RHEOLOGICAL METODOLOGIES

AND

RHEOLOGICAL CHARACTERIZATION

OF PAINTS

Author:
Rita Joana Batista Pinto

September to December

UNIÃO EUROPEIA
Fundo Social Europeu

RHEOLOGICAL METODOLOGIES

AND

RHEOLOGICAL CHARACTERIZATION

OF PAINTS

Author:

Rita Joana Batista Pinto

September to December

UNIÃO EUROPEIA
Fundo Social Europeu

Mais Educação

PART 1. RHEOLOGICAL METHODOLOGIES

CIN

Universidade do Porto

Faculdade de Engenharia

FEUP

TABLE OF CONTENTS

A. INTRODUCTION TO THE RHEOMETER

Bohlin rheometer can control the shear stress; i.e., a torque is applied (force) and is measured the resultant displacement (movement). It can also control the shear rate; i.e., the motor speed (movement) is regulate and is measured the resultant torque (force).

B. START UP OF THE RHEOMETER SYSTEM

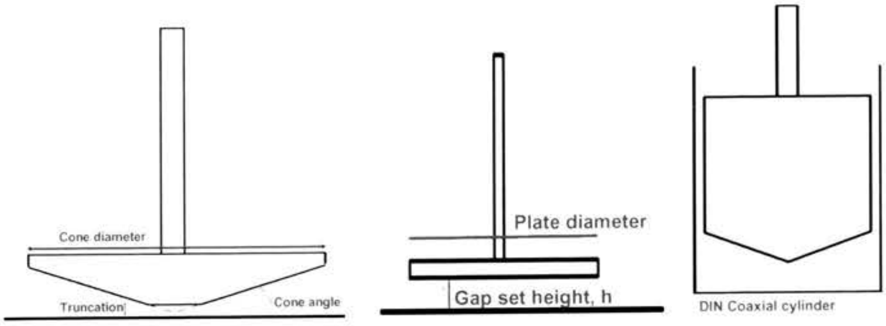
It is important that the rheometer system is started up in the right sequence to ensure correct operation.

1) Turn on the compressed air line and check that the pressure is accurately set at 3 bar (300 KPa) on the regulator unit
2) Switch on the computer and printer (if local).
3) If a temperature option is used that requires a thermocouple (such as an ETO, ETC, Melts Oven or Peltier), ensure that it is plugged into the correct yellow or green socket on the back of the instrument.
4) Switch on the rheometer (switch at the back).
5) Press the up arrow to start the initialisation. This will raise the air bearing to a reference height and then lower it to a rest position (c.7 mm).
6) Start the software as described on section F.

C. SELECTING THE CORRECT MEASURING SYSTEM

Many different measuring systems can be used on the rheometer. These fall broadly into three categories namely:

(i) Cone & plate
(ii) Parallel plate
(iii) Cup & bob (coaxial cylinder)



(a) (b) (c)

Figure 1 – Schematic diagram of basic tool geometries for the rotational rheometer:

(a) cone and plate, (b) parallel plate, (c) concentric cylinder

i) Cone & Plate

The cone and plate geometry consists of an inverted cone in near contact with a lower plate. The cone is usually designed with an angle of less than 4°.

This geometry offers absolute viscosity determinations with precise shear rate and shear stress information. The sample volumes required are very small and the sample cup is jackets for temperature control. The most important advantage of cone and plate geometry is that the shear rate doesn't depend on the radius.

ii) Parallel Plates

The parallel plate geometry can be considered a simplified version of the cone and plate, having an angle of 0°. The test fluid is constrained in the narrow gap between the two surfaces. This geometry can be used for stationary, as well as for transient experiments. Stress relaxation, recoil and creep test (stress controlled devices) are just a few examples. Oscillatory experiments are also possible with this type of geometry. The major disadvantage is that the shear rate is not constant throughout the material.

iii) Cup and bob (coaxial cylinder)

Cup and bob measuring geometries require relatively large sample volumes and are more difficult to clean. They usually have a large mass and large inertia's and so can produce problems when performing high frequency measurements.

Their advantage comes from being able to work with low viscosity materials and mobile suspensions. Their large surface area gives them a greater sensitivity and so they will produce good data at low shear rates and viscosities.

D. SAMPLE LOADING FOR CONE AND PLATE AND PARALLEL PLATE MEASURING GEOMETRIES

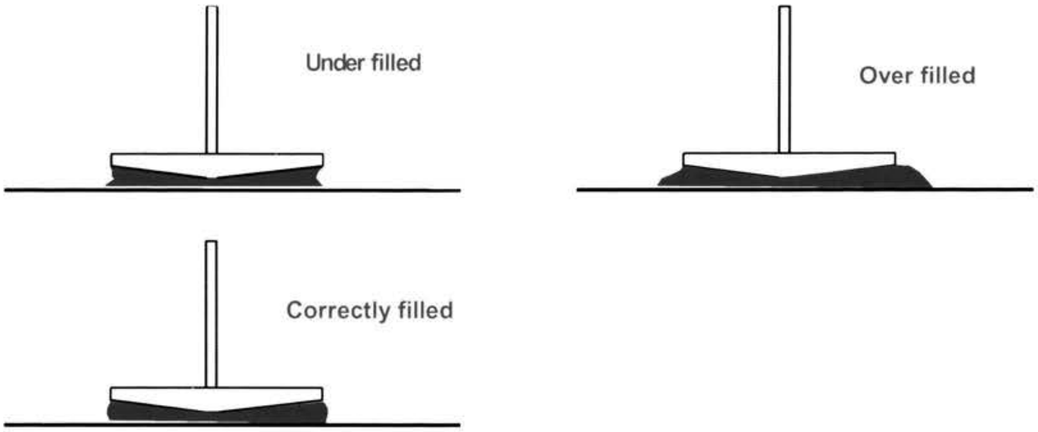


Figure 2 – Sample loading for cone and plate and parallel measuring geometries

The sample should just fill the gap between the upper and lower elements. If the sample is likely to shrink during the test (due to solvent loss, etc.), it is advisable to aim for a slight bulge as shown in Figure 2. If too much or too little sample is used, the torque produced will be incorrect, leading to the data being higher or lower, respectively.

When using stiff materials with parallel plates, the best results can often be obtained by pre-forming the sample into a disc of the same diameter of the upper plate. The thickness should be very slightly thicker than the required value so that the plates may be brought down such that they slightly compress the material, thus ensuring a good contact.

E. SETTING THE CORRECT GAP

It is very important to have the correct gap setting for each measuring system, since the correct gap between the upper and a lower measuring system is essential for accurate measurements. An incorrect gap will lead to errors in the results, especially when small gaps or small Cone angles are involved.

- Insert the cone and the plate into the rheometer;
- Place the chuck lock on;
- Press the key marked ZERO on the front panel. You must press and hold it for a short while before anything happens;
- The instrument will now find the zero position (i.e. where the Cone just touches the lower plate) automatically. Wait until the OK light comes on;
- Select the measuring system from the software (Figure 3). This will set the required gap of 0.15 mm. *Note – 150 µm is the truncation height for the 4° Cone (CP4/40)*;
- The gap light should go off and the OK light come on. The gap is now set.

Note: It is possible select the measuring system from the rheometer. Select GAP and change the measuring system. Select GAP again.

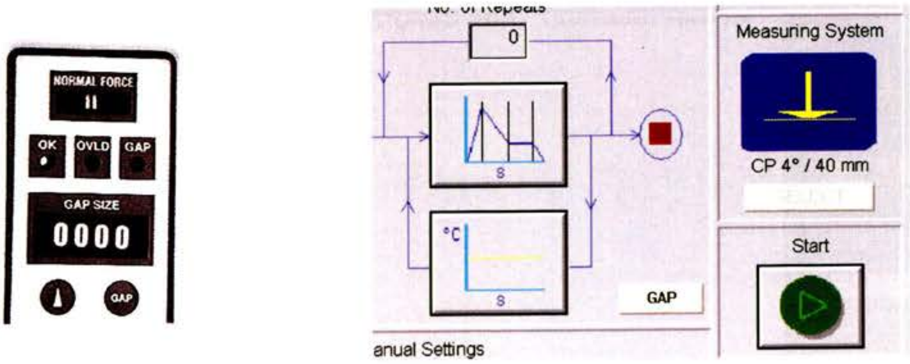


Figure 3 - Display when zero has been found

Note: 250 µm is the truncation height for the Cone PP20.

F. SELECTING A PROTOCOL

- Insert an username and password

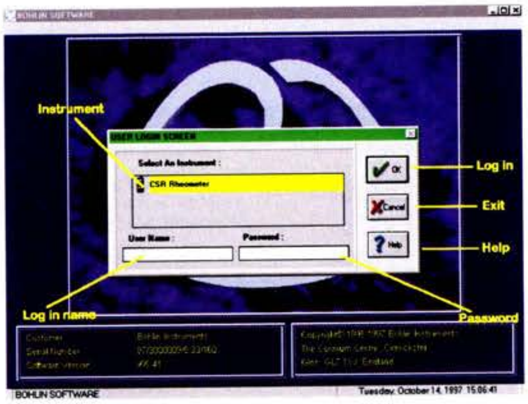
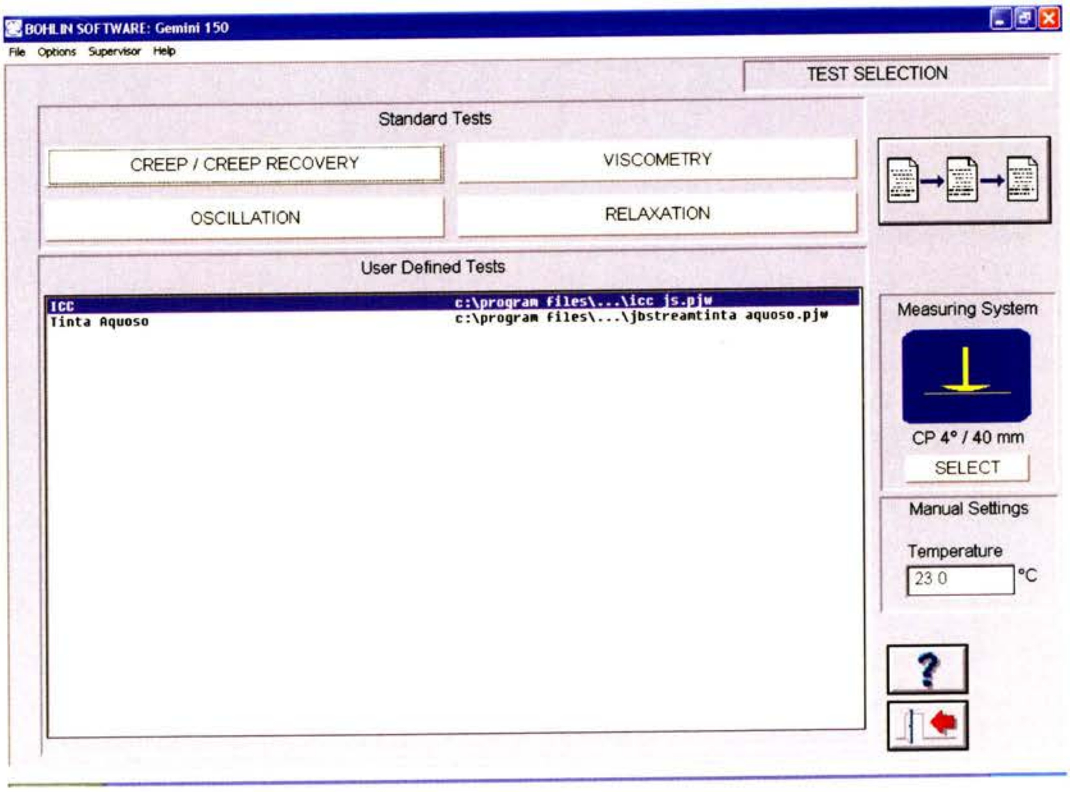


Figure 4 - The log-in screen

- Select one of the **standard tests**, the correct "**Measuring System**" and set the **temperature** at 23 ºC. [1]



```
ICC            c:\program files\...\icc js.pjw
Tinta Aquoso   c:\program files\...\jbstreamtinta aquoso.pjw
```

Measuring System: CP 4° / 40 mm

Temperature: 23 0 °C

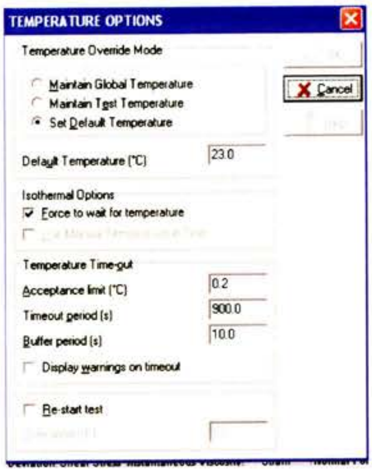
Figure 5 – The standard tests screen

---

1 – Based on NP EN 23 270, 1995 – *Temperatures and Humidities for conditioning and testing*

If measurement system is "PP", the gap should be at least 5 times larger than the largest particle of the sample.

It is important to verify if **Default Temperature** is set correctly (**Options**, **Temperature**).



Temperature Override Mode
○ Maintain Global Temperature
○ Maintain Test Temperature
● Set Default Temperature

Default Temperature (°C) 23.0

Isothermal Options
☑ Force to wait for temperature

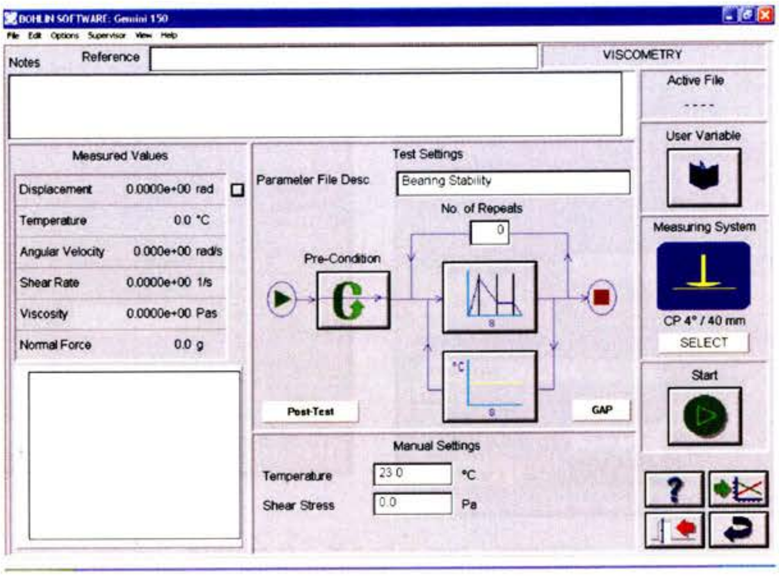
Temperature Time-out
Acceptance limit (°C) 0.2
Timeout period (s) 900.0
Buffer period (s) 10.0
☐ Display warnings on timeout

☐ Re-start test

Figure 6 – The temperature options screen

I. VISCOSIMETRY TESTS

- Select **Pre-condition** (pre-shear)



Displacement 0.0000e+00 rad
Temperature 0.0 °C
Angular Velocity 0.000e+00 rad/s
Shear Rate 0.0000e+00 1/s
Viscosity 0.0000e+00 Pas
Normal Force 0.0 g

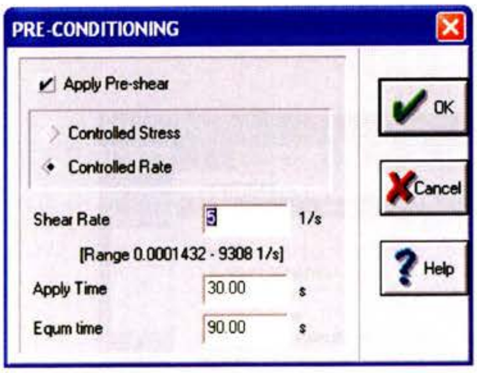
Parameter File Desc: Bearing Stability
No. of Repeats: 0
CP 4° / 40 mm

Temperature 23.0 °C
Shear Stress 0.0 Pa

Figure 7 – Viscosimetry screen

The pre-shear is always applied first followed by the equilibrium. Equilibrium time is the necessary time to recover the structure of materials.

- Select Apply Pre-shear, Controlled Rate. Insert **Shear rate**, **Apply Time** and **Equilibrium Time**.



