Temperature dependence of viscosity of non-Newtonian materials

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Introduction

A knowledge of rheological properties is of importance in processing, handling, process design, product development and quality control. During these two months of internship, I took an interest in temperature dependence of rheological behavior of non-Newtonian Material. The work was divided in two parts. For a first period, by studying a classic rheothinning material, toothpaste, I tried to find a generic model for the temperature dependence of viscosity. The second part of the work was about strain gage adhesives in cooperation with the Federal Institute for Materials Research, the aim was here to learn about the rheological behavior of the material and to connect the results with the industrial applications.

1. Rheology

Rheology is the material science of amorphous matter with viscous behavior. The response of the material can be measured with a rheometer, which is necessary to obtain a material model (cf. 1.2).

1.1. The rotational viscometer

The measurements have been performed with the rotational viscometer shown in Figure 1.

Figure 1: The rotational Viscometer

The material to test is placed in between two rotating plates. The device shears the material by controlling the angular velocity or the torque, and so we can study the evolution of the shear stress with the shear strain rate. The upper plate is turning, the bottom plate is fixed and can be heated from -20°C to 180°C. The plate is cooled by an external water supply. A compressed air system prevents frictions.

This device allows studying the rheological behavior of pasty material and its temperature dependency.

Liquid materials cannot be measured using this method, as it would not stay in-between the two plates.

Different types of viscometer

Two types of rotational viscometer are available in the Laboratory:

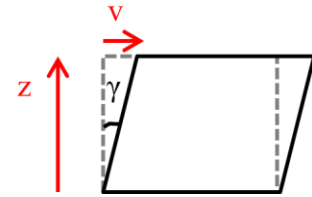- Parallel-plates viscometer
- Cone-plate viscometer

Figure 2: Pure shear test

For a purely sheared material, the angular shear strain γ (cf. Figure 2) is defined as follows:

$\tan(\gamma) = \dfrac{v\Delta t}{z}$, which implies when γ is small (approximately less than 5°C): $\gamma \approx \dfrac{v\Delta t}{z}$.

Hence the angular shear rate can be written: $\dot{\gamma} = \dfrac{v}{z}$.

Cone-plate viscometer: [1]

In the case of a cone-plate viscometer the upper plate, the upper plate is moved and has the shape of a cone and the bottom plate is fixed with a flat shape:
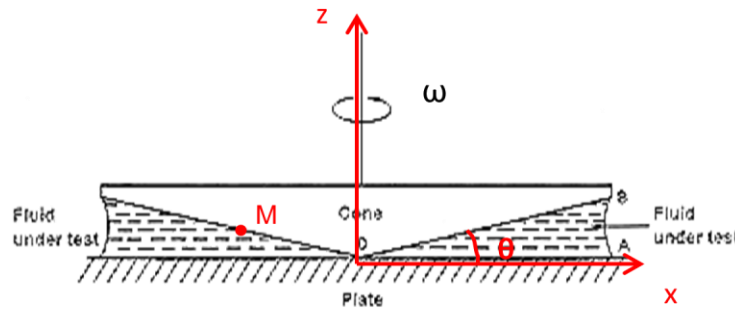
Figure 3: Sketch of a cone-plate viscometer

The angular shear rate is thus written: $\dot{\gamma} = \dfrac{v}{z} = \dfrac{x\omega}{x\tan(\theta)}$, and when θ is small: $\boxed{\dot{\gamma} \approx \dfrac{\omega}{\theta}}$.

So for a cone-plate viscometer, we have the same shear rate for any point M on the cone. That is of interest, since we want to measure one shear stress versus one shear rate at each instant.

However, for some very stiff materials, the cone may induce some shaping problems. We must also make sure that θ is small, in order to limit the edge effects.

Parallel-plates viscometer:

In the case of a parallel-plates viscometer, the sample is placed between the two plates and the angular shear rate can be written: $\boxed{\dot{\gamma} = \dfrac{v}{z} = \dfrac{x\omega}{d}}$
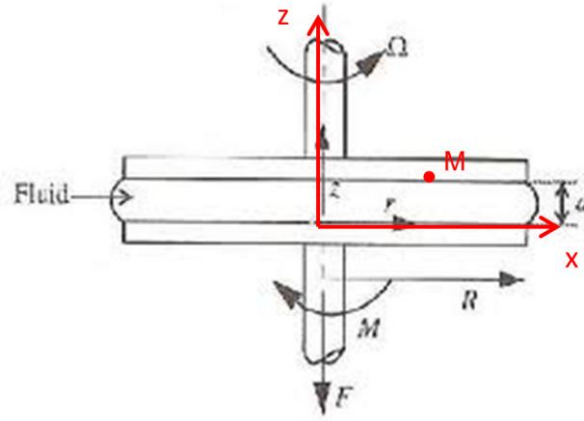
Figure 4: Sketch of a plate-plate viscometer

Thus on the upper plate, we have an angular shear rate ranging from 0 in the center to $\dfrac{R\omega}{d}$ at the edge.

For this reason is the cone-plate viscometer better than the parallel-plates viscometer. However we will have to use the parallel-plates for some stiff materials. Then it is better to choose a small R, so that the shear rate range is not large.

1.2. Rheological models

For a Newtonian material, the viscosity is defined as follows: $\sigma_{ij} = \mu d_{ij}$, where (σ_{ij}) is the stress tensor and (d_{ij}) is the velocity gradient tensor.

Here we assume that we have a two dimensional problem with only a shear force and strain. Thus the strain and velocity gradient tensor have the following form:

$$\sigma = \begin{pmatrix} 0 & \sigma_{12} & 0 \\ \sigma_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad d = \begin{pmatrix} 0 & d_{12} & 0 \\ d_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \text{where } d_{12} = \frac{\dot{\gamma}}{2}.$$

Since σ_{12} depends solely on the d_{12}, we will be able to use one-dimensional models.

Newtonian materials:
A Newtonian material is a purely viscous material with a constant viscosity. The stress depends then only on the strain rate and the viscosity μ is defined as follows: $\boxed{\sigma_{12} = \mu d_{12}}$.

Non- Newtonian materials:
The studied materials are supposed to be viscoelastic. Under a defined yield stress they behave like elastic solids. From this yield point, they flow like viscous non-Newtonian fluids, i.e., with a velocity dependent viscosity.

For those materials, we can define an apparent viscosity using the following models (for instance):

- Herschel-Bukley model [2]: $\boxed{\sigma_{12} = \mu (d_{12})^{n} + \tau}$

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- Ziegler Arctan model [3]: $$\sigma_{12} = \mu' d_{12} + \frac{2\tau'}{\pi} \arctan(\frac{d_{12}}{n'})$$,

where µ, µ', τ, τ', n, n' are constant parameters independent from σ_{12} and d_{12}.

A non-Newtonian material can be either rheothickening (i.e. it stiffers as the strain rate increases) or rheothining (i.e. it softens as the strain rate increases). Most non-Newtonian materials are rheothining and that will be also the case of the materials we will study.
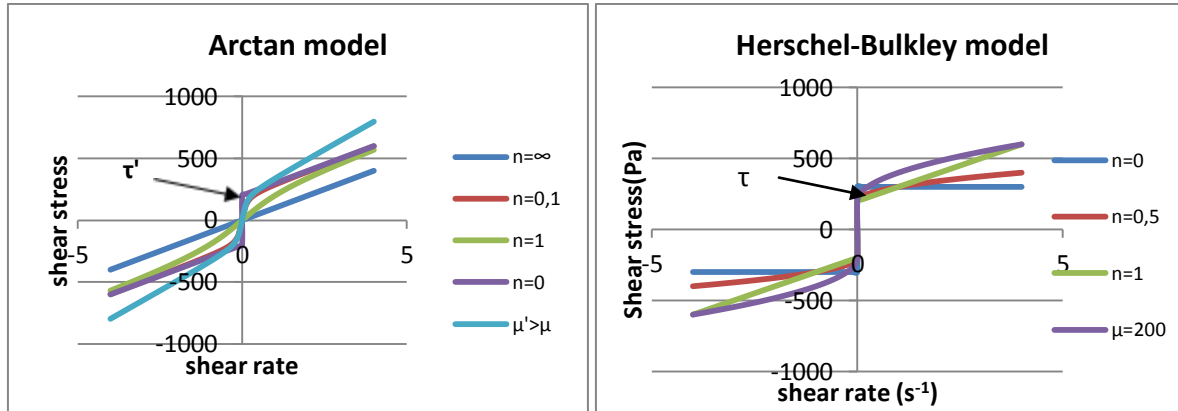
Influence of parameters:

Figure 5: Influence of parameters for the two models

In both cases, n is playing on the curvature, μ on the slope of the viscous part. For the Herschel-Bukley model, the material is rheothinning when n is between 0 and 1, and rheothickening when n is superior to 1. The Arctan model is only valid for rheothinning materials. The stress τ can be defined as a kind of yield stress. So by studying μ and τ evolution, we can expect to be able to quantify respectively the viscous and elastic moduli of the material.

1.3. Different experiments

1.3.1. Flow test

A flow test consists in imposing a ramp of stress (resp. strain rate) and measuring the strain rate (resp. shear stress). It is easy to fit the results (cf. 2.) of this test with the aforementioned models. Flows test are very easy to proceed and interesting for viscous and time independent materials. In the others case, we have to mind the fact that we also impose an increasing shear strain on the sample. For the material suited here, it may not be a problem as far as we have only viscoelacticity and no vicoplasticity. If we have a viscoplastic material, strain hardening can also happened. If the material is time dependent, we have the duration of the experiment can change the results.

