtained are shown in Figure 23.

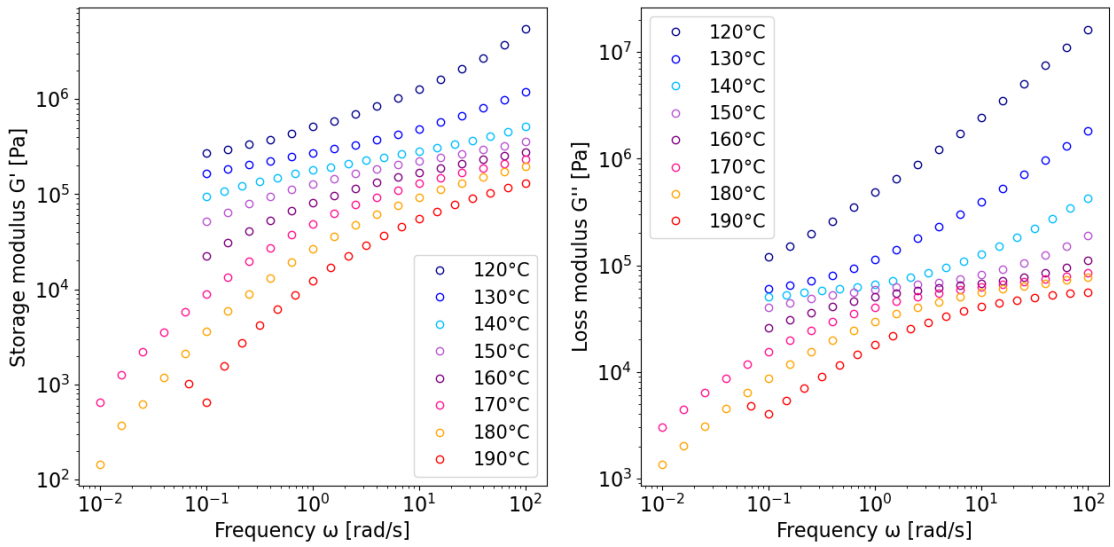

Figure 23: Experimental data for the storage and loss modulus from a SAOS experiment between 120°C and 190°C.

One of the data points at a frequency of 5.10^{-2} and a temperature of 190°C does not follow the trend of the curve, probably due to a very small error because it is performed at low frequencies and high temperature. For the rest of the analysis, data at 190°C will not be considered. Since experiments at temperatures of 170°C and 180°C are also carried out at frequencies lower than the other temperatures, down to a frequency of $10^{-2} rad/s$, the temperature of 190°C is not needed when the TTS is performed to see how polystyrene behaves at lower frequencies.

4.4.2 Time Temperature Superposition

The transformation of the raw data is done by applying the principle of TTS and shifting the data. Temperature-dependent shift values are obtained using the Williams-Landel-Ferry (WLF)

model, with $C_1 = 8.19$ and $C_2 = 89.53$, the values found in the literature for a specific reference temperature of 135°C [25].

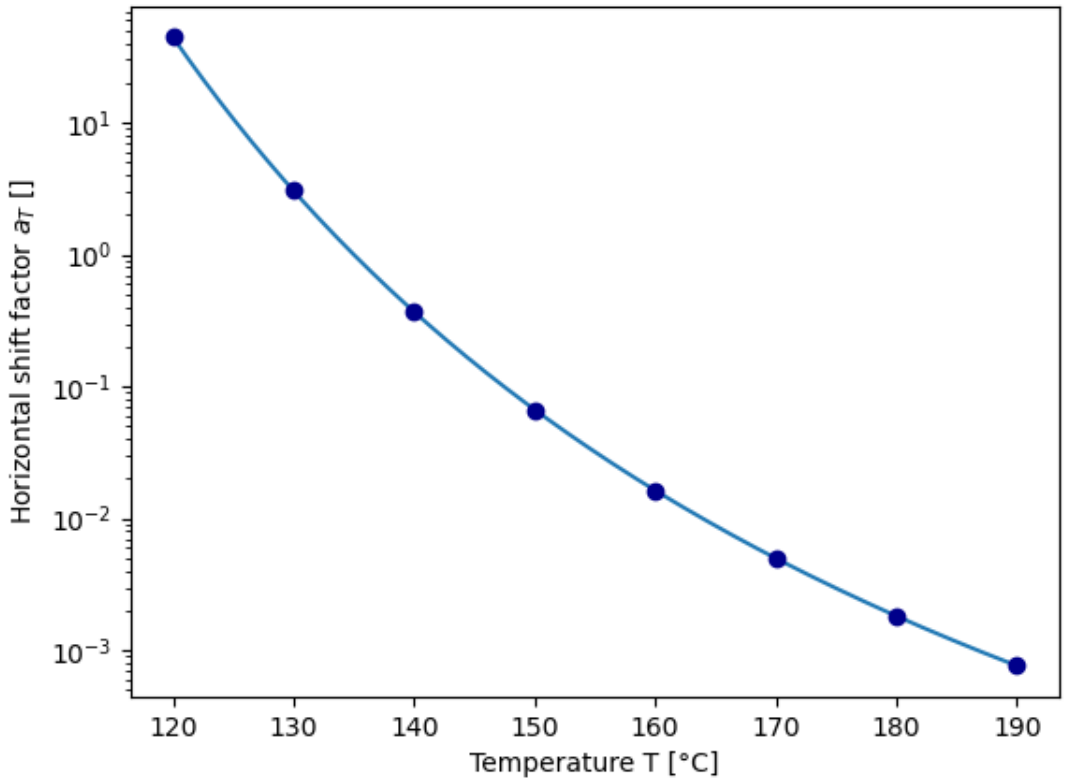

Figure 24: Horizontal shift factors.

By applying the right shift factor according to its temperature, it is possible to obtain the master curve for the reference temperature, as shown in Figure 25.

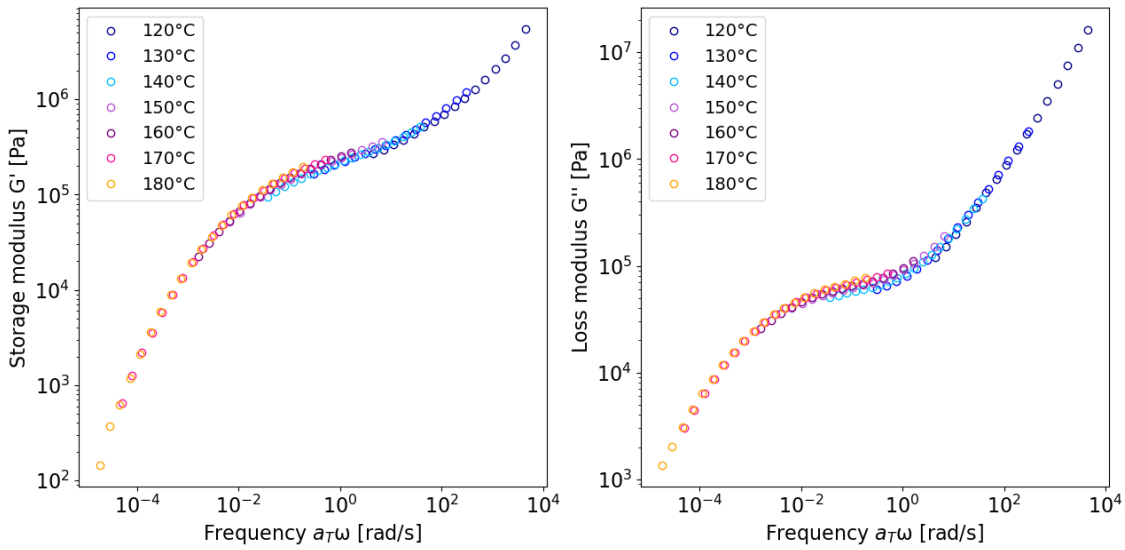

Figure 25: Master curve of the storage and loss modulus at a reference temperature of 135°C.

Firstly, it can be seen that the curves overlap almost perfectly at high temperatures (low frequency), whereas a shift is visible at intermediate and high frequencies. This discrepancy is probably due to the fact that this experiments is working close to the glass transition temperature, and that there may be other physical phenomena between the chains that come into account.

It is useful to look at the phase angle curve $\tan(\delta)$. The advantage of this curve is that possible vertical shifts appearing due to experimental problems are eliminated. This enables us to see the quality of the results obtained.