☑ Apply Pre-shear
○ Controlled Stress
● Controlled Rate
Shear Rate 5 1/s
[Range 0.0001432 - 9308 1/s]
Apply Time 30.00 s
Equm time 90.00 s

Figure 8 – Pre-condition screen

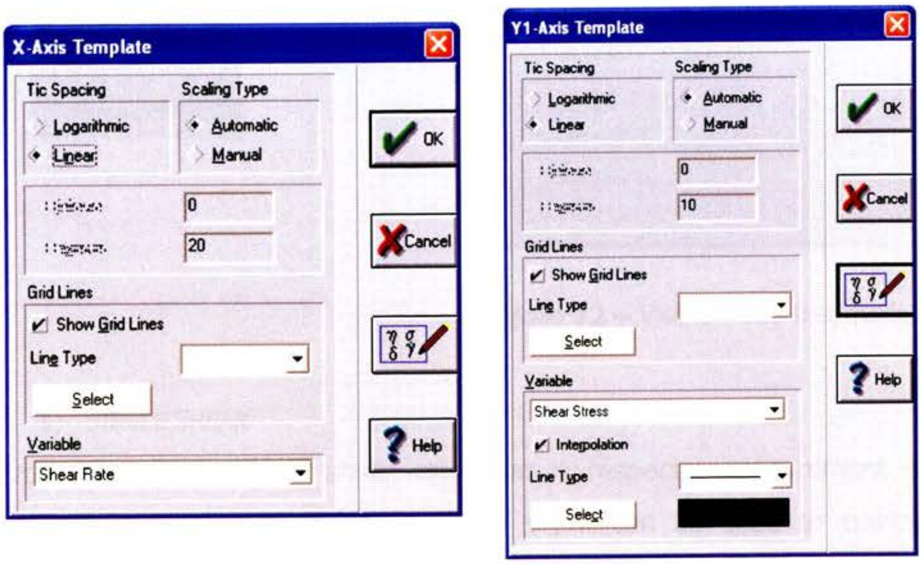
Table 1 – Measurements profile

Shear rate (s^{-1})	5
Apply time (s)	30
Equilibrium time (s)	90

It was chosen for "equilibrium time" 90 s because it was verified that the material studied in this project recovers in less time.

- Select Axis

With right button of mouse, click outside of the graph and choose X-axis and Y-axis.



X-Axis Template: Tic Spacing ○ Logarithmic ● Linear; Scaling Type ● Automatic ○ Manual; 0; 20; ☑ Show Grid Lines; Variable: Shear Rate

Y1-Axis Template: Tic Spacing ○ Logarithmic ● Linear; Scaling Type ● Automatic ○ Manual; 0; 10; ☑ Show Grid Lines; Variable: Shear Stress; ☑ Interpolation

Figure 9 – X and Y axis templates

- Select button and select axis variables.

- SELECT MEASUREMENTS WITH CSR OR CSS

1. Measurements with a **Controlled Shear Rate (CSR)**

- Select **Options**, **Viscosimetry** and select **controlled rate**

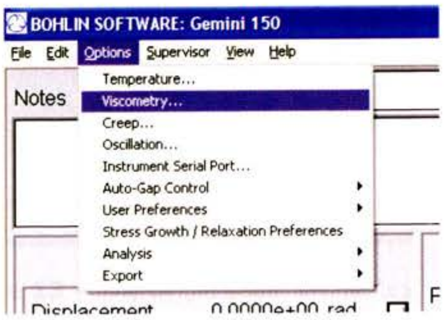
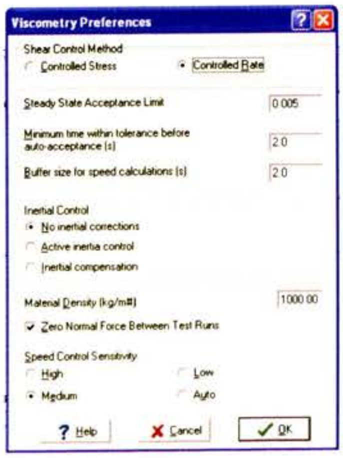


Figure 10 – Menu bar screen



Shear Control Method: ○ Controlled Stress ● Controlled Rate

Steady State Acceptance Limit: 0.005

Minimum time within tolerance before auto-acceptance (s): 2.0

Buffer size for speed calculations (s): 2.0

Inertial Control: ● No inertial corrections ○ Active inertia control ○ Inertial compensation

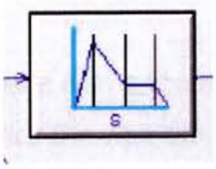
Material Density (kg/m#): 1000.00

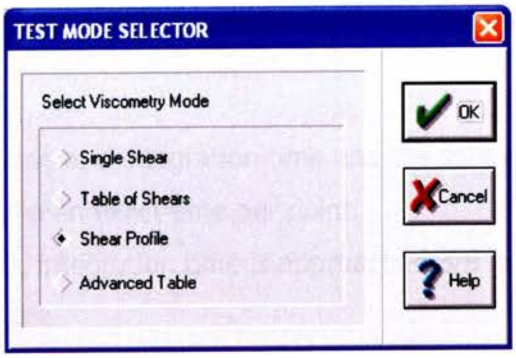
☑ Zero Normal Force Between Test Runs

Speed Control Sensitivity: ○ High ● Medium ○ Low ○ Auto

Figure 11 – Viscosimetry Preferences screen

- Select Viscosimetry sweep type (**Viscosimetry Mode**)





Select Viscometry Mode

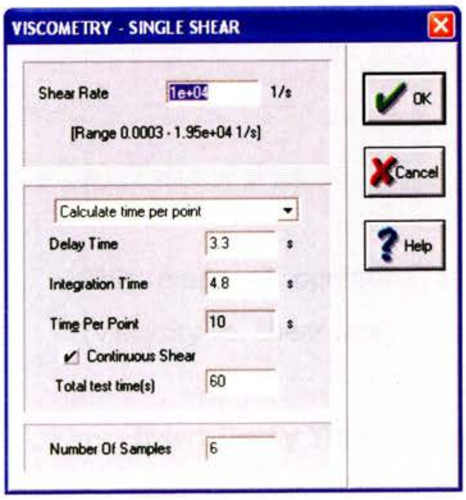
- ○ Single Shear
- ○ Table of Shears
- ● Shear Profile
- ○ Advanced Table

Figure 12 – Viscosimetry test mode window

a) SINGLE SHEAR

This mode applies a fixed shear rate that it respects measurement system. For example, if shear rate is equal to 10000 s^{-1}, it can be used to compare the ICI viscosity. It is important to see if Measurement system is PP 20 and a gap equal to 0.250 mm, when the biggest particles have a diameter of 50 μm.

- Insert **Shear rate**, **Delay Time**, **Integration Time**, **Total Time** and **Number of Samples**.



Shear Rate 1e+04 1/s
[Range 0.0003 - 1.95e+04 1/s]
Calculate time per point
Delay Time 3.3 s
Integration Time 4.8 s
Time Per Point 10 s
☑ Continuous Shear
Total test time(s) 60
Number Of Samples 6

Figure 13 – The single shear profile test

Table 2 – Measurements profile

Measurement system	PP 20
Temperature (ºC)	23 ºC
Shear Rate (s^{-1})	10000
Delay time (s)	3.3
Integration time (s)	4.8
Total time test (s)	60
Number of Samples	6
Time per point (s)	10

Use **Calculate time per point.**

The total time for the test is given by:

(Delay time + integration time + wait time) × Number of samples

This mode allows the user to enter delay time and integration time and the software calculates the wait time automatically to give an exact time per point.
For this case, delay time is approached 2/6, integration time is approached 3/6 and wait time is approached 1/6 of time per point.

The typical graph is illustrated in Figure 14.

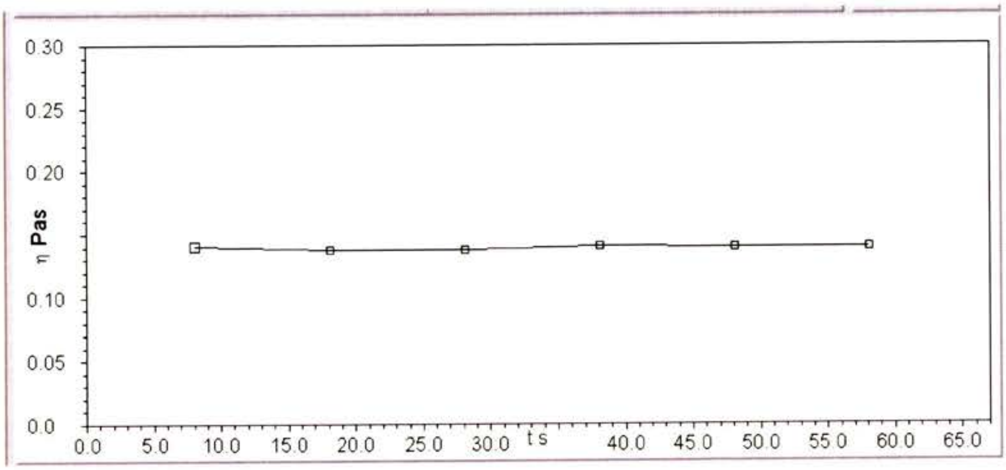
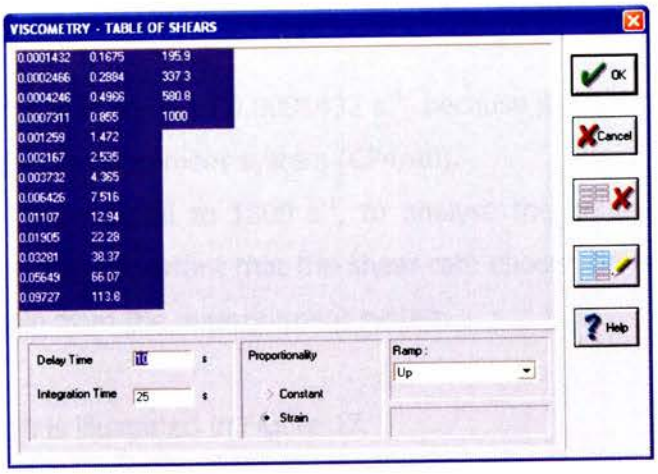


Figure 14 – An example of viscosimetry test with conditions from table 2

b) TABLE OF SHEARS

This mode of operation allows the realization of equilibrium flow curves (viscosity vs. shear rate).

- Insert **Delay Time**, **Integration Time**, **Proportionality** and **Ramp**.



0.0001432	0.1675	195.9
0.0002466	0.2884	337.3
0.0004246	0.4966	580.8
0.0007311	0.855	1000
0.001259	1.472	
0.002167	2.535	
0.003732	4.365	
0.006425	7.516	
0.01107	12.94	
0.01905	22.28	
0.03281	38.37	
0.05649	66.07	
0.09727	113.8	

Delay Time 10 s
Integration Time 25 s
Proportionality
○ Constant
● Strain
Ramp : Up

Figure 15 – Table of shears screen

Delay time is approached 2/5 and integration time is 3/5 of time per point.

It can be used on ramp: Up, Down, Up & Down or Down & Up.

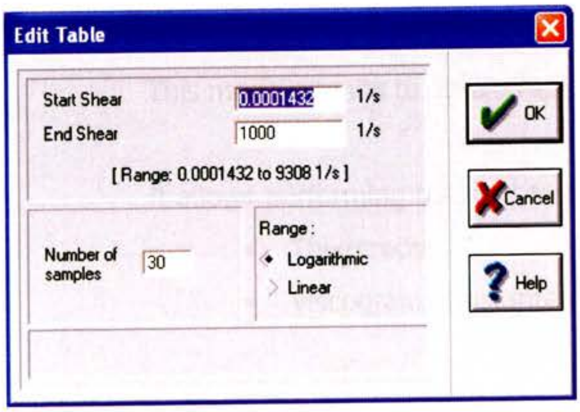
- Select **Proportionality "Strain"** and **Ramp "UP"**.

- Select button 

- Fill the next table

Table 3 – Measurements profile

Measurement system	CP 4º / 40 mm
Temperature (ºC)	23
Delay time (s)	10
Integration time (s)	25
Proportionality	strain
Ramp	Up
Start shear (s^{-1})	0.0001432
End shear (s^{-1})	1000
Number of Samples	30
Range	logarithmic



Start Shear 0.0001432 1/s
End Shear 1000 1/s
[Range: 0.0001432 to 9308 1/s]
Number of samples 30
Range :
● Logarithmic
○ Linear

Figure 16 – Edit table screen

It was chosen:

- Start Shear equal to 0.0001432 s^{-1}, because it is the minimum of range for this measurement system (CP4/40).
- End Shear equal to 1000 s^{-1}, to analyse the behaviour at high shear rates. It is important that the shear rate chosen do not throw away the sample from the measurement system.

The typical graph is illustrated in Figure 17.

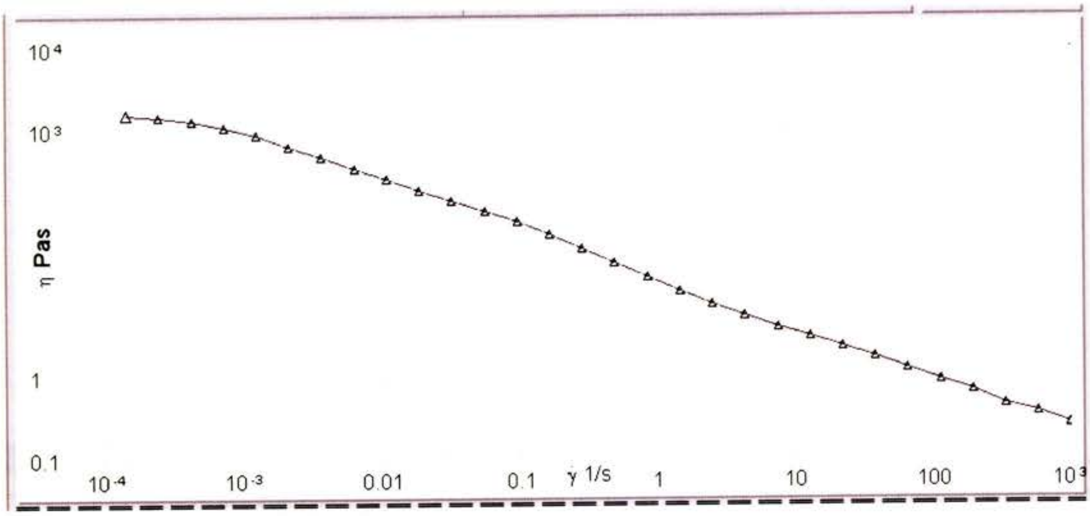


Figure 17 – An example of viscosimetry test with conditions from table 3

c) SHEAR PROFILE

This mode permits to obtain rapid flow curves.

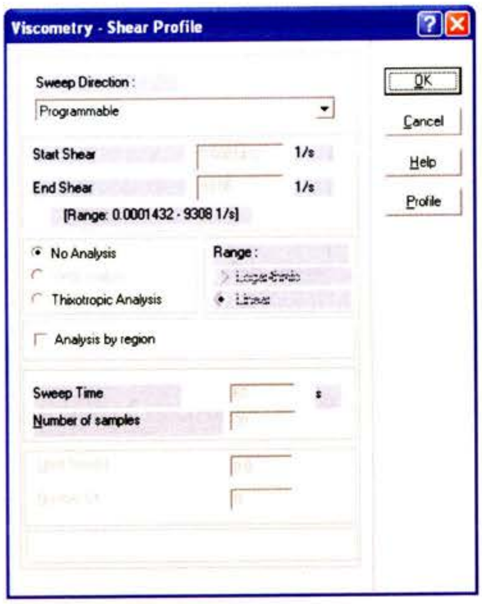
It allows performing the next tests:

- Thixotropy;
- Viscograms (instantaneous viscosity vs. shear rate).

For these tests, the measurement system used is CP 4° / 40 mm.

c1) THIXOTROPIC TEST

- Select, in **Sweep Direction**, **Programmable**.