1.3.2. Creep tests

A creep test consists in imposing and holding a constant stress during a given period of time on the sample and measuring the strain.
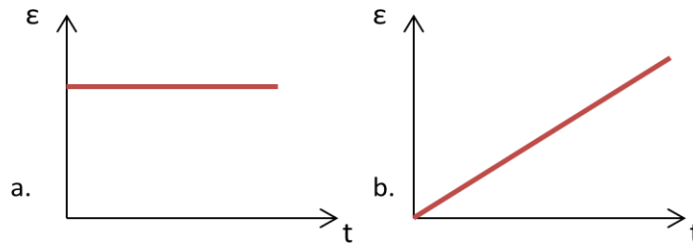
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Figure 6: Responses to a creep test for a purely elastic or plastic material (a.) and a purely viscous material (b.)

For a purely elastic or plastic solid, we would measure a constant strain, for a purely viscous fluid, a constant strain rate. This test is mainly useful to study time effect in the behavior of the material.

1.3.3. Oscillatory test

We give in input a shear strain $\gamma = \gamma_0 \sin(\omega t)$ on the sample. The shear rate can be written $\dot{\gamma} = \gamma_0 \omega \cos(\omega t)$.

Let us then define G' and G'' as $\sigma = \gamma_0 (G' \sin(\omega t) + G'' \cos(\omega t))$, we have thus : $\sigma = G'\gamma + \dfrac{G''}{\omega}\dot{\gamma}$.

For a purely elastic material, $G'' = 0$ and $G' = G$. For a Newtonian material, $G' = 0$ and $G'' = \mu\omega$.

For an oscillatory test, we can impose a sinusoidal strain to the sample with a constant amplitude γ_0 and a ramp of frequency ω and we get in output the two modulus G' and G'' vs. the frequency. This method is thus useful to separate the elastic response of the material (which can be studied with G') from the viscous response of the material (which can be studied with G'').

1.4. Quick tutorial for the utilization of the device

1.4.1. Test procedure
- Open the air pressure and the water cooling system before switching on the central unit.
- Software : TA Instrument
- Checking the plate geometry. To create a new one, click Geometry->New…
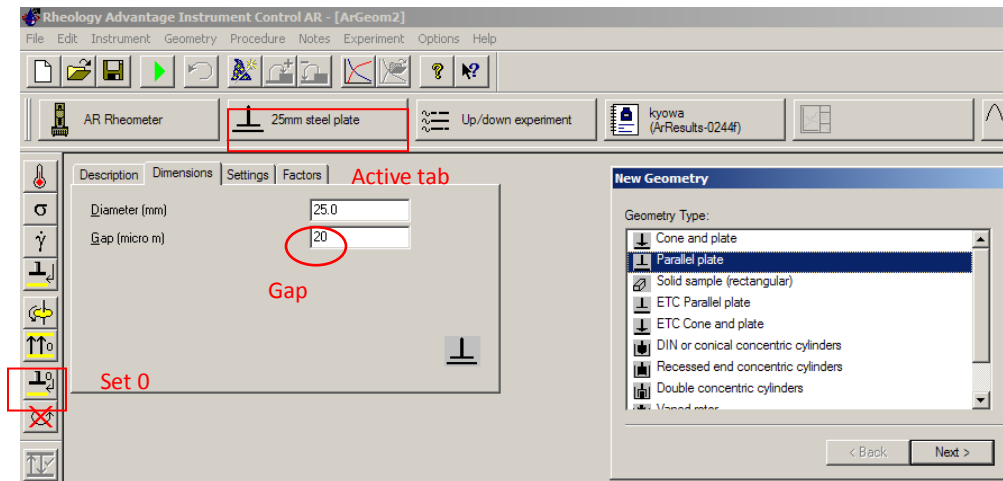

Figure 7: Setting of geometry

The gap (cf. Figure 12) entered as the parameter of the geometry has to match with the thickness of the sample. It will be used by the software to calculate the shear rate from the angular velocity.

It is possible to save and open geometries.

- Set the zero gap before putting the sample.

- Open an existing procedure or create a new one.
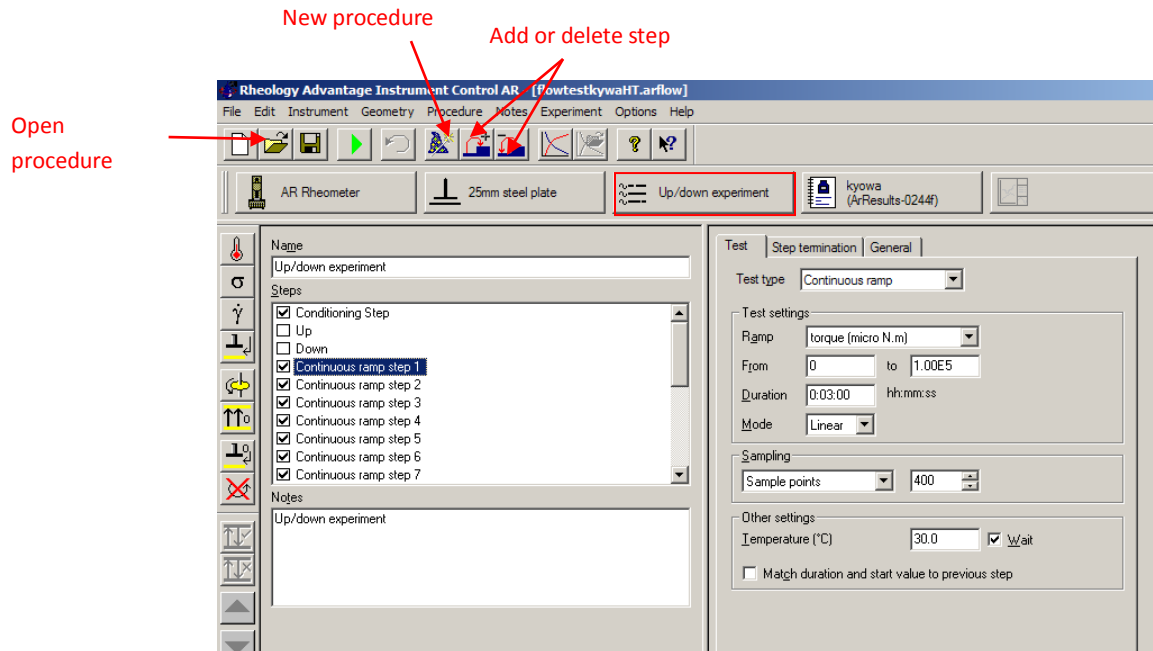
Figure 8: Creation of procedure

It is possible to add and change steps even when the experiment has been run.

- o Flow procedure: torque, shear stress, angular velocity and strain rate can be imposed.
  Maximum torque: 1E5 Nm .
  Maximum angular velocity: 100 rads^{-1} .
- o Creep procedure: Shear stress and torque can be fixed.
  The case "terminate on equilibrium" is checked by default. In this case, the experiment stops when strain gets linear vs. time, before the end of the indicated time.

- Once the experiment is launched, one can abort the procedure or only the current step which launches immediately the following step.
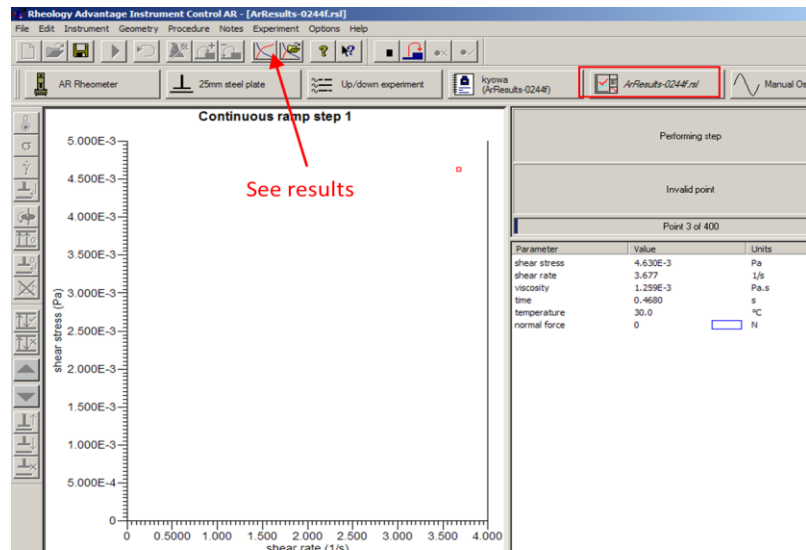
Figure 9: Experiment

- The Data Analysis software enables to get the data sheet and plot the curves.
- Data can be marked (Ctrl+A) and copied (Ctrl+C) to a spreadsheet program (Ctrl+V).
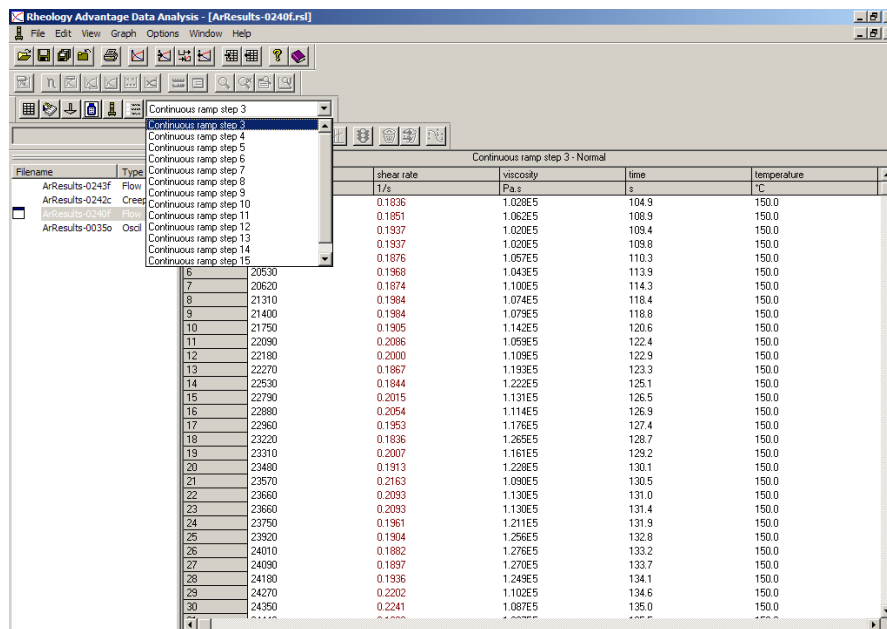
Figure 10: Data analysis

1.4.2. Tricks and notes

- The parameter controlled at best by the device is the torque. When we have to come close to the limits of the device, it is better to control the torque than the angular velocity, the shear rate, or even the shear stress.
- For high torques (from 5E4 Nm), the mechanism changes, that can induce perturbation in the curve.
- The data sheets do not contain every parameters of the procedure.

