In-depth analysis of viscoelastic properties thanks to Microrheology: non-contact rheology

Application

All domains dealing with soft materials (emulsions, suspensions, gels, foams, polymers, etc…)

Objective

Analyze the microrheological behavior at different stages during a product lifetime:

- Structure recovery ;
- Equilibrium ;
- Physical destabilization.

Device

RHEOLASER® LAB

Introduction

Viscoelastic properties are key parameters as they drive several end use properties of soft materials like consistency, spreadability, shape stability, or physical stability… Thus, it is crucial to characterize the rheological behavior using adequate technique.

Microrheology is a new domain of rheology to study the viscoelastic behavior of emulsions, suspensions, gels or colloidal dispersions at the micron length scale. It consists in measuring the displacement of particles which probe the elastic and viscous properties of soft materials. This technique offers many advantages :

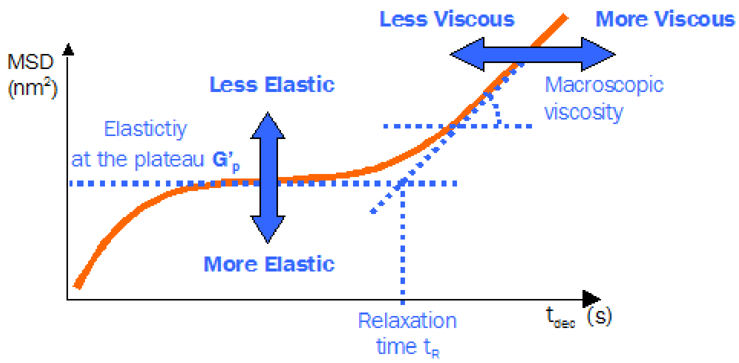
- Measurement at rest: zero shear ;
- Non contact measurement: no sample denaturing ;
- Measurement versus ageing time on the very same sample.

Indeed most of the conventional techniques like mechanical oscillation rheometers are complex to use because of practical constraints : choosing the adequate geometry, load precisely the right sample volume, determine the linear viscoelastic regime, slipping effect, motor torque inertia…

The microrheology analyzer Rheolaser LAB enables to solve these constraints as it does not require sample preparation, nor hardware or software configuration, and no external mechanical deformation is applied to the product. It also opens a new way to investigate the samples, as it works at the micron length scale.

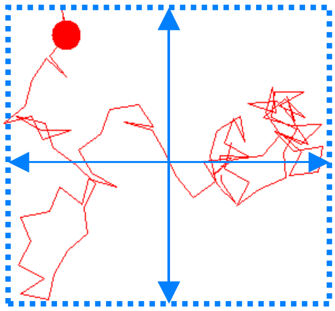
The purpose of this paper is to present the parameters that can be measured with Rheolaser Lab at different stage of the product lifetime such as the structure recovery, the viscoelastic equilibrium and the physical destabilization.

This is done thanks to the master curve which is obtained with Rheolaser: the Mean Square Displacement (MSD) in function of decorrelation time, which is the viscoelastic fingerprint of the studied product.



- The lower is the elastic plateau, the stronger is the elasticity ;
- The lower is the value of the slope for long decorrelation times, the stronger is the macroscopic viscosity ;
- The relaxation time is determined graphically ;

Note:



Brownian motion of a particle

The signal which is acquired, (decorrelation function), reflects how fast the particles move.

The signal in which it is translated (Mean Square Displacement) reflects how far the particles move.

I - GENERAL ANALYSIS

1. Acquisition

When launching an analysis, the first data obtained are the decorrelation curves (Figure 1). These curves are then converted to Mean Square Displacement (MSD) curves (Figure 2), allowing the user to monitor the viscoelastic behavior of his product.

The Mean Square displacement is the viscoelastic fingerprint of the product. It contains in one curve all the information which are necessary to fully characterize the microrheological behavior of a sample.