Sweep Direction : Programmable

Start Shear 1/s

End Shear 1/s

[Range: 0.0001432 - 9308 1/s]

● No Analysis

○ Thixotropic Analysis

Range : ● Linear

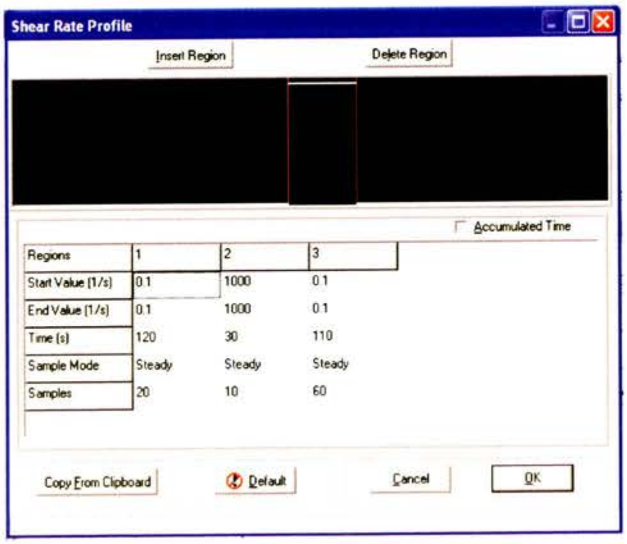
☐ Analysis by region

Sweep Time s

Number of samples

Figure 18 – Shear Profile screen

- Select **Profile** and fill the next table.



Regions	1	2	3
Start Value (1/s)	0.1	1000	0.1
End Value (1/s)	0.1	1000	0.1
Time (s)	120	30	110
Sample Mode	Steady	Steady	Steady
Samples	20	10	60

Figure 19 – The shear profile test

Table 4 – Measurements profile

Regions	**1**	**2**	**3**
Start value (s^{-1})	0.1	1000	0.1
End value (s^{-1})	0.1	1000	0.1
Time (s)	120	30	110
Sample Mode	Steady	Steady	Steady
Samples	20	10	60

The typical graph is illustrated in Figure 20.

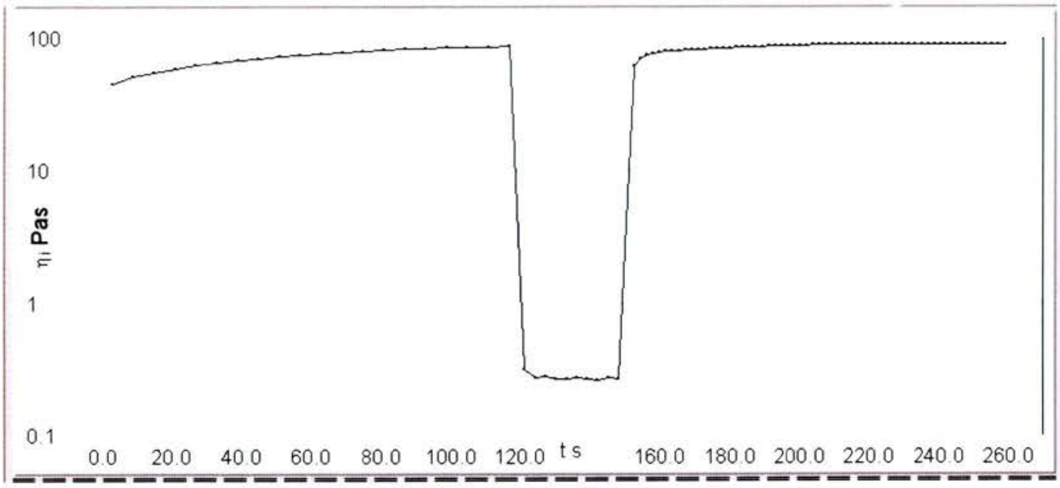


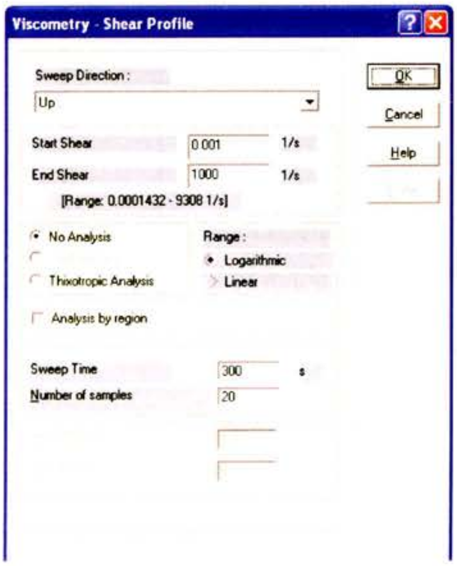
Figure 20 – An example of viscosimetry test with conditions from table 4

Table 5 – Estimation of recovery (%)

	Final of 1st interval ("low shear")	Final of 2nd interval ("high shear")	3rd interval after t=30s	3rd interval after t=60s	3rd interval after t=90s
η (Pa.s)					
Rec. (%)					

C2) VISCOGRAM TEST

- Select, in **Sweep Direction**, **Up**.



Sweep Direction : Up

Start Shear 0.001 1/s

End Shear 1000 1/s

[Range: 0.0001432 - 9308 1/s]

● No Analysis

○

○ Thixotropic Analysis

Range :

● Logarithmic

○ Linear

☐ Analysis by region

Sweep Time 300 s

Number of samples 20

Figure 21 – Viscosimetry shear profile

Table 6 – Measurements profile

Measurement system	CP 4º / 40 mm
Temperature (ºC)	23
Sweep Direction	Up
Start shear (s^{-1})	0.001
End shear (s^{-1})	1000
Range	logarithmic
Sweep Time	300
Number of Samples	20

The typical graph is illustrated in Figure 22.

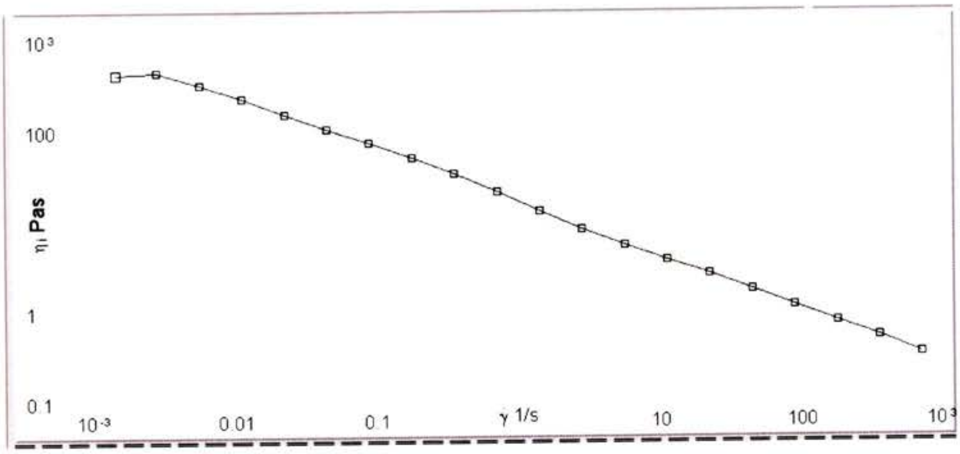


Figure 22 – An example of viscosimetry test with conditions from table 6

To determine the thixotropic behavior, it chooses sweep direction Up & Down, maintaining the same parameters.

Figure 23 illustrates an example of these conditions.

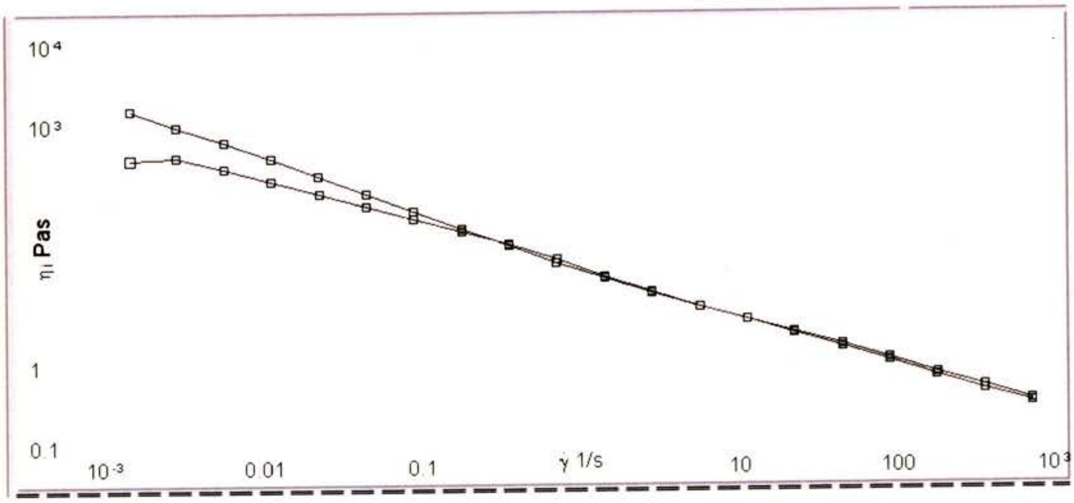
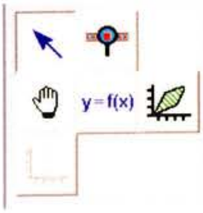
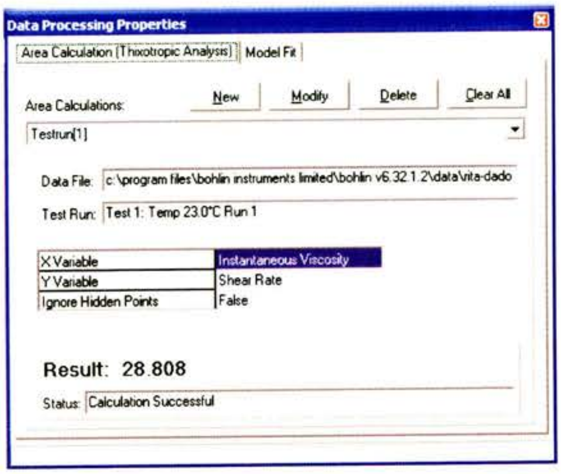


Figure 23 – An example of viscosimetry test with conditions from table 6 and sweep direction Up & Down

The Thixotropic Analysis dialog is accessed by clicking on y = f(x) of the TOOL BAR Select



The dialog that is displayed is shown below.



Area Calculations: Testrun[1]

Data File: c:\program files\bohlin instruments limited\bohlin v6.32.1.2\data\rita-dado

Test Run: Test 1: Temp 23.0°C Run 1

X Variable	Instantaneous Viscosity
Y Variable	Shear Rate
Ignore Hidden Points	False

Result: 28.808

Status: Calculation Successful

Figure 24 – Data processing properties of thixotropic analysis

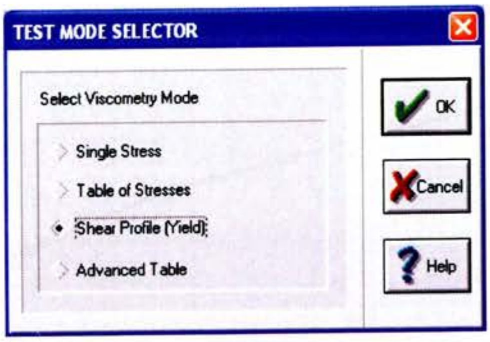
This dialog allows existing **area calculations** to be viewed.

2. Measurements with a **Controlled Shear Stress** (CSS)

It allows performing yield stress measurement with tensiograms.

The significant parameter for determining the yield point is that the result strongly depends on the resolution of the measuring instrument and thus on the minimum shear rate.

- Select **Options**, **Viscosimetry** and select **controlled stress** (see Figure 9 and 10).
- Select **Shear Profile (Yield)**



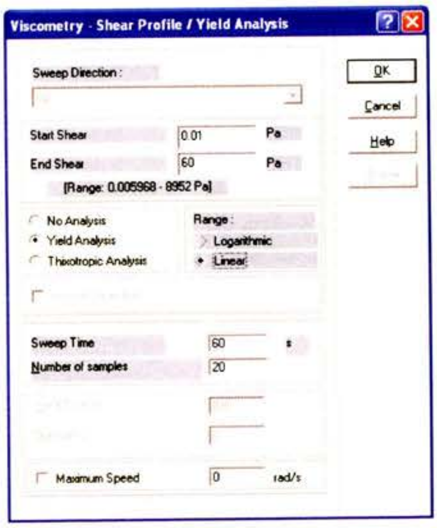
TEST MODE SELECTOR

Select Viscometry Mode

○ Single Stress
○ Table of Stresses
● Shear Profile (Yield)
○ Advanced Table

Figure 25 – Viscosimetry test mode window for CSS mode

- Select **Yield Analysis** for an automatic yield analysis (sweep direction will be set to UP) and select **linear range**.



Viscometry - Shear Profile / Yield Analysis

Sweep Direction :

Start Shear 0.01 Pa

End Shear 60 Pa

[Range: 0.005968 - 8952 Pa]

○ No Analysis
● Yield Analysis
○ Thixotropic Analysis

Range :
○ Logarithmic
● Linear

Sweep Time 60 s

Number of samples 20

☐ Maximum Speed 0 rad/s

Figure 26 – Viscosimetry shear profile / Yield analysis

Table 7 – Measurements profile

Measurement system	CP 4º/40 mm
Temperature (ºC)	23
Start shear (s^{-1})	0.01
End shear (s^{-1})	60
Sweep time (s)	60
Number of Samples	20

The typical graph is illustrated in Figure 28.

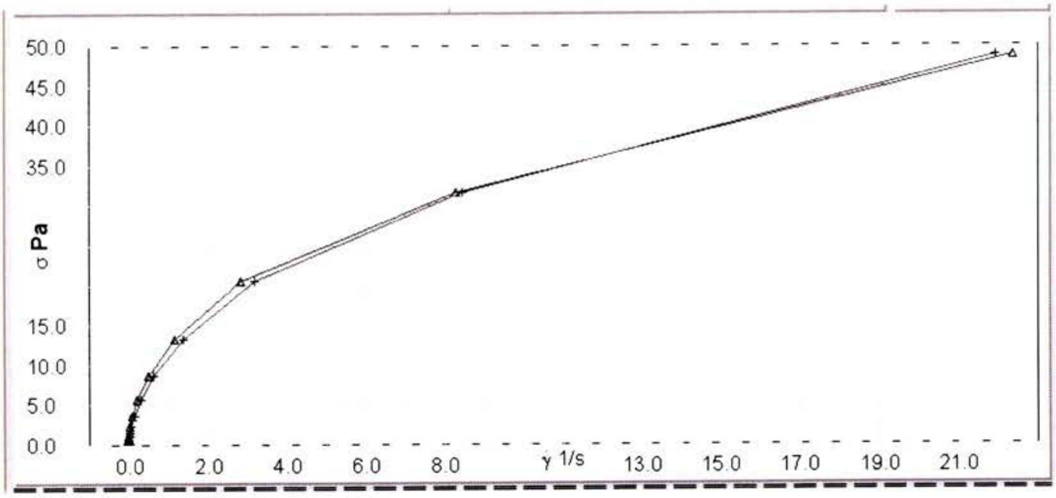


Figure 28 – An example of viscosimetry test with conditions from table 7

- In a Menu bar, select **View, Result Box** and it can be seen **Yield Stress**.