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2. Inverse analysis

The data measured have to be fitted with the models presented in chapter 1.2. Using the Inverse Analysis method, we can fit the shear stress to the shear rate by determining the three parameters μ, n and τ subject to minimizing the mean squared error (cost). This is a non-linear problem, hence a Newton-Raphson linearization has been utilized. This algorithm is called the Levenberg-Marquardt non-linear least squares error method. The solving is repeated a large number of times with randomly chosen starting parameters. Each step gives a new combination of parameters, which is saved if it has a cost less to the previous ones. This method is a Monte-Carlo method, since it uses a random choice of parameters. It does not give the best solution, but it approaches it with increasing number of steps increases. This algorithm is implemented in a Python code (using numpy and Scipy packages) shown in Appendix 3: SciPy Code.

3. Results

3.1. Toothpaste

Introduction

Toothpaste is a classic rheothinning and easy to handle material. By measuring toothpaste we can expect to find some generic model for other rheothinning materials.

3.1.1. Measurements

The measurements have been performed on Signal toothpaste with a cone-plate geometry (with a 6 cm diameter and an 2 ° angle) as shown in the Figure 1 in p.3.

They have been fit by inverse analysis. We could find out the parameters μ, n, τ minimizing at best the mean squared error with the Stress/Strain rate experimental curve.
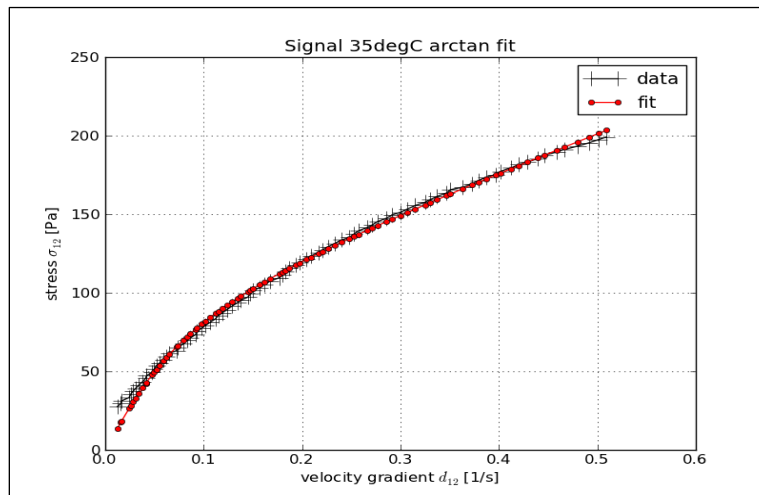

Figure 11: Arctan fit for signal toothpaste at 35°C

For the toothpaste, the Arctan model appears to fit better the data than the Herschel-Bukley one. It is thus the one that we will use in the following measurements.

3.1.2. Temperature dependence

Temperature dependence of the material coefficients plays a significant role. The material is softening as the temperature increases.
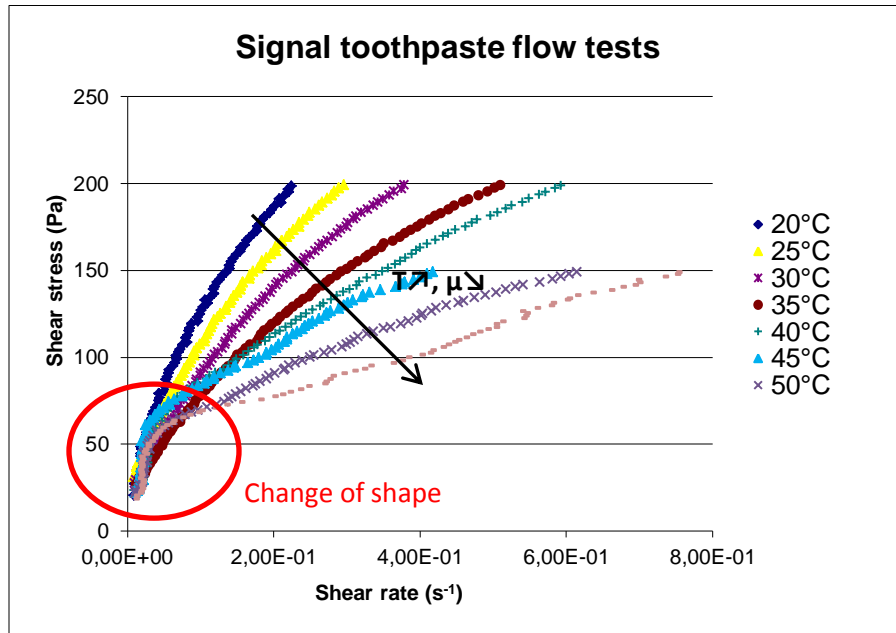
Figure 12: Flow tests on signal toothpaste

Those measurement have been modeled by using the parameter fit (cf. ch. 2) for different temperatures, the acquired results in Table 1 can also be presented as in Figure 13. The graphs of the fits are to be seen in Appendix 1: Signal Tooth paste Arctan fits.

Table 1: Temperature dependence of parameters for Signal toothpaste

T(°C)	T(K)	µ(Pa/s)	n	τ(Pa)
20	293	530	0.029	89
25	298	422	0.036	86
30	303	317	0.059	92
35	308	235	0.065	91
40	313	208	0.030	81
45	318	182	0.019	76
50	323	142	0.024	68
55	328	124	0.0093	56

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μ vs Temperature

$y = 9E+07e^{-0,041x}$
$R^2 = 0,9831$

τ vs Temperature
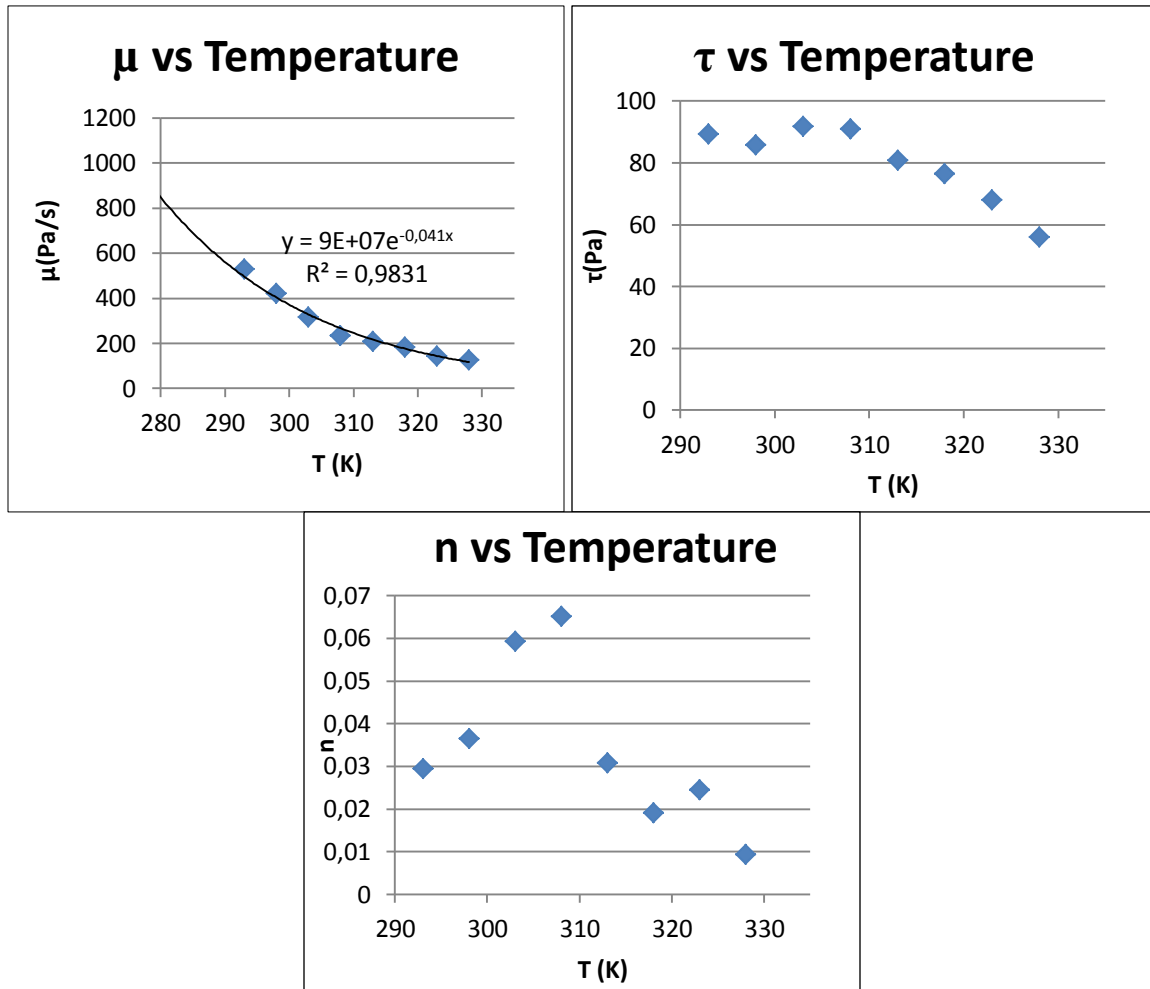
n vs Temperature

Figure 13: Temperature dependence of parameters for Signal toothpaste

For the apparent viscosity μ, we can find out an exponential behavior.