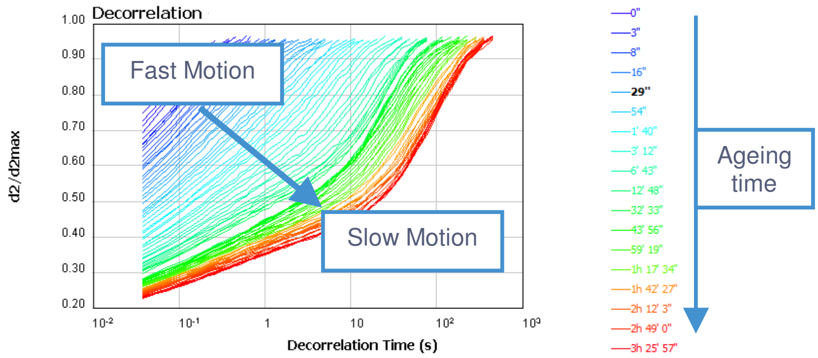


Figure 1. Decorrelation curves.

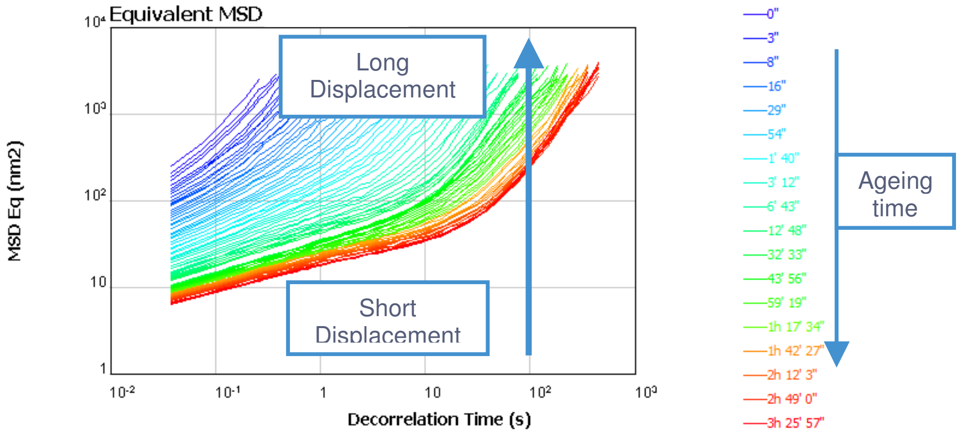


Figure 2. MSD curves.

Note:

The x-axis (decorrelation time) corresponds to the rheological time scale, that is to say, the exact inverse of the frequency which is used in general in mechanical rheology.

t_{dec} = 1 / frequency

In the example shown above, the product is a drilling mud, studied after a pre-shear. The user can observe an evolution of the decorrelation and MSD curves during the ageing time of the product:

- At the beginning (blue curves), the motion of the particles is very fast (decorrelation curves are short), and these particles travel a long distance in the sample (curves are high in the MSD graph).
- At the end of the analysis (red curves), the motion of the particles is slower (decorrelation curves are longer), and these particles travel a shorter distance for a given time of observation (curves are low in the MSD graph).

These information are linked to the microrheological behavior of the product:

- The further the particles travel, the less elastic is the product ;
- The faster the particles travel, the less viscous is the product.

In the example above, that means that elasticity and viscosity are increasing during the ageing time of the drilling mud after the initial shear (structure recovery).

2. Fluidity Index: identification of the visco-elastic state

From the decorrelation curves, it is possible to compute the Fluidity Index. The fluidity index (Fi) is computed directly from the decorrelation curve. The evolution of this parameter versus ageing time of the product enables to identify the viscoelastic state of the sample. It can usually be divided in 3 areas:

- **Structure recovery** of the product (Fi has a negative slope, the product recovers its viscoelastic properties) ;
- **Equilibrium** at rest (Fi reaches a plateau, the product is at viscoelastic equilibrium) ;
- **Physical destabilization** of the product (Fi has a positive slope, the product's viscoelasticity evolves).