Data File : yield stress lin2b

Test Run : 1

Temperature °C : --

Temperature Run : 1

Yield Parameter

Yield Index 0

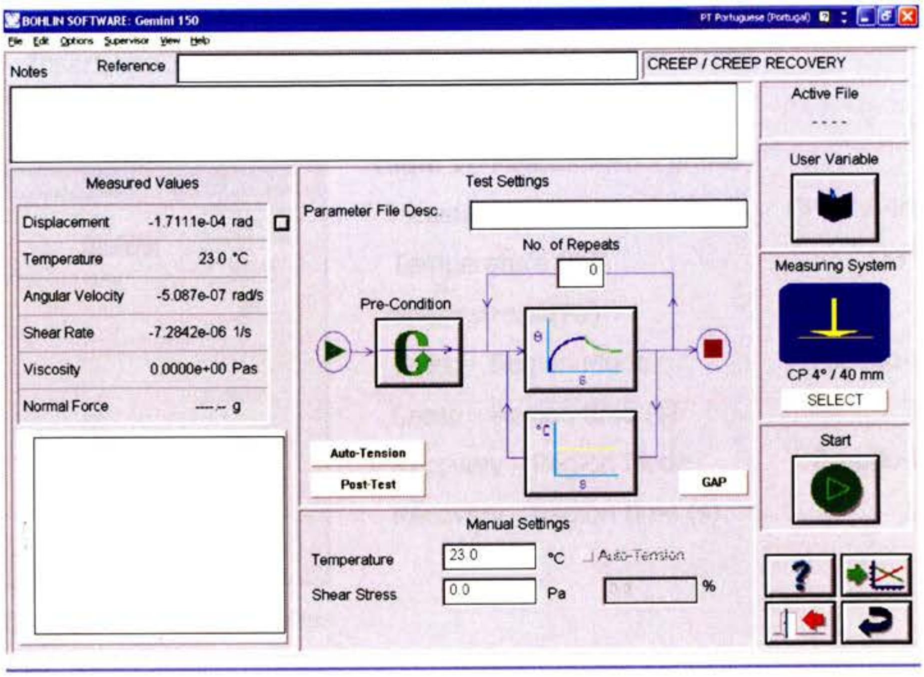
Yield Stress 1.508 Pa

Figure 29 – Yield Stress Results

Note: yield stress is very dependent on graph scale and the parameters of the test. When to compare products be sure that all the conditions are exactly the same.

II. CREEP TEST

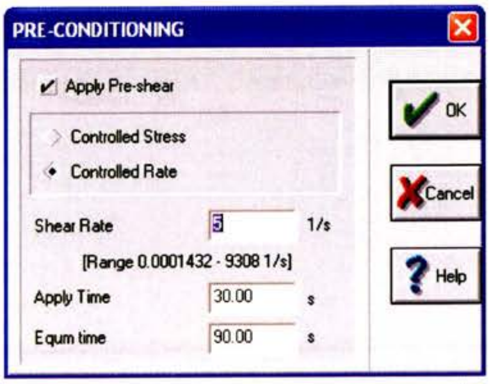
- Select **Pre-condition** (pre-shear)



Displacement -1.7111e-04 rad
Temperature 23.0 °C
Angular Velocity -5.087e-07 rad/s
Shear Rate -7.2842e-06 1/s
Viscosity 0.0000e+00 Pas
Normal Force ---.-- g
No. of Repeats 0
CP 4° / 40 mm
Temperature 23.0 °C
Shear Stress 0.0 Pa

Figure 30 – Creep/Creep Recovery screen

- Select Apply Pre-shear, Controlled Rate. Insert **Shear rate**, **Apply Time** and **Equilibrium Time**.



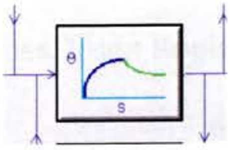
☑ Apply Pre-shear
○ Controlled Stress
● Controlled Rate
Shear Rate 5 1/s
[Range 0.0001432 - 9308 1/s]
Apply Time 30.00 s
Equm time 90.00 s

Figure 31 – Pre-condition screen

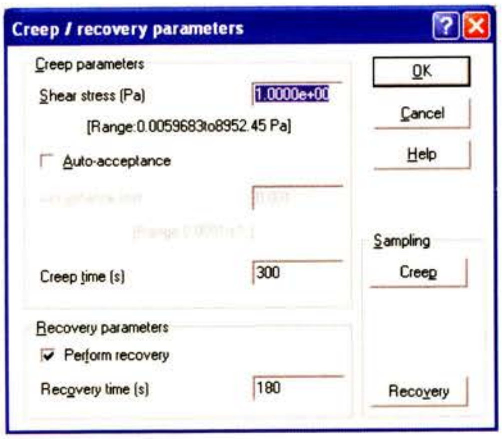
Table 8 – Measurements profile

Shear rate (s^{-1})	5
Apply time (s)	30
Equilibrium time (s)	90

- Select button



- Insert, in **Creep / Recovery Parameters**, shear stress.



Creep / recovery parameters

Creep parameters

Shear stress (Pa) 1.0000e+00

[Range:0.0059683to8952.45 Pa]

☐ Auto-acceptance

Creep time (s) 300

Recovery parameters

☑ Perform recovery

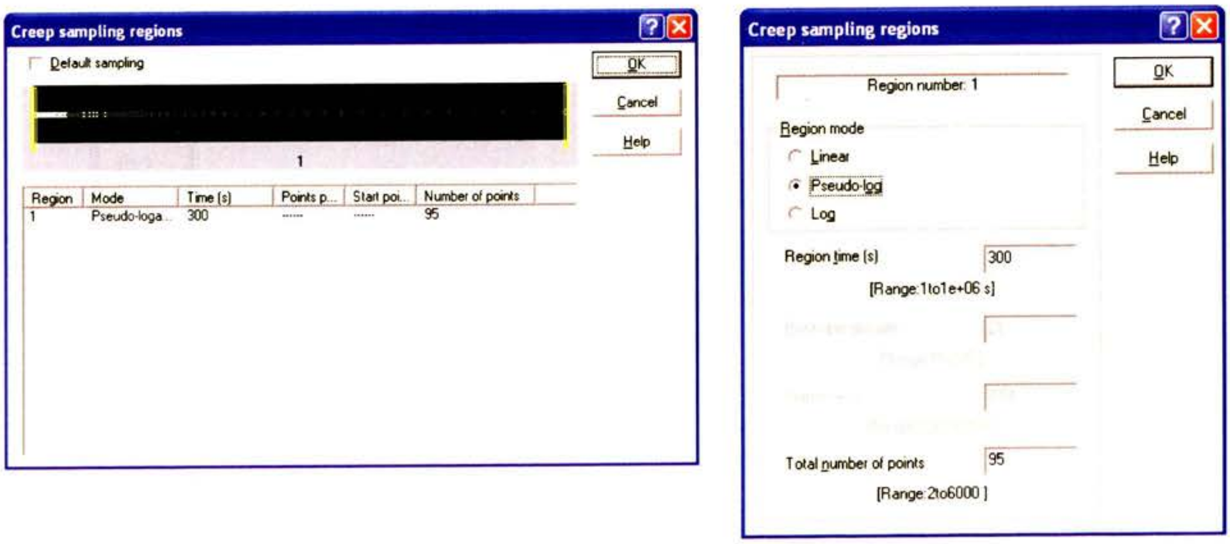
Recovery time (s) 180

Figure 32 – Creep / recovery parameters

Table 9– Measurements profile

Measurement system	CP 4º / 4mm
Temperature (ºC)	23 ºC
Shear stress (Pa)	5
Creep - Region Mode	Pseudo-log
Creep - Region time (s)	300
Recovery - Region Mode	Pseudo-log
Recovery - Region time (s)	180

- Select **Creep sampling**. With right button of mouse, click in blackboard and select region properties. Insert **Region mode** and **region time**.



Creep sampling regions

☐ Default sampling

Region	Mode	Time (s)	Points p...	Start poi...	Number of points
1	Pseudo-loga...	300	------	------	95

Creep sampling regions

Region number: 1

Region mode

○ Linear

● Pseudo-log

○ Log

Region time (s) 300

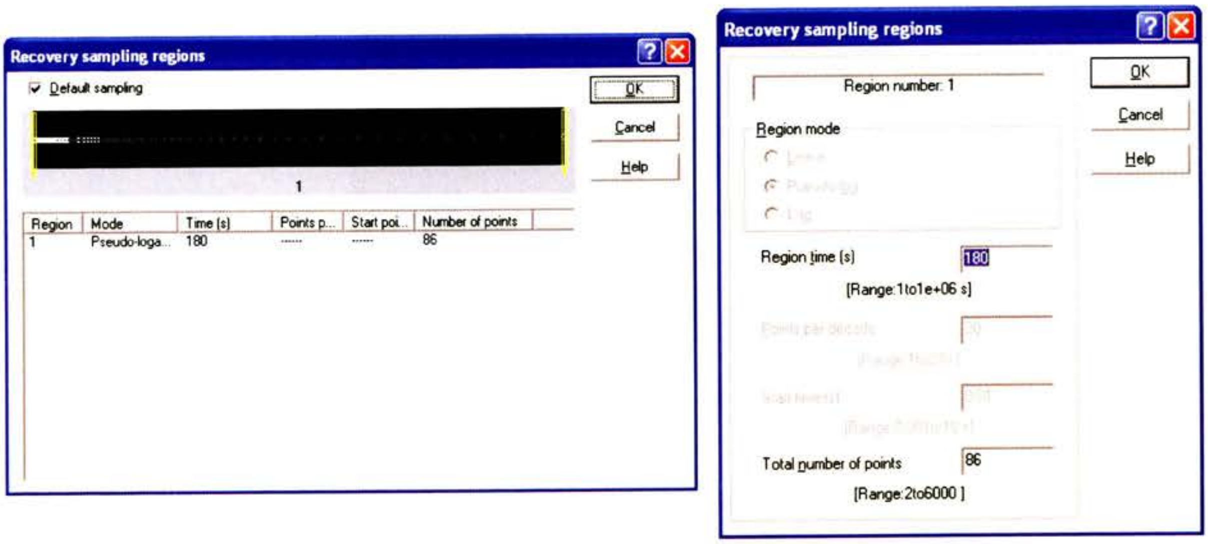
[Range:1to1e+06 s]

Total number of points 95

[Range:2to6000]

Figure 33 – Creep sampling regions

- Select **Recovery sampling**. With right button of mouse, click in blackboard and select region properties. Insert **Region mode** and **region time**



Recovery sampling regions

☑ Default sampling

Region	Mode	Time (s)	Points p...	Start poi...	Number of points
1	Pseudo-loga...	180	------	------	86

Recovery sampling regions

Region number: 1

Region mode

Region time (s): 180
[Range:1to1e+06 s]

Total number of points: 86
[Range:2to6000]

Figure 34 – Recovery sampling regions

The typical graph is illustrated in Figure 35.

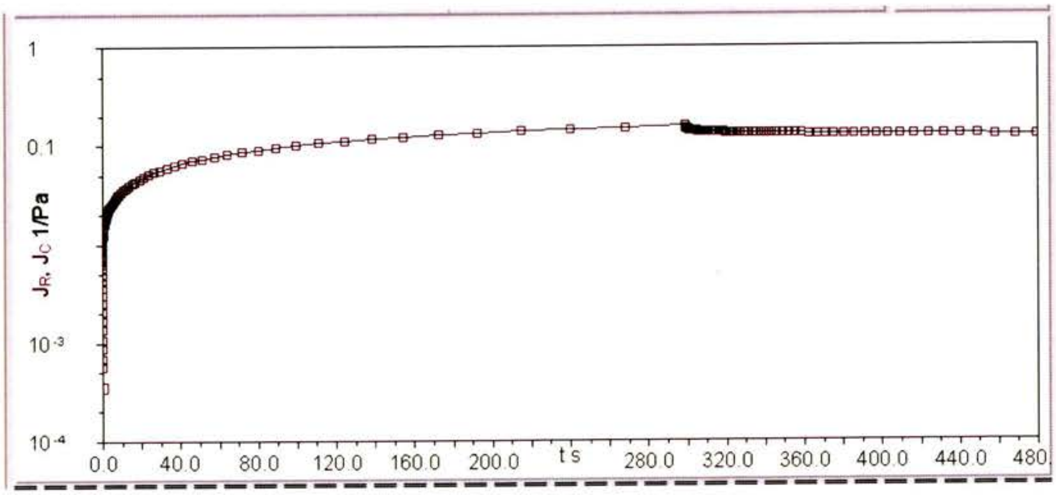
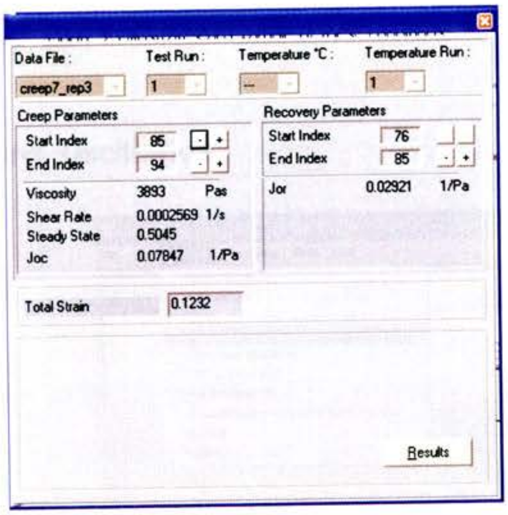


Figure 35 – An example of creep test with conditions from creep and recovery sampling regions

- In a Menu bar, select **View**, **Result Box** and it can be seen the value of viscosity. This value is important because it allows obtaining zero viscosity.



Data File : creep7_rep3
Test Run : 1
Temperature °C : --
Temperature Run : 1

Creep Parameters
Start Index 85
End Index 94
Viscosity 3893 Pas
Shear Rate 0.0002569 1/s
Steady State 0.5045
Joc 0.07847 1/Pa

Recovery Parameters
Start Index 76
End Index 85
Jor 0.02921 1/Pa

Total Strain 0.1232

Figure 36 – Recovery sampling regions

The curves can be quantified in terms of the steady compliance and zero-shear viscosity. When the curves are very closed, it means that the value of viscosity is the zero-shear viscosity.

Figure 37 illustrates an example of these conditions.

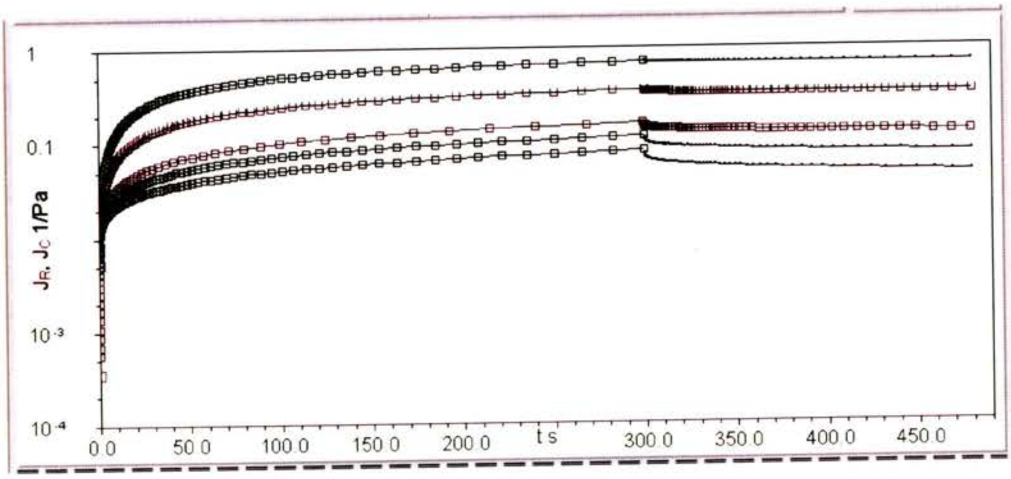


Figure 37 – Examples of creep test with conditions from creep and recovery sampling regions

III. OSCILLATION TESTS

- Select **Options**, **Oscillation**.

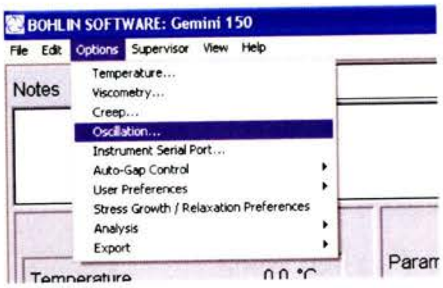
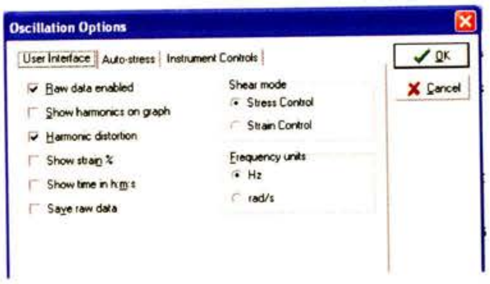


Figure 38 – Menu bar screen

- Fill the Oscillation Options like it is seeing in the Figure 39.



