Felix Hajek, BSc

Viscoelastic behaviour of paper

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Supervisor

Robert Schennach, Ao.Univ.-Prof. Mag. Dr.rer.nat

Co-Supervisor: Georg Urstöger, DI

Institut of Solid State Physics

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AFFIDAVIT

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1 Abstract

This work has been performed to gather the experimental data needed to improve paper models, to investigate the long term behaviour of paper under different relative humidities and to investigate the influence of capillary forces to the paper bonding system.

During the work for this thesis the sample size dimensions for paper suited for a Discovery TA Instruments DMA were calculated. Measurements at different relative humidities were performed to investigate the viscoelastic behaviour of paper.

The yield point of UNUT (untreated and unsized) paper has been investigated, by applying an increasing force, the sample goes from an elastic into a plastic region. In terms of creep recovery experiments, this has been studied with the result that no real yield point exists. UNUT paper seems to be in a not elastic region instantaneously (at the beginning of the measurement).

Two paper models have been improved with the results from creep relaxation experiments. One model is based on plasticity, the other one on viscoelasticity (Maxwell model).

The frequency dependence (long term behaviour) of UNUT has also been studied, intensive work was undertaken to clear the data from measurement artefacts. A hypothesis that one part stemps from activation, the other from resonance of the machine was stated.

A first try on creating a mastercurve and checking if UNUT is a "rheological simple" material has been made. Even though that the created mastercurve does look reasonable, the *Wicket-Plot* as well as the *Cole-Cole-Plot* (methods to check if the mastercurve worked correctly) do not.

The influence of capillary forces to the bonding system of paper has been studied by performing tensile tests under different conditions. By drying the paper completely it seems that the influence of capillary forces are of minor importance under dry conditions.

2 Acknowledgements

Before the reader of this thesis keeps his attention on science only, I want to thank the people who helped and supported me throughout my studies and especially throughout the process of writing my master thesis.

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3 Introduction

The time dependent (long term) behaviour of paper under different relative humidities is of interest for industry when it comes e.g. to printing with ink. This topic has been studied in terms of creep and relaxation from Niskanen et al. [16]. In terms of curl and injekt printing this has been studied by Hunstein [5], Richter [19] and Harter [4]. While they focused on ink on one side of the paper, this work is focusing on the paper environment by doing creep and relaxation experiments at different relative humidities.

The possibility of doing mechanical analysis measurements under several different conditions in terms of frequency sweep measurements has been studied by Gregorova et al. [1] and opens up new possibilities of investigating long term behaviour of paper. Frequency sweep measurements are an interesting procedure when it comes to modeling of paper. It provides a lot of information about short and long term behaviour of the investigated sample. By doing measurements at different temperatures the principle of TTS (time-temperature-superposition) has been investigated by Olsen et al. [13] and Fesko [2] investigating polymers.

To the best of our knowledge, the frequency response over humidity has not been studied so far and was studied as part of this work in the Christian Doppler Laboratory (CDL) for Fiber Swelling and Paper Performance at Graz University of Technology in collaboration with Canon Production Printing and Mondi Uncoated Fine Paper.

Frequency sweep measurements have been performed at different relative humidities in various frequency ranges and a mastercurve based on time-humidity-superposition (instead of TTS) has been made.

By focusing on the work of Hirn and Schennach [21] [22], who investigated the paper bonding system, the influence of capillary forces in this system was further investigated. This was done by performing tensile tests (breaking the sample) at standard conditions and with completely dry samples (pre-heated and 0 % relative humidity).

4 Materials and methods

4.1 Material

The material in use is a paper called UNUT, untreated and unsized paper. It is a wood free fine paper from an industrial supplier (Mondi). It is made from industrial bleached hardwood pulp and its characteristics have been measured by Krainer et. al [20] and are listed in tab. 1:

Table 1: Characteristics of UNUT paper measured by Krainer et al. [20]

Properties	**UNUT**
Grammage [$\frac{g}{m^{-2}}$]	97.2
Filler content [%]	21.51
Pigmentation [$\frac{g}{m^{-2}}$]	0
HSI surface treatment	No
Porosity [%]	40.3
Avg. pore diameter [μ m]	3.9

4.2 Material properties

4.2.1 Basics: Stress and strain

Stress and strain are the two most important terms for this work to describe paper behaviour.

Stress is used instead of force because it gives a clearer picture of what's happening when a force is applied. Force is defined as the mass of an object times its acceleration $F = ma$, which is called *Newton's law of motion*. This law tells us that eg. a golf ball of mass 1 g and velocity 100 m/s has the same force like a football of mass 100 g and velocity of 1 m/s. If you think about which ball you would rather like to catch, it for sure would be the football because the impact of the golf ball is higher. This impact can be described as the ratio of the force and the area it has an impact on, the so called stress [12] (see eq 1):

$$\sigma = \frac{F}{A} \tag{1}$$

With σ the stress, F the force and A the area. This stress causes a deformation which is called the strain and can be defined as in eq. 2:

$$\epsilon = \frac{\Delta Y}{Y} \tag{2}$$

ϵ the strain, Y the original materials dimensions and Δ Y the change in dimensions.

Theoretically it does not make a difference if an experiment is done by an applied stress or by an applied strain since these two quantities are related via eq. 3

$$\sigma = E\epsilon \tag{3}$$

E is called E-modulus or Young's modulus and tells you how a sample reacts if a stress is loaded. [12]

Looking at how stress causes strain or the other way around is a classical way of analysis in Rheology and gives the curve of interest, the stress-strain curve. This curve depends on the way for example how stress is applied (constant, constantly increasing/decreasing, oscillating,...). The way stress/strain is applied classifies different tests usually used in rheological experiments. [12]

4.2.2 Tensile test

A simple test which contains a lot of information is a tensile test.

During this test the sample gets stretched till it breaks, the stress is usually increased linearly. The stress and strain are recorded and normally plotted as a stress-strain curve which can have different forms but usually consist of a linear and a non linear region. The values of stress and strain in which the observed material behaves elastic (linear) or plastic (non linear) can be readout (see also sec. 6.1.2).

To make sure that a full tensile test can take place, the dimensions of the sample and the used machine have to be known. If for example the samples size is too big, the stress at break (force needed to break the sample) cannot be reached with the machine used.

4.2.3 Creep test

Creep tests are distinguished between creep-recovery (stress controlled) and stress relaxation tests (strain controlled) and investigate the time dependent changes of a loaded material [15].

In a creep recovery test a load is applied (force/stress on sample) and kept there for a desired amount of time and released afterwards. Imaginable just like putting a load on a spring and take it off again. During the whole process the strain corresponding to the load on the sample is recorded and plotted over time (see fig. 1, load blue, strain in green).

This test shows how long the sample needs to stabilize under loading (eg. under conditions of use). It also contains information on how the sample reacts

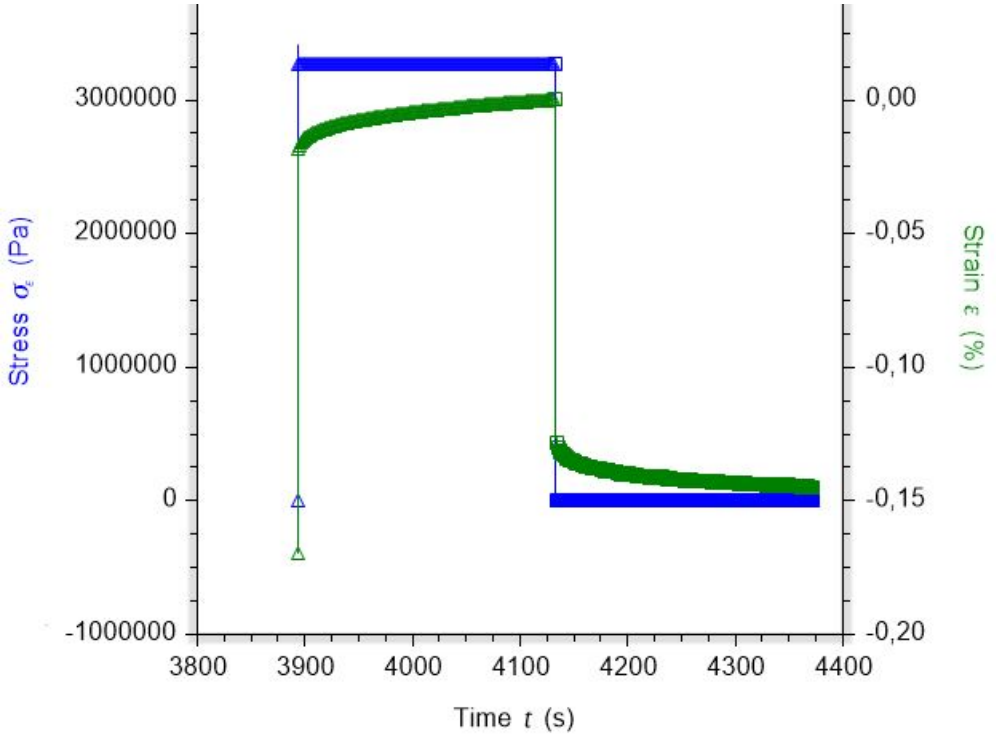


Figure 1: Schematic view of a creep recovery test. In blue the load in terms of a stress is shown and the corresponding recorded strain is shown in green.

when the load is released. Does it come back to its original shape? If yes, how long does it take the sample to recover completely? It is a very powerful tool to find the borders of the elastic and plastic region of a sample and to investigate the region in between (viscoelastic region).

There are different theoretical models to describe creep-recovery. [12] The one used for this work is the *Maxwell Model*. [8] [17]

This model describes paper behaviour with a spring and a dash pot in series. If a sample would be purely elastic, an ideal spring would be enough. Due to the fact that paper is not purely elastic a dash pot is also needed which represents the fact that paper does not recover fully if the load is high enough. This model shows the same curvature like real paper and thus can be used to describe it.

If we now take a look at stress relaxation tests we see that these two can be seen as reciprocal versions of each other (see eq. 4 [12]).

$$(\frac{\epsilon_t}{\epsilon_o})_{creep} \approx (\frac{\sigma_o}{\sigma_t})_{stress,relaxation} \tag{4}$$

With ϵ_o/σ_o the applied strain/stress and ϵ_t/σ_t the reaction of the material observed.

In a stress relaxation test the sample is quickly distorted to a set length and

decay of stress exerted by the sample is measured. The description is analog to the creep-recovery test.

From the descriptions above follows the definition of creep and relaxation [15]:

- Creep: Increase in strain over a time under a constant state of stress
- Relaxation: Decrease in stress over time under a constant state of strain

4.2.4 Frequency experiments

Frequency sweep measurements can be performed either stress controlled or strain controlled. The idea is to apply a sinusoidal load and measure the response of the observed material. If for example a stress/force is applied the response is measured in terms of strain. The shift of the strain depends on the materials properties. If the material is elastic the strain and the stress are overlapping: $\sigma(t) = E\epsilon_0 sin(\omega t)$ (with ω the frequency and t the time). If the material is viscous then there is a frequency dependent factor (ν) in front: $\sigma_0 = \nu\epsilon_0\omega$. [12]

It follows that:

$$\sigma(t) = \nu\frac{d\epsilon}{dt} = \nu\epsilon_0\omega cos(\omega t) \tag{5}$$

If the material is viscoelastic the material needs some time to respond, the same sinusoidal curvature like the load can be seen but a phase shift (δ) occurs. From this phase shift the complex modulus $E_{complex}$ can be calculated, illustrated in the following equations: [12]

The stress load can be written as

$$\sigma(t) = \sigma_0 sin(\omega t) \tag{6}$$

with this follows the corresponding strain as (also shown in fig. 2)

$$\epsilon(t) = \epsilon_0 sin(\omega t - \delta) \tag{7}$$

Since the E modulus is defined as the ratio between stress and strain, it can be written in terms of real and imaginary parts,

$$E' = \frac{\sigma_0 cos(\delta)}{\epsilon_0} \tag{8}$$

$$E'' = \frac{\sigma_0 sin(\delta)}{\epsilon_0} \tag{9}$$

These two moduli define the complex modulus and represent the in-phase and out-of-phase parts of the materials response. The storage modulus (E′)

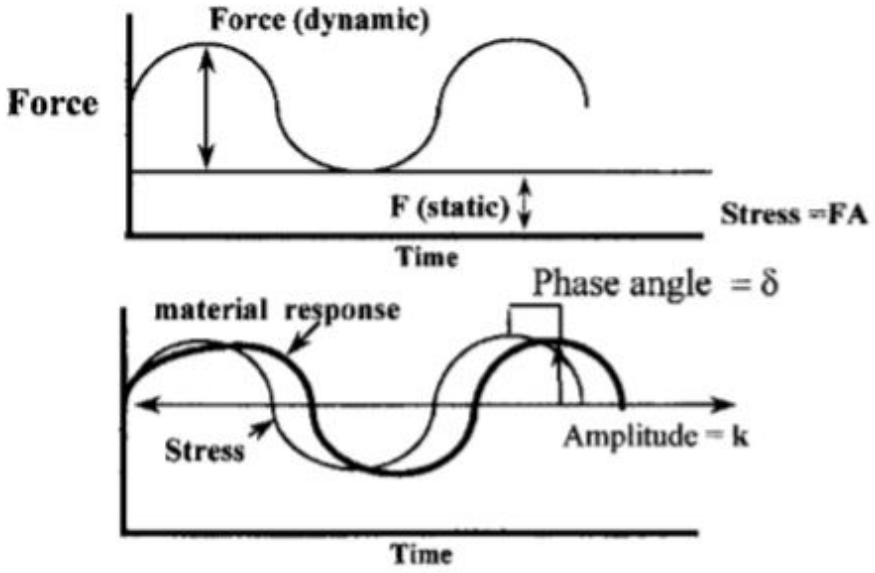


Figure 2: An illustration of what is happening when a sinusoidal force is applied on a viscoelastic sample. A phase shift δ is measured. [12]

is the in-phase part which is completely elastic. The loss modulus (E″) is the out-of-phase part and results in dissipation energy. Those two combined give the complex modulus

$$E_{complex} = E' + iE'' \tag{10}$$

Their frequency dependence can best be seen if the above equations are substituted so equation 11 follows.

$$\sigma(t) = \epsilon_0(E'sin(\omega t) + E''cos(\omega t)) \tag{11}$$

To sum this up and clarify the picture of what is happening at frequency sweep measurements:
A sample is oscillated sinusoidal with a certain frequency. The sinusoidal responds of the material are measured and the complex modulus is calculated. This modulus contains information about the elastic behaviour (storage) and the dissipated energy (loss).

4.2.5 Mastering

The concept of mastering is based on time-temperature-superposition (TTS). This technique uses the time-temperature equivalence to create a master curve

out of a set of frequency scans, by shifting the curves relative to a reference. These curves must all be of the same material but at different temperatures. The reference is chosen arbitrary but traditionally a temperature in a range between the glass transition temperature T_g and $T_g \pm 100$ K is taken because TTS was originally defined in this region [12].

These curves are plotted usually with the frequency on the x-axis and the E-modulus in the y-axis. The curve shifting is happening in the x-axis, on the frequency/time scale, in a way that the curves overlap and form a new smooth mastercurve for the chosen reference temperature.

The shift factor can be calculated via the WLF model (Williams-Landel-Ferry) and is given by eq. 12: [11]

$$log(a_T) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \tag{12}$$

With a_T the shift factor, T the temperature of the curve I want to shift, T_g in this case the glass transition temperature chosen as reference and C_1&C_2 are material constants. This equation was generated for polymers and holds in the above defined temperature limit. It is useful to generate a fit after the curves have all been shifted but the shifting is often done empirical. The curves are shifted horizontal till they overlap and build a smooth mastercurve.

The whole procedure of mastering is performed to overcome the limits of the used machine. By shifting the curves in the frequency axis, lower and higher frequency ranges can be predicted. Often the lower frequency ranges are of interest because the time dependence after long time periods can be seen. Since the frequency is often given in Hz and Hz = 1/s, by inverting the frequency dependent curve you get the time dependent one (the low frequency ranges equal the long time ranges).

Mastering is a very strong tool which can help to predict the behaviour of a material outside the measurable range of your machine but this technique does not work for all materials. The materials of choice are "rheological simple" materials. When a material is "simple" is not clearly defined.