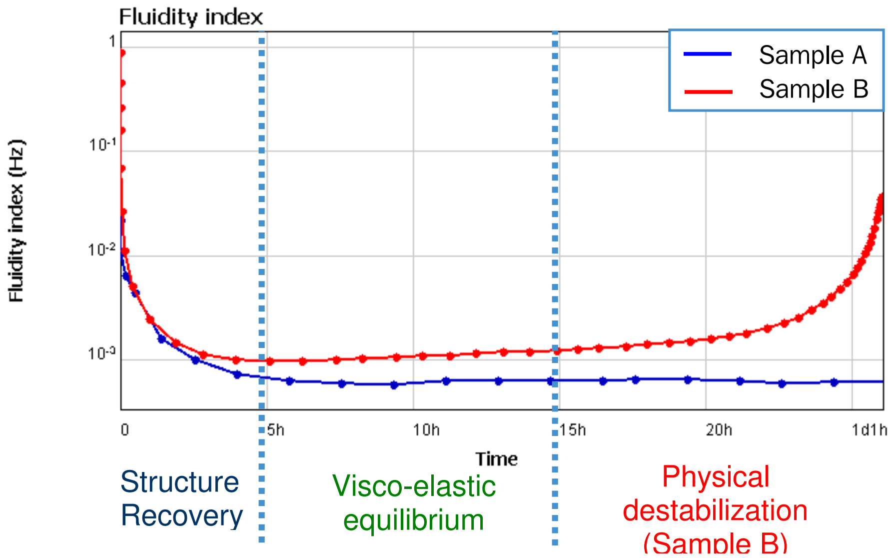


Figure 3. Fluidity Index for 2 drilling muds.

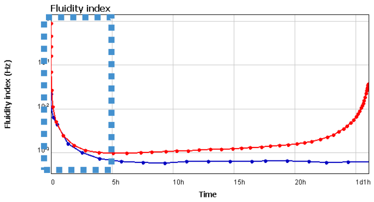
In the example shown above, 2 drilling muds are compared thanks to the Fluidity Index.

The one displayed in blue recovers its structure during the first 5 hours (decrease of the Fluidity Index), then reaches its microrheological equilibrium (the Fluidity Index reaches a plateau).

The product displayed in red also recovers its structure during the first 5 hours, then reaches its microrheological equilibrium, during 10 hours. After 15 hours, the Fluidity Index begins to increase, reflecting the physical destabilization of the product.

Thanks to this parameter, it is easy to identify the stable formulations and the ones with physical destabilizations, and then rank their stability.

Reminder:
This study is done in the following lifetime of the product (using the Fluidity Index curve):



II - Structure Recovery

1. Definition

The purpose of the recovery analysis is to monitor how a product recovers its structure after an initial pre-shear (pouring sample, pressing a toothpaste tube, pumping the sample in pipes, etc…).
Does the product recover its initial structure ? And if so, how fast does it ?

The main assets brought by Rheolaser are the following :

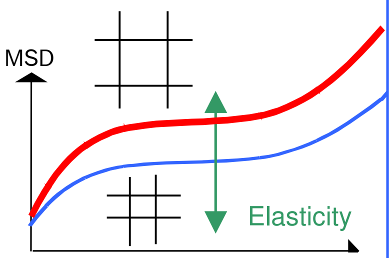
- Recovery is monitored at rest (zero-shear) ;
- Analysis of fragile materials (non-contact measurement) ;
- Possibility to monitor the very same sample versus long ageing time.

2. How do you see the structure recovery with Rheolaser?

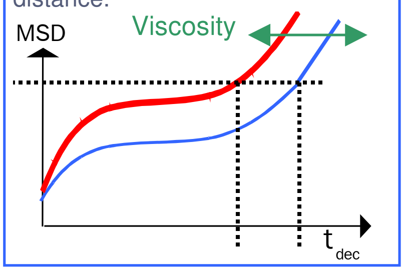
Recovery can be easily detected using the Rheolaser LAB® as it induces a change of the MSD curves versus ageing time:

- With the recovery of elasticity, MSD curves will move toward lower values of MSD at short decorrelation times (left part of the graph). Indeed, the structure is rebuilding, thus tightening the network ;
- With the recovery of viscosity, MSD curves will move toward longer decorrelation times (right part of the graph). Indeed, a particle will need a longer time to reach a given distance when the viscosity increases.

Increase of elasticity: the network is tightening:



Increase of viscosity: the particles take longer time to reach a given distance.