☑ Raw data enabled
☐ Show harmonics on graph
☑ Harmonic distortion
☐ Show strain %
☐ Show time in h:m:s
☐ Save raw data

Shear mode
● Stress Control
○ Strain Control

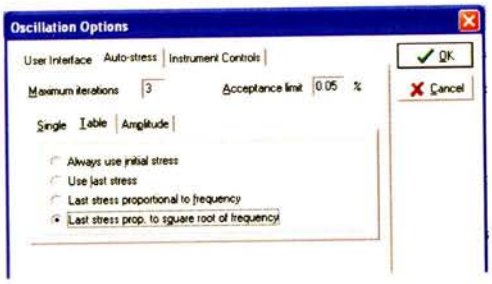
Frequency units
● Hz
○ rad/s

a) Set parameters – User Interface

Maximum iterations 3
Acceptance limit 0.05 %

○ Always use initial stress
● Use last stress
○ Curing

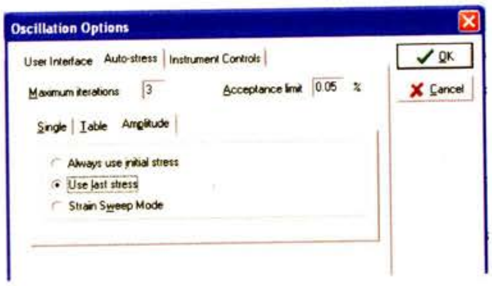
b) Set parameters – Auto-Stress, Single



Maximum iterations 3
Acceptance limit 0.05 %

○ Always use initial stress
○ Use last stress
○ Last stress proportional to frequency
● Last stress prop. to square root of frequency

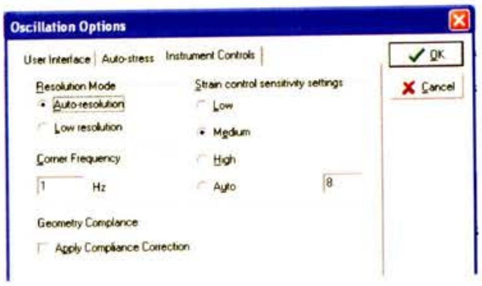
c) Set parameters – Auto-Stress, Table



Maximum iterations 3
Acceptance limit 0.05 %

○ Always use initial stress
● Use last stress
○ Strain Sweep Mode

d) Set parameters – Auto-Stress, Amplitude



Resolution Mode
● Auto-resolution
○ Low resolution

Corner Frequency
1 Hz

Strain control sensitivity settings
○ Low
● Medium
○ High
○ Auto 8

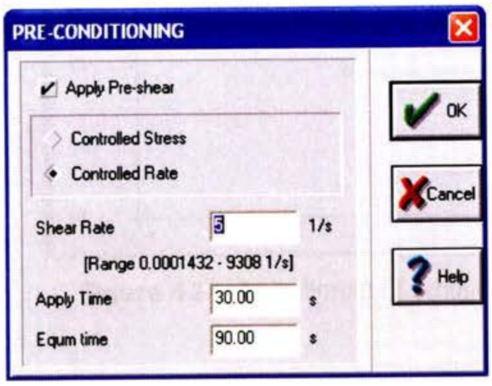
Geometry Compliance
☐ Apply Compliance Correction

e) Set parameters – Instrument Controls

Figure 39 – Menu bar screen

A. Amplitude Sweep

- Select Apply Pre-shear, Controlled Rate. Insert **Shear rate, Apply Time** and **Equilibrium Time.**


PRE-CONDITIONING

☑ Apply Pre-shear

○ Controlled Stress

● Controlled Rate

Shear Rate 5 1/s

[Range 0.0001432 - 9308 1/s]

Apply Time 30.00 s

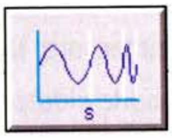
Equm time 90.00 s

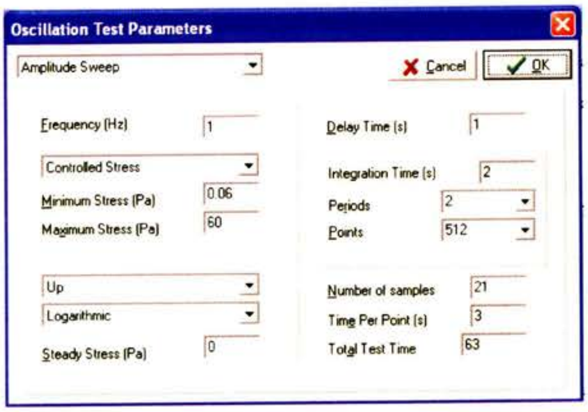
Figure 40 – Pre-condition screen

Table 10 – Measurements profile

Shear rate (s^{-1})	5
Apply time (s)	30
Equilibrium time (s)	90

- Select button




Oscillation Test Parameters

Amplitude Sweep

Frequency (Hz) 1

Controlled Stress

Minimum Stress (Pa) 0.06

Maximum Stress (Pa) 60

Up

Logarithmic

Steady Stress (Pa) 0

Delay Time (s) 1

Integration Time (s) 2

Periods 2

Points 512

Number of samples 21

Time Per Point (s) 3

Total Test Time 63

Figure 41 – Pre-condition screen

Table 11 – Measurements profile

Measurement system	CP 4º / 4mm
Temperature (ºC)	23 ºC
Frequency (Hz)	1
Minimum stress (Pa)	0.06
Maximum stress (Pa)	60
Steady Stress (Pa)	0
Delay Time (s)	1
Periods	1
Points	512
Number of Samples	21

Note: Minimum Stress is 10 x min of range. It means 10 x Minimum stress to CP 4º / 40 mm (10x*0.006*).

The typical graph is illustrated in Figure 42.

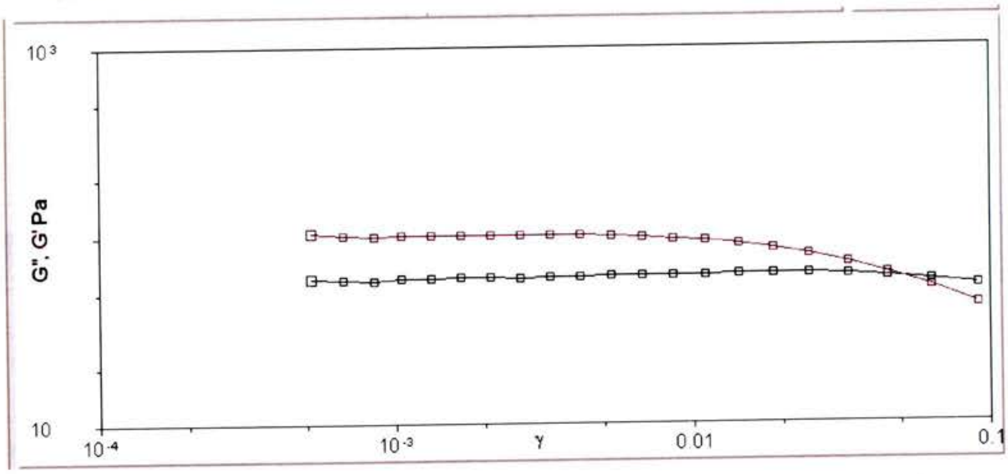
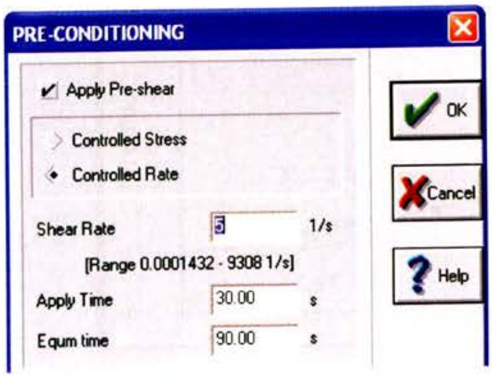


Figure 42 – An example of amplitude sweep test with conditions from table 11

Controlled Strain mode is generally used for all multiple frequency tests, since the strain can be kept within the linear response region for the sample. However, since the software adjust the stress at each reading using iterative techniques, you can not be certain of the shear history of the sample. For measurements on any material where you must guarantee a repeatable shear history, it is recommended that you use either stress proportional to frequency or stress proportional to square root of the frequency.

B. Frequency Sweep

- Select Apply Pre-shear, Controlled Rate. Insert **Shear rate**, **Apply Time** and **Equilibrium Time**.



☑ Apply Pre-shear

○ Controlled Stress

● Controlled Rate

Shear Rate 5 1/s

[Range 0.0001432 - 9308 1/s]

Apply Time 30.00 s

Equm time 90.00 s

Figure 43 – Pre-condition screen

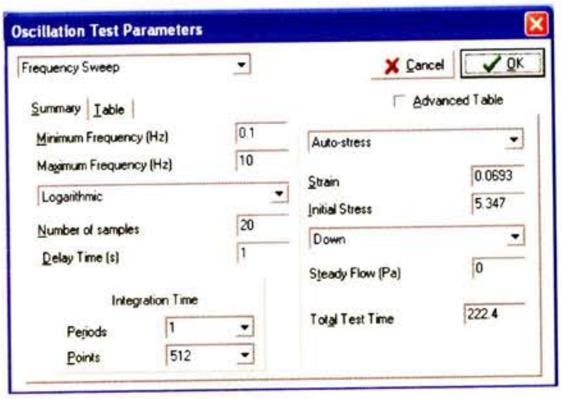
Table 12 – Measurements profile

Shear rate (s^{-1})	5
Apply time (s)	30
Equilibrium time (s)	90

- Select button

Table 13 – Measurements profile

Measurement system	CP 4º / 4mm
Temperature (ºC)	23 ºC
Frequency (Hz)	1
Minimum Frequency (Pa)	0.1
Maximum Frequency (Pa)	10
Number of Samples	21
Delay Time (s)	1
Periods	1
Points	512
Strain	**Obtained from A.S.**
Initial Stress	**Obtained from A.S.**
Steady Flow (Pa)	0



Frequency Sweep
☐ Advanced Table
Minimum Frequency (Hz) 0.1
Maximum Frequency (Hz) 10
Logarithmic
Number of samples 20
Delay Time (s) 1
Integration Time
Periods 1
Points 512
Auto-stress
Strain 0.0693
Initial Stress 5.347
Down
Steady Flow (Pa) 0
Total Test Time 222.4

Figure 44 – Oscillation Test Parameters

Note: use a point of strain and stress:

- crossover point, ± 5 % preceding or following (Figure 45);
- inside LVR (Figure 46);
- after the crossover point (Figure 47).

Figure 45 illustrates an example of conditions of Figure 44.

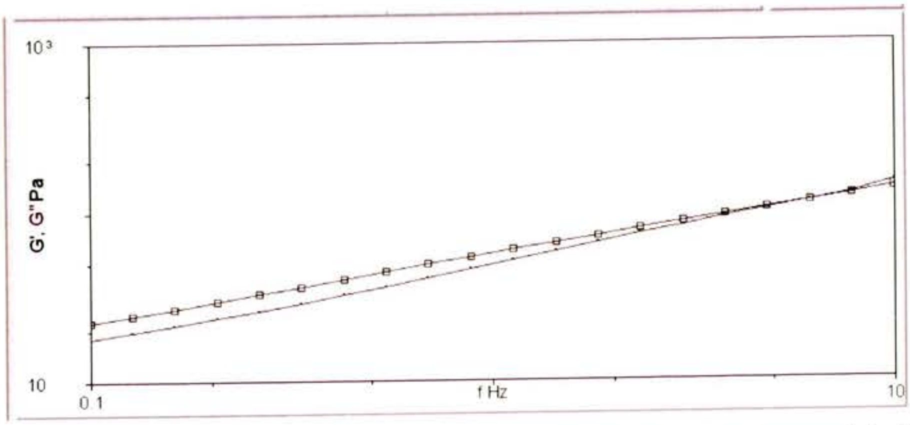


Figure 45 – An example of frequency sweep test with conditions from table 13

To confirm the elastic behaviour, it is used a point inside LVR; as it is showed on the next typical graph. It allows showing the storage stability. If it is used a point preceding the crossover point, it allows to evaluate the transport of material.

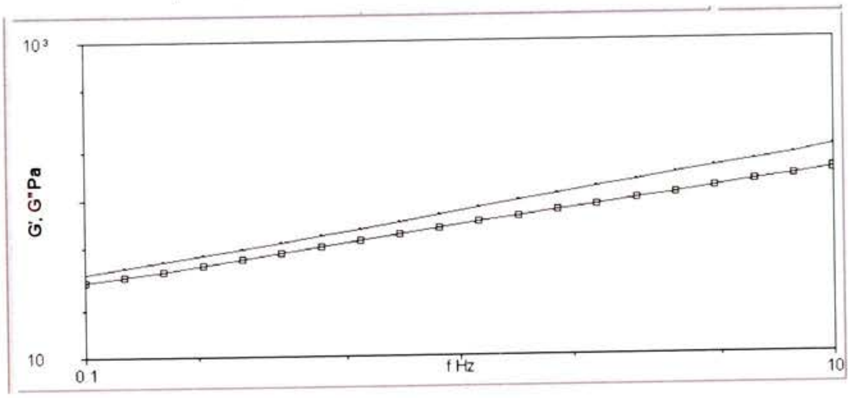


Figure 46 – An example from frequency sweep test

On the other side, it is used a point after the crossover to confirm the viscous behaviour; as it is showed on the next typical graph.

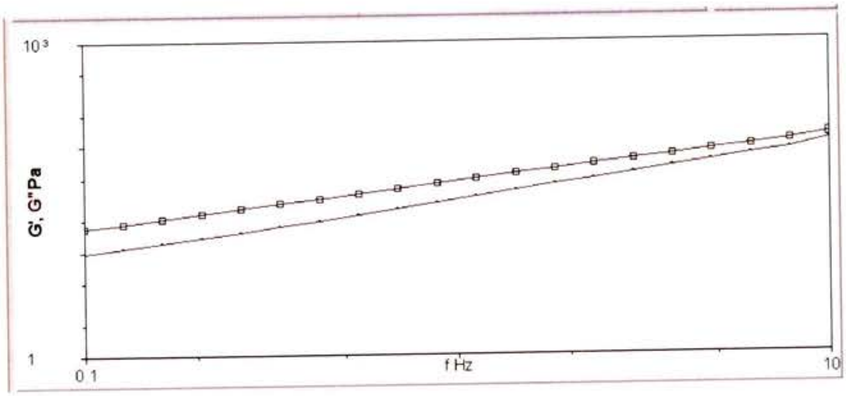
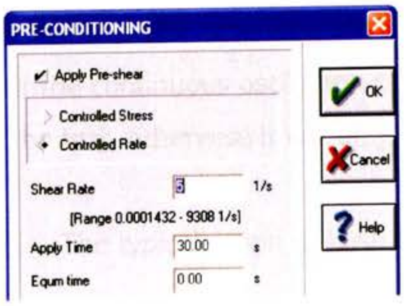


Figure 47 – An example from frequency sweep test

C. Single Frequency

i. Select **Pre-condition** (pre-shear)



☑ Apply Pre-shear

○ Controlled Stress

● Controlled Rate

Shear Rate 5 1/s

[Range 0.0001432 - 9308 1/s]

Apply Time 30.00 s

Equm time 0.00 s

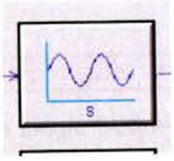
Figure 48 – Pre-condition screen

Table 14 – Measurements profile

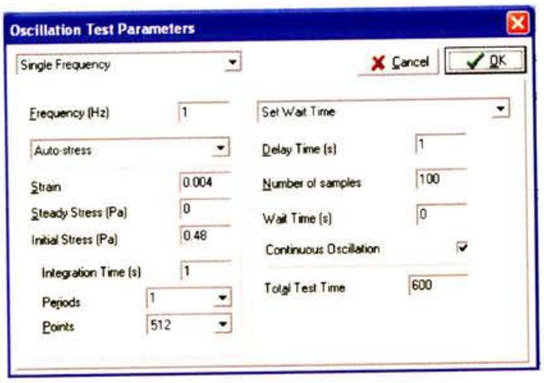
Shear rate (s^{-1})	5
Apply time (s)	30
Equilibrium Time (s)	0

NOTE: The required pre-shear time can be obtained from single frequency test, by running a constant shear rate (5 s^{-1}) and plotting G′ against time, Figure 50. When the viscosity reaches a plateau, the recovery time can be used in pre-shear.
Another way to evaluate the thixotropic behavior is applying a shear rate = 1000 s^{-1} (to simulate practical application) and measure the recovery time.

ii. Select button



iii. Fill the Oscillation Parameters.