One way to define and at the same time test, if the mastercurve is trustworthy is a *Wicket plot* [18]. In a Wicket plot the loss modulus is plotted (on a loglog scale) vs $tan\delta$, which is defined as the ratio between the loss and the storage modulus ($tan\delta = \frac{E_{stor}}{E_{loss}}$). This is done for all temperatures measured and plotted in a single figure. If the shape looks like a smooth inverted U the material can be set as "rheological simple" and the mastercurve can be generated. [18]

Another but similar way to check your material is the so called *Cole-Cole plot* [9]. It is basically the same approach but the plot is a loss modulus vs storage modulus plot. Again an inverse U shape should be visible if the used

material is ”simple” [9]. An example of a mastercurve procedure is shown in fig. 3 [10] and a *Wicket plot* is shown in fig. 4 [23]

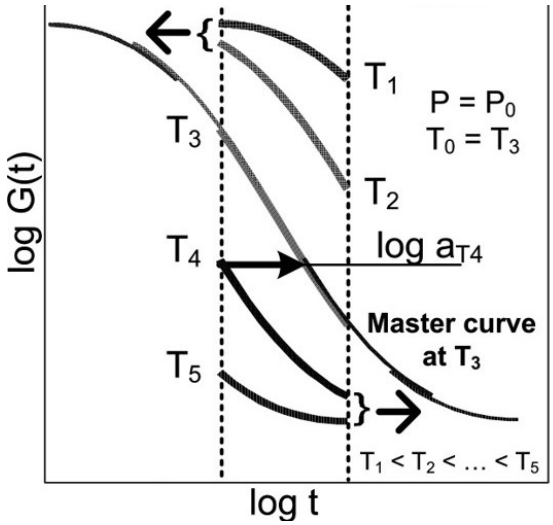


Figure 3: A theoretical procedure how a mastercurve is created. Shifting the curves below and above the reference so a smooth curve is made. [10]

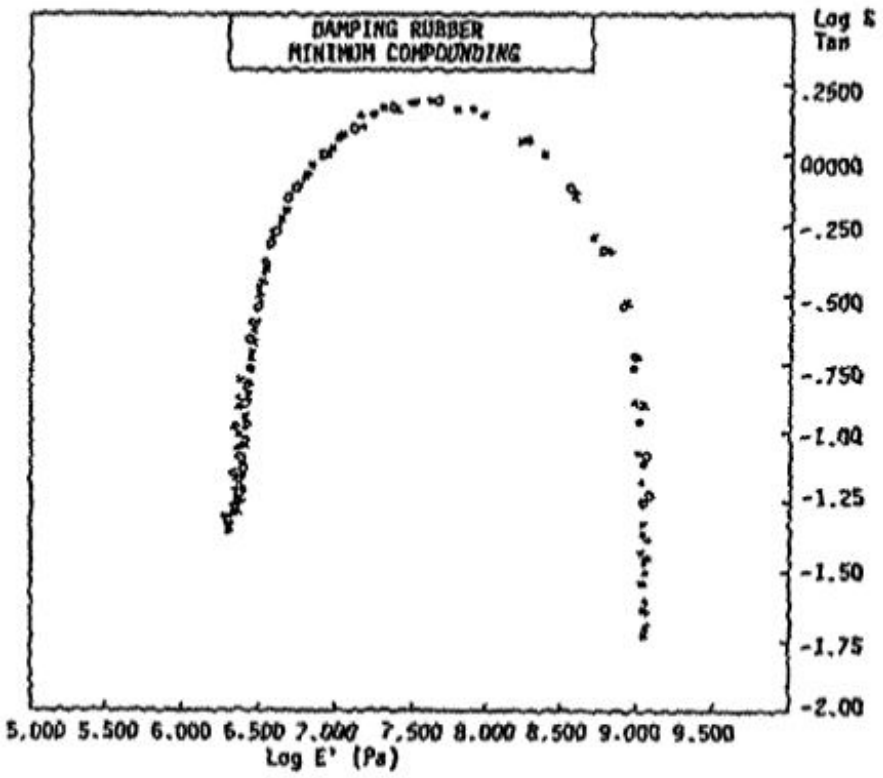


FIG 9. Wicket plot of damping rubber at -56°C

Figure 4: *Wicket plot* made by [23] from rubber. It shows a perfect inverse U like shape.

4.3 TA- Instruments, Discovery DMA 850

Besides the first tests to discover the stress and strain in break of UNUT paper, all measurements have been performed with the *Discovery DMA 850*. Some of the most important properties are listed in tab. 2 [6]:

Table 2: Discovery DMA 850, properties

Property	**Value**
Maximum force	18 N
Minimum force	0.0001 N
Force resolution	0.00001 N
Frequency range	(0.001 - 200) Hz
Dynamic strain range	$(\pm 0.005 - 10000)\ \mu$m
Strain resolution	0.1 nm
Modulus range	$(10^3 - 3 \cdot 10^{12})$ Pa
Modulus precision	±1 %
Temperature range, standard	$(-160 - 600)\ ^\circ C$
Temperature range, RH-equipment	$(5 - 120)\ ^\circ C$
Temperature change	±1 $\circ$**C** /min
Relative humidity range	(5 – 93) %

This machine not only allows mechanical operation but also the control of the surrounding conditions like relative humidity and temperature. It can be operated in various ways by providing a set of different clamps. The one used for this work is a pull clamp ("Zugklemme" [6]) and is used for one axial displacements. A picture of the used *Discovery DMA 850* can be seen in fig. 5.

With this machine the measurements described above, tensile test, creep test and frequency sweeps, can be done.

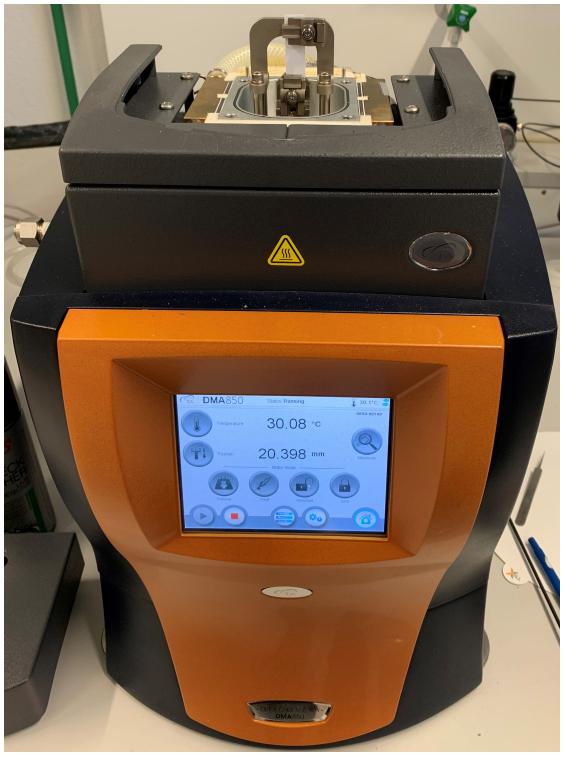


Figure 5: Used *Discovery DMA 850*.

5 Experimental procedure

5.1 Sample size

The right sample size is an inevitable sample property which has to be known before the experiments can take place. To make sure that the used paper sample can be broken with the DMA, the strain and force at break have to be evaluated. Therefore, a pulling/tensile test has been performed with a "L&W Tensile Tester" ,series number: C10644. This measurement has been done for machine and for cross direction (MD and CD, respectively) at standard conditions, 23 °C and 50 % relative humidity, with a sample width of 15 mm. The results can be seen in tab. 3 and tab. 4.

Table 3: First tensile test for UNUT paper, cross direction

F.....Force, ±2 N
σ.....stress, ±71 Pa
ϵ.....strain at break, ±0.1 %
TEA.....tensile energy absorption, ±4 $\frac{J}{m^2}$

	F / [N]	σ **/ [Pa]**	ϵ **/ [%]**	**TEA /** $[\frac{J}{m^2}]$
	62	2214	1.4	39
	59	2107	1.2	31
	60	2143	1.3	35
	59	2107	1.3	34
	56	2000	1.2	29
Mean values	59	2107	1.3	34

Table 4: First tensile test for UNUT paper, machine direction

F.....Force, ±2 N
σ.....stress, ±71 Pa
ϵ.....strain at break, ±0.7 %
TEA.....tensile energy absorption, ±16 $\frac{J}{m^2}$

	F / [N]	σ **/ [Pa]**	ϵ **/ [%]**	**TEA /** $[\frac{J}{m^2}]$
	31	1107	3.6	57
	35	1250	5.2	91
	35	1250	5.3	92
	35	1250	5.3	92
	35	1250	5.3	92
Mean values	34	1214	5	85

The sample thickness of 0.11 mm has been evaluated with a measuring stick produced by ”Flower” called ”Ultra Cal V”.

With this information and the knowledge that the DMA can only hold a maximum sample length of 28 mm and can apply a maximum force of 18 N, the diameters for the used samples was calculated and set to a width of 5 mm in cross direction and 3 mm in machine direction.

5.2 Conditioning time

An appropriate conditioning time is important to keep the duration of equilibration as short as possible but as long as necessary.

A measurement has been performed with UNUT paper in cross direction to evaluate this time. Here the paper has been held at constant force and constant relative humidity of 0 % for 24 h. A zoom-in perspective can be seen in fig. 6. What is illustrated there is, that after a conditioning time of 3 h the paper is approximately equilibrated and after 1 h the paper has already reached 93,75 % of that state.

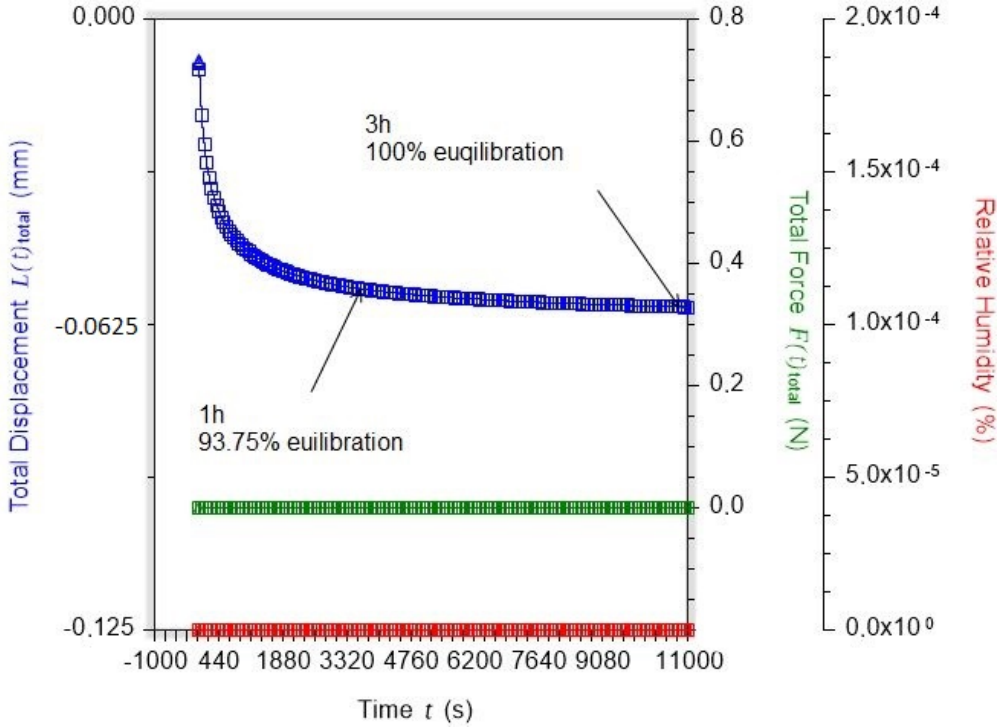


Figure 6: 24 h measurement with UNUT paper in CD to evaluate the needed conditioning time. The displacement happening during conditioning is shown in blue. The relative humidity is constantly held at 0 % shown in red. Also the total force stays at 0 N during the conditioning process which can be seen in the green curve. 93,75% of equilibration is completed after 1 hour.

The conditioning time has been set to 1 h to keep the measuring time as short as possible while giving the sample enough time for equilibration.

5.3 Yieldpoint evaluation

After a reasonable conditioning time and a functional sample size has been set, the actual measurements can take place. The first sample property of interest is the yield point.

The yield point defines the border of a material between its elastic and its plastic region, usually shown in a stress-strain diagram. A schematic example is shown in fig. 7.

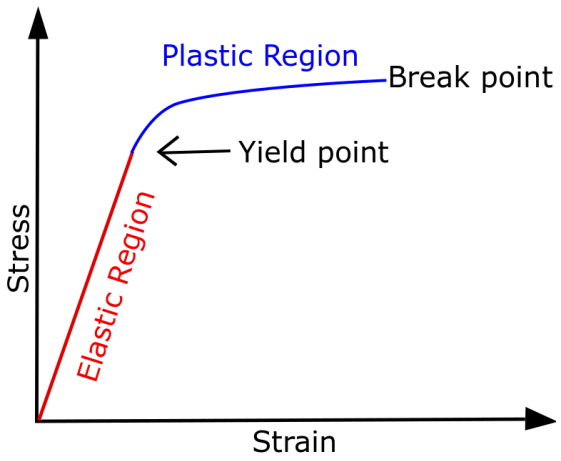


Figure 7: Schematic view of a stress-strain curve with the yieldpoint marked as the border between the elastic and plastic regions.

As long as the sample is in the elastic region, the used material always comes back to its original shape after deformation, just like a rubber band. When the material gets into its plastic region, plastic deformation takes place and hinders the material to get back to its shape before deformation. This is usually illustrated with springs and dash pots (see sec. 4.2).

In the case of this work it is important to find the yield point of UNUT paper to stay in the elastic region at later experiments. While working with paper a lot of uncertainties come into account, like plastic deformation, the influence of the paper orientation and so on. To decrease the number of uncertainties which have to be taken into account it is important to stay elastic. With this the number of needed measurements can be minimized while still having a good statistic.

5.3.1 Yield point evaluation, tensile test

Different methods have been used to investigate the yield point of UNUT paper. The first method was a simple tensile test, stretching the sample till it breaks.

By taking the derivative of the stress with respect to the strain, one optains the E-modulus (see eq. 13),

$$E = \frac{d\sigma}{d\epsilon} \tag{13}$$

The E-modulus shows the reaction of a material when a stress or strain is applied. By looking at its maximum the yield point can be defined as the corresponding stress or strain at that point.

5.3.2 Yield point evaluation, creep test

Another method, later used as the method of choice, is a series of creep tests. These are made in a way that the following creep test applies a higher load than the previous one. Each load is held for 5 min and a relaxation time of 10 min was provided after the load was released. This creep test series was first made strain controlled and later done stress controlled due to conditioning problems with the DMA (for more information see sec. 6.1.2). All series were done at various relative humidities and both paper directions. The load has been increased linearly from 0 N up to 5 N, a zoom-in example can be seen in fig. 8.

The above green curve represents the creep step and the lower green curve the relaxation step, both in strain. The blue lines are the corresponding stress values.

The yield point has been set to a remaining strain in the relaxation step of 0.05%. The stress and strain values in the creep step before give the wanted yield point values.

5.4 Theoretical plastic model

For the two theoretical models, in house programmed MATLAB routines were used.

The one based on plasticity is called "hardCalc.m" and uses a rate-independent nonlinear hardening plasticity model [7] shown in fig. 9.