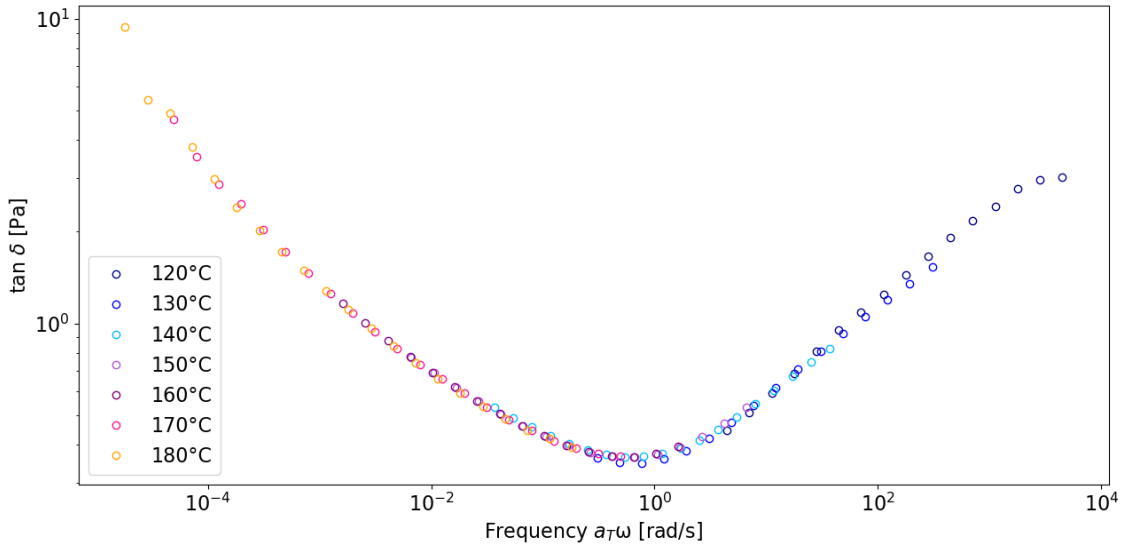

Figure 26: Master curve of the $tan(\delta)$ for the reference temperature of 135°C.

With the TTS method with the loss factor (see Figure 26), using the values at 135°C found in the literature. It is seen that the experiments are carried out with very good precision, since the different curves superimpose well. This is very good evidence of the quality of the results obtained at different temperatures. These results are useful to discuss the viscoelastic properties of the sample in the non-linear domain.

The TTS with the loss factor, *i.e.* $tan(\delta)$, highlights a good superposition of the curves (see Figure 26). One can therefore apply additional vertical shift factors on the data of the storage and loss moduli (G' and G'') to successfully align the curves (see Figure 27) and remove the discrepancies observed previously (see Figure 25).

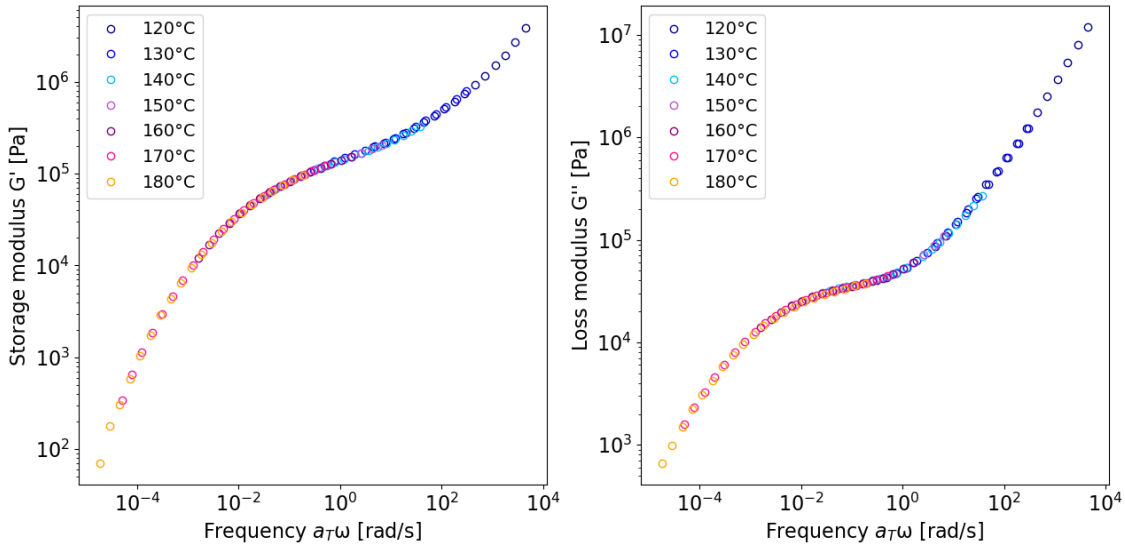

Figure 27: Corrected master curve of the storage and loss modulus at a reference temperature of 135°C.

4.5 Versatile Accurate Deformation Extensional Rheometer (VADER 1000)

Firstly, to see if the elongation results obtained with the VADER seem correct, the curves obtained with the small amplitude oscillatory shear experiment (SAOS) results are compared. Since the short time data of the elongation curves are always in the linear regime, the two curves should overlap before diverging when the elongating sample enters the non-linear regime. To achieve this, the master curve obtained earlier in Figure 27 needs to be transformed into a viscosity versus time curve, as detailed in Section 2.3. This gives the linear viscoelastic curve (LVE), which is the limit of the linear region.

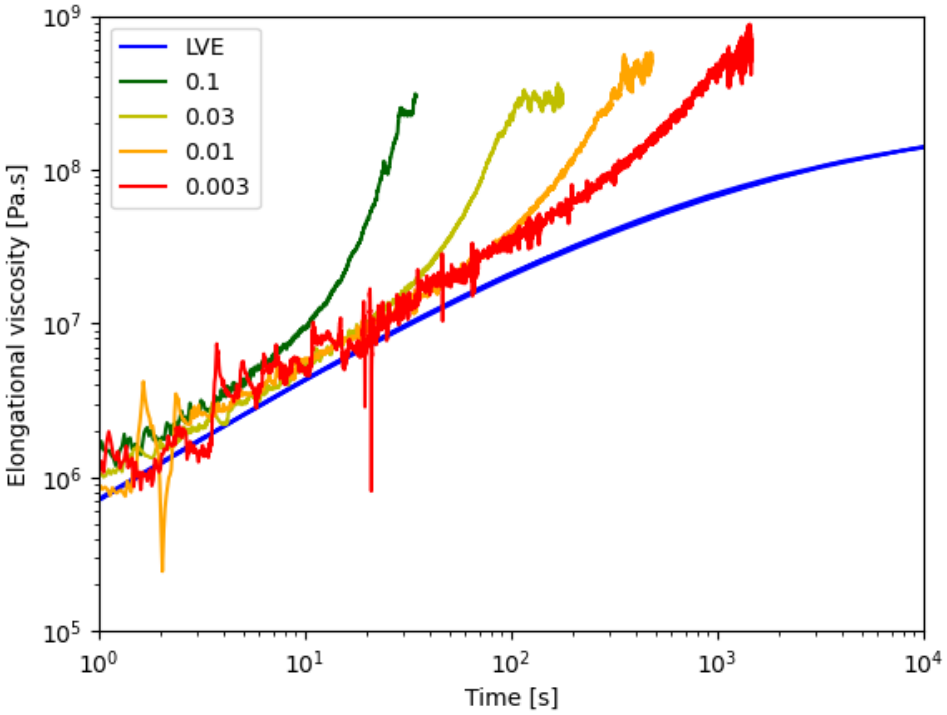

Figure 28: Transient response of PS1160 under elongational flow at 130°C for different strain rates of 0.1, 0.03, 0.01, 0.003 s^{-1}.

Therefore, it can be observed that the transient response follows well the linear envelope curve at short times, for all curves. The lower the strain rate, the longer the elongation curve superimpose to the LVE data. At higher strain rates, the elongation curves deviate more rapidly from the LVE curve, and their viscosity increases much more rapidly. This is expected, since the chains are

aligned and stretched much faster in the direction of traction, leading to higher transient hardening.

At the end of the experiments, the four curves show a strain hardening, which is rather important for a linear sample. Indeed, it is observed that this strain hardening reaches a higher viscosity value than at lower strain rate. This is attributed to the sample polydispersity, and in particular, to the presence of shorter chains.

These data are obtained for experiments carried out at a temperature of 130°C. It may therefore be interesting to compare them with other temperature ranges to see the possible effects of temperature. This comparison can be useful when it is known that a small difference in temperature in the field of rheology can lead to completely different results.