Single Frequency

Frequency (Hz): 1

Auto-stress

Strain: 0.004

Steady Stress (Pa): 0

Initial Stress (Pa): 0.48

Integration Time (s): 1

Periods: 1

Points: 512

Set Wait Time

Delay Time (s): 1

Number of samples: 100

Wait Time (s): 0

Continuous Oscillation ☑

Total Test Time: 600

Figure 49 – Oscillation Test Parameters

Table 15 – Measurements profile

Measurement system	CP 4º / 4mm
Temperature (ºC)	23 ºC
Frequency (Hz)	1
Stain	**From LVR**
Steady Stress (Pa)	0
Initial Stress (Pa)	**From LVR**
Periods	1
Points	512
Delay Time (s)	1
Number of Samples	100
Wait Time (s)	0

For controlled stress rheometers, must use the **Auto Stress** option that allows to enter a strain, otherwise the software will accept a stress value.
If the continuous oscillation option is selected, the oscillation will be applied throughout the test, otherwise it will only be applied whilst a measurement is being made.

The typical graph is illustrated in Figure 50.

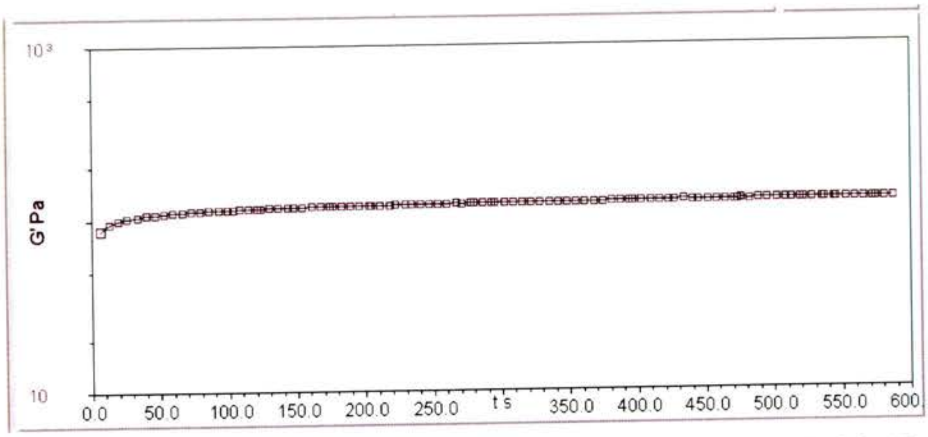


Figure 50 – An example of single frequency test with conditions of table 15

IV. RELAXATION TEST

Stress relaxation can give much useful information about viscoelastic materials.

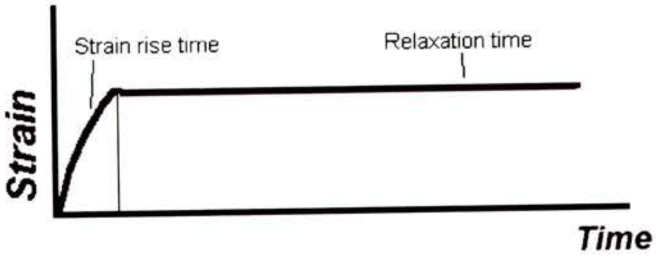


Figure 50 – The relaxation test

This test method is mostly used to examine chemically unlinked and unfilled polymers in the form of melts and solutions, but it also suitable for determining the behavior of chemically cross-linked polymers, gels and dispersions with a physical network of forces. It is not used for paints.

The test sample is subjected to a rapidly applied strain which is then held for the remaining of the test. The relaxation behaviour is then studied by monitoring the steadily decreasing value of shear stress.

For a pure Newtonian material, the stress will decay instantaneously whereas for a pure Hookean material there will be no decay. The simplest type of viscoelastic response is an exponential decay.

For long time scale tests the stress relaxation method is substantially faster than standard oscillation testing to obtain the viscoelastic response as a function of time.

The stress relaxation test is also useful in quality control to obtain a 'finger print' which may indicate several rheological properties - viscosity, initial modulus and decay time.

Spite the rheometer allows to make this kind of testing, it is not very used in paints; therefore at this point, there is no particular interest in trying to better understand this kind of test.

PART 2. RHEOLOGICAL CHARACTERIZATION OF PAINTS

CIN

Universidade do Porto

Faculdade de Engenharia

FEUP

TABLE OF CONTENTS

LIST OF TABLE

LIST OF FIGURES

A. INTRODUCTION

1.1 DEFINITION OF RHEOLOGY

Rheology is the science of understanding the flow and deformation of materials. It is a study of the change in form and flow of matter, embracing elasticity, viscosity and plasticity.

Because the cost of new product development is considerable, it makes sense to introduce rheological measurements as a means of reduce both development time and cost.

Rheological phenomena are found in many coatings operations. Because coatings are complex structured fluids, it is necessary to be able to apply a variety of tests to examine their complex behaviour.

1.2 RHEOLOGICAL TEST TYPES

Rheometers are instruments for measuring the shear stress and viscosity and also permit the measurement of additional viscoelastic parameters.

Rotational Tests

High precision, continuously-variable-shear instruments in which the test fluid is sheared between rotating cylinders, cones or plates, under controlled-stress or controlled-rate conditions, are termed rotational rheometers.

There are two basic methods: controlled shear rate (CSR) and controlled shear stress (CSS).

In the first case, which may be termed "controlled rate", the applies angular velocity is the independent variable and the viscous drag torque the dependent variable. In the second case, termed "shear stress", the applied torque is the dependent variable and the measured angular velocity the dependent variable.

Both measuring methods allow measuring either single viscosity values or a full viscosity curve.

Oscillatory Tests

Oscillation mode in a rheometer is required to provide further information about the viscoelastic behaviour. The material to be measured is exposed to an oscillation frequency. Mostly, the oscillations are performed at very low shear loads in order not to destroy the internal structure of the sample while the test is running.

Creep Test

One unique capability to controlled-stress rheometers is the creep test, whereby a constant load is applied to the material and the deformation is recorded with time. Creep has defined as "the slow deformation of a material, usually measured under a constant stress". The creep test records the information from the moment that it applies and hence gives measure elastic, viscoelastic and viscous components. It allows to obtain viscosity at low shear rates, therefore it is possible to determine zero viscosity.

1.3 PRODUCTION AND PROCESSING OF PAINTS

To allow proper production of paints, these have to be stirrable, mixable, dispergable as well as pumpable and flowable while being transported.
Dependent on the kind of application, these paints have to be spreadable, brushable, knife-coatable, rollable, pourable, sprayable or printable, respectively.

i) Viscous Flow

The paint flows at all the processes referred above. In rheology, rotational tests are used to simulate flowing processes. Flow curves and viscosity curves describe the dependence of the measured substance on the intensity and the duration of shearing load.

ii) Viscoelastic effects

If elastic effects – such as e.g. stringing or adhesion – should occur during processing, the cohesion forces within the color are too high. Usually, a "short break-off" is desired. Creep or oscillation tests often are well suitable to evaluate effects occurring during practical operation. The measured results help to optimize the paints. The relationship between viscous and elastic properties has to be optimal - a measurement of the viscosity only is insufficient. Both the viscous and elastic properties of the substance have to be known to be able to set such parameters that are required for achieving optimal product behaviour. Here, oscillation tests are very suited for considerably improving the behaviour of paints or pastes.

1.4 STABILITY OF THE DISPERSION

The sedimentation stability is a very significant aspect for the judgment of dispersions. For most of these products, long-term storage ability as well as closed-circuit stability in the pipeline is required over weeks or even months. The following paragraphs describe three different methods of investigating the stability of the dispersion.

i. Yield Point

The yield point can be determined by measuring the flow curve, preferably according to the CSS-method. As an example, imagine a network of forces between the different components of the dispersion. The stronger a network of a substance is developed, the lower is the sedimentation tendency of particles or fillers. The stronger these particles are embedded into the superstructure, the higher is their yield point.

The yield point denotes the highest shear stress value of the flow curve, at which still no movement is measured, i.e., the shear rate $\dot{\gamma} = 0$. The significant parameter for determining the yield point is that the result strongly depends on the resolution of the measuring instrument and thus on the minimum number of revolutions or the minimum shear rate.

ii. Storage Modulus G′

Many users of oscillation rheometers judge the dispersion stability of a substance with the help of the storage modulus G′. Comparison with the yield point model: also here, the storage modulus stands for the stability of the dispersion thus characterizing the internal structural forces. A higher structural strength in rest which is measured under minimum load in the linear-viscoelastic range provides improved particle compound and counteracts a phase separation. The increased stiffness of the superstructure avoids sedimentation processes and is indicated through higher G′-values.

iii. Zero Viscosity

Usually, three different test types can be used to determine the zero viscosity of substances containing polymer components, provided that the disperse character is not predominant: Using the rotational test – measurement of flow curve and viscosity curve at minimum shear rates. Using the oscillation test – running the frequency sweep at lowest frequencies. Using the creep test – evaluation of the curve gradient is based on the model of shear viscosity at rest.

1.5 BEHAVIOUR AFTER APPLYING THE PAINTS

After applying the paint, especially the surface levelling characteristics and the sagging behaviour will significantly affect the quality of the coating. The internal superstructure must be built up within a certain period of time. During this period there should be enough time for gas bubbles to escape. Often, a smooth and glossy surface without any splashes or other inhomogenities is required.

1.5.1 Structural recovery, thixotropy

For today's quality control measurements, often the area between up and down flow curves of the diagram is evaluated to determine the thixotropic behaviour.
The internal structural re-formation of a good paint is performed not too fast to allow appropriate levelling of probably occurring splashes. However, if the internal structural re-formation is performed too slow, then too much paint will run down thus providing a too thin layer.

1.5.2 Thickness of the wet layer

After applying a coat, a definitive layer thickness should remain on the underground. Also here, the yield point, the storage modulus G' and the zero viscosity represent the most significant parameters. As already mentioned for the stability of the dispersion, it deals with condition at rest. An appropriate thick layer will remain as soon as the internal network of forces, the structural strength or the shearing viscosities at rest of the layer meet the requirements. The following rule is valid: the higher the yield point, the storage modulus G' or the zero viscosity, the thicker is the remaining layer applied on the underground.

B. EXPERIMENTAL RESULTS / CORRELATION APPLICATION

The results are split into three main sections. For each case, the tested paints are the following:

☐ (black) – Styrene-Acrylic Paint
△ (red) – Acrylic Paint
+ (blue) – PVAveova Paint

First, it is important to know the major differences between the three formulations (Table 1).

Table 1 – Type of thickeners, density, volume of solids, weight of solids and PVC for each paint

	Acrylic Paint	Styrene-Acrylic Paint	PVAveova Paint
Type of thickeners	HMHEC PEPO	HMHEC PEUP	HMHEC PEUP
Density	1.338	1.338	1.415
Volume solids (%)	34.6	34.2	37.3
Weight solids (%)	51.2	51.0	55.8
PVC (%)	53.1	76.2	66.8

that:

HMHEC – hydrophobically modified cellulose;
PEUP – hydrophobically modified polyether urea polyurethane;
PEPO – Hydrophobically modified polyether polyols.

The first section will include rotational measurements performed in higher performance testing equipment that is able to use CSR-mode (controlled shear rate) as well as CSS-mode (controlled shear stress). In the second section, Amplitude/Frequency Sweep were studied and in the third and final section will allow to find zero viscosity, Creep Test.

In the present work, some practical essays have been performed, namely:

- height of phase separation and sedimentation;
- level of sagging;
- levelling;
- determination of ICI viscosity;
- determination of Stormer viscosity;
- roller practical application (levelling; spattering; wet layer thickness).

Table 2 – Application features of the tested paints

Application feature	Δ (Acrylic Paint)	□ (Styrene-Acrylic Paint)	+ (PVAveova Paint)
Height of phase separation (cm)	1.5	1	~ 0
Sedimentation	None	None	None
Levelling	0	3	0
ICI Viscosity (Pa.s)	0.111	0.09	0.105
Stormer Viscosity (UK)	105	104	114
Theoretical Stormer Viscosity (Pa.s)	1.942	1.885	2.520

that:

η_S – Stormer Viscosity in UK;
η – Stormer Viscosity in Pa.s.

2.1 ROTATIONAL TESTS WITH RHEOMETER GEMINI OF BOHLIN INSTRUMENTS

Gemini rheometer allows measurements with a controlled shear rate and controlled shear stress. Both methods can be combined by defining several subsequent measuring segments in one test.

With a suitable test procedure flow properties can be determined in one test allowing statements regarding the different test modes. For the tested paints the viscosity behaviour was to be determined regarding:

- low to high shears rate (viscograms);
- small deformations (yield points);
- shearing time dependent behaviour (thixotropy).

---

[1] – one coat roller

2.1.1 Viscogram

As measuring geometry the plate-cone-system CP 4º/40 mm was used. The measurements were performed at T = 23 ºC. The measurement for the characterization of the viscosity behaviour was therefore defined as shown in Table 3.

Table 3 – Parameters for measurement of viscosity behaviour with CSR-mode and table of shears

Measurement system	CP 4º / 40 mm
Temperature (ºC)	23
Delay time (s)	10
Integration time (s)	25
Proportionality	strain
Ramp	Up
Start shear (s^{-1})	0.0001432
End shear (s^{-1})	1000
Number of Samples	30
Range	logarithmic

The behaviour of the tested paints is now shown in Figure 1. In this case, one can evaluate the flow behaviour of the paints from 0.0001432 s^{-1} to 1000 s^{-1}. From this viscograms it can be concluded that all paints display pseudoplastic behaviour. i.e., the viscosity decreases with an increasing shear rate.

It is possible to analyse the low shear rate region (10^{-4} – 10^{-1} s^{-1}), giving a parameter of extreme importance to evaluate sedimentation, phase separation, levelling and sagging of the tested paints.

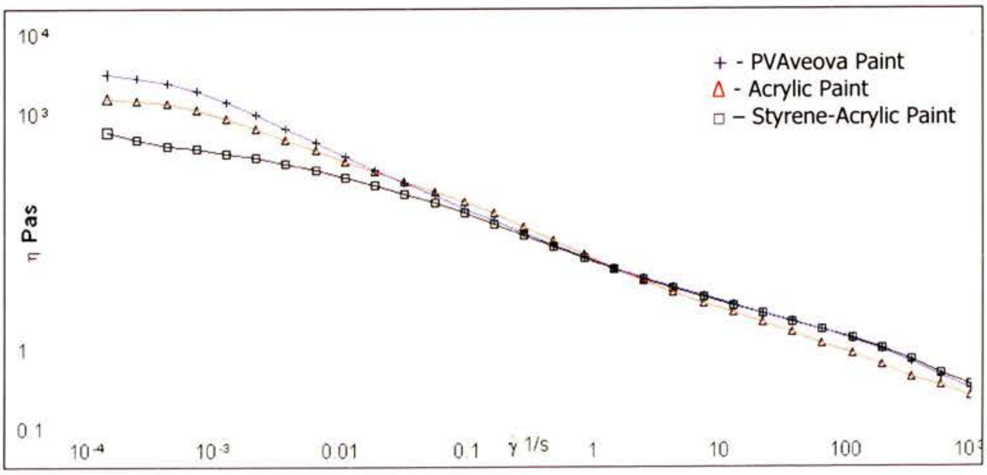


Figure 1 – Viscosity as function of the shear rate for the three tested paints in logarithmic scale

Analysing the viscosity at 1.4×10^{-4} s^{-1}, it is verified that the paints differ from each other, as shown in Figure 2.

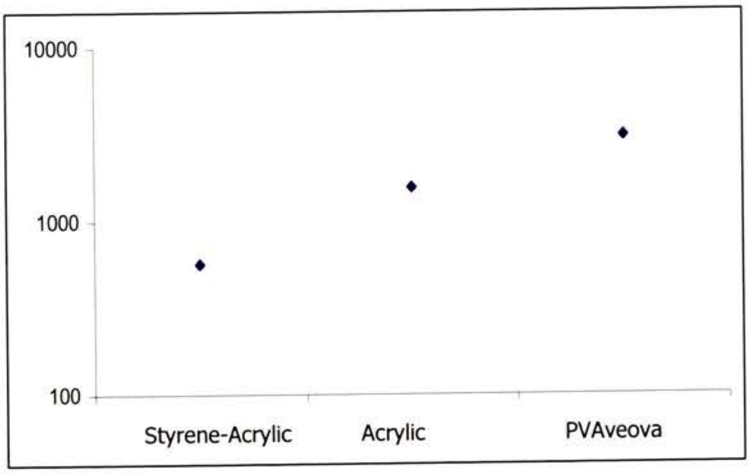


Figure 2 – Viscosity at a shear rate of 10^{-4} s^{-1} for each tested paints

It is known that the higher the viscosity at very low shear rates, the higher is the resistance against sedimentation. The viscosity obtain is quite higher, it should not exists sedimentation, as determined in the practical tests.