For τ and n, there is no easy to find trend but we can notice a decrease in the value of τ from 40°C. This fall coincide with the change in the shape of the curve that happens on Figure 12: Flow tests on signal toothpaste from 40°C. For this reason, we can assume that there exists a sort of glass transition at this temperature.

We could not find anything on glass transition of toothpaste in the literature. However, regarding the composition of the toothpaste, this value coincides with transition temperature of some of the components.

The supplier gives the following composition:

Calcium Carbonate, Aqua, Sorbitol, Hydrated Silica, Sodium Lauryl Sulfate, Sodium Silicate, Sodium Monofluorophosphate, Aroma, Cellulose Gum, Potassium Citrate, Benzyl Alcohol, Sodium Saccharin, Calcium Glycerophosphate, PEG-32, Limonene, CI 73360

Among this component, the ones that are often used as thickeners are hydrated Silica and cellulose gum. Mechanical properties of hydrated Silica depend strongly on the water content, which is unfortunately not given in the composition. The cellulose gum (or Carboxymethyl cellulose) have a higher glass transition temperature (about 200°C) according to the temperature. The PEG-32 is a polymer (Polyethylene glycol). It should melt at 42-46°C (cf.[6]). Hence, the structural change occurring at 40°C could be due to the melt of PEG-32. However, we don't know the percentage of each ingredient in the toothpaste, and a mixture doesn't necessarily react the same way as each component separated.

3.1.3. Oscillatory Test

The apparent viscosity μ and the yield stress τ seem to have two different behaviors. Hence, it would be interesting to perform some oscillatory measurement, to be able to study independently the elastic response (characterized by the τ) and the viscous response of the material (characterized by the μ).

We thus performed some oscillatory tests on the toothpaste (cf. 1.3.3) and we tried to fit it with the fractional Zener model, which were using Aditya Desai:

$$\sigma_{ij} + \tau_0{}^\alpha \frac{d^\alpha \sigma_{ij}}{dt^\alpha} = G_e(\varepsilon_{ij} + \tau_0{}^\alpha \frac{d^\alpha \varepsilon_{ij}}{dt^\alpha}) + G_0\tau_0{}^\beta \frac{d^\beta \varepsilon_{ij}}{dt^\beta}$$ (cf. [7]).

Starting from this equation can be found the expressions of the two modulus G' and G'':

$$G' = G_e + G_0 \frac{y^\beta(\cos(\beta\pi/2) + y^\alpha(\cos((\beta-\alpha)\pi/2))}{1 + 2y^\alpha \cos(\alpha\pi/2) + y^{2\alpha}}$$

$$G'' = G_0 \frac{y^\beta(\sin(\beta\pi/2) + y^\alpha(\sin((\beta-\alpha)\pi/2))}{1 + 2y^\alpha \cos(\alpha\pi/2) + y^{2\alpha}}$$

with $y = \omega\tau_0$.

As the device give in output G', G'' and ω, we can use the inverse analysis method to fit the result with the two expression above. Unfortunately, as it is to be seen on the Figure 14 below, we cannot get a good fit for this data (the other fit graphs are to be found in Appendix 2: Fit graphs for the oscillotary model and the signal toothpaste
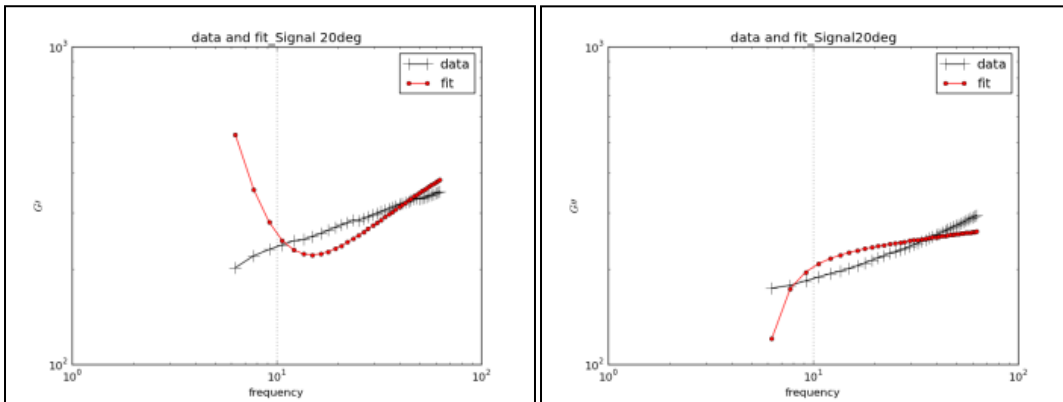

Figure 14: Fit of the results of oscillatory tests on Signal toothpaste at 20°C with the fractional Zener model- to the left: G' vs. ω, to the right: G'' vs. ω

The fractional Zener model does not seem to suit the behavior of Signal toothpaste, but it will be interesting to find a suitable model in further research.

Signal toothpaste has a very large dependence on temperature. By fitting with the Arctan model, the experimental results at different temperature, we could find out two different trends for µ and for τ: the apparent viscosity µ follows an exponential behavior with temperature, the yield stress τ decrease from 40°C, which could be due to a kind of glass transition. It could be interesting in further research to find a suitable oscillatory model to be able to separate those two trends and to make further tests to investigate this transition at 40°C.

3.2. UHU glue

Introduction

Studying the rheology of adhesives is necessary to be able to foresee their response to stresses in a current utilization. In this respect, it is interesting to study the rheological behavior of the fixed adhesive. The measuring procedure will not be exactly the same as for toothpaste. First the fixed glue is much stiffer than toothpaste, so we will not use a cone-plate geometry anymore but a parallel-plates geometry (25mm diameter). The hardening reaction is also to mind and can make the measurement more complicated.

3.2.1. Hardening of UHU glue

Before starting off the experiment, the adhesive has to be hardened fully.

Flow tests:

By performing the same sort of flow tests, as being the case for toothpaste, we can notice that the hardening process is a thermally activated reaction, which can be seen in the Figure 15 below.
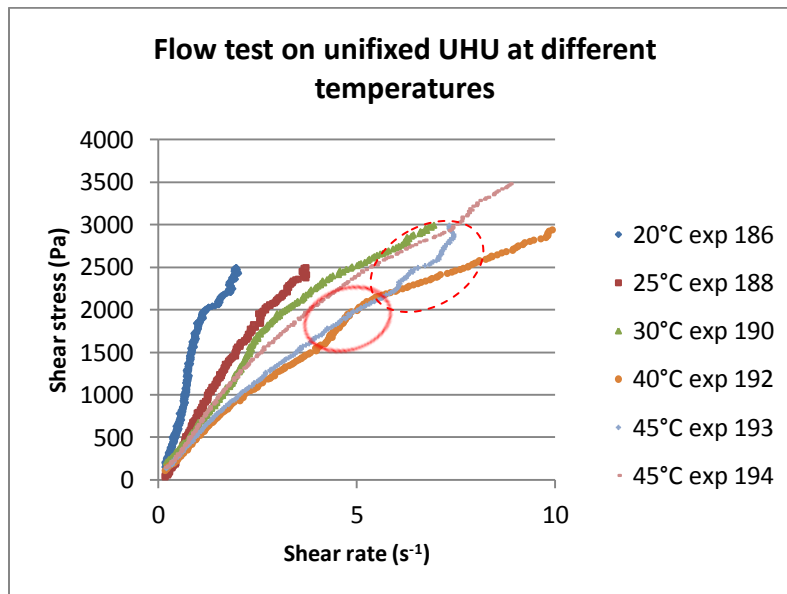

Figure 15: Flow tests on UHU glue

At higher temperature, we can observe a very fast hardening at the scale of one experiment (each measurement is performed in 3 minutes). For the first measurement at 45°C (light blue curve), we can

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see a rise at the end of the curve (dashed red circle), and with the following measurement at 45°C (pink curve), we can see that the material is actually stiffer. There is also a rise in the orange curve (full red circle) which represents the measurement at 40°C.

We have then two phenomena in competition:
- the hardening reaction, which tends to stiffen the material faster when the temperature increases,
- the softening of the material when the temperature increases, as it was observed in toothpaste.

Creep Test:

We made then some creep test to study further this hardening reaction.
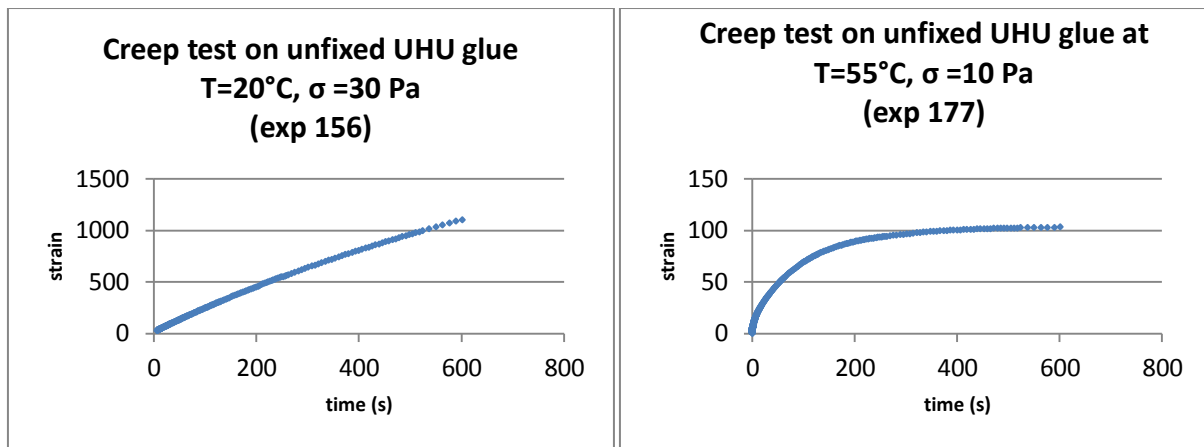
Figure 16: Creep tests on UHU glue at 20°C and 55°C

The value of strain in those two measurements shown in Figure 16 cannot be compared, as the stresses imposed are different. However, we can notice a difference in the shapes of the curves. At 20°C, the strain vs. time is linear, as it is expected to be for a viscous material (cf. ch. 1.3.2). At 55°C, however, we can observe a decrease of the strain rate, which shows that the material is stiffening.