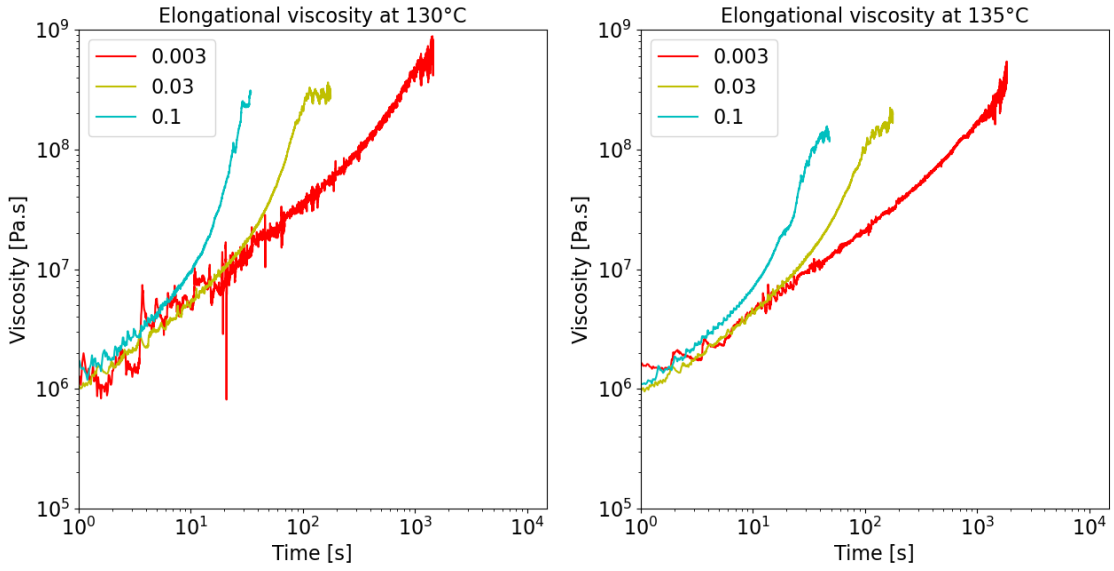

Figure 29: Transient response of PS1160 under elongational flow at 130°C and 135°C for different strain rates 0.1, 0.03, 0.003 s^{-1}.

When the transient response at 130°C is compared to the one at 135°C, a decrease in the maximum viscosity that the curves can reach is noticed. Strain hardening therefore occurs at a lower viscosity value as the temperature is increased, but strain hardening occurs at the same experimental time.

In order to compare the results obtained with the VADER and the tensile test machine, it may be interesting to see if it is possible to obtain consistent results with the VADER at temperatures

closer to the glass transition temperature. Experiments are therefore carried out at 125°C, *i.e.* around 20°C above T_g, if they could be obtained. The probability of delamination is greater, since polystyrene has poorer adhesion, but it is possible to carry out experiments at 125°C.

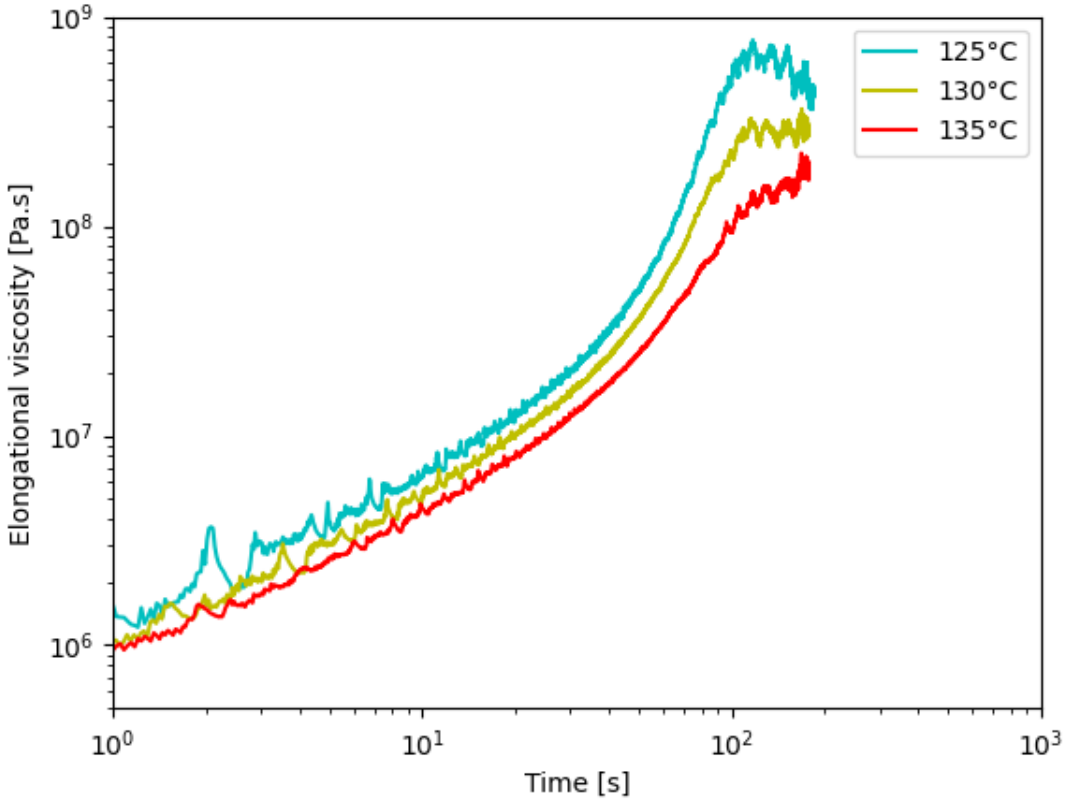

Figure 30: Transient response of PS1160 under elongational flow at 125°C, 130°C and 135°C at a strain rates of 0.03 s^{-1}.

Figure 30 shows the plot of experiments carried out at 125°C, 130°C and 135°C for a strain rate of 0.03 s^{-1}. The strain hardening always occurs at the same time which is in fact not expected, it is probably correct only if nothing can relax and the sample behaves as an elastomer. It can also be seen that the lower the temperature, the more strain hardening occurs at higher viscosity values.

With all the data obtained at different strain rates, but also at different temperatures, it can be interesting to bring them together in the same temperature range for comparison. The reference temperature chosen is 125°C. To achieve this, the curves at 130°C and 135°C are shifted. This

shift is applied not only to the time and elongational viscosity, but also to the strain rate applied during the experiment.

The shifted curves are plotted in Figure 31 below. The reference curve [E], at 125°C with a strain rate of 0.03 s^{-1}, is shown in purple. Curves in the orange-red range have an experimental temperature of 130°C, while the curves in the blue color range have an experimental temperature of 135°C. In the legend, in addition to the experimental temperature, the new strain rate calculated when moving from their base temperature to 125°C is shown.

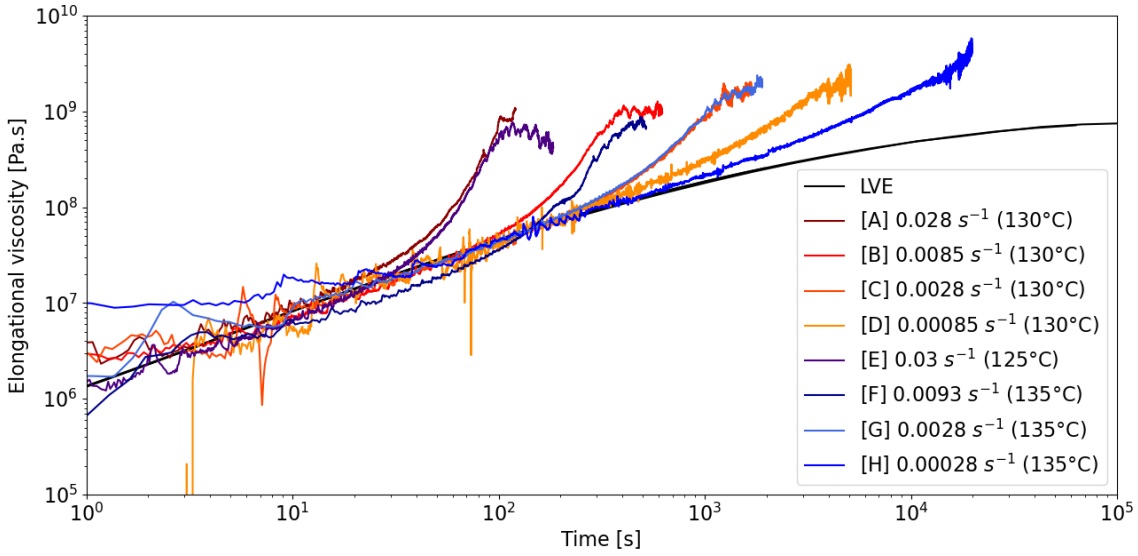

Figure 31: Transient response of PS1160 under elongational flow at 130°C, 135°C shifted at a reference temperature of 125°C, together with the unshifted data at 125°C.