If one tries to correlate phase separation with this parameter, it is shown that the highest viscosity is the only paint that does not have any phase separation. It will also try to correlate this performance with oscillatory tests.

For viscosity at low shear rates (10^{-2} s^{-1}), Figure 3 shows the respective values for each other tested paints.

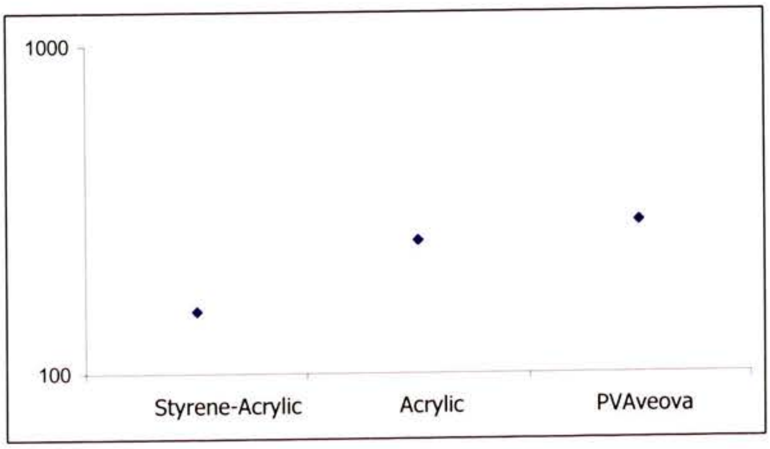


Figure 3 – Viscosity at a shear rate of 10^{-2} s^{-1} for each tested paints

At this shear rate, it is possible to analyse levelling and sagging behaviour. It is known that the higher the viscosities at low shear rates, less sagging, therefore worst levelling. This is according with practical essays: levelling test and roller practical application (see Table 2).

To compare ICI viscosity with viscosities obtained in the rheometer at the same constant shear rate (10000 s^{-1}), it was necessary to apply a different measurement system, plate-plate PP 20. The gap it is equal to 0.250 mm. The measurements were performed at T = 23 ºC. Table 4 shows the parameters for these measurements.

Table 4 – Parameters for measurement of viscosity behaviour with CSR-mode and single shear

Measurement system	PP 20
Temperature (ºC)	23 ºC
Shear Rate (s^{-1})	10000
Delay time (s)	3.3
Integration time (s)	4.8
Total time test (s)	60
Number of Samples	6
Time per point (s)	10

Figure 4 shows the viscosities of tested paints at shear rate 10000 s^{-1}.

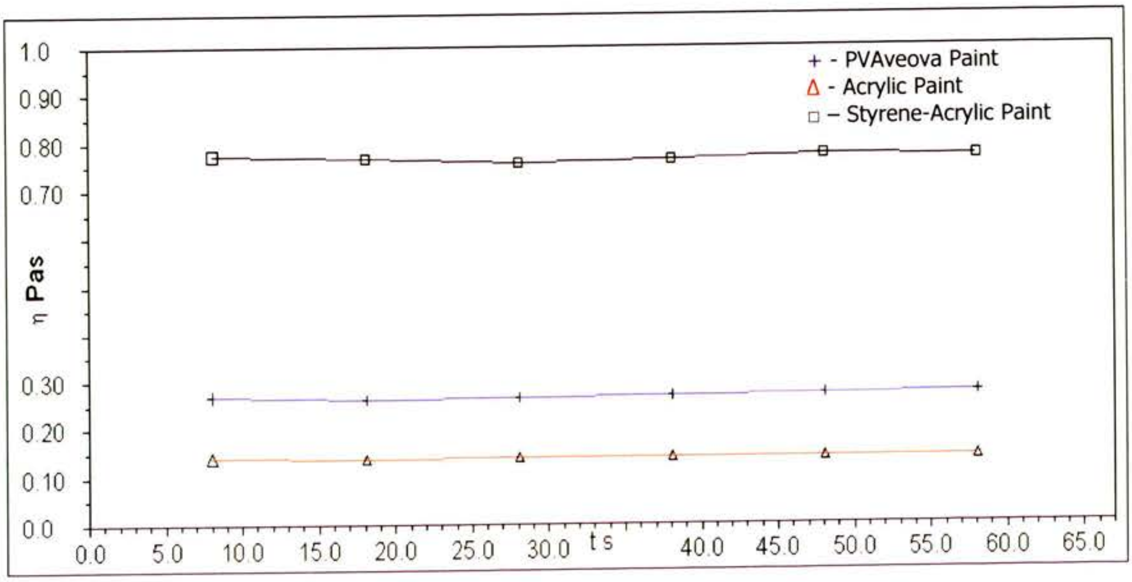


Figure 4 – Viscosity at a shear rate of 10000 s^{-1} for each tested paints

Comparing the viscosities at a shear rate of 10000 s^{-1} (see Table 5) with the ICI viscosity presented in Table 1, there are significant differences, probably due to gap of ICI viscometer.

Table 5 – Viscosity at shear rate equal to 10000 s^{-1}

Paints	**η (Pa.s)**
Δ (Acrylic Paint)	0.139
□ (Styrene-Acrylic Paint)	0.756
+ (PVAveova Paint)	0.265

2.1.2 Tensiogram

The measurement for the characterization of viscosity behaviour with CSS-mode was defined according table 6.

Table 6 – Parameters for measurement of viscosity behaviour with CSS-mode and shear profile

Measurement system	CP 4º/40 mm
Temperature (ºC)	23
Start shear (s^{-1})	0.01
End shear (s^{-1})	60
Sweep time (s)	60
Number of Samples	20

Figure 5 shows the viscosity behaviour of the tested paint as function of the preset shear stress in linear scale.

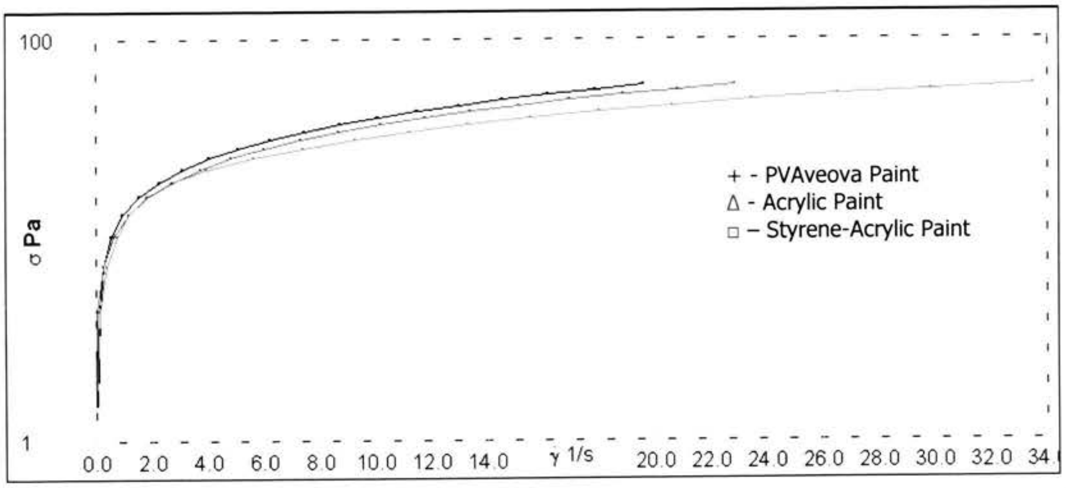


Figure 5 – Shear stress as function of the shear rate for the three tested paints in linear scale for the yield point determination

The viscosity behaviour was considered as function of the shear stress in order to detect a yield point. The yield point corresponds to the shear stress which is needed to bring a substance to flow. It was obtained looking with basis on Figure 6.

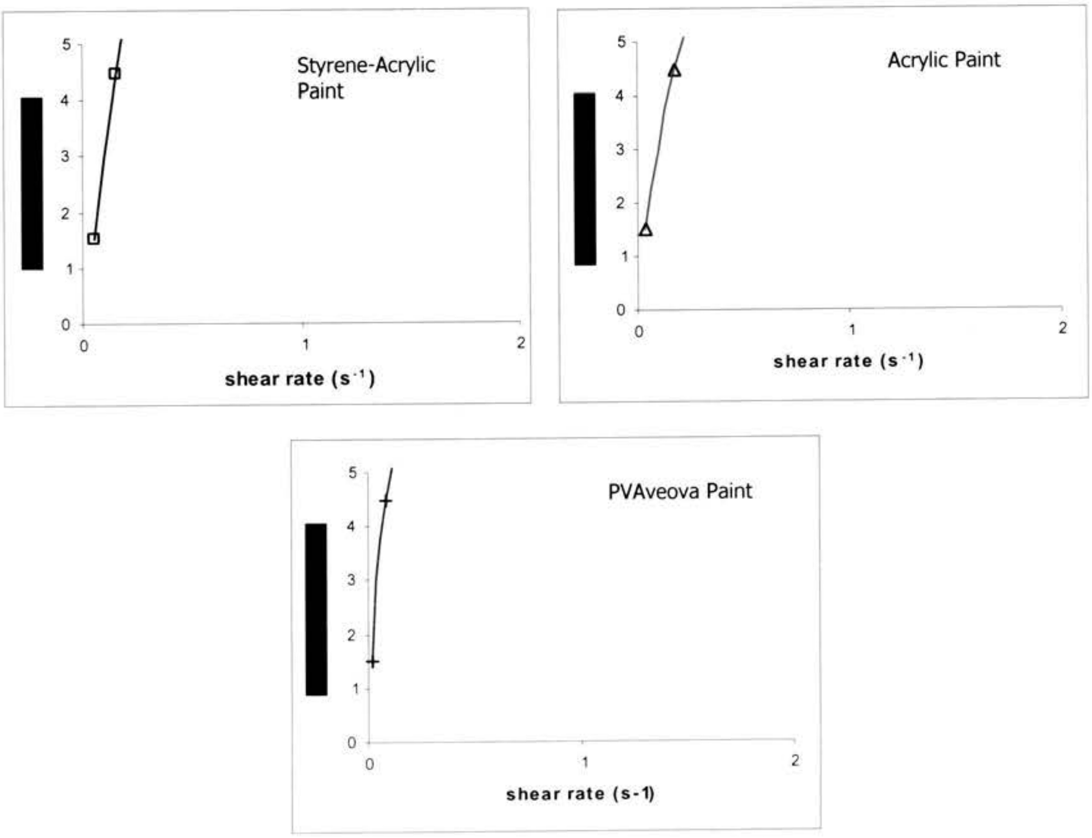


Figure 6 – Shear stress as function of the shear rate for the three tested paints in linear scale for the yield point determination

From the analysis of the Figure 6, it can be seen that the paints (□) and (Δ) show no yield point and paint (+) shows a yield point at 1.508 Pa. In practical test of phase separation, the paint (+) showed no phase separation, whereas the others two paints did not.

2.1.3 Thixotropy

In a thixotropic fluid, the viscosity is not only dependent on the shear rate but also the time period through which the fluid is being sheared.
Here, the levelling behaviour of a coating surface, the sagging behaviour on a vertical wall and the thickness of a wet layer are influenced distinctively.

In Figure 7 three measuring curves of paint coatings are presented. The test conditions are:

Table 7 – Parameters for measurement of viscosity behaviour with CSR-mode and shear profile

Regions	1	2	3
Start value (s^{-1})	0.1	1000	0.1
End value (s^{-1})	0.1	1000	0.1
Time (s)	120	30	110
Sample Mode	Steady	Steady	Steady
Samples	20	10	60

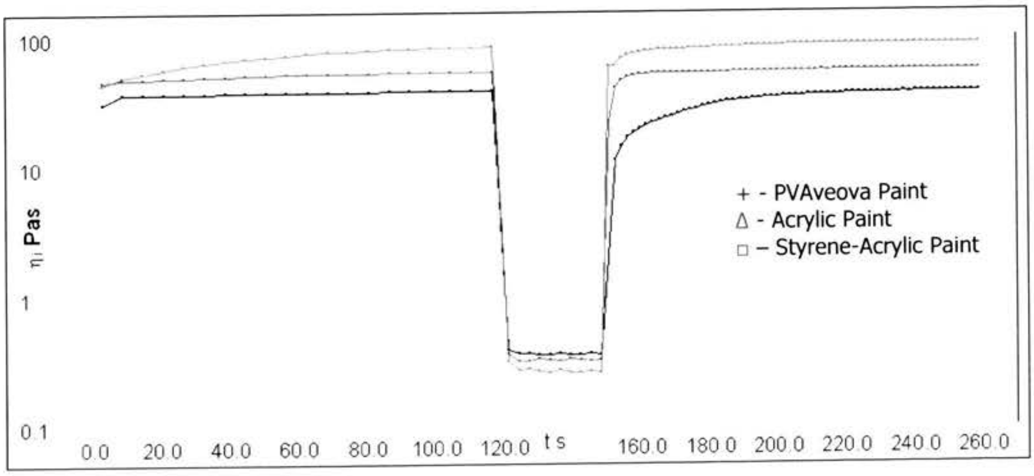


Figure 7 – Instantaneous viscosity as function of the time for the three tested paints for analyse thixotropic behaviour

Table 8 shows the estimation of recovery.

Table 8 – Estimation of recovery (%)

		Final of 1st interval ("low shear")	Final of 2nd interval ("high shear")	3rd interval after t=30s	3rd interval after t=60s	3rd interval after t=90s
Δ	η (Pa.s)	85.995	0.264	83.111	88.319	89.208
	Rec. (%)			96.6	102.7	103.7
□	η (Pa.s)	39.173	0.3580	29.062	35.455	37.037
	Rec. (%)			74.2	90.5	94.5
+	η (Pa.s)	54.703	0.32566	53.655	54.918	55.793
	Rec. (%)			98.1	100.3	102.0

Paints (Δ) and (+) exhibits full recovery in an application relevant time (t = 60 s). In contrast, after t = 90 s, the viscosity of paint (□) has recovery 94% of the values determined in interval 1. This one presents the best levelling (see Table1).

Paints with fast structural regeneration displayed no sagging and insufficient levelling, whereas a too slow recovery causes sagging but a better levelling of paint.

Comparing this behaviour of paints showed in Figure 7 and Table 6 with the practical essay of levelling, it is verified that paints (Δ) and (+) showed insufficient levelling and displayed no sagging, as its structure regenerates too fast after application. Paint (□) showed a better levelling, due to a slow recovery.

2.2 OSCILLATORY TESTS WITH RHEOMETER GEMINI OF BOHLIN INSTRUMENTS

2.2.1 Amplitude Sweep

The amplitude sweep is used to determine the limit of the linear viscosity range (LVE).

Table 9 gives the parameters selected for the accomplishment of this test.

Table 9 – Parameters for characterization of amplitude dependency of the tested paints

Measurement system	CP 4º / 4mm
Temperature (ºC)	23 ºC
Frequency (Hz)	1
Minimum stress (Pa)	0.06
Maximum stress (Pa)	60
Steady Stress (Pa)	0
Delay Time (s)	1
Periods	1
Points	512
Number of Samples	21

Figures 8 and 9 illustrate, for each tested paints, the storage modulus (G′) and loss modulus (G″) as functions of strain and shear stress, respectively.