The program calculates the hardening function (which is the stress-strain curve above the yield point) from experimental data. It subtracts the elastic strain (ϵ_e) from the total strain ($\Delta\epsilon_{tot}$) to get the plastic strain ($\Delta\epsilon_p$). Shown in fig. 9 left. Then it computes the stress in terms of the plastic strain as illustrated in eq. 14 and 15:

$$\sigma(\epsilon_{tot}) \rightarrow \sigma(\epsilon_p) \tag{14}$$

$$\epsilon_p = (\epsilon_{tot} - \epsilon_{tot}(y_0))\frac{\Delta\epsilon_p}{\Delta\epsilon_{tot}} \tag{15}$$

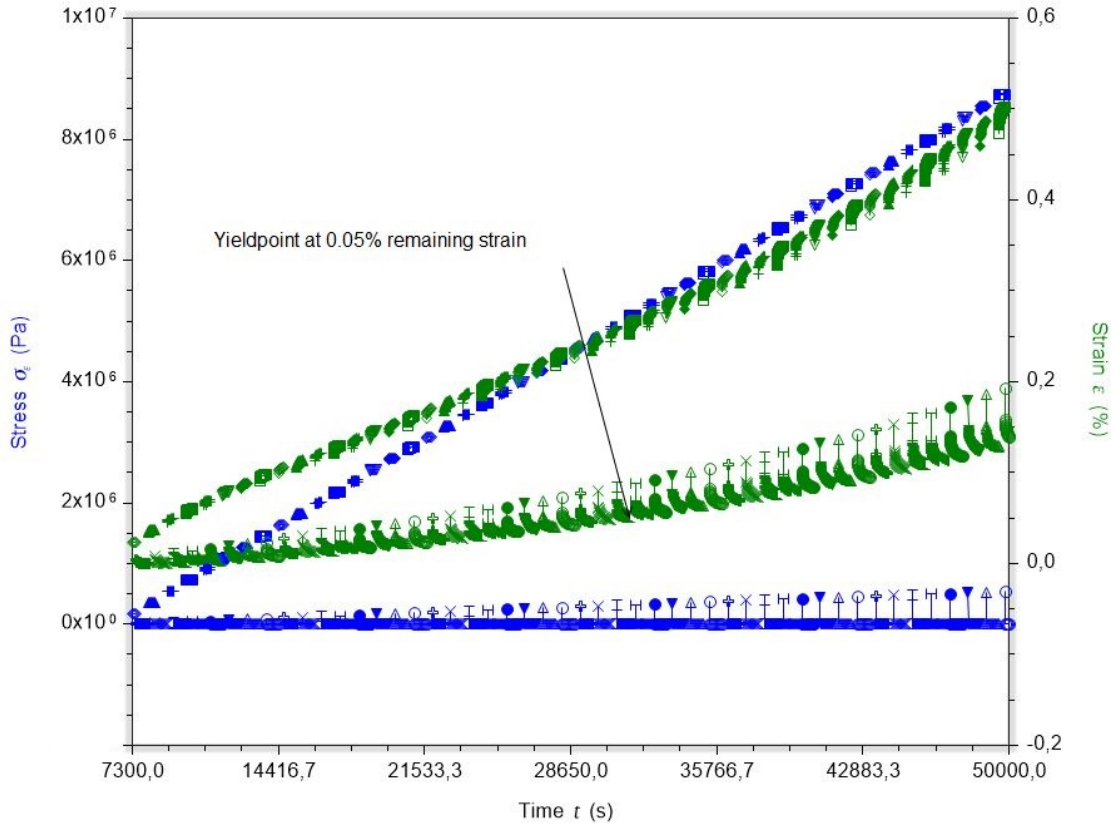


Figure 8: Series of creep tests, stress controlled. The upper green curve represents the creep and the lower green curve the relaxation step. The blue lines shown the corresponding stress values at either the creep or the relaxation step. The yield point has been set to a remaining strain of 0.05%.

From these equations it creates a table of stress and strain values for the desired hardening function. So "hardClac.m" simply recalculates the experimental data based on the E-modulus since the elastic strain and stress are related via $\Delta\epsilon_e = \frac{\Delta\sigma}{E}$.

As input parameters it needs obviously the experimental data gained from tensile tests and the yield point of the used paper at the desired relative humidity. Variable parameters are the way of loading (using a stress/force as a load or a strain/deformation), the resolution time, the maximum number of iterations and aborting criteria. The tensile tests needed for this program have been done in machine and cross direction and at relative humidities of $(0, 50, 90)$ %.

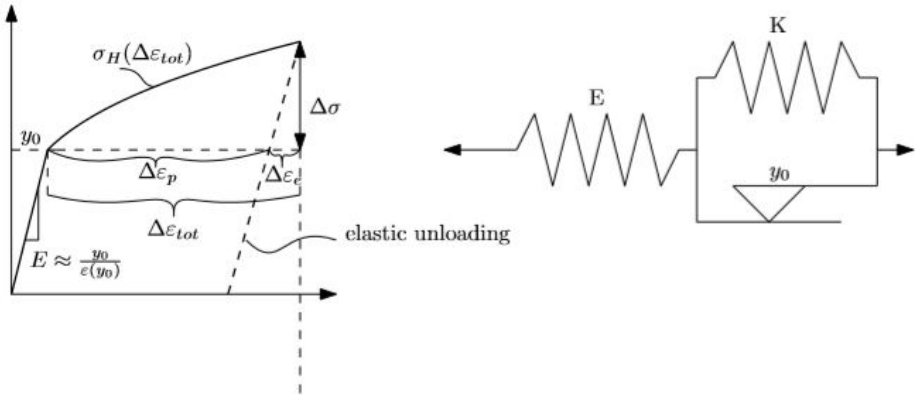


Figure 9: Schematic description of the plastic region in a stress-strain curve (left). An independent plastic model to describe the paper behaviour (right).

5.5 Theoretical viscoelastic model

The second program made in house focuses on viscoelasticity and is called "REHAfit". The program is based on a generalized Maxwell model shown in fig. 10 and it operates according to [8] and [17].

The generalized Maxwell model consists of an infinte number of Maxwell elements. Each Maxwell element has a spring and a dash pot in series. By stretching the sample (increasing the strain) step by step all the Maxwell elements get activated and their corresponding E-moduli can be read out.

Based on the experimental data gained from a single creep test this program makes a fit using this model and calculates the E-moduli and relaxation times of each Maxwell element. There are several optional settings applicable to make the fit better, but the most important are:

The number of Maxwell elements, which can be read out of the number of decades of time needed for the creep test, and the option if a stress relaxation creep or a strain relaxation creep test have been performed.

For the case of this experiment a stress relaxation creep test has been performed at the yield point stress obtained from the yield point experiments described above. To get a better statistic the sample size has been increased to the maximum measurable size which the DMA can handle ($(10x22x0.11)$ mm). The loading time as well as the relaxation time have been changed to standard 4 min. This measurement has been performed for $(0, 50,$ and $90)$ % relative humidity.

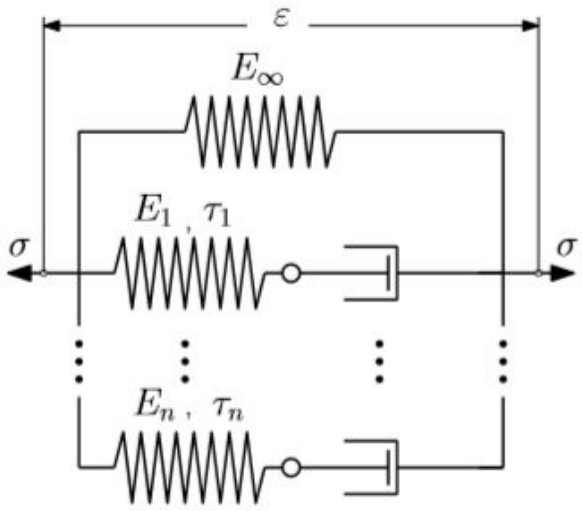


Figure 10: Generalized Maxwell model with n elements

5.6 Frequency sweep measurements

The motivation to make frequency sweep measurements was to create a mastercurve of UNUT paper as a function of relative humidity. As described in sec. 4.2.5 mastering is based on Time-Temperature-Superposition not on Time-Humidity-Superposition. This phenomenon has been investigated with wool fibers already [3] but not with paper samples.

Frequency sweep measurements have been performed in a range from (0.1 – 100) Hz and from (1 – 50) Hz, at various relative humidities to gather information about the complex modulus and to later create a mastercurve.

Those tests have been performed with UNUT paper in cross and machine direction and with PET to get a feeling of mastering and TTS. Due to unexpected results (artefacts visible in the complex modulus explained later in sec. 6.4) also measurements at a range from (10^{-2} – 1) Hz have been performed as well as reverse frequency ranges and time sweeps where the frequency is held constant (0.1 Hz) over a set amount of time (2.5 h). The influence of the amplitude used was also investigated by using stress sweeps, which were made with a constant frequency of 1 Hz and a varying amplitude force from (0.1 – 2) N.

All measurements have been done with the maximum sample size possible and force controlled. A schematic view is illustrated in fig. 11.

A pre-force has been applied 20 % above the measured pseudo yield point and afterwards a cycle ±20 % around the pseudo yield point has been done. Usually this setup is arranged in a way that the cycle is way below the pre-force to stay elastic, but at this point it was already shown that UNUT paper has no

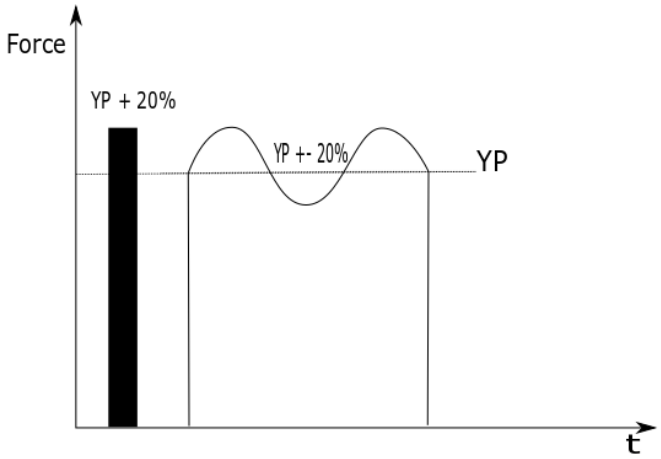


Figure 11: A schematic view of the frequency sweep measurements done. A 20 % cycle around the pseudo yield point has been chosen.

real yield point because it is never fully elastic. It is later shown that the choice of pre-force and amplitude makes no significant change in the values of the complex modulus optained.

5.7 Capillary forces

The last project of this theses is the influence of capillary forces to the fiber bonding in paper. Tensile tests with cross direction samples, diameters ($5x22x0.11$) mm, were made. Those tensile tests were performed under 3 different conditions:

- 50 % relative humidity
- 0 % relative humidity
- 0 % relative humidity with preheating

The tests themselves were always performed at 23 °C. At the preheating step the sample has been heated up to 110 °C, held there for 20 h, cooled down to operation temperature again before the tensile test was done. During this this conditioning step, the force has been held constant at 0 N by the DMA.

The idea is to get rid of all the water stored in the paper and with this, neglect the capillary forces from the paper bonding system. By comparison of the resulting stress-strain curves the influence of capillary forces in paper can be observed.

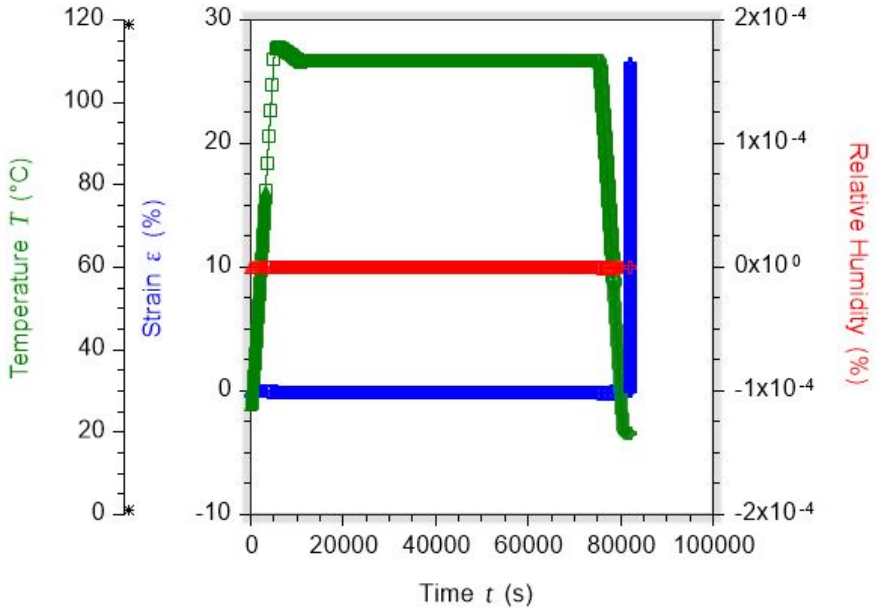


Figure 12: A schematic view of the third condition with preheating step in it. In red the constant relative humidity can be seen. In blue the strain is shown which stays 0 till the actual tensile test starts. In green the temperature is shown which increases at the beginning to 110 °C, held there for 20 h and cooled down to operation temperature again.

A schematic view of the third condition is shown in fig. 12 for better understanding.

As can be seen, the relative humidity (red) is held constant during the whole procedure at 0 %, the temperature (green) is raised up to 110 °C, kept there for 20 h and brought back to 23 °C again before operating and the strain (blue) shows a steep increase at the end which corresponds to the actual tensile test taking place.

6 Results and discussion

6.1 Yieldpoint evaluation

6.1.1 Yield point evaluation, tensile test

An example of the results of the tensile tests is shown in fig. 13

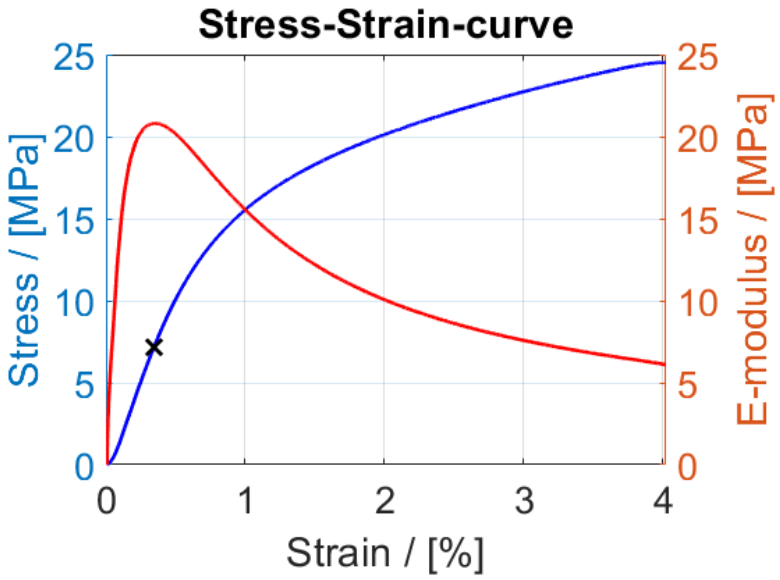


Figure 13: Tensile test shown as stress-strain curve (blue). The calculated E-modulus via eq. 13 is shown in red. The black cross points at the developed yield point.

The blue line shows a stress-strain-curve of a UNUT sample in CD, the red curve is the calculated E-modulus and the green cross shows the the yield point corresponding to the maximum of the E-modulus. This method is only based on a definition, that the yield point can be defined as the maximum of the blue lines slope and gives no information about plasticity. Therefore, it was replaced by another method, creep tests.

6.1.2 Yield point evaluation, creep test

In fig. 14 a creep test series, strain controlled, of a CD sample is shown.

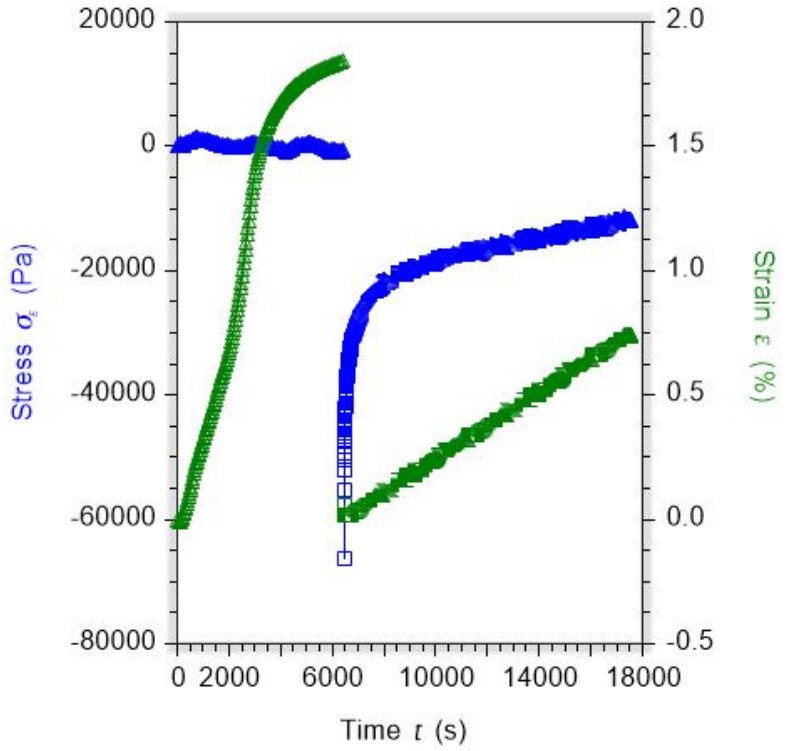


Figure 14: Strain controlled creep test, UNUT, CD, 93 % relative humidity. DMA holds stress constant during conditioning step which leads to a jump in strain before the creep measurement starts. Stress shown in blue, strain in green.