For clarity, a table is provided for each temperature, the strain rate during the experiment and the strain rate calculated with the shift to 125°C for each curve.

N°	Experimental Temperature	Experimental Strain Rate	Shifted Strain Rate
A	130°C	0.1 s^{-1}	0.028 s^{-1}
B	130°C	0.03 s^{-1}	0.0085 s^{-1}
C	130°C	0.01 s^{-1}	0.0028 s^{-1}
D	130°C	0.003 s^{-1}	0.00085 s^{-1}
E	125°C	0.03 s^{-1}	0.03 s^{-1}
F	135°C	0.1 s^{-1}	0.0093 s^{-1}
G	135°C	0.03 s^{-1}	0.0028 s^{-1}
H	135°C	0.003 s^{-1}	0.00028 s^{-1}

Table 1: Values of the temperature, experimental and calculated strain rate for each curves of the Figure 31.

Starting by comparing the reference curve [E], it is observed that the curve with a strain rate of 0.1 s^{-1} at 130°C [A] overlaps with it. Their strain rate values are relatively close, with a difference of 0.002 s^{-1}. Nonetheless, it is notable that the plateau is slightly higher for [A] and less pronounced, as the strain rate is highest for this curve, and sample breakage occurs more quickly, preventing a well-defined plateau.

The F-curve is slightly lower than the B-curve, this F-curve also being performed at 0.1 s^{-1} but here at 135°C. The higher strain rate in this case could also be the reason for this lower value. Curves with a higher strain rate could have values that fit the other curves less, since it is more complicated to keep a constant high strain rate since the deformation is much faster.

Two curves overlap perfectly, C-curve and G-curve, respectively 0.01 s^{-1} at 130°C and 0.03 s^{-1} at 135°C. Their strain rate shifted to 125°C is also exactly the same, with a value of 0.0028 s^{-1}, demonstrating not only the validity of the data shift method between different temperatures, but also the validity of the results obtained. All this shift data provides a good basis for future comparison with tensile tests.

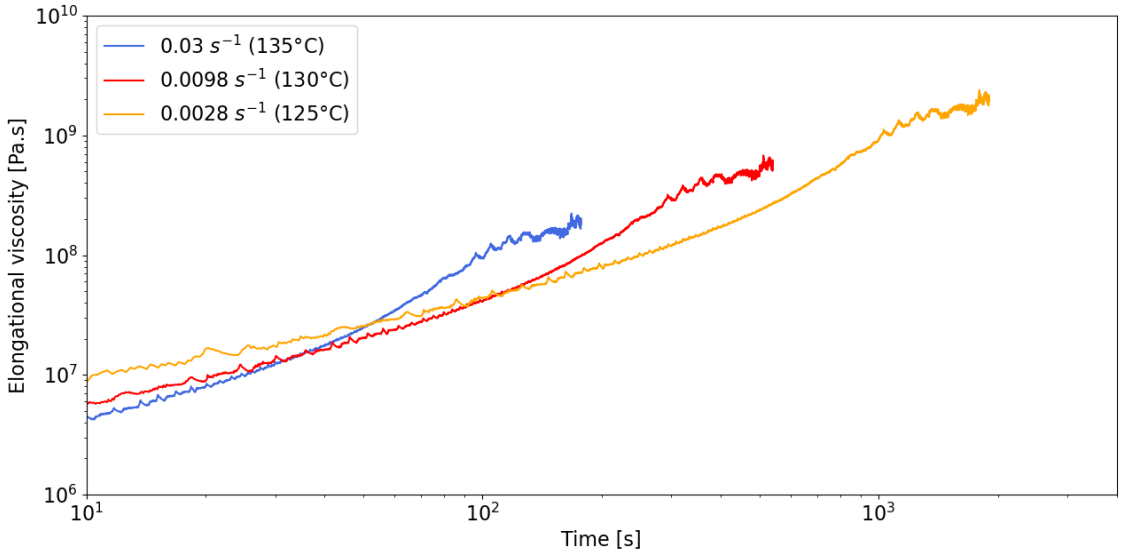

Figure 32: Transient response of PS1160 under elongational flow with original data at 135°C shifted to a reference temperature of 125°C and 130°C for a rate of 0.03 s^{-1}.

To better understand how the curves shift when the reference temperature is changed, it may be interesting to look at Figure 32. The reference experiment is performed at 135°C with a strain rate of 0.03 s^{-1}, this curve is then shifted to 130°C and 125°C. It can be seen that when shifted to lower temperature values, strain hardening appears at longer times and higher elongational viscosity. This means that for the same applied force, it is more difficult for the polystyrene to flow at 125°C than at 135°C. This is logical, since the same material have a higher viscosity at lower temperatures.

As the curves obtained in the tensile machine are stress versus strain curves, it is useful to represent the results in this form for a comparison between the two techniques. In Figure 33 and Figure 34, the effects of strain rate and temperature for true stress - true strain curves are analyzed.

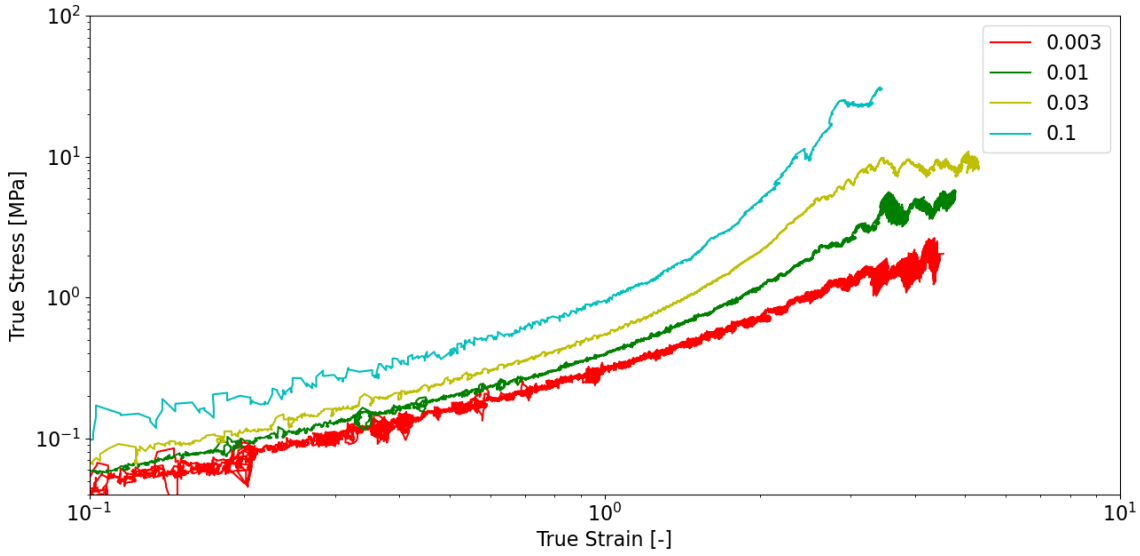

Figure 33: True stress-True strain curves of PS1160 under elongational flow at 130°C for different strain rates of 0.1, 0.03, 0.01, 0.003 s^{-1}.

The effect of the strain rate is compared in Figure 33, showing that when the strain rate is lower, the stress applied to achieve the same strain is lower. The faster the desired deformation for the polystyrene, the higher the stress that must be imposed. It is also observed that the strain rate at 0.1 s^{-1} does not reach a plateau at the end of the curve like the other strain rates. This could be due to the fact that the filament tends to break faster, since the stress applied is very high and the chains are stretched faster.