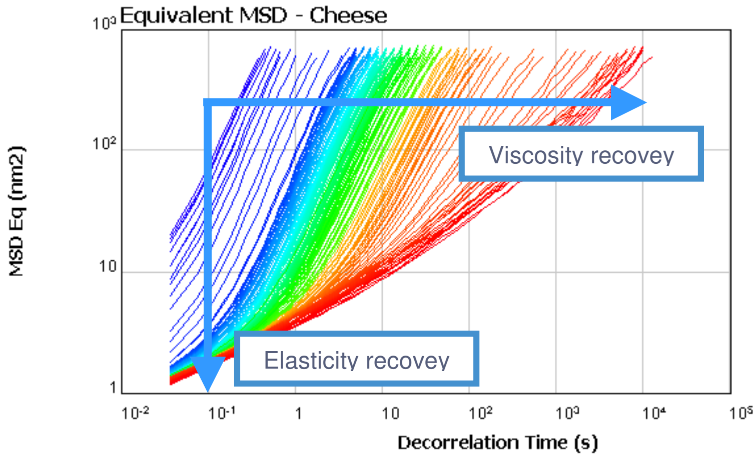


Figure 4. MSD curves during structure recovery of a drilling mud.

In the example shown above, a cheese is recovering after a pre-shear. Both elasticity and viscosity are increasing during ageing time (curves are moving to the lower part of the graph (distance traveled by the particle is shorter), and to the right (the motion is slowing down)).

3. What can you compute?

In order to monitor the structure recovery of a product, the interesting parameters to compute are:

- **Elasticity Factor** (EF) and **Viscosity Factor** (VF) versus ageing time ;
- **Elastic and Viscous moduli** (G' and G'') or their ratio (G'' / G') versus ageing time at a given frequency ;
- **The moduli spectrum** (moduli versus frequency) at several ageing time.

Elasticity and Viscosity Factors give a first clue about the speed of structure recovery in the studied sample.
It is therefore possible to determine characteristic times (such as 80% of recovery) in terms of elasticity and/or viscosity.

In the example shown below, a same **cheese** is monitored during its structure recovery, after an initial shear rate (1000 s^{-1}).

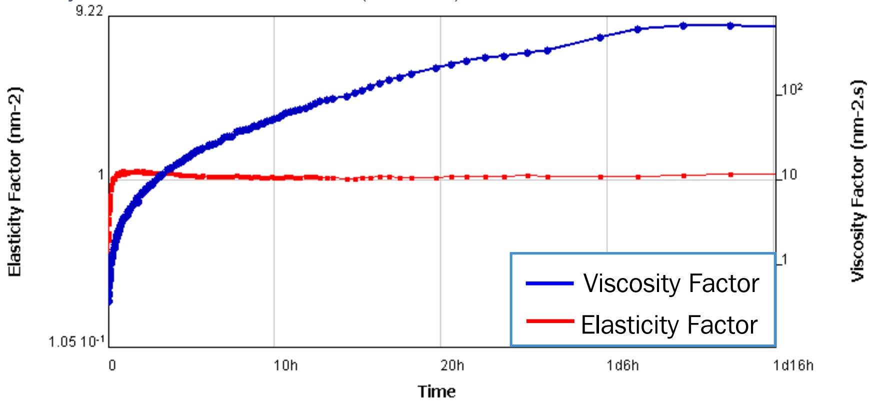


Figure 5. Recovery of EF and VF

To fully characterize the recovery, it is possible to compute elastic and viscous moduli at various frequencies, versus ageing time.

Additionally, the ratio between G'' and G' and its evolution can be computed at any frequency.