What can be seen here is a sample in cross direction at 93 % relative humidity. A jump in stress and strain is clearly visible which comes from the way the DMA is operating. When a conditioning step is applied, the DMA holds the desired sample at constant stress/force. By changing the relative humidity und holding the sample at constant stress, a strain is created inside the sample. In the case of fig. 14 the relative humidity has been increased which leads to an increase in strain. The first creep test starts at 0 % strain so the DMA "corrects" the accrued strain by pushing the sample together. This leads to a jump in stress and strain. Unfortunately, this effect can not be corrected in the used DMA and since one does not know the precise values of strain after equilibration, the setup had to be corrected to a stress controlled creep test.

The way to go stayed the same, a series of creep tests with increasing load after each step and 5 min of load and 10 min of relaxation. The only thing that

has been changed is the way the load is applied. Instead of a strain, a force has been applied. This works perfectly with the way the DMA is operating and thus leaded to the desired results. An example is shown in fig. 15.

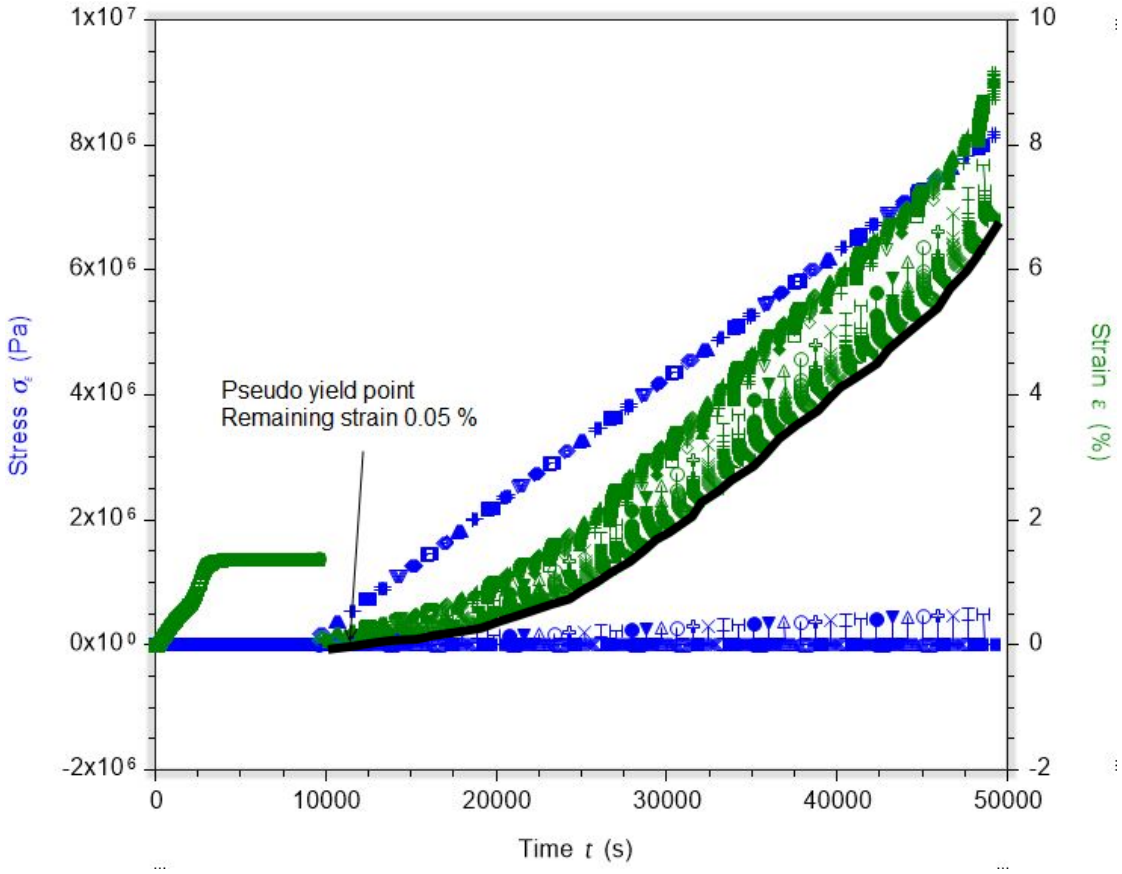


Figure 15: Stress controlled creep test, UNUT, CD, 90 % relative humidity. Upper green curve represents the creep steps, lower ones the relaxation steps. Blue points give the corresponding stress values. The pseudo yield point is marked at a remaining strain of 0.05%. Compared to the measurement which was strain controlled, no jump in the driving force (stress) is visible which indicates that the measurement worked correctly.

Again a cross direction sample is shown at 90 % relative humidity. The force was increased linearly from 0 N up to 5 N and the resulting strain was measured. The black curve on the bottom green one represents the relaxation during this experimental series and thus the information about plasticity. This curve was used to define the yield point of the used UNUT paper. What can be seen is that there is no pure elastic region visible in fig. 15. The black curve does not stay constant at the beginning, instead it starts to increase immediately after the

measurement has been started. It follows, because there is no pure elastic region visible, that UNUT paper has no ”real” yield point, so it is impossible to stay elastic during measurements and it is not possible to define a yield point.

Nevertheless a yield point had to be defined to have an orientation point for later experiments, so that the relative strain and stress at different relative humidities is equal.

The pseudo yield point has been defined as the point where a change of $0,05$ % of the strain in recovery appears. The corresponding strain and stress values for the pseudo yield point can be written out of the curve above (creep curve).

The results are show graphically in fig. 16 (stress, strain and E-modulus) and are listed in tab. 5 (stress and strain values).

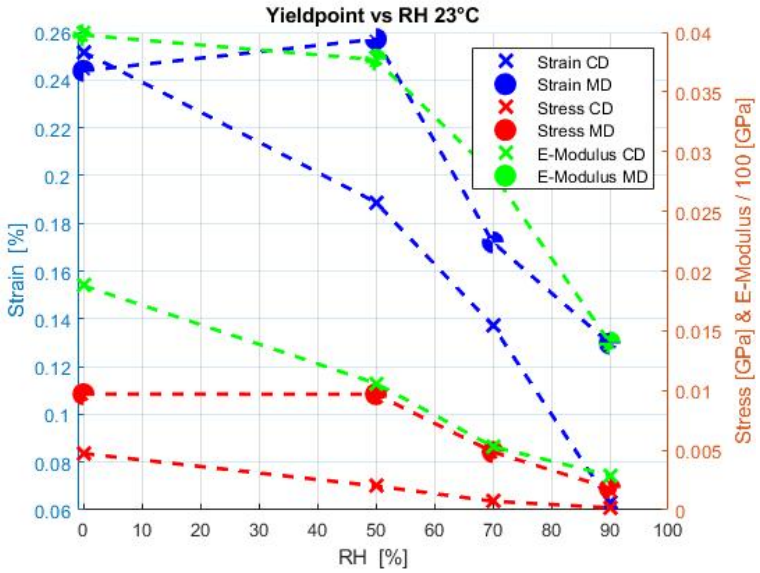


Figure 16: Defined yield points for CD and MD at different relative humidities in stress, strain and E-modulus.

Table 5: Yield points for CD and MD at different relative humidities in stress and strain

σ.....stress
ϵ.....strain
RH.....Relative humidity
CD.....Cross direction
MD.....Machine direction

Paper direction	*RH* / [%]	ϵ / [%]	σ / [*MPa*]
CD	0	0.25	4.7
CD	50	0.18	2.0
CD	70	0.14	0.7
CD	90	0.06	0.2
MD	0	0.24	9.7
MD	50	0.26	9.7
MD	70	0.17	4.8
MD	90	0.13	1.8

As can be seen in fig. 16 the pseudo yield point and thus the paper behaves as expected. With increasing relative humidity the strain, the stress and the calculated E-modulus decrease.

6.2 Theoretical plastic model

An example of the recalculated hardening functions obtained from ”hardCalc.m” is shown in fig. 17.

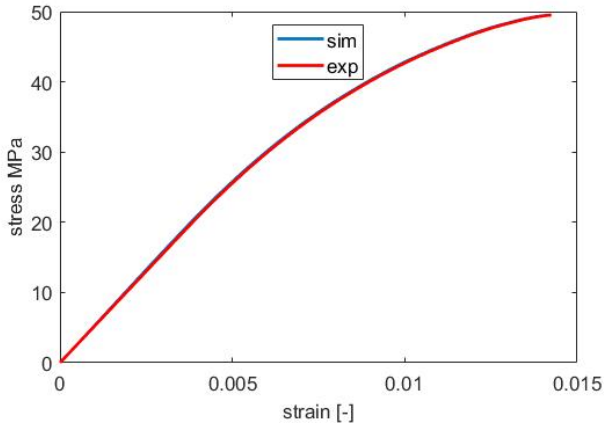


Figure 17: A stress-strain curve of the experimental data in red and the recalculated hardening function in blue. They relate 1:1.

What can be seen here is that the recalculated curve and the experimental data relate 1:1. Since the used UNUT paper has no real yield point, the obtained hardening function is nearly the full stress strain curve. The strain in fig. 17 is the total strain of the tensile test made.

A comparison of the different paper directions and relative humidities can be seen in fig. 18.

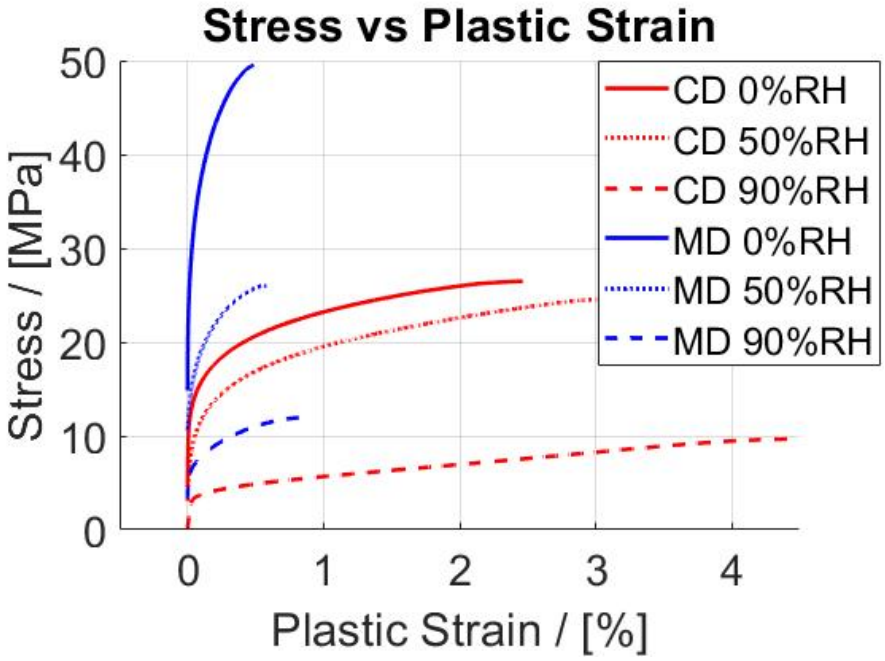


Figure 18: A comparison of the obtained hardening functions for CD and MD and various relative humidities. Red curves show the CD samples and blue ones the MD samples. Yield point differs for different humidities (starting point of the curves) and break point differs too.

Clearly visible in fig. 18 is the behaviour of the paper while changing the relative humidity. Just like shown in the yield point experiments, with increasing relative humidity the strain at break increases for both paper directions while the stress at break as well as the yield point stress decrease. This means that the paper can get more stretched when the humidity is higher but at the same time one needs less force to break it.

6.3 Theoretical viscoelastic model

The way how the creep tests for ”REHAfit.m” were made can be seen in fig. 19.

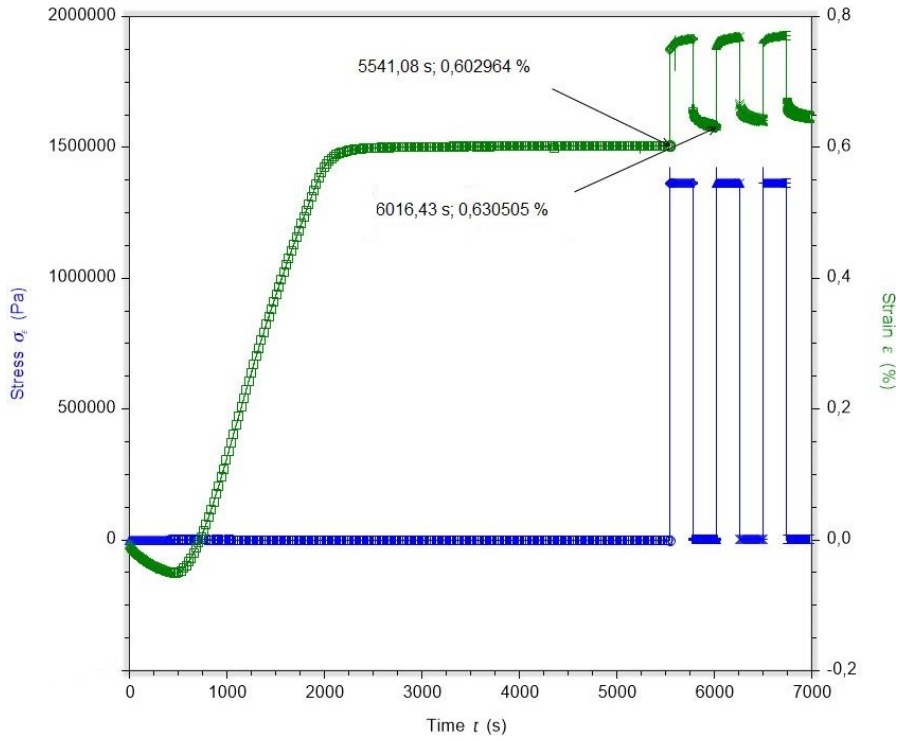


Figure 19: Creep test in cross direction for the maximum measurable size possible at 50 % relative humidity.

This test has been made at standard conditions of 23 °C and 50 % relative humidity. If a closer look at the values marked in the picture is taken it can be seen that the difference in plastic strain before and after the measurement is less than the defined yield stress of 0.05 %.

All three of these creep tests has been taken and put into ”REHAfit.m”. The results, here plotted as strain vs time, can be seen in fig. 20.