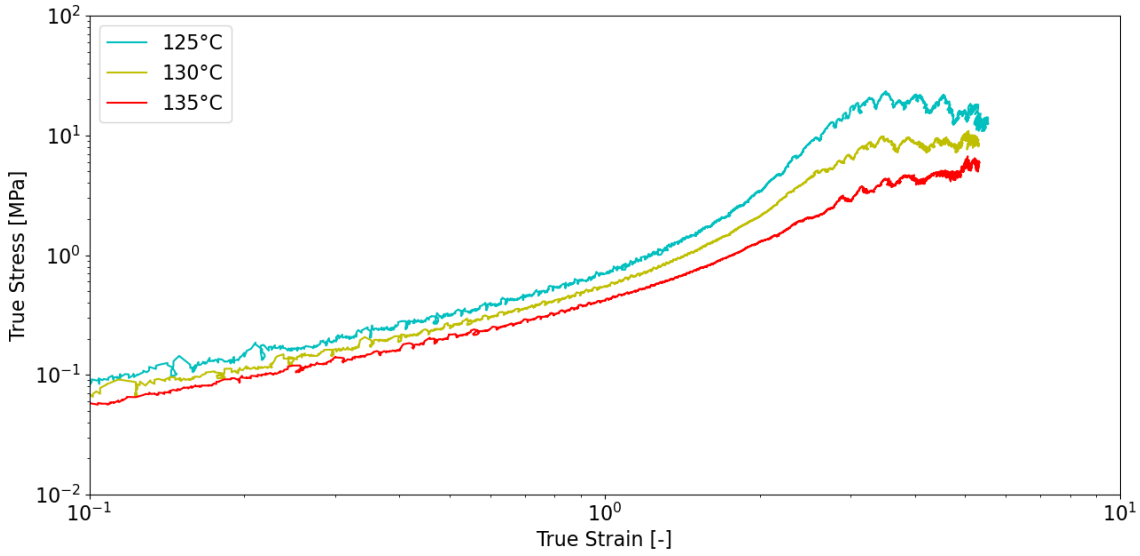

Figure 34: True stress-True strain curves of PS1160 under elongational flow at 125°C, 130°C and 135°C for a strain rate of 0.03 s^{-1}.

For the effect of temperature, data at temperatures of 125°C, 130°C and 135°C are compared in Figure 34. The curves show similar patterns, with a decrease in true stress as temperature rises, to reach the same value of true strain. This effect is due to the fact that, at higher temperatures, a lower stress must be applied because polystyrene is easier to deform, as it becomes less viscous and flows more.

4.6 Tensile Test

To be able to compare the tensile test with the VADER, it is needed to find a temperature compatible between the two techniques. At a too low temperature, the VADER causes adhesion problems between the polystyrene and the plates. In the case of the tensile test, however, at a too high temperature, the effects of flow and relaxation are likely to be too great, as the risk of the sample to slip out of the jaws.

But it may also be interesting to look at the behavior of polystyrene at temperatures below the glass transition temperature, as the tensile machine allows us to do so. Experiments will therefore be carried out, starting at room temperature (25°C) and rising to 100°C. At 100°C, the temperature is increased by 5°C between each experiment. The increase is only of 5°C because the temperature gets close to T_g, and so the impact of temperature is greater on the results. The aim would be to increase the temperature to at least 125°C (minimum value obtained from the VADER) and, in the best case, to 135°C. The experiments are carried out at a tensile rate of 50 mm/min. The experiments are run at least twice to check validity, and repeated more times if results are not reproducible. As the time required to produce the samples is very long, it is decided in advance to carry out a minimum of two experiments per set of conditions.

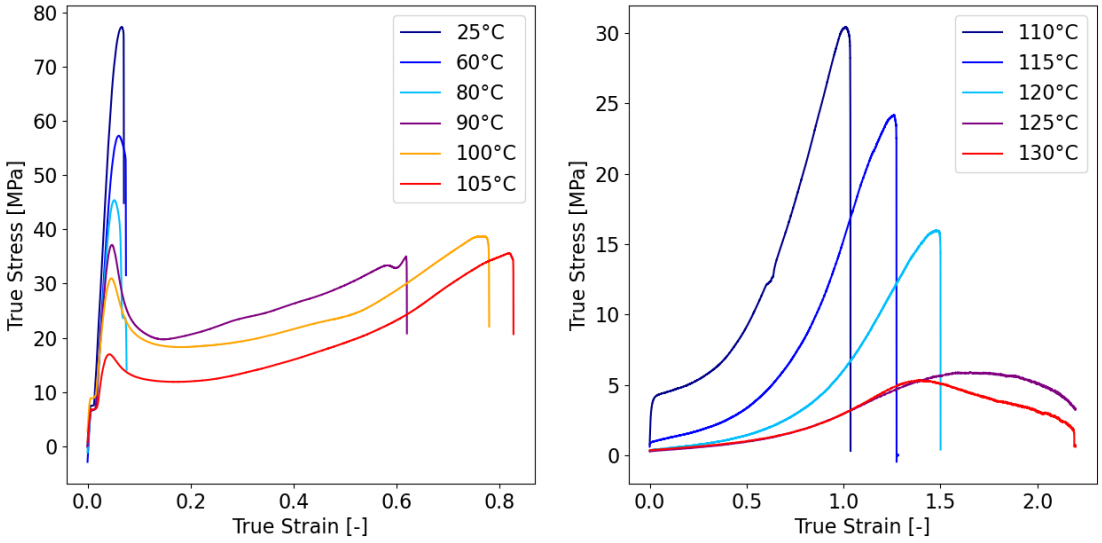

Figure 35: Tensile tests over a temperature range from 25°C to 130°C at a tensile rate of 50 mm/min. Left : Below T_g experiments. Right : Above T_g experiments.

First, by analyzing the curves below the glass transition temperature, it is observed that Young's modulus does not decrease much between the different curves, but remains more or less constant. On the other hand, the maximum value of yield strength decreases sharply with temperature, which means that the material enters plasticity or breaks at lower tensile values. However, plasticity does not occur sooner, as the maxima of the different curves are located at approximately the same displacement value. A smaller force must therefore be applied to reach the non-linear zone.

The main visible difference is the appearance of a plateau at 90°C. Below this temperature, the sample breaks before it can enter plasticity. Above 90°C, the material enters the plastic region before breaking. Just after the yield point, the stress decreases to a minimum, a phase known as strain softening. This is followed by a strain hardening phase, illustrated by an increase in the true strain. Material failure occurs at higher strains as temperature increases.

Then, for the curves above the glass transition temperature, it is noticed, as is expected, a completely different behavior. The linear zone is almost non-existent at higher temperatures, which means that at very low strain, polystyrene is almost directly in the plastic phase. Here, it is noticeable that deformation at the moment of failure is greater with increasing temperature, which is not the case below 90°C.

On the other hand, above 120°C, there is no fracture of the sample, which is due to the fact that the maximum deformation by the machine has been reached, and a larger oven would be required to reach fracture or also a higher rate. However, a different behavior is seen, with a drop in true stress, meaning that a lower force is required to obtain the same displacement. This behavior would be similar to strain softening.

The two curves at temperatures at 125°C and 130°C have a similar starting. However, the curve at 130°C decreases at lower strain. It may therefore be interesting to compare these data with data at intermediate temperatures, to see in more details the influence of temperature on the maximum true stress. But first, a defect in the curves is detected and will be detailed below.

At very short deformation, a shoulder is observed in the tensile curves. Figure 36 shows that this leads to a deviation of around 0.3 mm and occurs when the force reaches a value of more or less 60 N at temperatures below T_g.

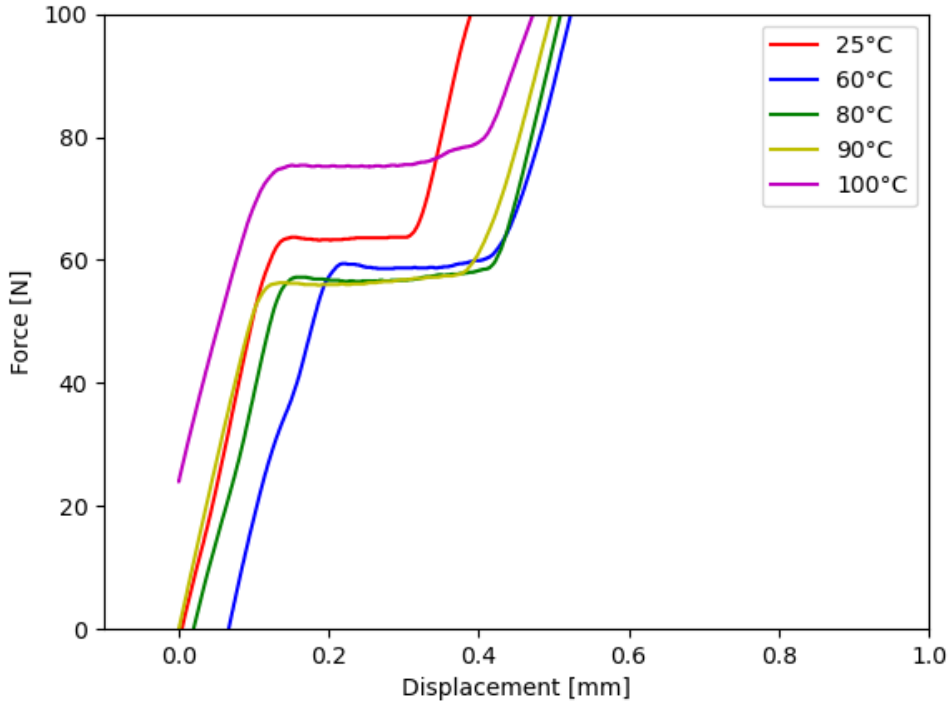

Figure 36: Zoom in on the shoulder detected at low displacements for temperatures below T_g.