Figure 17: Creep test on UHU glue at 55°C-exp 181

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The Figure 17 above represents a creep test performed just after the creep test at 55°C of the Figure 16. Here we can observe a decrease in the strain, which shows that the material is stiffening very fast. The material has stiffened and its yield stress became superior to the stress imposed. The glue has thus an elastic behavior and, as it goes on stiffening, the strain decreases.

Definitive method:

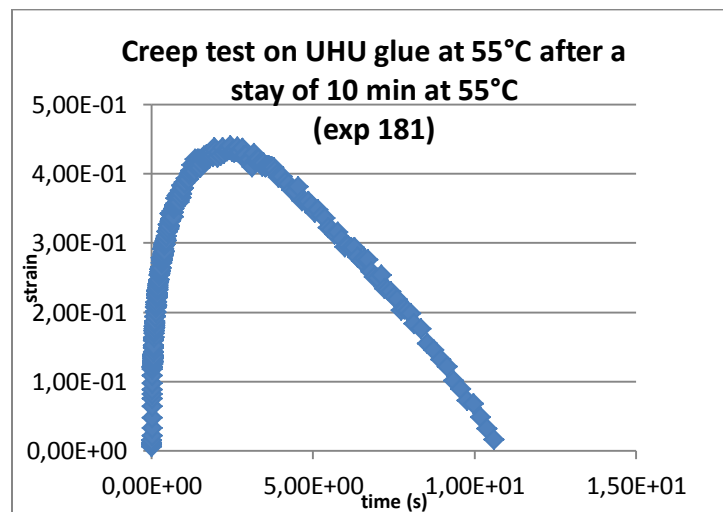It is of interest to do creep test to see when the glue hardens. However, to repair the moment when the glue is hardened fully, it is better to do successive flow tests as shown in the Figure 18 below.
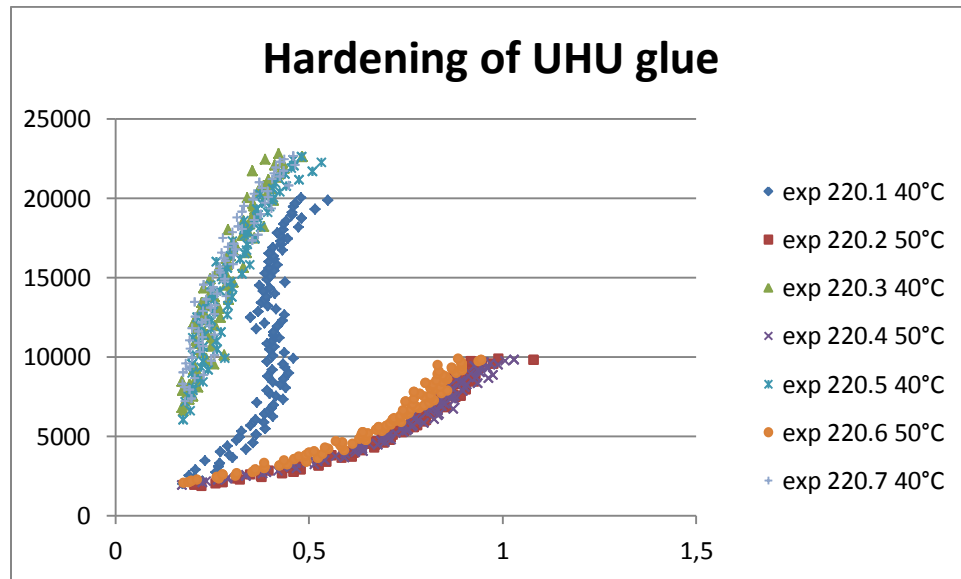
Figure 18: Flow tests on the hardening UHU glue

The Figure 18 shows the end of a series of flow tests at 40°C and 50°C. The last curves at 40°C are approximately the same, we can thus suppose that the glue is fixed. The temperature of 50°C is chosen to accelerate the hardening without damaging the material.

3.2.2. Test on hardened glue

Once the glue is fixed, we could make several flow tests at different temperature to observe the temperature dependence (cf. Figure 19 below). Those tests have been performed over 40°C as below this temperature the glue becomes too stiff for the device to be able to measure anything.

Evolution with temperature of hardened UHU glue

Legend:
- exp 221.13 40°C
- exp 221.1 45°C
- exp 221.2 50°C
- exp 221.3 55°C
- exp 221.4 60°C
- exp 221.5 65°C
- exp 221.6 70°C
- exp 221.8 75°C
- exp 221.9 80°C
- exp 221.10 85°C
- exp 221.11 90°C

Axes: Shear stress (Pa) vs Shear rate (s^{-1})

Figure 19: Temperature dependence of UHU glue

As for toothpaste, the temperature plays an important role on the stiffness of the material. However, the shapes of the curves are not the same, and we could not get any good fit neither with the Arctan model nor the Herschel-Bulkley model.
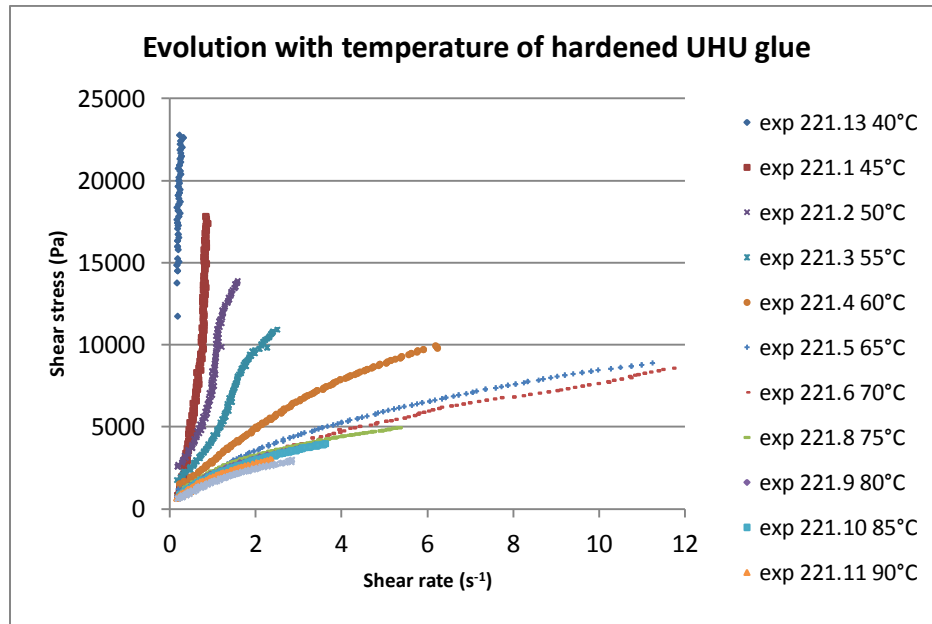
Conclusion

To study the rheology of adhesive, the first step is to ensure that they are hardened. Adhesives tend also to be much more sensitive to temperature, which induces not only a softening but can also play on the kinetic of chemical reactions. Those elements and methods have to be used for the study of strain gages' adhesive.

3.3. Strain Gages' Adhesive

A strain gage is a device used to measure strains. The strain gage is stuck on the object to study. The material is conductive and its electric conduction depends on geometry. It is thus possible to calculate the strain by measuring the electronic conduction. In this respect, it is important to know the mechanical properties of the adhesive used, as it can have an influence on the results.

3.3.1. Context

The strain gages' adhesive studied is the adhesive Kyowa CC33A. The samples have been supplied by the BAM (Federal Institute for Materials Research and Testing) regarding to a cooperation project. This adhesive is used for drop test of storage and transport containers. It needs to resist to temperatures from -60°C to 100°C. The Figure 20 below shows two different types of stain gages.

Figure 20: Strain gages- linear DMS (left) and biaxial DMS (right)

3.3.2. Flow tests

Figure 21: The adhesive Kyowa CC33A

We began the rheological study of the material with flow tests. The adhesive Kyowa CC33A is a pressure sensitive adhesive. It hardens pretty fast at room temperature subject to a simple pressure with the thumb. It also hardens with the pressure of the upper plate going down on the sample, so we did not have the same sort of problem as with UHU glue.

However this adhesive is much stiffer than UHU glue, which has caused two different problems:

- The maximum shear stress we can obtain with a 25mm flat plate, regarding the limit of the device, is around 32kPa. The only measurements we could get were from 150°C. Below this temperature, the material is too stiff and imposing a stress of 32 kPa does not enable to measure any strain rate. This temperature is unfortunately not in the utilization temperature range. However, it could be still interesting to measure and we can at least say that the adhesive does not show significant strain for a stress below 32 kPa and a temperature below 150°C.
- The adhesive is difficult to unstick at the end of the experiment. We had to use several tricks to clean it away, as the normal force of the device was not big enough.

Measurement on the prehardened sample:

The first flow test was performed with a prefixed sample from 150°C to 180°C. The data obtained are not very interesting as far as the sample was much slipping. However we can see on the Figure 22 below that the sample was kind of "burned" in some places. It was at first totally transparent whereas after the test we could observe a brown coloration. We can thus assume that there is change occurring in the sample at this temperature, which we will try to confirm in the following experiment.