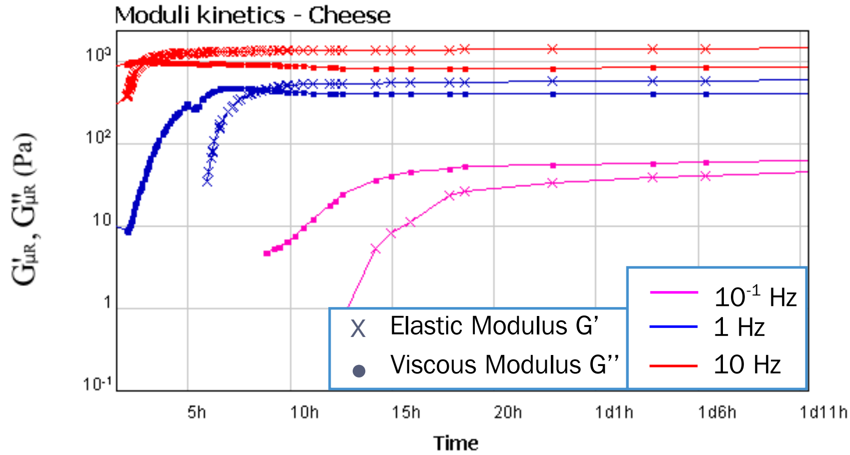


Figure 6. Recovery of Elastic and Viscous moduli at various frequencies

Using the previous computation, it is also possible to display the moduli spectra versus frequency, for various ageing times.
It is therefore possible to monitor the complete evolution of viscoelastic behavior during the recovery process.

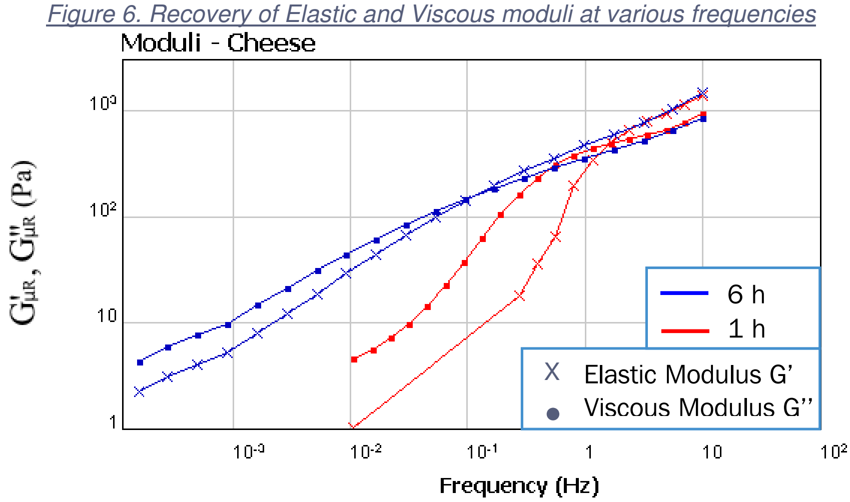
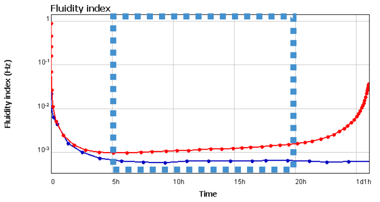


Figure 7. Moduli spectra at various ageing time of the sample

It is noticeable that elasticity and viscosity don't increase at the same speed, it takes 30 minutes to reach an equilibrium for the elasticity, and 34 hours to reach an equilibrium in terms of viscosity (see kinetics of EF and VF, and also of the moduli G' and G'').
Determination of the full moduli spectrum can be done at any time of the analysis (see Figure 7, displaying spectrum for 2 distinct ageing times), thus allowing a complete characterization of the sample (recovery of G' and G'', evolution of the cross-over point, etc…)

Reminder:
This study is done in the following lifetime of the product (using the Fluidity Index curve):



III - Characterization at the viscoelastic equilibrium

1. Definition

The purpose of the characterization analysis is to determine the viscoelastic properties of a product at rest, and at its equilibrium.
The main assets brought by Rheolaser are the following:

- Characterization is possible at rest (real zero-shear) ;
- Measurement is non-destructive (characterization is possible on the very same sample at different ageing times, without diluting prior to analysis) ;

2. How can you quickly characterize a product with Rheolaser?

The master curve which is obtained with Rheolaser is the Mean Square Displacement (MSD) in function of decorrelation time.
In the example below, the MSD curve is the one corresponding to a toothpaste sample, at microrheological equilibrium.