Our first thought was to see if there was a problem with the tensile machine, such as a loose jaw or a calibration error. The force is noticed to be always around the same value of force of 60 N and a displacement of 0.2 mm. Looking above T_g, this shoulder is still observed at a temperature of 110°C, as shown on Figure 37. At this temperature, the force at which the shoulder occurs is still around 60 N but since it is above T_g, the displacement when the shoulder occurs is greater, above 20 mm. So this problem occurs when it exceeds a certain force, not after a certain displacement or experience time.

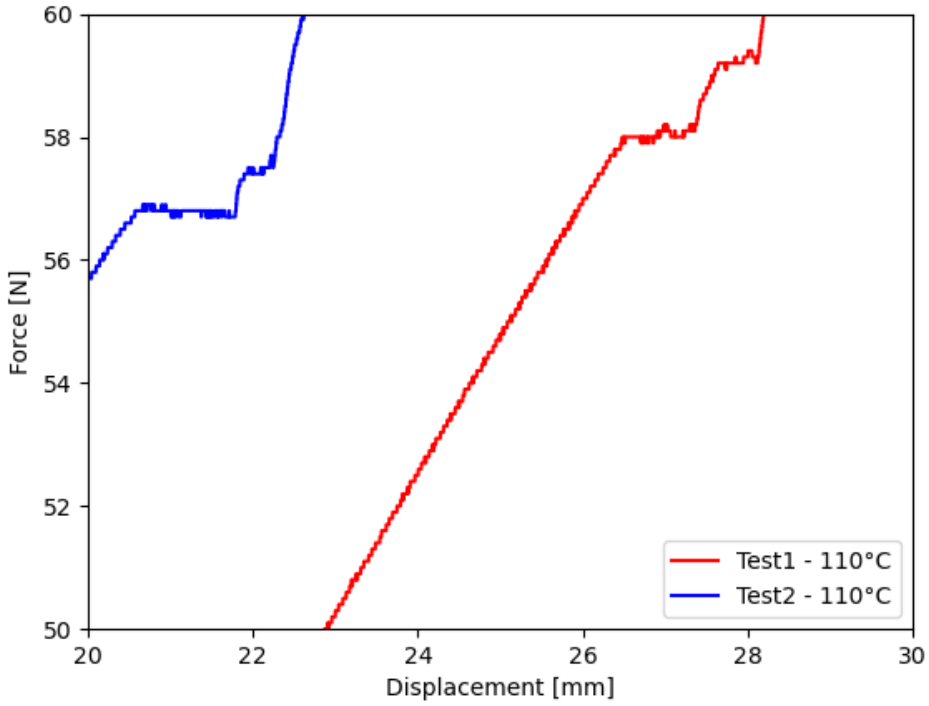

Figure 37: Zoom in on the shoulder detected for temperatures above T_g for two experiments performed at 110°C.

To avoid this deviation, a pre-force of 60 N was applied on the sample before the tensile test. Such protocol leads to more accurate results at short time. Nevertheless, although working at high temperatures (above T_g), this mechanical problem does not have a large impact on the data. This pre-force was applied from experiments at 115°C, which is why the shoulder is not visible from this temperature on Figure 35.

Another observation that is made at low temperature (below T_g), and which could have an influence on the mechanical properties of the sample, is that the dogbone fracture appears only at the bottom of the sample represented as the B side on the Figure 38. However, the test is still valid since the fracture occurs in the central part of the dogbone. In order to check that the problem is not related to the molding of the samples, the samples were flipped to have the top of the dogbone [A] in the lower jaw. But the fracture continued to occur in the lower part of the sample [B], and always approximately at the same place.

This phenomenon could therefore be due to the molding process, *i.e.* a defect in the mold, or in the suboptimal molding conditions under which defects are created at this precise point, leading to an increase in internal stresses in this area and hence to premature failure of the sample. At high temperatures, rupture is not observed at this precise location, probably due to the flow of polystyrene, so there should be no problems for future analysis above T_g.

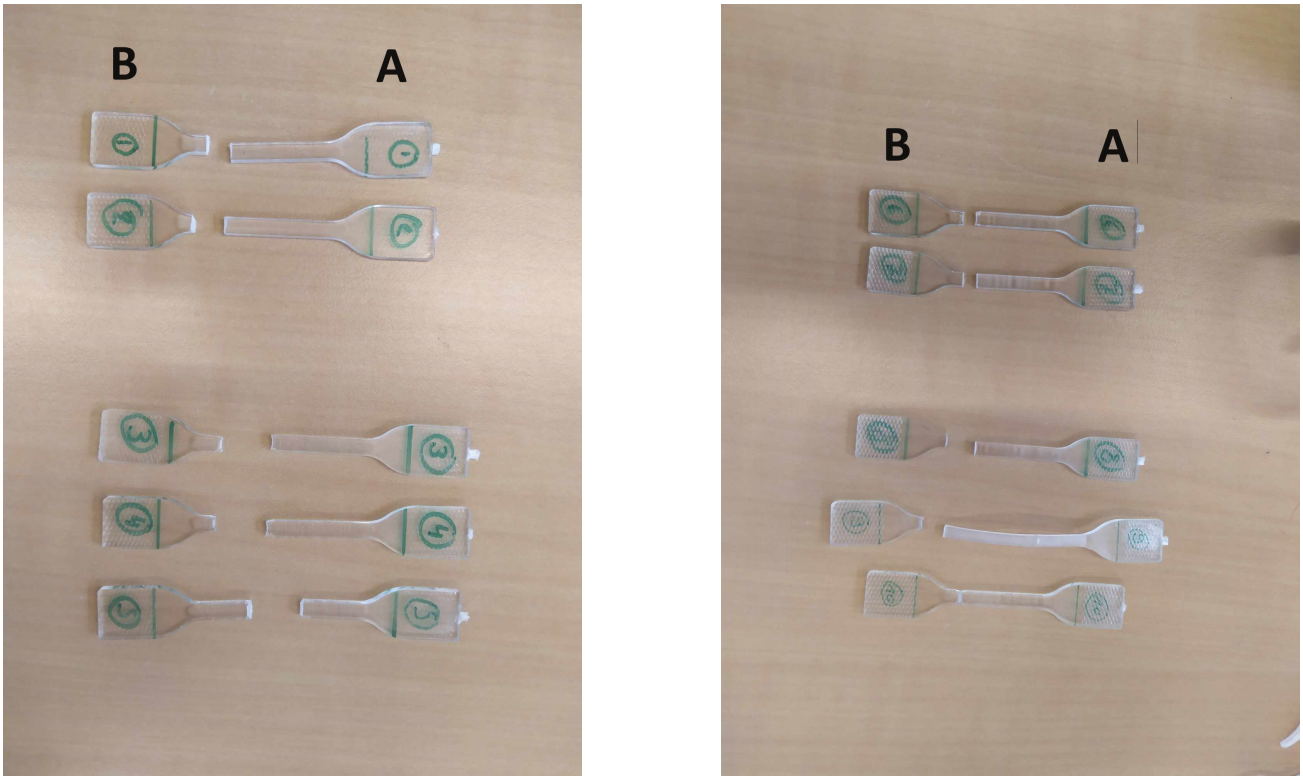

Figure 38: Recurrence of rupture in the lower part of the sample under T_g.