Figure 22: Prefixed sample after flow tests up to 180°C

Measurements using steel disks:

To protect the bottom plate, we first performed the measurements using one steel disk. The disk is put on the bottom plate and we use it to set the zero gap. We put then the adhesive to test on the disk. The measurement shown in Figure 23 has been performed with this steel disk, a 25mm diameter parallel-plates geometry and a gap of 20µm.
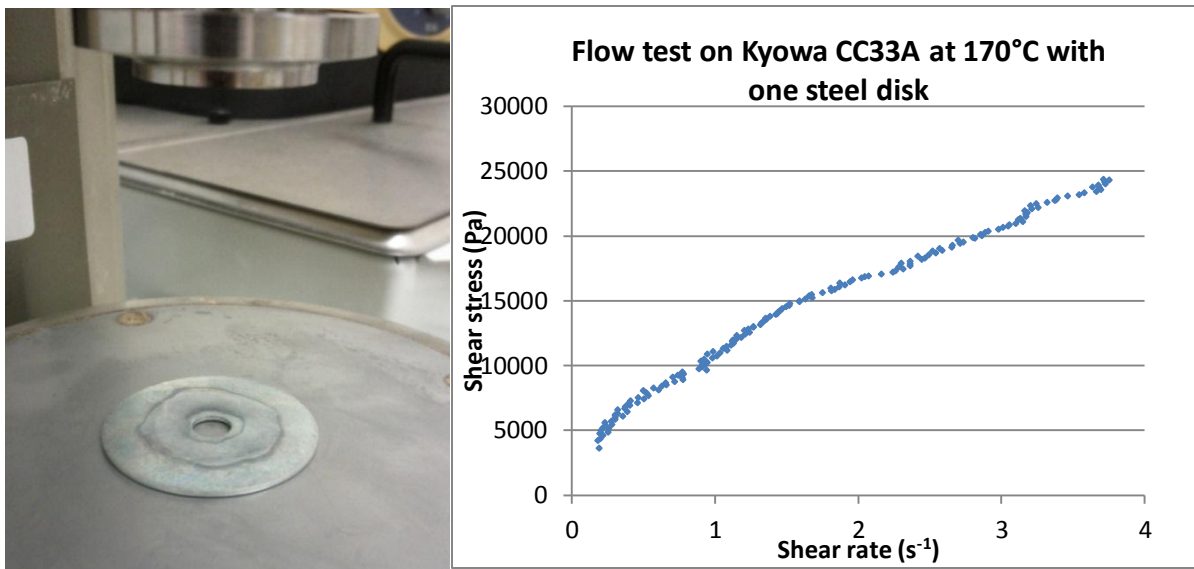

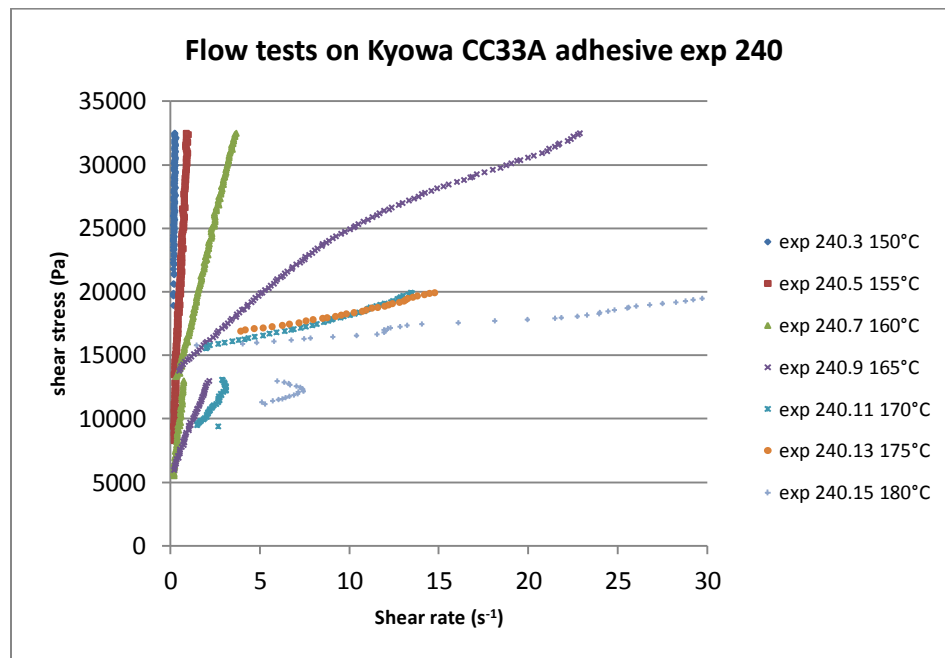Figure 23: Measurement on Kyowa adhesive using a steel disk

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We make two hypotheses by using this disk:

- The steel can be considered as a part of the device, which is reasonable as the plate is also made of steel, so the mechanical properties must be close.
- The disk does not slip on the upper plate, which is much more hazardous. Regarding the results of the measurements made without the disk (cf. Figure 24), we can assume that on the Figure 23, we measure both the response of the sample and the solid friction between the steel disk and the bottom plate.

Measurement without disk:

By making the measurement with disks, we could notice that the adhesive was much easier to unstick after having been kept long enough at high temperature. All the following measurements have thus been performed using the classic method with a 25 mm diameter parallel-plates geometry and a gap of 20 μm. To unstick the glue, we had been waited at 180°C until we could raise the plate.

We performed three successive series of flow tests (with the same sample) at temperature ranging from 150°C and 180°C. The Figure 24 below shows the results for the second and the third series.

Flow tests on Kyowa CC33A adhesive exp 240

- exp 240.3 150°C
- exp 240.5 155°C
- exp 240.7 160°C
- exp 240.9 165°C
- exp 240.11 170°C
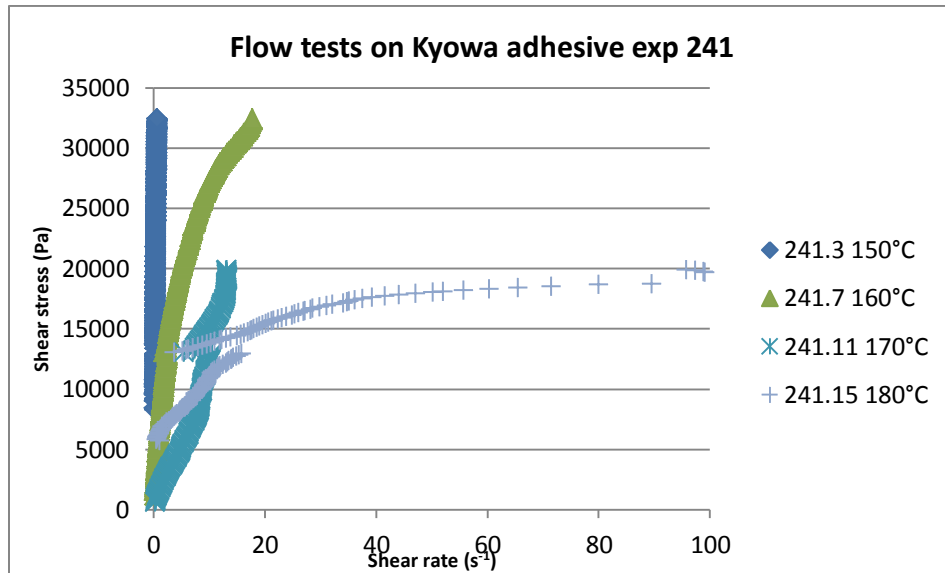- exp 240.13 175°C
- exp 240.15 180°C

Figure 24: Flow tests on Kyowa adhesive - exp 240 & 241

We did not get any data point for the first series of measurements, the material was still too stiff. We can thus assume that there is a time dependent softening reaction occurring in the material at high temperature, which induces a structural or a chemical change. Besides this reaction, we can notice the same sort of reversible softening we could have seen in toothpaste or in UHU glue. As in the case of UHU glue, we cannot fit those curves with the Herschel-Bulkley or the Arctan model, all the more so as there is a default in the curves around 12kPa, induced by the device.

3.3.3. Resistance to temperature

We made some creep tests to study its resistance to temperature. We can see on the Figure 25 and Figure 26 below the results of a creep tests on the adhesive at 180°C. First we imposed a shear stress of 20kPa during 30 minutes (cf. Figure 25). Then for the relaxation step, the stress is put back to 0, and we have measured the response and the material during 5 minutes (cf. Figure 26).
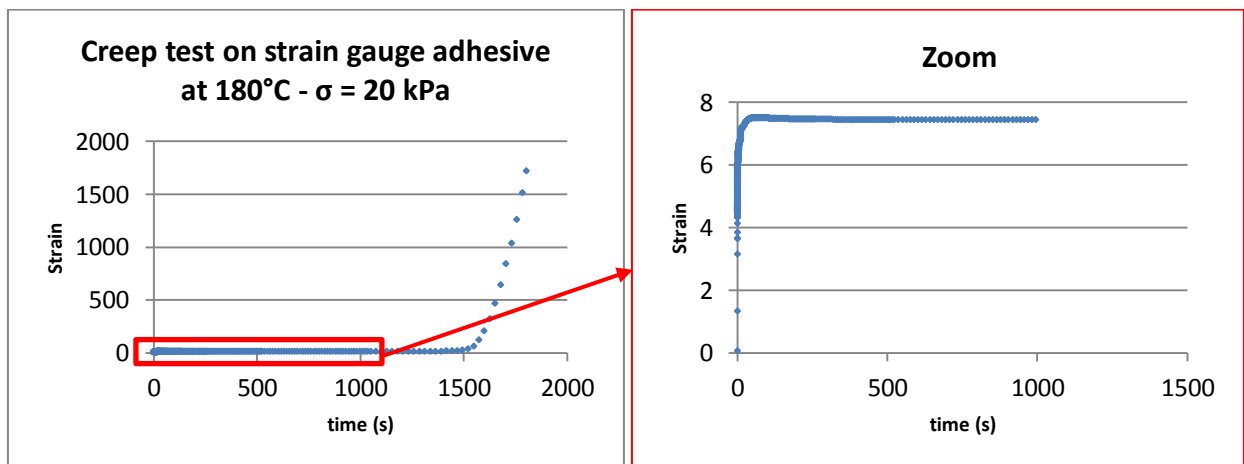