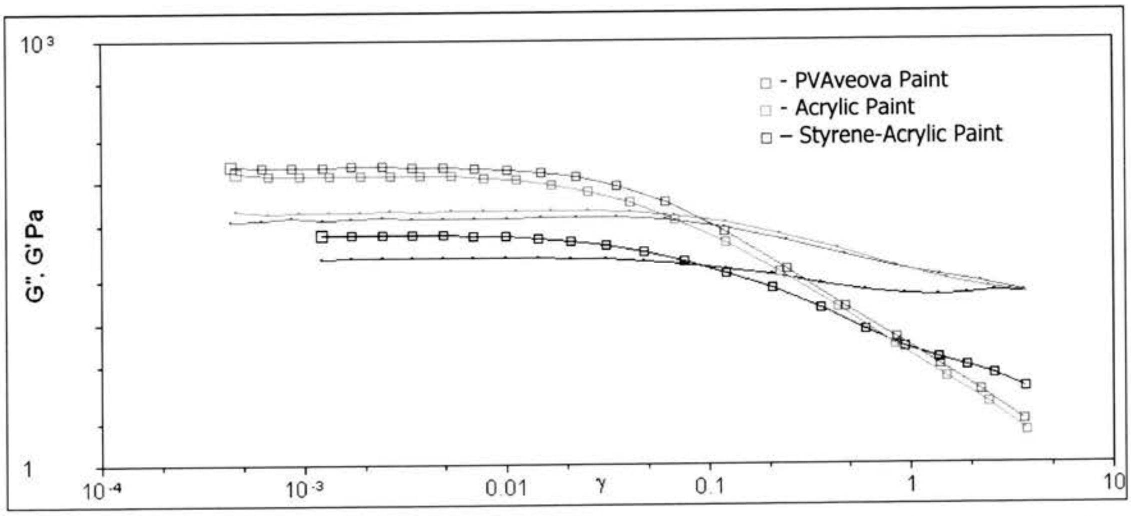


Figure 8 – Amplitude sweep, Storage modulus G′ and loss modulus G″ as function of strain

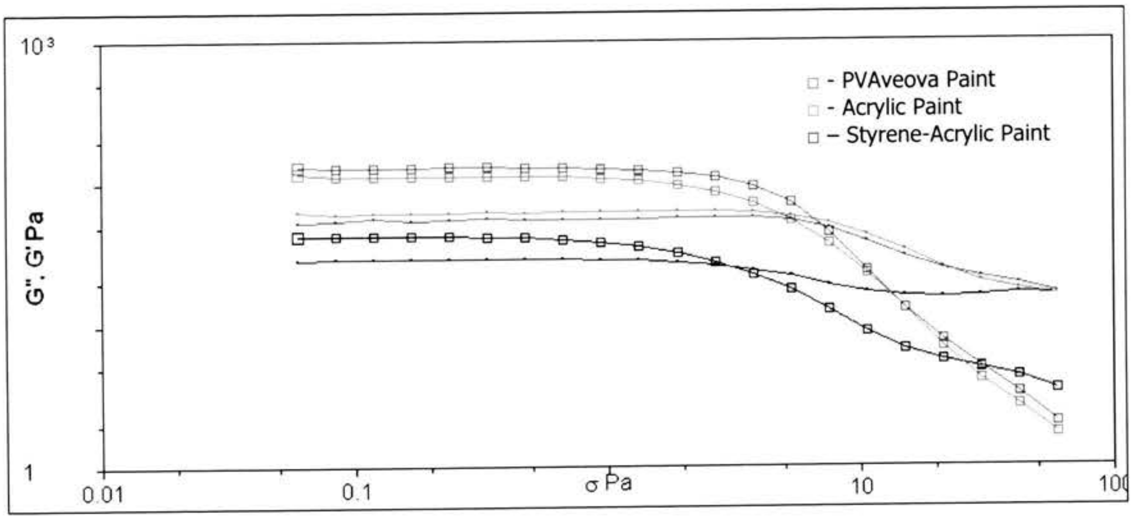


Figure 9 – Amplitude sweep, Storage modulus G′ and loss modulus G″ as function of shear stress

In the LVE range (i.e. under low shear conditions) all paints show G′ > G″, so the elastic portion dominates over the viscous portion. All paints display a gel character and therefore have a certain amount of structure stability. When the G′ and G″ curves intersect, the paints change from a gel-like to a liquid character. This intersection is usually taken as the criterion for regeneration time of the structure.

Table 10 indicates the crossover point and respective strain and shear stress for each paint and their yield stresses.

Table 10 – Yield stress; shear stress, strain, G′ and G″ at crossover point for each paint

Paints	σ_y (Pa)	σ_{co} (Pa)	γ_{co}	G′ = G″ (Pa)
Δ	0.673	4.93	0.0618	58.76
□	0.337	3.21	0.0987	24.86
+	1.343	7.21	0.1119	48.14

that

σ_y – shear stress at yield point

σ_{co} – shear stress at crossover point

γ_{co} – strain at crossover point

The shear stress at the limit of the LVE range could be determined as the yield point. The higher the yield point the more stable is the paint. Values of yield point above 1 Pa could show a preventing sedimentation of particles, no phase separation. Once again, it is verified that paint (+) has a value of yield point higher than the others two paints. As already shown, paint (+) do not display phase separation.

The wet layer thickness of a coating which remains on the vertical wall can be calculates as:

$$WLT = \frac{\sigma_y}{\rho\, g}$$

that

WLT – wet layer thickness;

ρ - density (g/m^3);

g – gravitational acceleration ($9.81 m/s^2$).

These values are represented in next table:

Table 11 – yield stress and wet layer thickness for each paint

Paints	σ_y (Pa)	WLT (μm)
Δ	0.673	51.3
□	0.337	25.7
+	1.343	96.7

The calculated values should only be seen as rough indication, because other factors. The thickness of the wet layer also depends a lot on its time-dependent behaviour during structural regeneration after the shear-intensive application.

These values give the maximum wet layer thickness that sagging will not occur for coatings.

As it can be seen in Figure 8, for a strain equal to 0.01 (one value of LVE range for all paints), G′ and G″ modulli are different for each paint. The G′ value of paint (+) is higher and G′ value of paint (□) is lower. That way, the higher G′ and G″, the greater is the consistency of the paints.

It can be seen, in Table 10, that shear stress of crossover point is lower for paint (□). It can show that this paint has a better levelling than others two paints but it can lead to undesired sagging. As already shown in practical tests, paint (□) has a better levelling.

2.2.2 Frequency Sweep

The frequency test provided significant information for the investigation of internal structures. Frequency sweep tests were provided in order to study the variation of G' and G" as function of the frequency at a constant amplitude (inside the LVE range).

Table 12 gives the parameters selected for the accomplishment of this test.

Table 12 – Parameters for characterization of frequency dependency of the tested paints

Measurement system	CP 4º / 4mm
Temperature (ºC)	23 ºC
Frequency (Hz)	1
Minimum Frequency (Pa)	0.1
Maximum Frequency (Pa)	10
Number of Samples	21
Delay Time (s)	1
Periods	1
Points	512
Strain	Obtained from A.S.
Initial Stress	Obtained from A.S.
Steady Flow (Pa)	0

Figure 10 illustrates, for each tested paints, the storage modulus (G') and loss modulus (G") as functions of frequency.

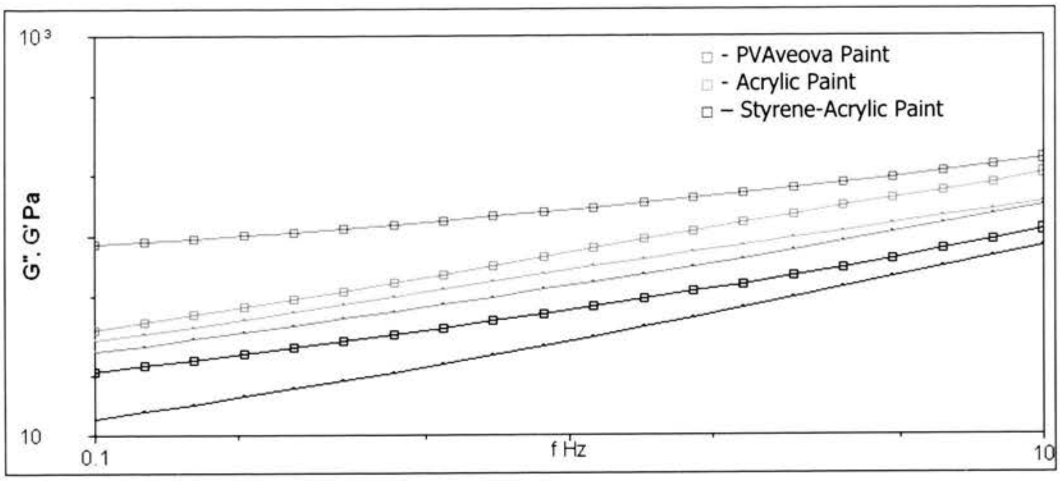


Figure 10 – Frequency sweeps, Storage modulus G' and loss modulus G'' as functions of frequency

All paints show the following behaviour: over the whole frequency range the storage modulus G' is higher than the loss modulus G'', i.e., the sample elastic properties prevail at small, as well as at high stress. This is an indication for the strong suspension character of these paints, with particular strong interactions; therefore there is a great resistance against sedimentation. Figure 11 shows the relative importance of viscous to elastic contributions for a material at a given frequency (tan δ = G''/G').

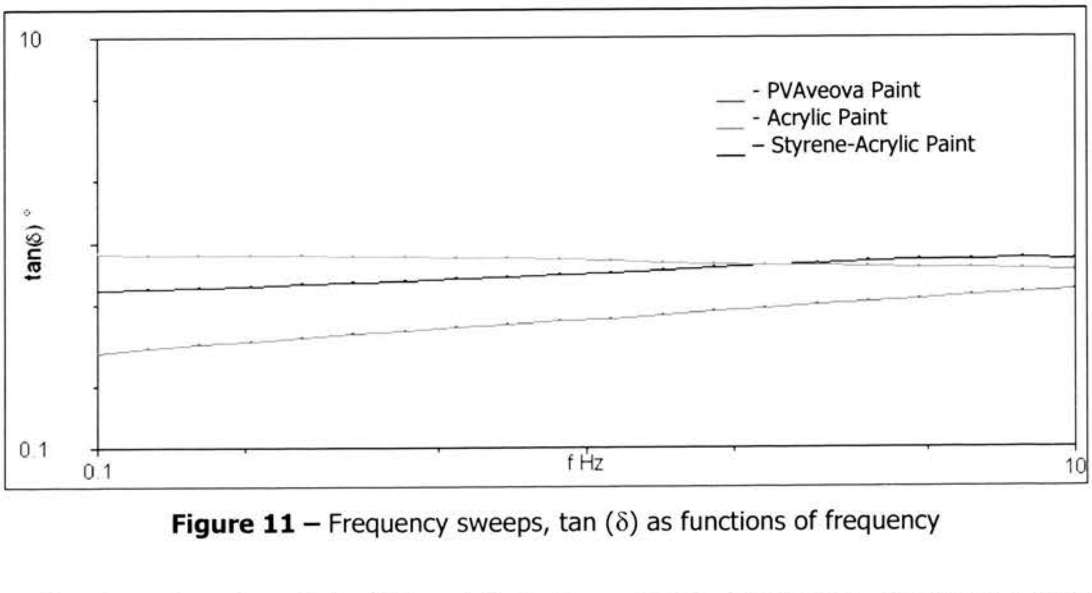


Figure 11 – Frequency sweeps, tan (δ) as functions of frequency

As already referred, paints (Δ) and (□) show phase separation. Comparing these results with zero viscosity, one believes it can be better understood the different behaviour in phase separation of the three paints. The higher the value for tan δ, less strongly associated dispersed particles, therefore it is more probable to occur phase separation.

2.3 CREEP TEST WITH RHEOMETER GEMINI OF BOHLIN INSTRUMENTS

A Creep test consists of applying a constant non-destructive shear stress to the sample and monitoring the compliance as a function of time. The compliance (J) is defined simply as the ratio of the strain to the applied stress.

A creep and recovery curves provide information about the viscoelastic behaviour of the test sample. The results can be confidently used to predict the sagging and levelling.

Table 13 gives the parameters selected for the accomplishment of this test.

Table 13 – Parameters for characterization creep test

Measurement system	CP 4º / 4mm
Temperature (ºC)	23 ºC
Shear stress (Pa)	5
Creep - Region Mode	Pseudo-log
Creep - Region time (s)	300
Recovery - Region Mode	Pseudo-log
Recovery - Region time (s)	180

The results are plotted in Figure 12.

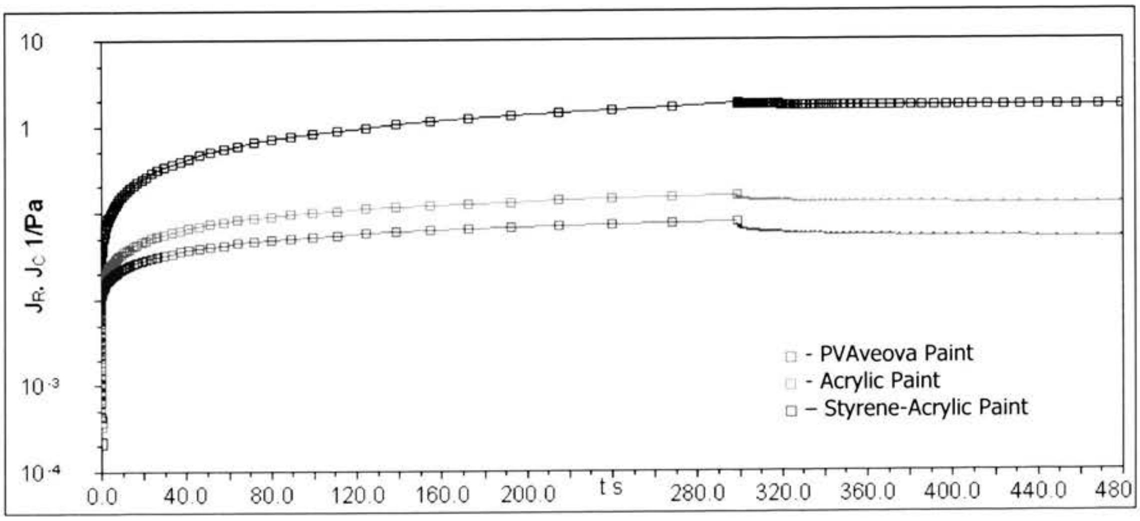


Figure 12 – Creep test, compliance as function of time

At shear stress equal to 1 Pa, it obtains a value of viscosity (Table 14).

Table 14 – Viscosity at a shear stress equal to 1 Pa

Paints	**η (Pa.s)**
Δ (red)	3894
□ (black)	312
+ (blue)	8337

As it can see, paint (+) displays a higher viscosity and paint (□) displays a lower viscosity. The higher compliance, the lower viscosity. For paint (+), biggest η, it does not show sedimentation or phase separation. Paint (□) starts to flow first than others; comparing with practical tests, it displays a better levelling.

As a summary, Table 15 shows the values of different parameters that were studied in this work.

Table 15 – Studied parameters for each tested paint

Paints	η (Pa.s)	σ_y (Pa)	WLT (μm)	σ_{co} (Pa)	γ_{co}	G′ = G″ (Pa)
Δ	1570	0.673	51.3	4.93	0.0618	58.76
□	568	0.337	25.7	3.21	0.0987	24.86
+	3110	1.343	96.7	7.21	0.1119	48.14

C. CONCLUSION

Important rheological characteristics have been reviewed on several different coatings.

The main results are:

- all tested paints display shear thinning flow behaviour;
- the higher the viscosity at low shear rates, the higher is the resistance against sedimentation, worst levelling and less sagging.
- the higher yield point, worst levelling and less sagging;
- yield point can also allows to predict the maximum wet layer thickness of the paint, before it starts to sag;
- the best method, in this work, to correlate phase separation, was obtained with the Frequency Sweep, representing tan δ as function of frequency;
- the higher the viscosity at high shear rates, the higher the force necessary for stirring and brushing (ex. worst roller application);
- the higher yield point or G' or zero viscosity, the stronger is the structure of the paint, being more difficult a substance to flow.

In this work, the aim is to compare rheological measurements with practical tests for three different products. The results obtained are very satisfactory; one can predict, with a certain degree of security, the performance of paints according to certain rheological parameters.

APPENDIX

DETERMINATION OF STORMER VISCOSITY IN PA.S

$$\ln(\eta_S) = 1.8118 + 0.596 \times \ln(0.1938\eta + 36) - 0.0206 \times [\ln(0.1938\eta + 36)]^2 ;$$

according to www.cannon-ins.com/ConversionsAndCalculations.htm.