An experiment at 127°C is carried out to compare it with the values already obtained at high temperatures. As shown in Figure 39, the curves at 125°C, 127°C and 130°C are rather similar, contrary to lower temperatures at which large differences appear. Up to a true strain of 1.0, the curves at 125°C, 127°C and 130°C follow the same trend, and it is only above this value that the data slightly differ. It is observed that the curves at 125°C and 127°C follow the same trend, *i.e.* a decrease and a shift to the right of the curve maximum, as can be seen at lower temperatures. On the other hand, the curve at 130°C behaves differently from the other curves, reaching a maximum stress which is higher than at 127°C, located at a lower strain.

It can be concluded that at too high a temperature, it is more difficult to obtain curves con-

sistent with the rest of the experiments carried out. This may be due to the partial flow of the sample, which is held vertically for more than 10 minutes before starting the experiment.

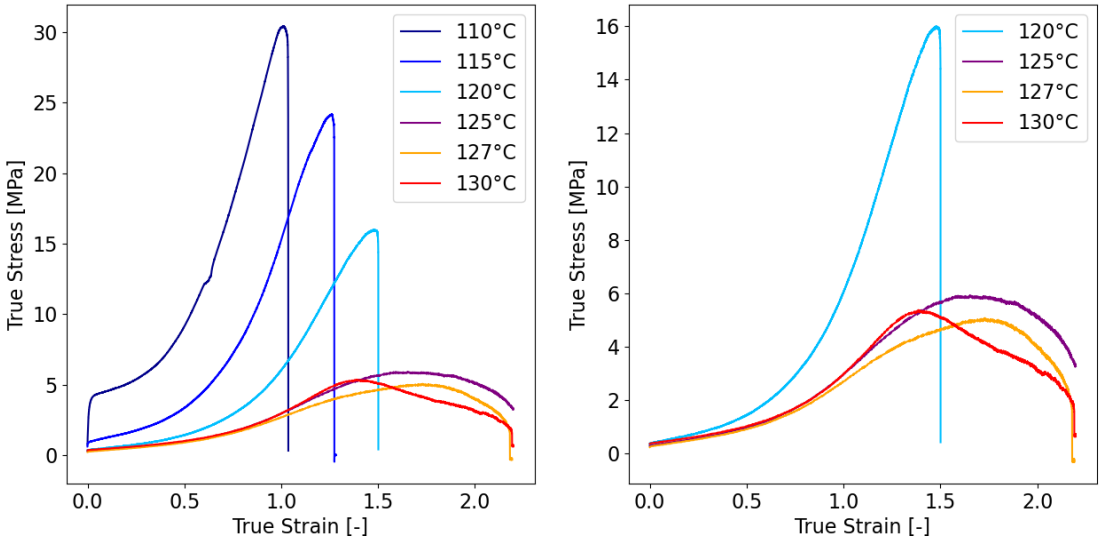

Figure 39: Tensile tests over a temperature range from 110°C to 130°C at a tensile rate of 50 mm/min.

The temperature of 125°C is the most interesting to analyze, since the sample does not break too early in the experiment, hence allowing a more accurate analysis of the transient response of the material. It also appears as the most appropriate value to compare the tensile test results with the elongational data obtained with the VADER. At lower temperature, the risk of sample detachment in the filament stretching rheometer is high. On the other hand, experiments at too high temperature in the tensile test lead to unexpected results, attributed to the sample flowing. Therefore, the temperature of 125°C is chosen as the temperature for comparison between the tensile test and the VADER.

Before moving on to the comparison between the two techniques, an analysis of the impact of tensile rate is carried out to further understand the behavior of polystyrene in tension. Different rates of deformation have been applied, at 125°C.

The data collected at different rates are taken with our first protocol of measurement, *i.e.* without waiting long enough at 125°C to ensure a homogeneous heating of the sample. Due to a lack of

time, it was not possible to carry out these experiments with the new protocol. Hence, the results can only be analyzed qualitatively.

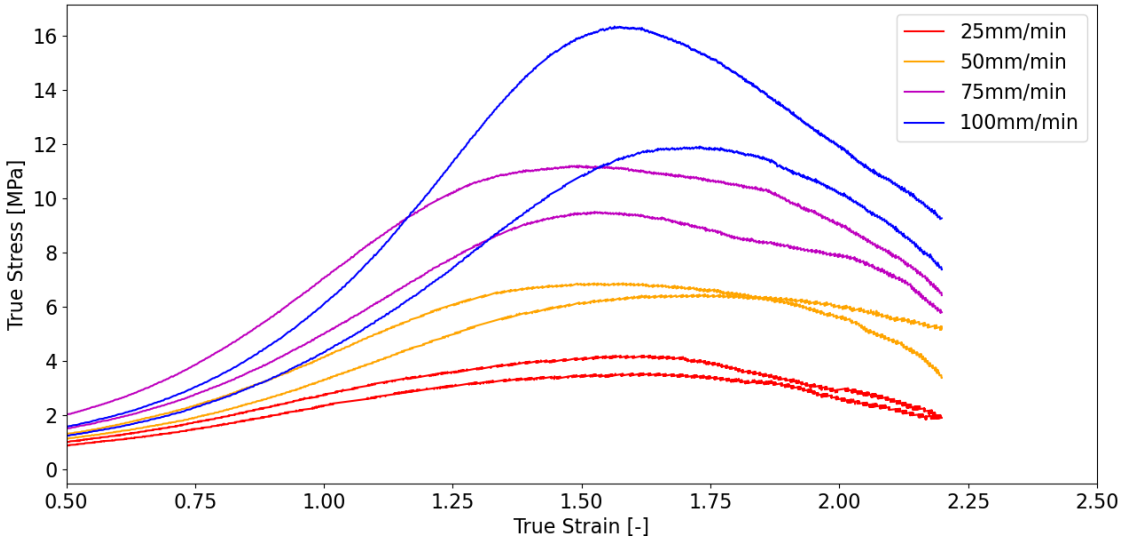

Figure 40: Tensile tests at different traction rate at 125°C.

Firstly, the higher the traction rate, the greater the maximum true stress, which is logical since the force applied to the sample is greater at higher rates. It is noticed that the gap between the curves at low rate are smaller than at high rate. This is interesting for the reproducibility of the results, as it is harder to obtain identical curves when the traction rate is too high. It is therefore preferable to work with a rate of 50 mm/min or 25 mm/min.

4.7 Comparison between elongation rheology and tensile test results

The aim of this section is to compare the two methods detailed in the previous sections. The temperature for comparison is set at 125°C, as this provides reproducible results for both methods. At too high temperatures, there is a lack of consistency in the data obtained in the tensile test. Whereas at lower temperatures, the adhesion between the VADER plates and the polystyrene is too weak, making it more difficult to obtain results.

It is interesting to compare the data obtained from the VADER and Instron experiments in a true-stress/true-strain plot. Figure 41 illustrates two respective curves at a temperature of 125°C. The Instron experiment (red curve) was performed at a speed of 50 mm/min, equivalent to an engineering strain rate of 0.03 s^{-1}. The VADER experiment (cyan curve) was carried out at a true strain rate of 0.03 s^{-1}. One observes that the two curves do not overlap. The VADER curve reaches a plateau at around 20 MPa, while the Instron curve shows a clear maximum at 6 MPa. These discrepancies are expected due to the differences in true strain rates (and Weissenberg numbers) between the two experiments, leading to variations in how the polymer chains are stretched. Indeed, in the Instron experiment, the Weissenberg number decreases over time, allowing for polymer relaxation during the test. Consequently, the maximum stress observed for the red curve is lower than that of the cyan curve. In the case of VADER, the Weissenberg number remains (almost) constant throughout the duration of the experiment.