Figure 25: Creep test on Kyowa adhesive at 180°C exp 241.1

We can observe two periods in this first creep test (cf. Figure 25). First, the material reacts like an elastic solid, i.e., after a short transitory period, the strain tends to be constant, which can be seen in the zoom (Figure 25-2). From t=25 minutes, the material begins to flow. We can then assume that from this moment, the yield stress became inferior to 20 kPa, due to this change in the material at high temperature.
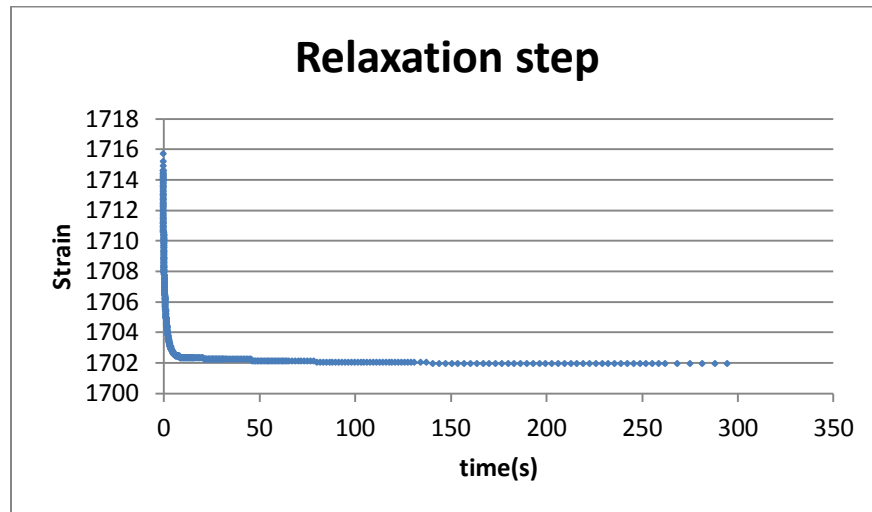
Figure 26: Creep test on Kyowa adhesive at 180°C, Relaxation step - exp 241.2

For the relaxation step, we have a short elastic response at the beginning, and then the strain remains at 1702, which shows the viscous behavior of the adhesive.

We made then a second creep test of 5 minutes with an imposed stress of 20kPa on the same sample, the results are shown on the Figure 27 below.
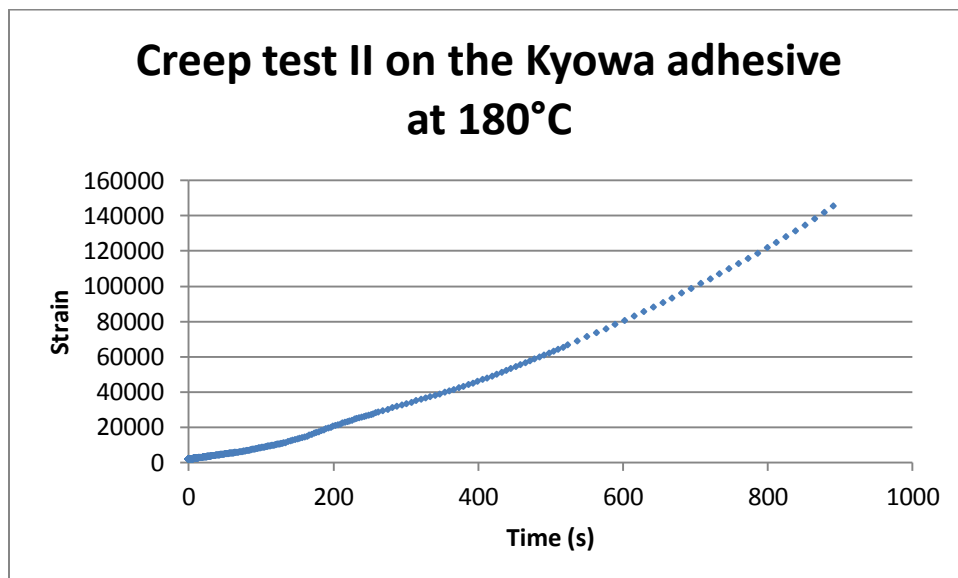

Figure 27: Creep test on Kyowa adhesive at 180°C - exp 242

We can see that the flow of adhesive accelerates, i.e. the strain rate increases. This is the effect of the softening reaction.

Conclusion:

The device does not enable to study the adhesive at its utilization temperatures. However, we can characterize its resistance at high temperature by performing a creep test.

Conclusion

We had different results by studying Signal toothpaste and adhesives. For Signal toothpaste, we performed some flow tests at different temperatures and we noticed that the material was softening with an increasing temperature. After having fit these flow curves with the Arctan model, we have found two different tendencies for the coefficients μ and τ: an exponential trend for μ between 20°C and 55°C and a linear decrease from 40°C for τ, which corresponds to a kind of glass transition. We also performed oscillatory tests and tried to fit it with the fractional Zener model, but this model is unfortunately not suitable for toothpaste. Further investigations could be useful to study this transition at 40°C and to find a suitable oscillatory model. It would also be interesting to see if the thermal behavior observed for toothpaste could be extended to other materials, as a generic model.

The adhesives were much more difficult to study with the rotational viscometer, as we reached the limits in torque of the device. For the strain gages' adhesive, we only managed to get measurements above 150°C. We could not find any fit for the Kyowa adhesive. However we could notice two different phenomena occurring in the material at high temperature: a reversible softening at high temperature, as it was the case for toothpaste, and a degradation of the material at high temperature, which can be observed with creep tests. We could notice a fast degradation of the Kyowa adhesive from 25 minutes at 180°C, with a significant decrease in its mechanic properties. In this respect, there are further tests to be made on the resistance at high temperature of the Kyowa adhesive, maybe by using a more powerful device.

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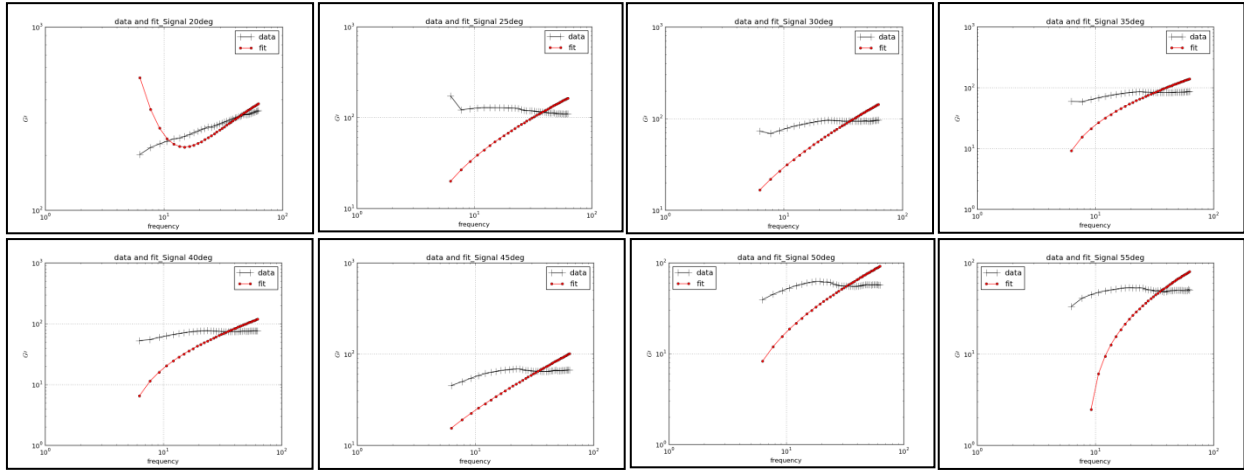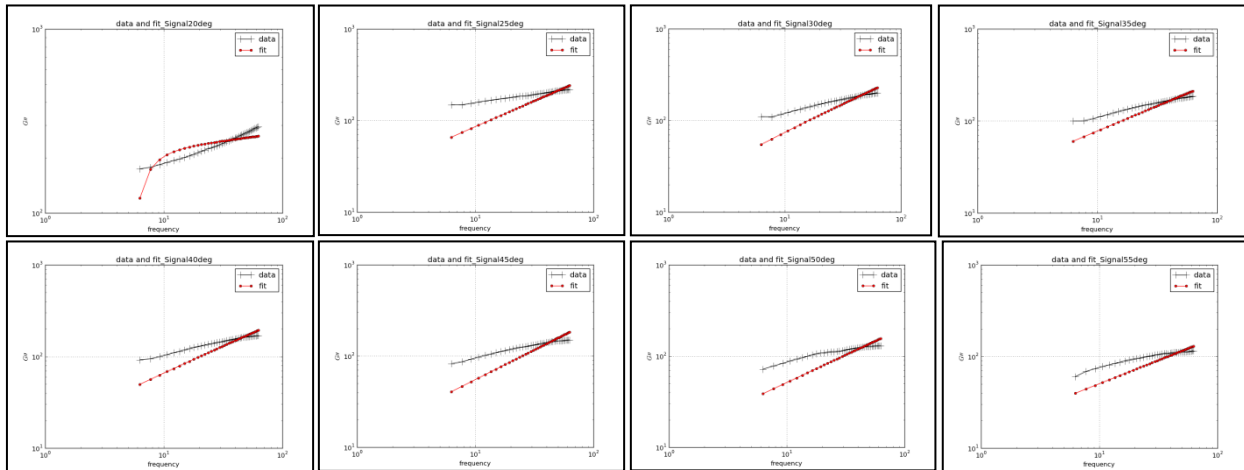
Appendix