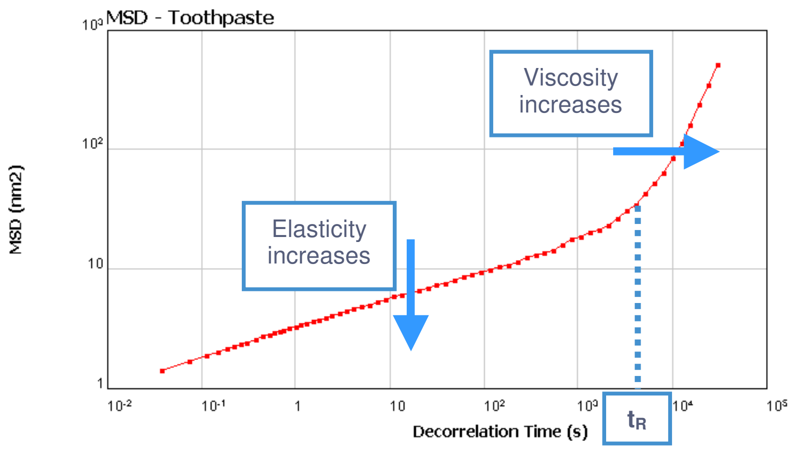


Figure 8. MSD is the viscoelastic signature of a product

For a given product :

- The lower is the elastic plateau, the stronger is the elasticity ;
- The lower is the value of the slope for long decorrelation times, the stronger is the macroscopic viscosity ;
- The relaxation time can be determined by looking at the decorrelation time which corresponds to the inflection point reflecting the transition between solid-like and liquid-like behavior ;

3. What can you compute?

In order to fully characterize a product at rest, here are the parameters that can be computed :

- The final **MSD curve at the equilibrium** ;
- The values of **Elasticity and Viscosity Factors** (EF and VF);
- The spectrum of **elastic and viscous moduli** G' and G'' and/or their ratio versus frequency ;
- The values of Generalized Maxwell parameters such as **relaxation time** (t_R), **macroscopic viscosity** (η_m) or **elasticity at the plateau** (G'_p).

Note:
This section also deals with the comparison of several similar samples. The figures in this page show the result one may obtain by comparing 3 toothpastes.

This section also deals with the comparison of several similar samples. In the example below, the user analyses 3 different toothpastes with Rheolaser® LAB.

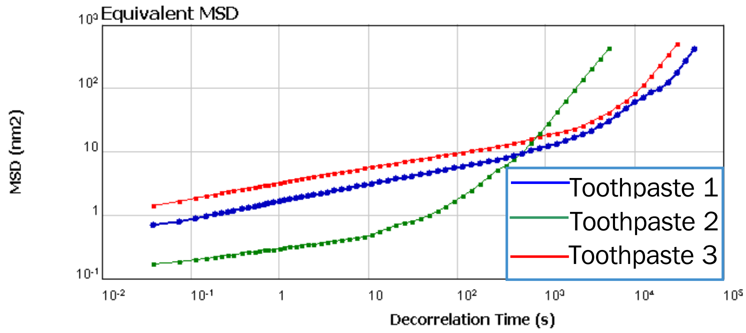
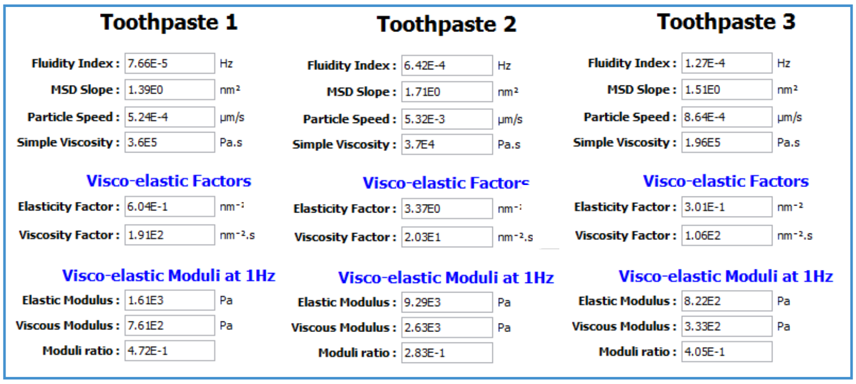