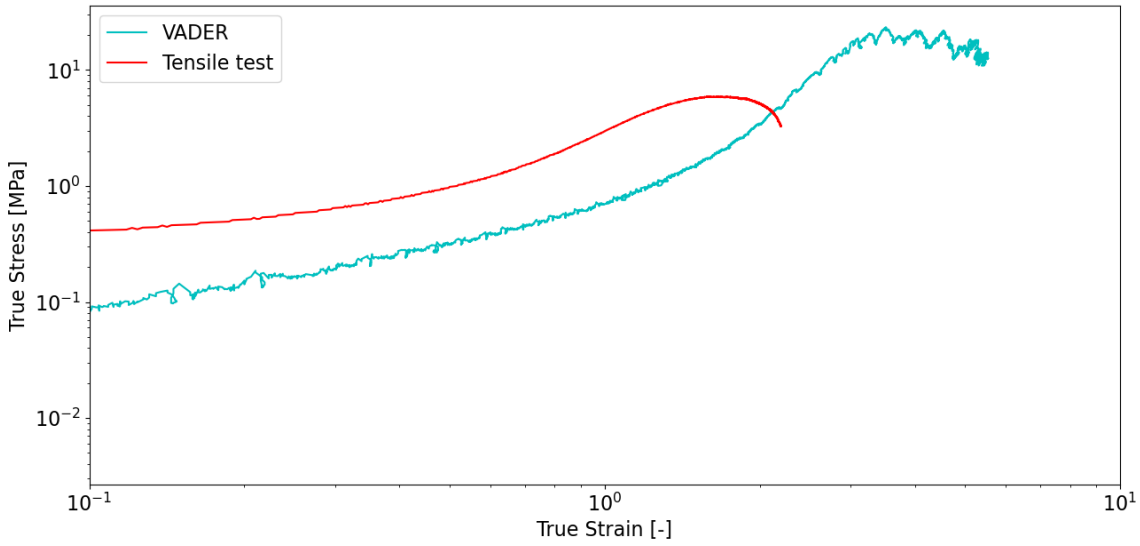

Figure 41: Comparison between VADER (true strain rate of 0.03 s^{-1}) and tensile test (rate of 50 mm/min) at 125°C.

As indicated in Section 2.5, we proposed a new method of measurement for the tensile tests, which would allow a direct comparison with the rheological data. This method has been discussed with the manufacturers of the tensile machine (Instron), to be implemented in their instrument. This was achieved very recently.
While no conclusion can be drawn at this stage, a first test with the new velocity profile imposed to the tensile machine led to similar stress-strain curves as the ones obtained with the VADER.

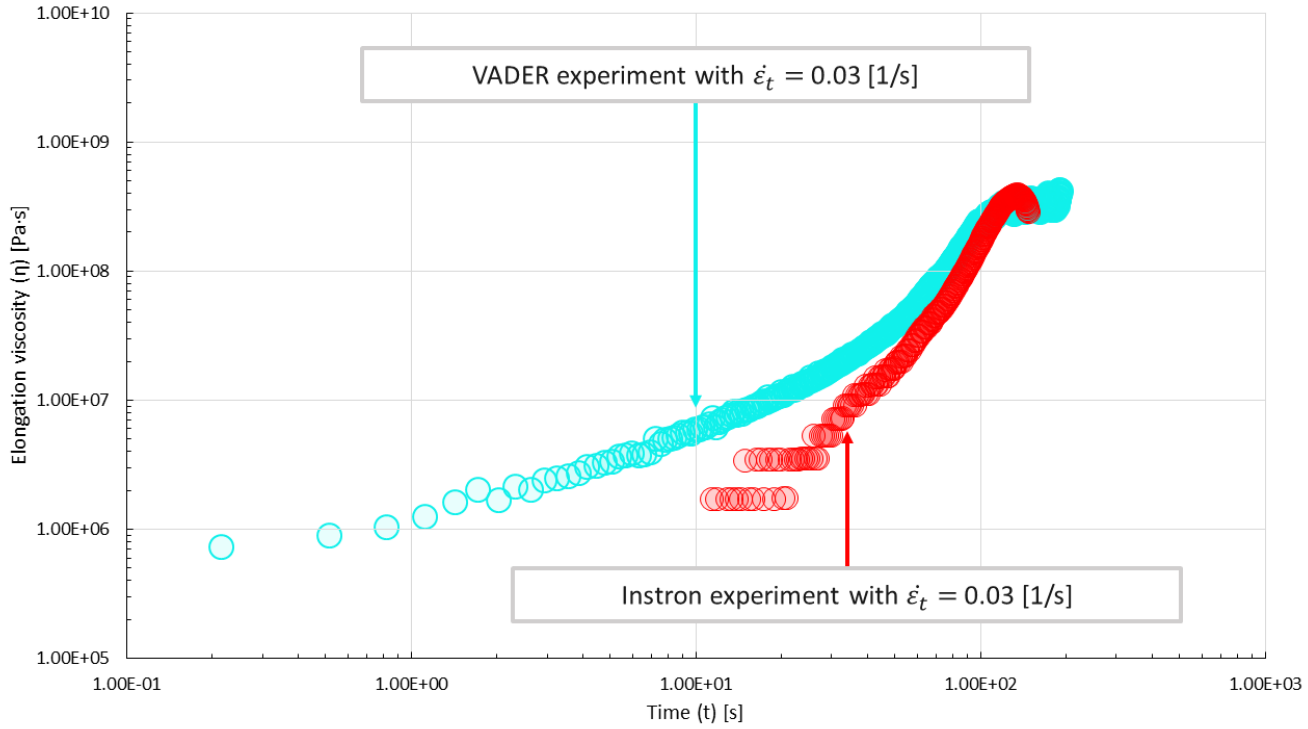

Figure 42: Comparison between VADER and tensile test at 125°C with a true strain rate applied in the two techniques. These experiments have been performed by Alexandru Tudor Boborodea.

A first preliminary result is shown in Figure 42, based on this new method, at a true strain rate set at 0.03 s^{-1}. The resulting curve was compared with the curve determined using the VADER. One observes that the two curves are in good agreement, as they display similar trends and converge at the same value for the maximum elongation viscosity. Interestingly, the maximum elongation viscosity achieved with the Instron method appears to be more precisely defined compared to the VADER curve, which shows some data noise that renders the determination of the steady-state value a bit difficult.

Hence, this step is important as it opens a new road to bridge rheological and mechanical response of a viscoelastic material. In particular, this allows us to apply rheological models to analyze the tensile data, from high temperatures towards lower ones, not accessible with a rheometer.

5 Conclusion and perspectives

The elongation flow of polymers plays a very important role in certain applications and in industry. But the behaviors that take place in the non-linear elongational regime are highly complex and not yet as well understood as the phenomena that take place in the linear regime. The primary objective was therefore to study a polymer in the non-linear elongation regime. This polymer is a polydisperse linear polystyrene (PS1160). The elongation study of polystyrene is carried out using two different techniques, namely rheology and mechanical tests. The final objective is to see if it is possible to compare the results obtained with these two different techniques.

The sample was first characterized based on the small amplitude oscillatory shear experiment (SAOS), *i.e.* in the linear regime of deformation. Once the data were obtained, the master curve of the sample could be successfully performed using the TTS principle with the Williams-Landel-Ferry (WLF) model.

The rheological study of polystyrene under non-linear elongation was achieved using the VADER. This has enabled the analysis of the transient response and strain hardening of the polystyrene. The dependence of the elongational properties on strain rate and temperature was rationalized. These two parameters influence the time at which the steady state is reached and the maximum elongational viscosity value of the polystyrene. The VADER data were validated using the data obtained in the linear regime and the Trouton's rule to obtain the linear viscoelastic curve (LVE).

The mechanical properties of polystyrene were then analyzed using a tensile test machine. This machine was used to study tensile behavior from room temperature up to 130°C. The influence of engineering strain rate and temperature was investigated, to determine their impact on the mechanical behavior of polystyrene. A method of analysis at 125°C was developed to maintain the homogeneity of the temperature gradient, while avoiding the sample to be heated for too long at high temperatures, which could lead to flow.

The final objective is to use the data collected with the VADER and the tensile machine to compare these methods and link the results obtained with a rheological and mechanical method. A method of implementation was therefore discussed with Instron (designer of the tensile machine) to enable a true strain rate to be imposed.

To continue this project, several points and experiments could be interesting to realize. Firstly, it

is possible to find a more optimal technique to improve the production of samples for the tensile machine. Since the injection molding method is long and tedious, with a non-negligible percentage of failures due to burnt polystyrene or lubricant, or to the presence of bubbles. It may be possible to use a press heated at high temperature. Then, with more samples produced, it would be possible to check the validity of the results by carrying out five experiments per parameter's set.

The discussions with Instron to find a method for analyzing samples with a true strain rate are finished, but there was not enough time left to test this approach. Such comparison will be performed in the near future. To take the subject, it may also be possible to study polystyrene with impurities to see the effects on mechanical and rheological properties.

This in-depth characterization of the rheological and mechanical properties of a polystyrene sample, has also highlighted a series of possible experimental issues, which have been solved all along this work, to provide a 'standard polystyrene' to use as reference in the rheology lab.
With the proposition of a new measurement protocol for the mechanical test, this work opens the door towards the investigation of the mechanical properties of a viscoelastic sample, based on a rheological point of view.

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