The same sample as in fig. 19 is shown but the strain is plotted as a function of time. In blue the experimental data points are shown and in red the fit from ”REHAfit.m”. What can be seen here is that there are 5 decades of time which tells us that 5 Maxwell elements are needed to make a proper fit, which leads to 5 relaxation times (τ) and 5 E-moduli plus the instantaneous E-modulus (E_{inst}). When those 3 fits are compared, there is no difference visible between them, but if a look at tab. 6 is taken, this changes. The corresponding instantaneous modulus as well as the E-moduli of each Maxwell element is shown there. The

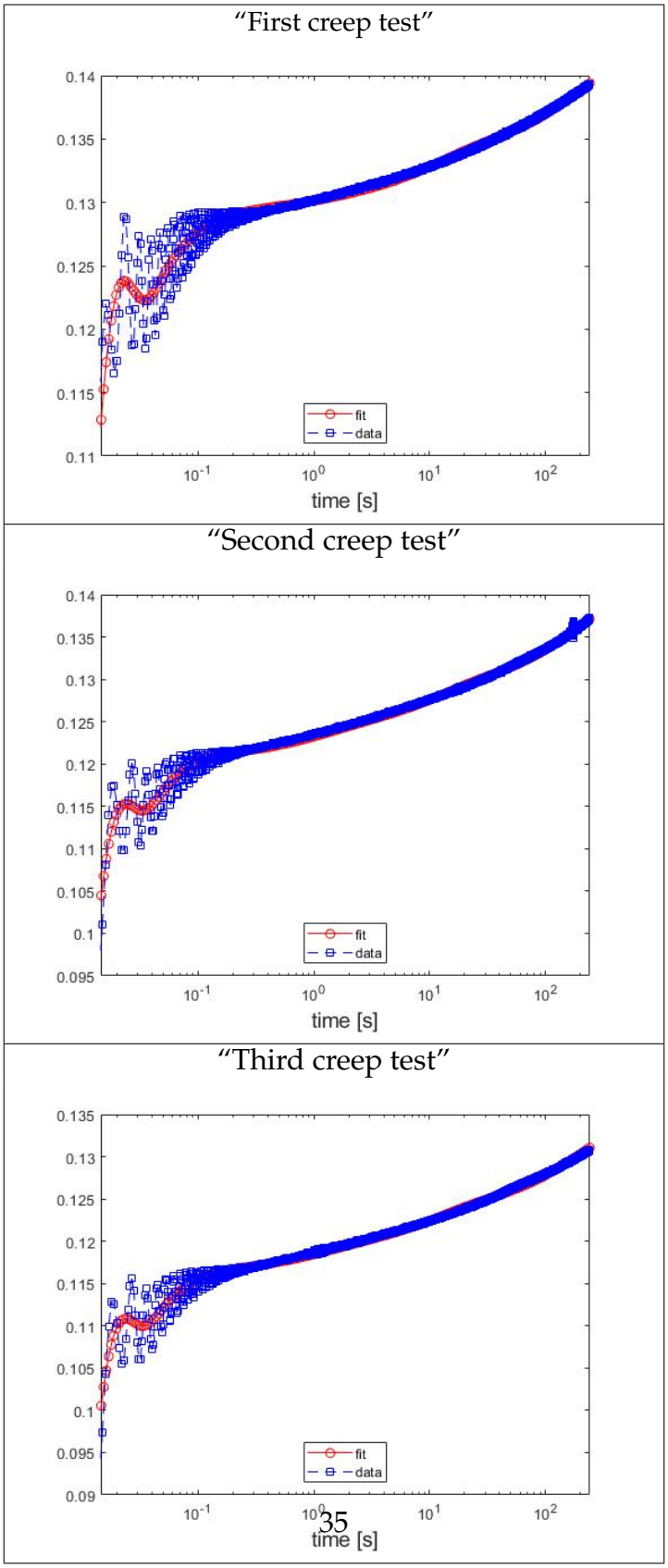


Figure 20: Comparison of the fits obtained from "REHAfit.m" for the three creep tests in series.

Table 6: Fit parameters for 3 creep tests in series get from "REHAfit.m"

All units in GPa

Parameter	Creeptest 1	Creeptest 2	Creeptest 3
E_{inst}	10.6556	13.5774	13.1050
E_1	1.1031	2.4933	0.8132
E_2	$1.8 \cdot 10^{-10}$	0.0012	0.7751
E_3	$6.6 \cdot 10^{-17}$	0.0090	$2.1 \cdot 10^{-15}$
E_4	0.6144	0.5814	0.5761
E_5	0.9162	0.8124	0.7973

values of E_{inst} and the other E-moduli differ after each creep test. To be able to compare the later results for different relative humidities and paper directions correctly, it is important to compare the same creep test. So for later comparisons only the first creep test has been taken and put into "REHAfit.m".

The resulting relaxation times to all creep tests put into "REHAfit.m" are listed in tab. 7:

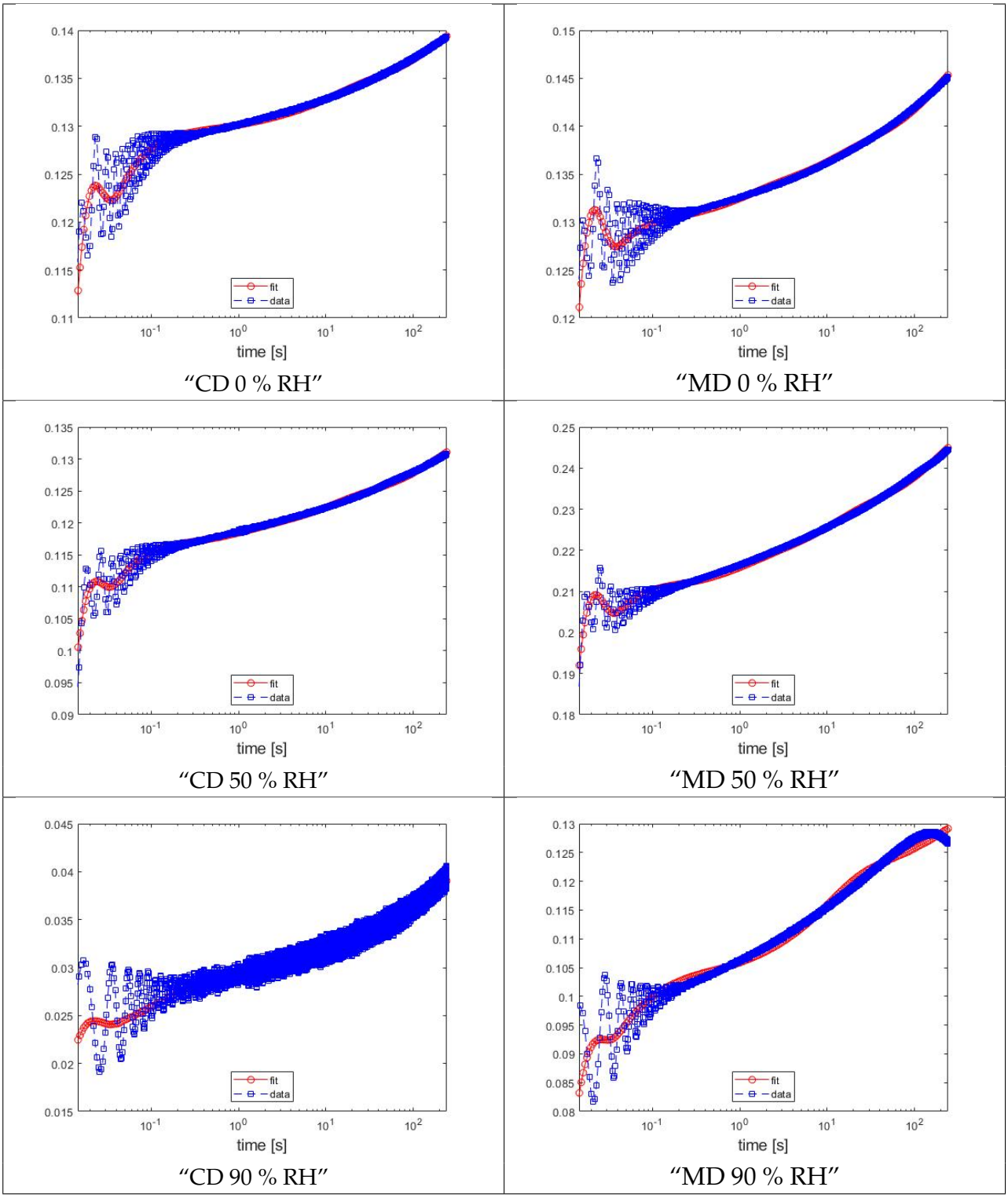
Table 7: Relaxation times from "REHAfit.m"

Relaxation time	s
τ_1	0.03
τ_2	0.1
τ_3	1
τ_4	10
τ_5	200

These relaxation times are valid for all samples measured.

In fig. 21 a comparison of the fits obtained, for different relative humidities and paper directions, is shown. Here UNUT samples in cross direction and machine direction are shown, with relative humidities of $(0, 50, 90)$ %. The fits do relate to the experimental data except for the first decade. Here the signal to noise ratio is too bad to have a good resolution. Especially if a closer look at the sample in cross direction with 90 % relative humidity is taken, the yield point stress for this sample is the lowest and with this the signal to noise ratio throughout the whole measurement is quite bad. But nevertheless the curvature of the fit does suit the curvature of the experimental data.

A graphical view of the E-moduli corresponding to the Maxwell elements activated at each relaxaion time is shown in fig. 22. Here the very first data points on the left are the instantaneous moduli (E_{inst}) for the different samples observed. The next points on the right are the E-moduli corresponding to each



"CD 0 % RH" "MD 0 % RH"

"CD 50 % RH" "MD 50 % RH"

"CD 90 % RH" "MD 90 % RH"

Figure 21: Comparison of the fits obtained from "REHAfit.m" for cross and machine direction and for various relative humidities.

Maxwell element activated, at their relaxation times, and subtracted from E_{inst}. So the E-modulus value at the relaxation time τ_n can be written as:

$$E = E_{inst} - E_{\tau_1} - ... - E_{\tau_n} \tag{16}$$

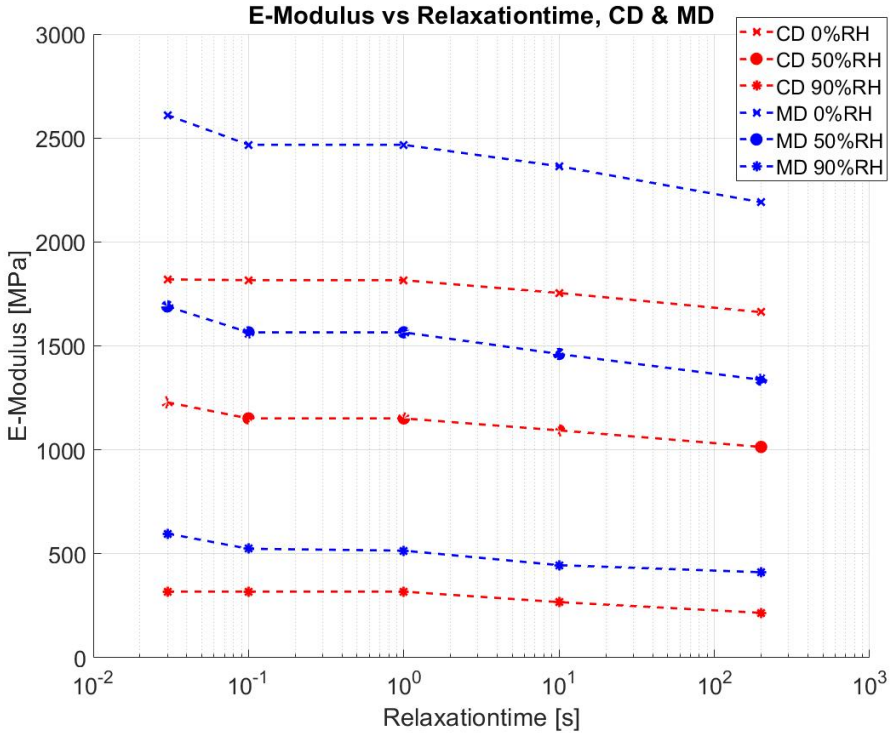


Figure 22: E-moduli vs τ plot. The E-modulus of each Maxwell element is subtracted from E_{inst} when it gets activated.

The corresponding values of the E-modulus are written in tab. 8

Typical E-modulus values for paper according to [14] lie between $2-20$ GPa. These values are obtained by looking at the force per specimen width for a given strain: $E = \frac{F}{W} d\epsilon$. This means that the sample thickness plays an important role. Nevertheless the range for the E-mdoulus values does suit tab. 8.

Table 8: E moduli from "REHAfit.m"

All units in GPa

E modulus	**CD** 0 %	**CD** 50 %	**CD** 90 %	**MD** 0 %	**MD** 50 %	**MD** 90 %
E_{inst}	$2.12 \cdot 10^{1}$	$1.3 \cdot 10^{1}$	$4.8 \cdot 10^{0}$	$2.61 \cdot 10^{1}$	$1.69 \cdot 10^{1}$	$6.14 \cdot 10^{0}$
E_1	$3.0 \cdot 10^{0}$	$8.13 \cdot 10^{-1}$	$1.62 \cdot 10^{0}$	$2.7 \cdot 10^{-18}$	$1.03 \cdot 10^{-14}$	$1.66 \cdot 10^{-1}$
E_2	$4.05 \cdot 10^{-2}$	$7.75 \cdot 10^{-1}$	$5.42 \cdot 10^{-13}$	$1.43 \cdot 10^{0}$	$1.25 \cdot 10^{0}$	$7.32 \cdot 10^{-1}$
E_3	$2.15 \cdot 10^{-16}$	$2.13 \cdot 10^{-15}$	$1.79 \cdot 10^{-15}$	$5.31 \cdot 10^{-22}$	$1.28 \cdot 10^{-17}$	$9.01 \cdot 10^{-2}$
E_4	$6.13 \cdot 10^{-1}$	$5.76 \cdot 10^{-1}$	$5.04 \cdot 10^{-1}$	$1.03 \cdot 10^{0}$	$1.04 \cdot 10^{0}$	$6.99 \cdot 10^{-1}$
E_5	$9.24 \cdot 10^{-1}$	$7.9 \cdot 10^{-1}$	$5.16 \cdot 10^{-1}$	$1.73 \cdot 10^{0}$	$1.24 \cdot 10^{0}$	$3.39 \cdot 10^{-1}$

6.4 Frequency sweep measurements

As a result of frequency sweep measurements the complex modulus is recorded as a function of frequency. An example of a UNUT sample in cross direction at 0 % relative humidity can be seen in fig. 23.

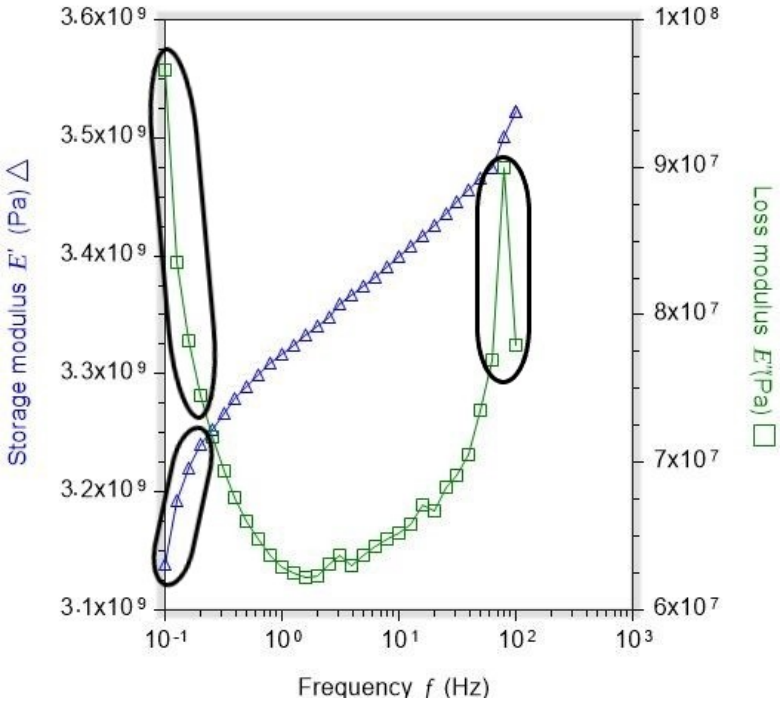


Figure 23: Frequency sweep measurement, (0.1 – 100) Hz, cross direction. Artefacts (circled in black) at the beginning and the end of complex modulus. Storage modulus in blue and loss modulus in green.

Looking at fig. 23 there are three artefacts visible which have to be clarified because they are present at all relative humidities and other frequency sweep measurements. There is a steep increase in the storage modulus (blue) and a drop as well as a peak visible in the loss modulus (green). These artefacts open a lot of new questions concerning frequency sweep measurements. A series of other experiments have been made to get a better understanding of what causes these artefacts.

At first an equilibration effect was investigated. As mentioned in sec. 5.2 UNUT paper needs at least 3 h to be fully equilibrated. The conditioning time, as described in sec. 5.2, has been set to 1 h to make the measurement as short as possible. One frequency sweep, excluding the conditioning time, lasts for 45 min, so an equilibration effect sounds like a possible action that can take place.

To see if this is the cause of the first artefacts a frequency sweep measurement with a conditioning time of 3 h has been made at the same frequency range and again at standard conditions. The result in comparison with the example from before can be seen in fig. 24.