Appendix 1: Signal Tooth paste Arctan fits
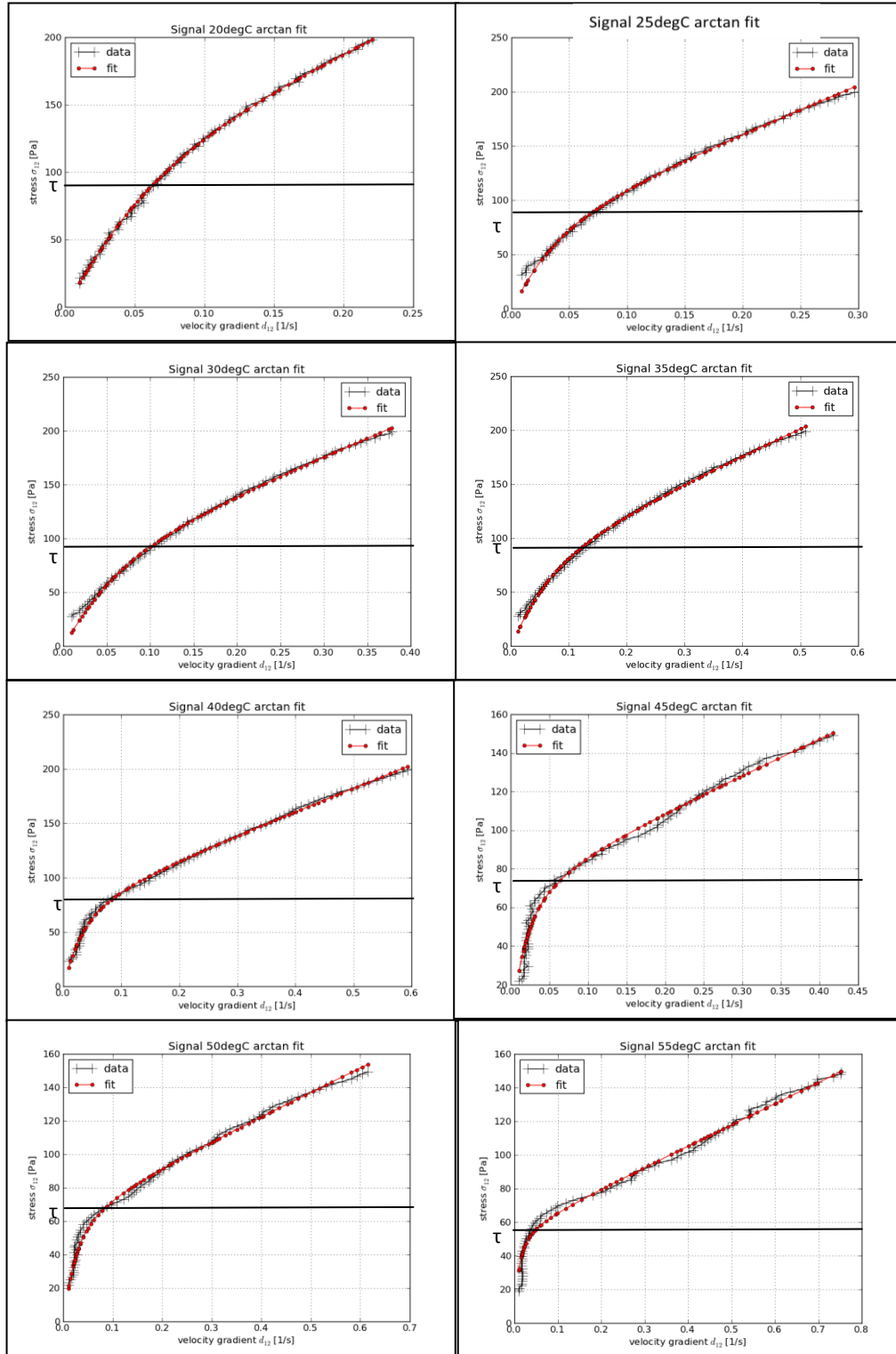
Appendix 2: Fit graphs for the oscillotary model and the signal toothpaste

G'

G''

Appendix 3: SciPy Code

```python
"""parameter fit"""

__author__ = "B. Emek Abali (abali@tu-berlin.de)"

__date__ = "2012-03-23"

__copyright__ = "Copyright (C) 2012, B.E.A."

__license__ = "GNU GPL Version 3 or any later version"


#--------------------------------------------------------------
#---run like: python fit_compute_plot.py
#---from shell after installing FEniCS and SciPy (matplotlib), such that:
#sudo apt-get install python-scipy python-matplotlib
#under Ubuntu
#please refer to:
#---www.fenicsproject.org
#---www.scipy.org
#--------------------------------------------------------------
from dolfin import *
import numpy
#------------reading the data from experiment
#the data Signaldata.py is to be found under Comp.Real. website
shear_stress, shear_rate, viscosity, t, temperature = \
 numpy.loadtxt('test.py', unpack=True)


import scipy
import scipy.interpolate
import scipy.optimize
stress = scipy.interpolate.interp1d(shear_rate, shear_stress, bounds_error=False, \
```

```
    fill_value=0.0)


#----------------------------------------parameter identification of the fit equation

def fit2find_param(constitutive_model):

        #---model in 1D to be used

        def fit(d12,mu,n,tau):

                if constitutive_model=='herschelbulkley': sigma = mu*d12**n + tau

                if constitutive_model=='arctan': sigma = mu*d12 + \

                 2.*tau/numpy.pi*numpy.arctan(d12/n)

                return sigma


        def residual(param, h, G, hypothesis):

                return h(G) - hypothesis(G,*param)


        def cost(param, h, G, hypothesis):

                return numpy.sum(residual(param, h, G, hypothesis)**2,axis=0)


        #-----------number of experiments

        m=shear_rate.size

        #-----------number of them to be taken for fit

        m=round(m*0.7)


        #-----------initial guess

        #as a range, param = [ mu , n , tau ] due to the def fit(d12,mu,n,tau)

        prange=[numpy.arange(0,1000,1),numpy.arange(0,1,0.1),numpy.arange(0,10,0.5)]


        numpy.seterr(all='ignore')
```

```python
#------------------------fitting on a random set and testing with another set


montecarlo = 6

number_of_trials = 0

error_min = 10e10

penalty = 10e6

from copy import deepcopy

rate_s=deepcopy(shear_rate)

while number_of_trials < 15000.0:

        if montecarlo>5:

                p1 = prange[0][numpy.random.random_integers(0,len(prange[0])-1)]

                p2 = prange[0][numpy.random.random_integers(0,len(prange[0])-1)]

                p3 = prange[0][numpy.random.random_integers(0,len(prange[0])-1)]

                param0 = [p1,p2,p3]

                montecarlo = 0

        numpy.random.shuffle(rate_s)

        param_lsq = scipy.optimize.leastsq(residual, param0, \

        args=(stress , rate_s[:m], fit))

        param=param_lsq[0]

        montecarlo +=1

        error=cost(param, stress , rate_s[:m], fit)

        if param[0]<0: error += penalty #we force tp get k>0

        if param[2]<0: error += penalty #we force tp get mu>0

        if error<error_min:

                chosen_param = param

                error_min = error

                print 'parameters: ', param, '  error on test set: ', error, \

                ' @ ', number_of_trials
```

```python
            number_of_trials +=1

    return chosen_param


#-----------------------------------------parameter identification of the fit equation


#------------------------------------------------------------------------visualization
import matplotlib as mpl
mpl.use('Agg')
import matplotlib.pyplot as pylab
def visualize(constitutive_model,chosen_param):

    def fit(d12,mu,n,tau):

                if constitutive_model=='herschelbulkley':

                        sigma = mu*d12**n + tau

                if constitutive_model=='arctan':

                        sigma = mu*d12 + 2.*tau/numpy.pi*numpy.arctan(d12/n)

                return sigma

    pylab.cla()

    pylab.plot(shear_rate, shear_stress, color='black', marker='+', \

    markersize=13, label='data')

    pylab.plot(shear_rate, fit(shear_rate,chosen_param[0],chosen_param[1],\

    chosen_param[2]), color='red', marker='o', markersize=5, label='fit')

    pylab.ylabel('stress $\sigma_{12}$ [Pa]')

    pylab.xlabel('velocity gradient $d_{12}$ [1/s]')

    pylab.title('Experiment vs. fit')

    pylab.legend(loc='best')

    pylab.grid(True)

    return pylab
#------------------------------------------------------------------------visualization
```

```python
#-------------------------------------------------------------fit & compute & plot


fit_a = fit2find_param('arctan')

fig_a = visualize('arctan',fit_a)

fig_a.savefig('fit_arctan.png')


"""

fit_hb = fit2find_param('herschelbulkley')

fem_shearrate_hb, fem_stress_hb = compute('herschelbulkley',fit_hb[0],fit_hb[1],fit_hb[2])

fig_hb = visualize('herschelbulkley',fit_hb,fem_shearrate_hb, fem_stress_hb)

fig_hb.savefig('fit_herschelbulkley.ps')
"""


print 80*'-'

print 80*'-'

print 'For arctan model, mu: ',fit_a[0],' n:',fit_a[1],' tau:',fit_a[2]

print 80*'-'

print 80*'-'
"""

print 'For Herschel Bulkley model, mu: ',fit_hb[0],' n:',fit_hb[1],' tau:',fit_hb[2]

print 80*'-'
"""

#-------------------------------------------------------------------------end of file
```

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