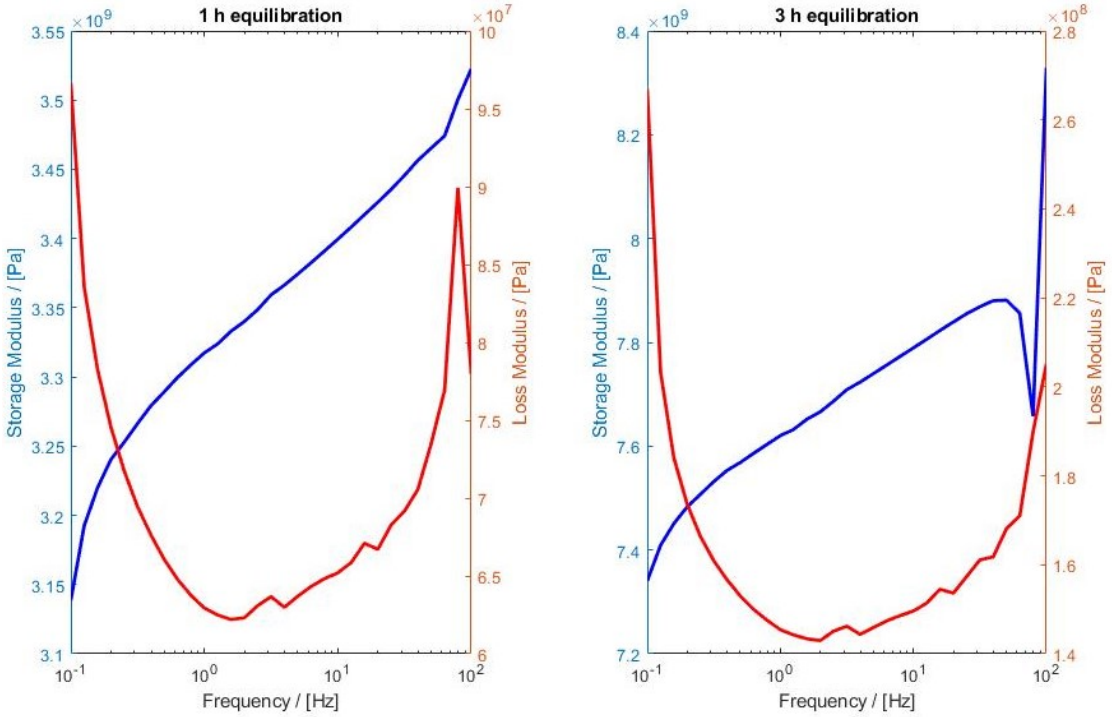


Figure 24: Comparison frequency sweeps with 1 h (left) and 3 h (right) of conditioning time. They have the same curvature and artefacts.

Those two curves seem to have the same curvature and do show the same artefacts (beside their different values which is explained later). As there is still this steep increase in storage and drop in loss modulus, the equilibration does not cause those two artefacts.

The next investigation step was to look more closely at the frequency range of these first artefacts. So a frequency sweep in a range from $(10^{-3} - 1)$ Hz has been made. The result in comparison with the very first measurement can be seen in fig. 25.

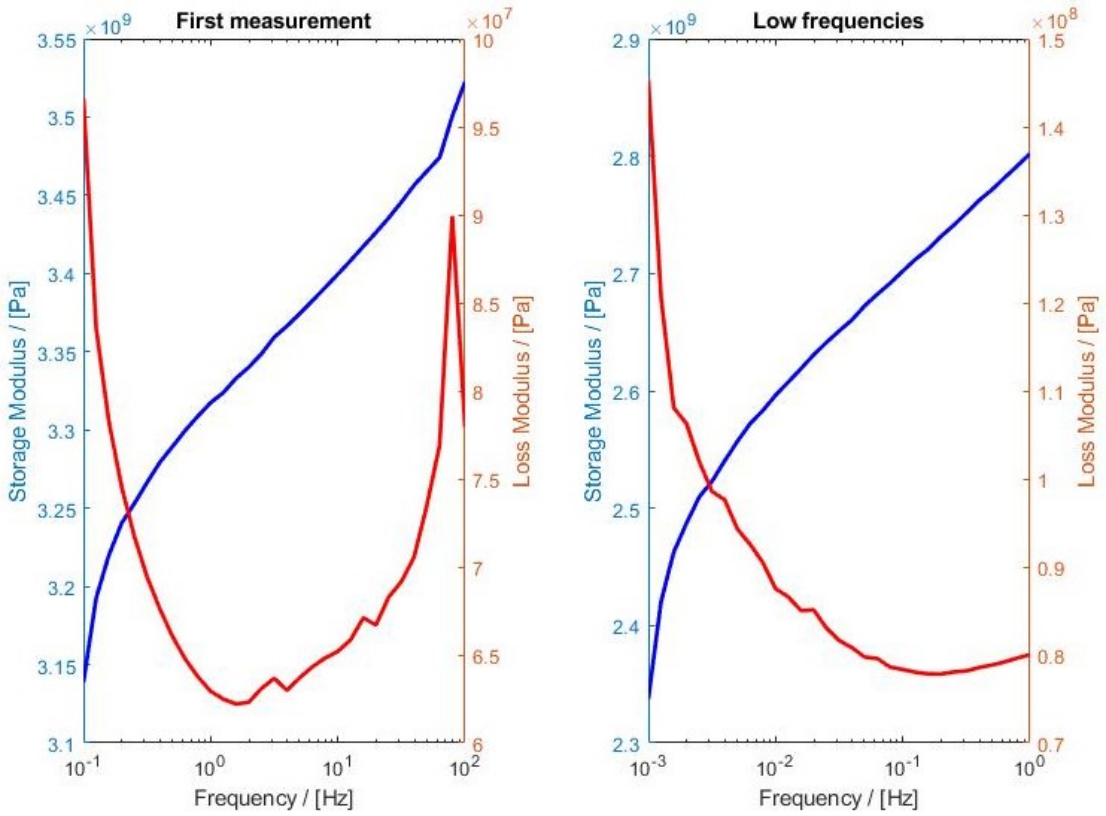


Figure 25: Comparison frequency sweeps: First measurement (left) and the one at low frequencies ($(10^{-3} - 1)$ Hz, right). Same curvature but last artefact is gone.

Again if we take a look at the curvature of those two measurements they do look alike. They have different values obviously because they are in different frequency ranges but what is clearly visible is that the last artefact, the peak in the loss modulus, is gone. Does that mean that this peak is frequency dependent while the other artefacts do not seem to be?

Next two sweeps after each other were made. The result can seen in fig. 26.

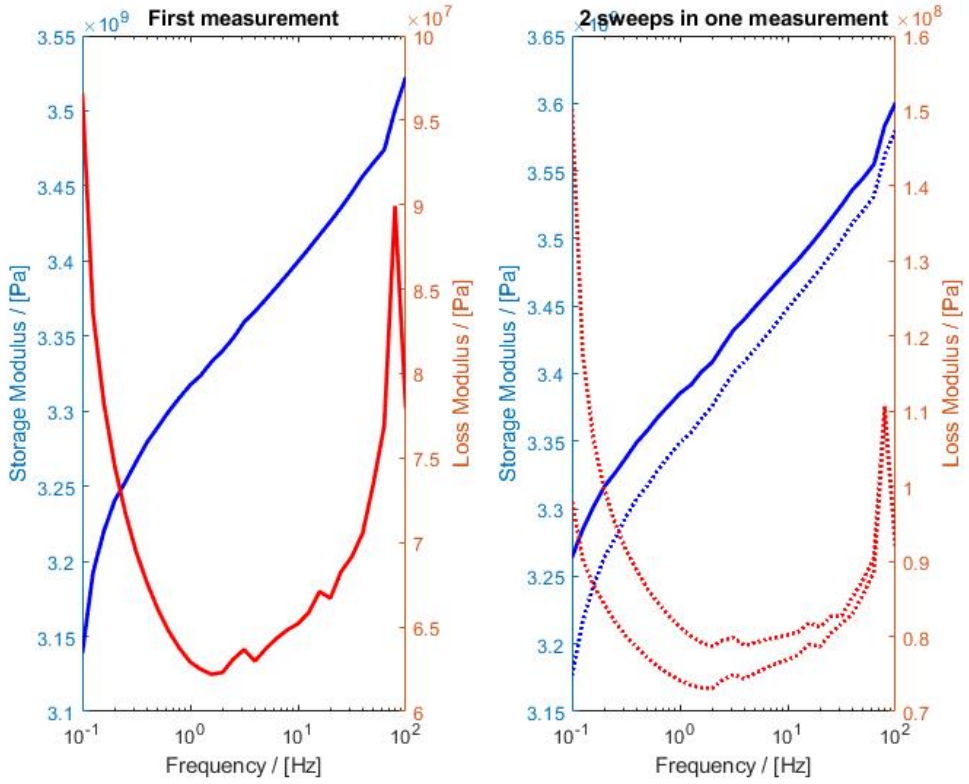


Figure 26: Comparison frequency sweeps: First measurement (left) and two sweeps in series (right). Same curvature but at the second sweep (not dotted line right, blue) the artefacts at the beginning are smaller.

Again the curvature looks the same, there are all three artefacts visible in both sweeps (right picture, dotted one is the first, not dotted one the second sweep), but at the second sweep the first two artefacts look like they got narrower (steep increase/ drop). Is this an indication that the first artefacts are an activation effect?

To see this picture more clearly another measurement has been done in which the frequency range has been flipped around. So the measurement has been done in a range from (100 – 0.1) Hz to see if the same results occur. The measurement can be seen in fig. 27.

Now the first artefact at the storage modulus is completely gone and in the loss modulus this artefact got narrower (green curves). This indicates that the first artefact is indeed an activation effect of the paper. When the DMA makes a frequency sweep, it does at every frequency 7 build up cycles and 6 measurement cycles. At high frequencies it changes from counting cycles to counting seconds

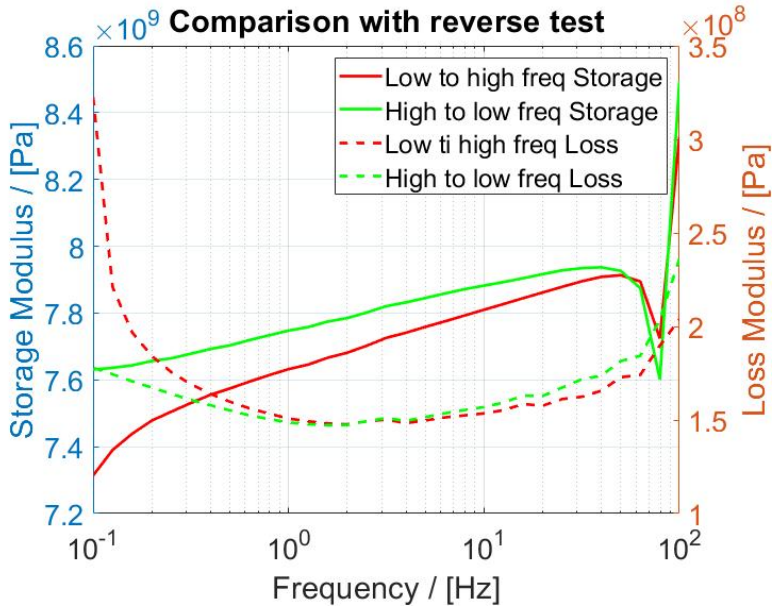


Figure 27: Comparison frequency sweeps: First measurement (red) and reverse measurement (green). Storage modulus is a straight line and loss modulus first artefact got narrower too. Still the second artefact at 100 Hz is present.

because at high frequencies it would have no time to measure data points. So when a measurement is made starting at 0.1 Hz, the DMA makes about 130 cycles in the first decade ((0.1 − 1) Hz). If the chronology is twisted, already at the very first data point (100 Hz) the DMA measures about 1300 cycles. So 10 times more then before. That it is a matter of activation is furthermore shown in the next measurement, where a time sweep has been made. During this time sweep the frequency was held constant at 0.1 Hz for 2.5 h (see fig. 28).

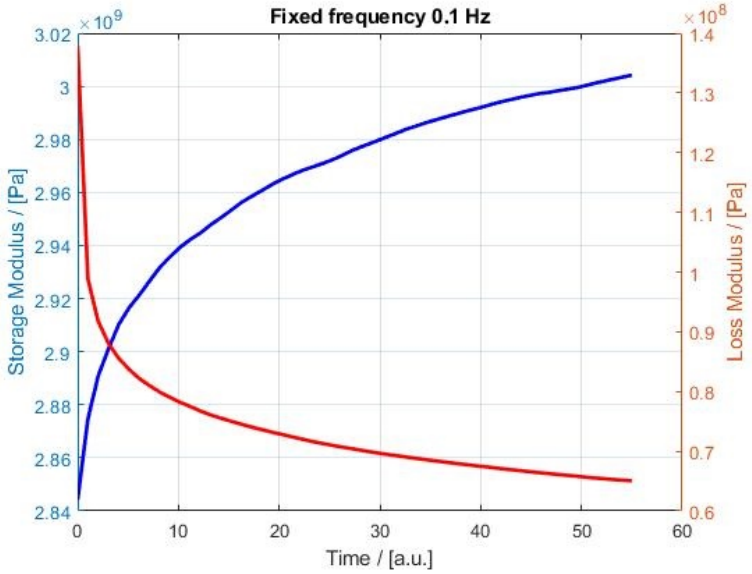


Figure 28: Time sweep, cross direction sample at 0 % relative humidity. Held at 0.1 Hz for 2.5 h.

The time sweep shows clearly the same behaviour as the frequency sweep before, this suggests that the first artefacts are activation effects, otherwise the complex modulus should stay constant during the time sweep measurement.

Looking at all the measurements made so far, the peak in the loss modulus seems to appear only at a certain frequency. A hypothesis has been stayed that this peak may correspond to a resonance effect of the used DMA.

As a side effect the influence of the amplitude and the pre-force has been investigated too. Therefore, stress sweeps have been performed with a constant frequency of 1 Hz and an amplitude range of $(0.1 - 2)$ N. Two series of measurements have been made, one with a pre-force of 3 N and one with a pre-force of 7 N. A machine direction sample has been chosen with a pseudo yield point of 5 N. So one measurement series has a pre-force above and one has a pre-force below the pseudo yield-point. The result can be seen in fig. 29.

Here it can be seen that the influence of the pre-force is of no significant magnitude. The influence of the amplitude is bigger but comparing to the storage and loss modulus values of the figures above, it is still not a big effect. The error bars have been calculated with a 95 % confidence interval. These results show that the way of doing frequency sweeps with UNUT paper is not significantly influenced by the amplitude or the pre-force (in a range ±40 % around the pseudo yield point).

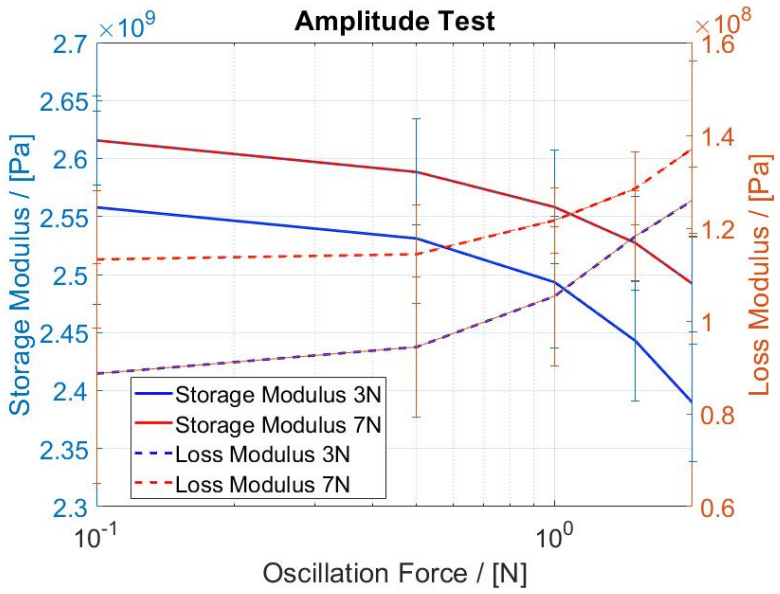


Figure 29: Stress sweep with a constant frequency of 1 Hz, an amplitude range of $(0.1 - 2)$ N. One test with a pre-force of 3 N, one with 7 N. Looking at the complex moduli values the influence of the pre-force is rather small compared to the influence of the amplitude. Both do not seem to have a significant e4ffect on the other measurements.

6.4.1 Angle influence

During the measurements made to get a better understanding of how frequency sweep measurements function with a paper sample, an important set up fact about the operation of paper has been investigated.

As can bee seen in fig. 24 the values of the measured storage and loss modulus do vary. This variation has been clarified by taking a closer look on how the paper sample is fixed in the DMA. Even a slight change (like shown in fig. 30) in the paper orientation leads to a massive change in the complex modulus values, illustrated in fig 31.

Looking at those two figures shows, how important it is to fix the paper in the same way/orientation at every measurement. Otherwise the results are not comparable!

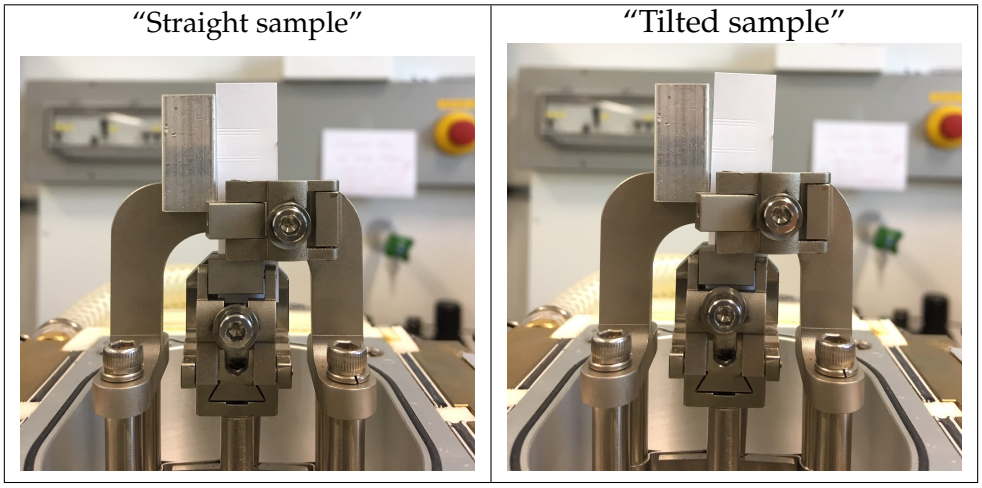


Figure 30: Comparison of a straight and a slightly tilded sample.

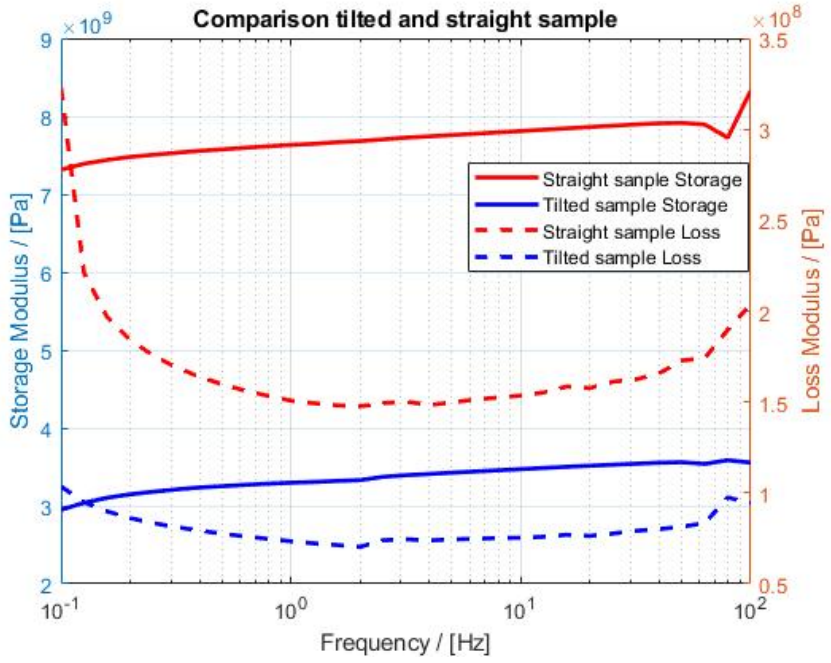


Figure 31: Frequency sweep measurements with a straight (red) sample and a tilted (blue) sample. A clear difference in complex modulus values is visible.

6.5 Mastering

Even though not all mysteries about frequency sweep measurements have been cleared yet, a first try to generate a UNUT paper mastercurve was part of this work too.

Therefore, frequency sweep measurements in a range of (0.1 - 100) Hz where performed at relative humidities of (0, 25, 50, 70, 75, 80, 85, 90) %, with the biggest sample size possible to handle with the used DMA (in cross direction). The results in terms of storage and loss modulus can be seen in fig. 32.

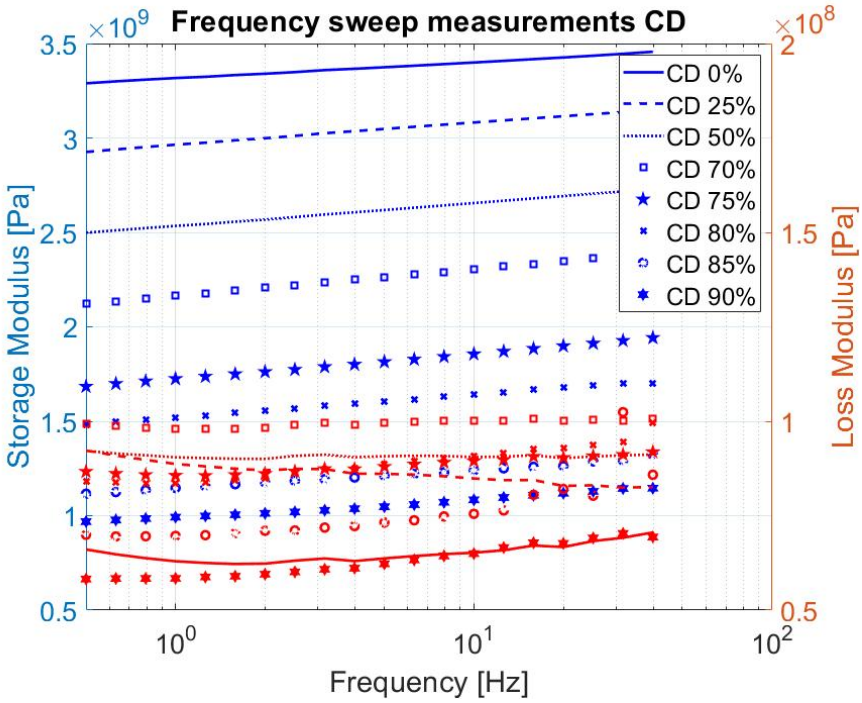


Figure 32: Frequency sweep measurements at various relative humidities in a frequency range of (0.1 - 100) Hz. Storage modulus blue and loss modulus red.

These curves where shifted (only looking at the storage modulus) with respect to standard conditions (50 % relative humidity). The result can be seen in fig. 33.

Here the mastercurve looks well if only the storage modulus is taken into account. As described above the frequency range is expanded tremendously from a range of (0.1 - 100) HZ up to a range of (10^{-20} - 10^{10}) Hz. This means that the behaviour of paper could, theoretically, be described over a time period of about 10^{20} s which are $1.\dot{6} \cdot 10^{18}$ h.

To see if this first try of generating a UNUT mastercurve truly worked, a look

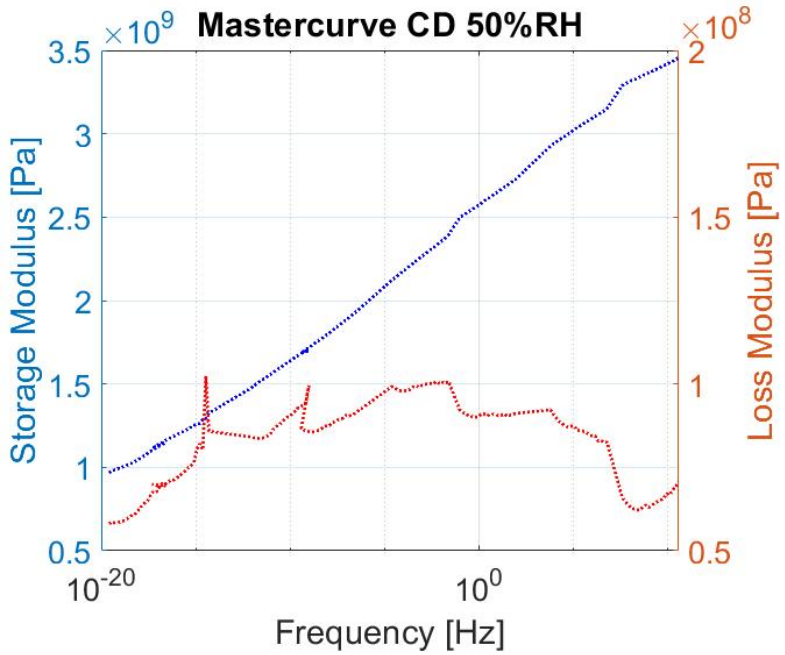


Figure 33: First try to generate a mastercurve with UNUT in cross direction and with a reference of 50 % relative humidity. Storage modulus blue and loss modulus red. Peaks visible in the loss modulus correspond to the artefacts discussed in sec. 6.4.1.

at the shift factor, the *Wiked-plot* and the *Cole-Cole-plot* have been taken.

As described in sec. 4.2.5, the generation of a mastercurve is based on TTS and the WLF-equation. One can either use the WLF equation given in sec. 4.2.5, eq. 12 or use an *Arrhenius-Ansatz* to make a proper shifting. To see if the empirical shifting done above suits the theory, the shift factor has been plotted as a function of relative humidity, together with the theoretical shift factors given by WLF and the *Arrhenius-Ansatz*. the result can be seen in fig. 34.

The three curves shown here do not agree, which indicates that the shifting has not been done correctly.

As a next check if the mastercurve dose make sense, a *Wicket-Plot* as well as a *Cole-Cole-Plot* have been performed. These plots should look like an inverse U and if so are in indicator that the used material is "rheological simple" which means masterable.

An example of an ideal *Wicket-Plot* generated with a rubber can be seen in fig. 4 [23].

The results of the *Wicket-Plot* and *Cole-Cole-Plot* generated with the observed data can be seen in fig. 35.

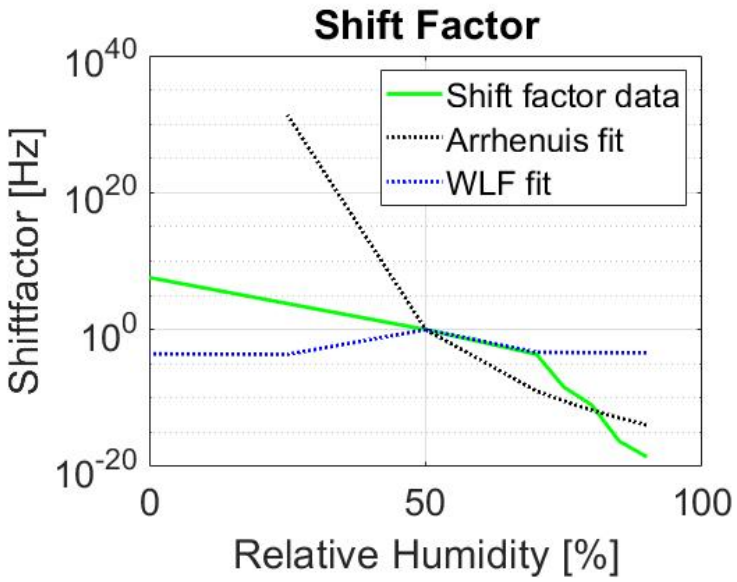


Figure 34: Shift factor from fig. 33 plotted in green, as well as the WLF fit (blue dotted) and the *Arrhenius-Ansatz* (black dotted). The three curves do not agree.

As can be clearly seen, those two plots do not look like a smooth inverse U, which is necessary to make a mastercurve.

Concluding this small journey into the world of mastering and TTS:

Even though the mastercurve generated with UNUT paper does look properly, the shift factor as well as the *Wicket-Plot* and *Cole-Cole-Plot* do not. At the current state of the art it cannot be said if UNUT is masterable or not. The frequency sweep measurements do show some unsolved mysteries and as long as they are present no further mastering does make sense. When the frequency sweep measurements no longer leave open questions behind, a further investigation of generating a mastercurve can be done.

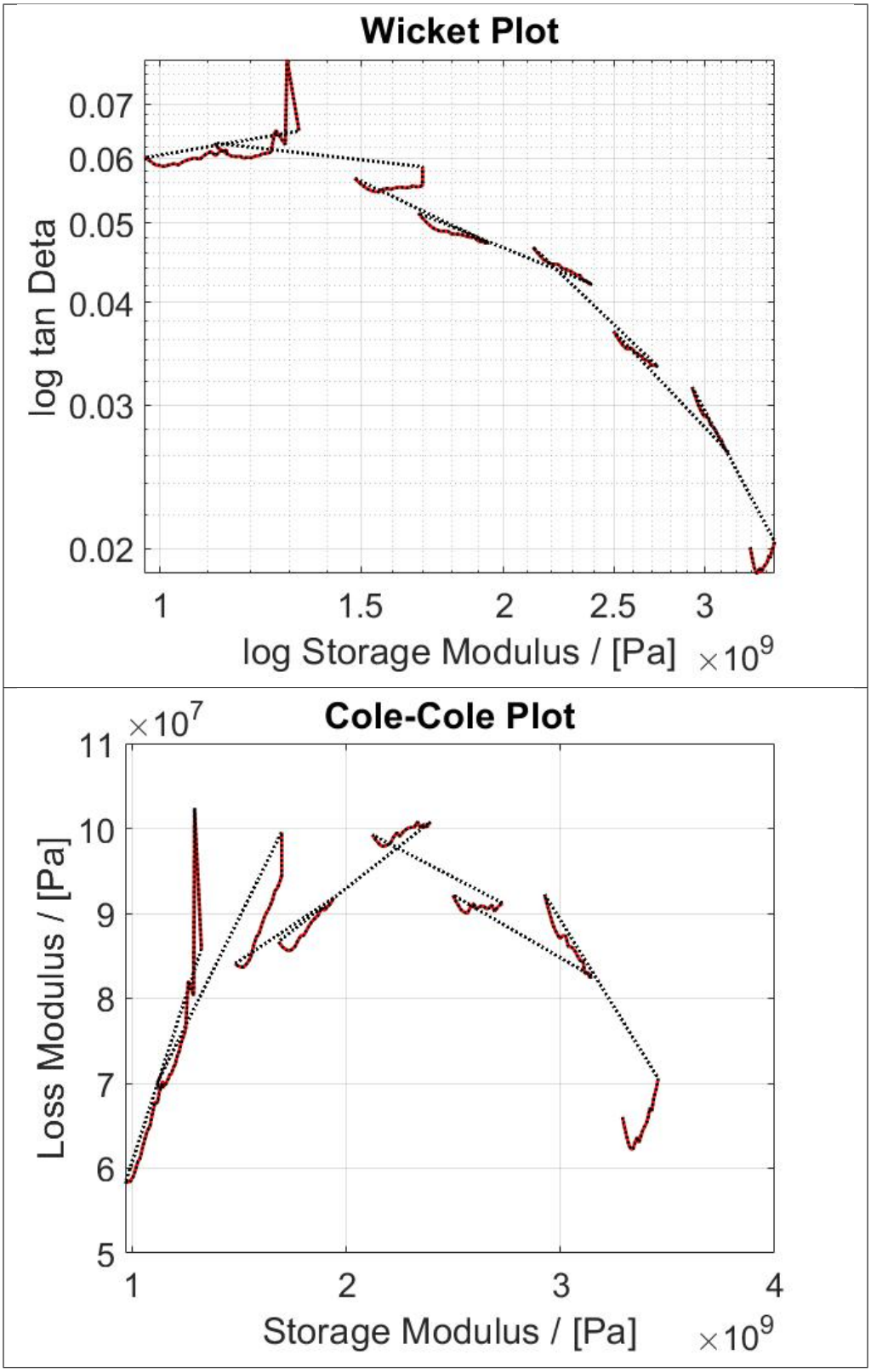


Figure 35: *Wicket-Plot* and *Cole-Cole-Plot* of the data generated with UNUT paper.

6.6 Capillary forces

Under every condition, described in sec. 5.7, 10 measurements have been performed. An example is shown in fig. 36.

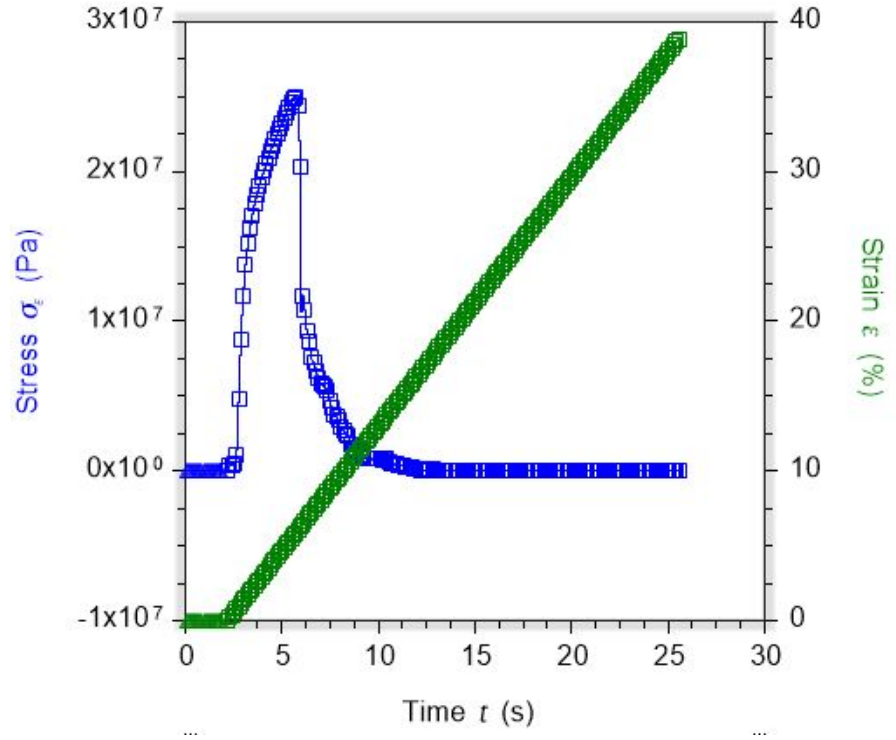


Figure 36: Tensile test at standard conditions, stress (blue) and strain (green) vs time

It is clearly visible that the measurement was strain driven because the strain increases linearly. At the beginning of the measurement the stress should increase linearly (elastic region) till it bends over (plastic region) and drops to 0 at the point of break. In the case of this experiment the paper was not fully stretched before starting. It is nearly impossible to overcome the fact that the sample has a fractional curvature after it is fixed in the DMA. This curvature is stretched out at the beginning of the tensile test and causes this up bending at the beginning. Also it is visible that the measurement shows stress values despite zero after the point of break (they should drop to zero after that point is reached). This is due to the way paper breaks. When the point of break is reached not all paper fibers break at the same time, there is still some connections between the two halves of the sample. Those fiber-bonds break later on individually which causes this bottom out effect. For the aim of this thesis this regions of the curve

are irrelevant so the curve has been cut to only look from the linear region to the point of break. The result is shown in fig. 37.

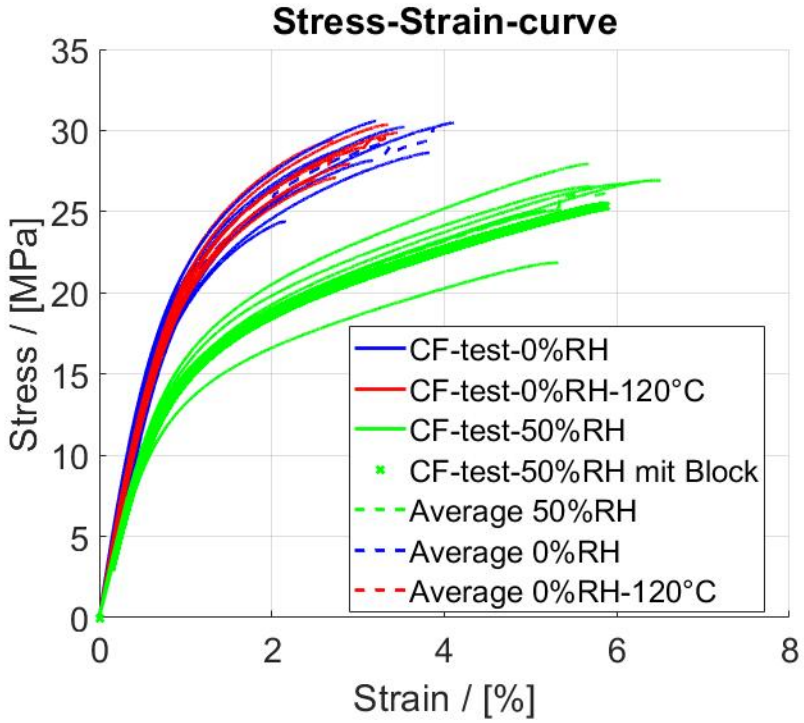
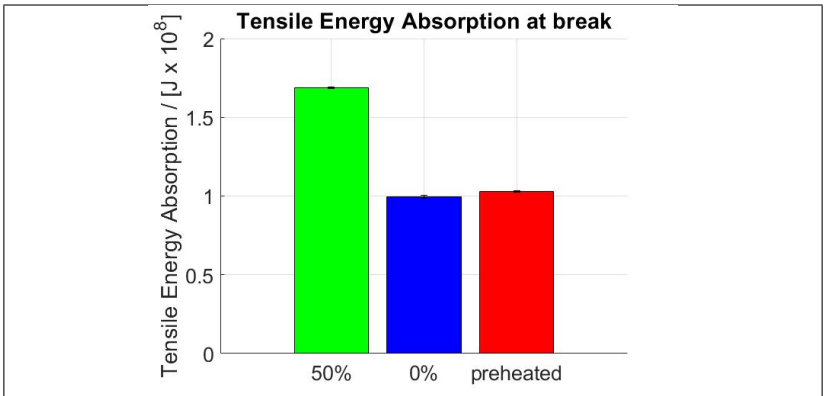


Figure 37: Comparison of the 3 different conditions. Relative humidity: 50 % (green), 0 % (blue), 0 % + preheating (red)

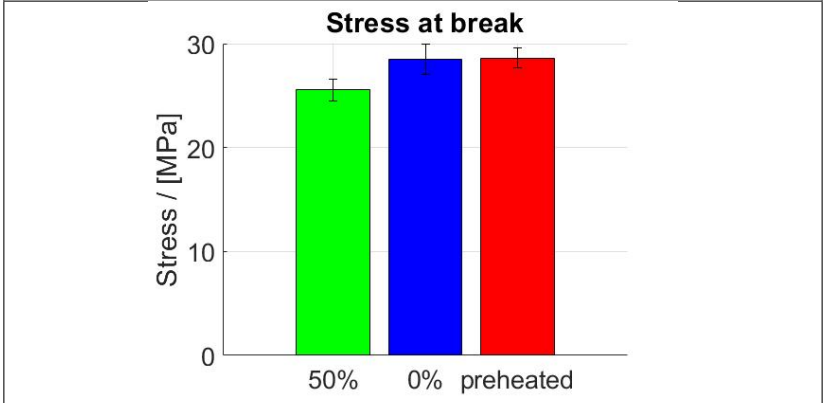
A comparison of all 3 different conditions is presented. The green curve represents the standard condition test, the blue one the 0 % relative humidity test and the red one corresponds to the one with a preheating step in it. As can be seen, changing the relative humidity to 0 % does change the paper. The strain at break decreases and the stress at break increases. This means that more strength is needed to break the paper but at the same time the paper does not stretch as much as before.

If the water inside the paper is taken out completely (red curve) no major change is visible.

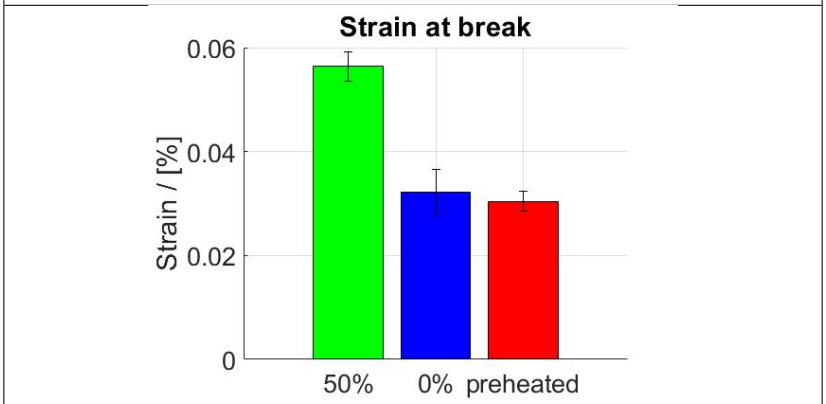
In fig. 38 the tensile energy absorption as well as the stress and the strain at break are shown explicitly. The color mapping stays the same as in fig. 37. The error bars have been calculated with 95 % confidence interval. It can clearly be seen that the strain at break decreases while changing the relative humidity and taking out the water (even though there is no significant change between the blue and the red bar). The same holds for the stress at break but the stress increases



"Tensile energy absorption, error: 95 % convidence intervall"



"Stress at break, error: 95 % convidence intervall"



"Strain at break, error: 95 % convidence intervall"

Figure 38: Comparison of the tensile energy absorption, the stress and the strain at break. No significant change between the red and the blue bar in TEA. The stress at break constantly increases with less amount of water in the sample. The strain at break constantly falls with less water in the sample.

while taking out the water. If a closer look at the tensile energy absorption is taken there is no significant change between the blue and the red bar visible, which means that it looks like the paper does get more brittle but not convincing. So the influence of capillary forces to the bonding system of paper is of minor importance with dry samples.

7 Summary/ Conclusion

7.1 Discovery DMA 850

A meaningful setup for paper experiments with the used TA- Instruments, Discovery DMA 850 has been found.

The used DMA worked pretty well with most of the used applications but some problems have appeared.

The temperature control of the DMA does not work correctly when the furnace is open. This has been seen when measurements were performed with an open furnace. The used DMA stands in a climate room which is held at constant 23 °C and 50 % relative humidity. When the furnace is open the DMA does show 27 °C which indicates a wrong temperature control.

Another problem during this work was the force driven operating way of the DMA. It was not possible to overcome the problem described in sec. 6.1.2. During conditioning the sample is held at constant stress which generates a strain while changing the relative humidity.

Also an appearing artefact was visible during creep measurements. It seems that either the sample slipped through the pull clam or that an electronic failure took place. While looking at fig. 39 this artefact can be seen as a vertical blue line.

The last problem with the used DMA appeared during mastering. Since the frequency sweep measurements still open up some questions, it was important to measure all sweeps at different humidities with the same sample, without opening the DMA. The problem here was that the DMA does not allow a change in conditions (such as temperature or relative humidity) once it worked in its frequency mode (it seems that the DMA works, depending on the measurement, in different operation modes. In the ones needed e.g. for creep tests, it is possible to change conditions, while for making frequency sweeps, it is not). This problem had to be solved by putting in some pseudo-creep tests so the DMA changes into another mode where it can change conditions, but this did not work always, so 2-3 pseudo steps had to be included to let the DMA change conditions (while doing this experiments it seemed to be arbitrary if the DMA changes into the desired mode or not). These pseudo-creep tests neither applied a force on the samples nor caused some deformation, they are only digital steps to change the mode the DMA is operating in (they had no influence on the results of further done experiments).

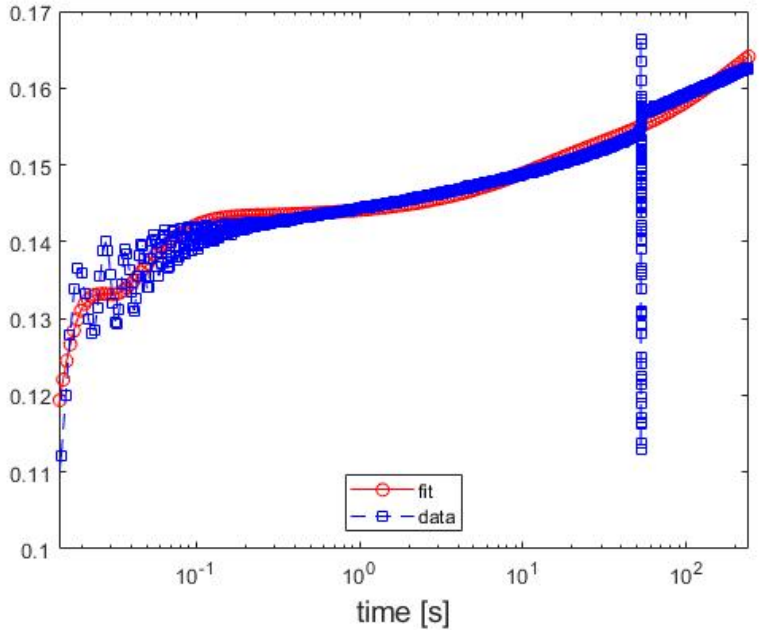


Figure 39: Creep test at the pseudo yield point. Blue points are measurement data and red curve is a fit gathered through ”REHAfit.m”. A artefact in form of a vertical line is visible in the measurement data.

7.2 Yield point

The elastic and plastic phase of UNUT paper has been investigated and no pure elastic phase has been found. That means that UNUT paper does not seem to have an elastic phase and with that no real yield point (see fig. 15).

7.3 Theoretical paper models

An in house made MATLAB routine to recalculate the hardening function has been tested and further improved. The theory behind it and the experimental data do correspond to each other (see fig. 17).

Another in house made MATLAB routine focusing on the viscoelastic behaviour of paper has also been tested and improved with experimental data gathered during this work. 5 decades of time and with this, 5 Maxwell elements and 5 corresponding E-moduli besides the instantaneous modulus have been found (see fig. 21 and tab. 8). If a close look at the E-moduli calculated with ”REHAfit.m” is taken, it can be seen that one E-modulus (E_3 in this case) is very low. In comparison with the other E-moduli, it seems vanishing small. Does that mean that this E-modulus and with that the corresponding Maxwell element is

not needed? This could further be tested if the same simulations but with one Maxwell elements less are done.

7.4 Frequency sweeps

Even though that a lot of measurements to investigate the paper behaviour during frequency measurements have been performed during this work, there are still some open questions about the artefacts visible. The first drop/ steep increase in loss/ storage modulus could be explained as an activation term, which can be overcome by either measuring from high frequencies to low ones, or by giving the paper more time (e.g. more build up cycles) before measuring. This idea is just a hypothesis and has to be proven in further work.

The second artefact which is a peak visible in the loss modulus may be connected to a resonance effect of the used DMA. This hypothesis was stayed because the peak seems to appear only at a certain frequency (see fig. 23).

7.5 Mastering

A first try of creating a relative humidity dependent mastercurve has been done. The mastercurve with standard conditions as refernce (see fig. 33) does look reasonable, but the shift factor as well as the *Wicket-Plot* and *Cole-Cole-Plot* compared to theory show that this first try of creating a mastercurve did not work correctly (see fig. 34, fig. 35). Further experiments in this section have to be done, to get a better understanding of the behaviour of paper during frequency sweep measurements. For now it seems that UNUT paper is not ”rheological simple” and with that not masterable.

7.6 Capillary forces

The influence of capillary forces to the bonding system of paper has been investigated using tensile tests at different humidities and with completely dried samples. A problem which was present during this work was that the paper could not be fixed stretched in the DMA. If a close look at the tensile tests is taken (fig 12) it is visible that the stress does not increase linearly at the beginning. This is due to the stretching of the paper at the beginning of the measurement.

In fig. 38 the influence of capillary forces in terms of the tensile energy absorption is shown. It looks like the paper does get more brittle but not convincing. So the influence of capillary forces to the bonding system of paper is of minor importance.

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