Figure 9. Comparison of the equilibrium MSD curve between various toothpastes



	Toothpaste 1		Toothpaste 2		Toothpaste 3	
Fluidity Index :	7.66E-5	Hz	6.42E-4	Hz	1.27E-4	Hz
MSD Slope :	1.39E0	nm²	1.71E0	nm²	1.51E0	nm²
Particle Speed :	5.24E-4	µm/s	5.32E-3	µm/s	8.64E-4	µm/s
Simple Viscosity :	3.6E5	Pa.s	3.7E4	Pa.s	1.96E5	Pa.s
Visco-elastic Factors						
Elasticity Factor :	6.04E-1	nm⁻²	3.37E0	nm⁻²	3.01E-1	nm⁻²
Viscosity Factor :	1.91E2	nm⁻².s	2.03E1	nm⁻².s	1.06E2	nm⁻².s
Visco-elastic Moduli at 1Hz						
Elastic Modulus :	1.61E3	Pa	9.29E3	Pa	8.22E2	Pa
Viscous Modulus :	7.61E2	Pa	2.63E3	Pa	3.33E2	Pa
Moduli ratio :	4.72E-1		2.83E-1		4.05E-1	

Figure 10. Comparison of the microrheological properties of the different toothpastes

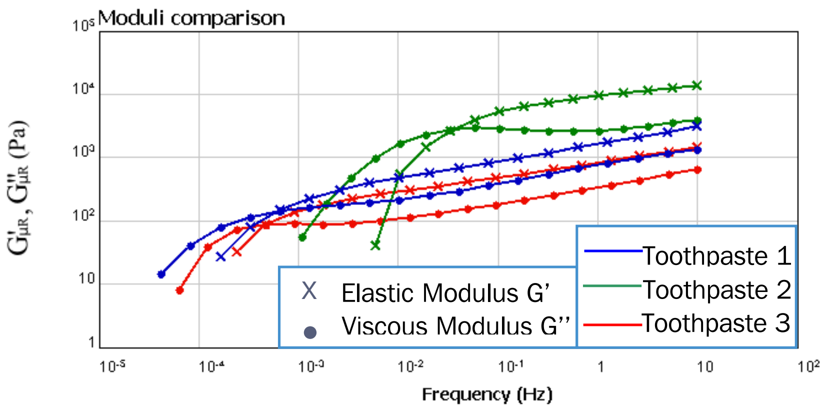


Figure 11. Elastic and Viscous moduli spectra for the 3 toothpastes

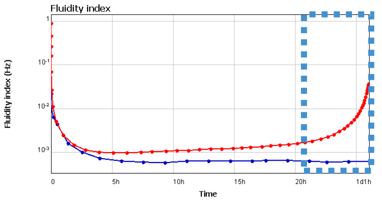
Visual observation of the MSD curves (Figure 9) gives the user information about the products. Indeed, toothpastes 1 and 3 have a very similar rheological behavior (their MSD curves are approximately the same), while toothpaste 2 is completely different: the elastic plateau is lower (meaning a stronger elasticity) and the linear increase happens at a shorter decorrelation time (meaning a lower viscosity). The user can then classify these various products depending on viscosity and elasticity:

Elasticity: Toothpaste 2 > Toothpaste 1 > Toothpaste 3
Viscosity: Toothpaste 1 > Toothpaste 3 > Toothpaste 2

It is possible to compute various parameters directly taken from these MSD curves to quantify these differences of microrheological behavior, such as the **Elasticity Factor**, or the **Viscosity Factor**, as shown in Figure 10.

A complete characterization of these products is also possible, by computing its **full viscoelastic spectra** (Figure 11).

Reminder:
This study is done in the following lifetime of the product (using the Fluidity Index curve):



IV – Physical stability analysis

1. Definition

The purpose of the stability analysis is to monitor the evolution of the product after it has reached its equilibrium. The main assets brought by Rheolaser are the following:

- ➢ Microscopic scale analysis, allowing to detect the very beginning of destabilization process ;
- ➢ Possibility to monitor the very same sample versus long ageing time.

2. How do you characterize the stability with Rheolaser?

Stability can be easily monitored using the Rheolaser® LAB as it induces a change of the MSD curves versus ageing time. As shown before (see paragraph III-1), thanks to the Fluidity Index curve, the user can know in which "age" is the product (recovery, equilibrium, destabilization). If the product faces a destabilization:

- ➢ MSD curves will move to shorter decorrelation times (to the left), i.e. the viscosity or relaxation time decrease ;
- ➢ MSD curves will move up if the elasticity decreases ;
- ➢ The MSD slope at long decorrelation times will change and becomes higher than 1 if the motion becomes ballistic (e.g. sedimentation).

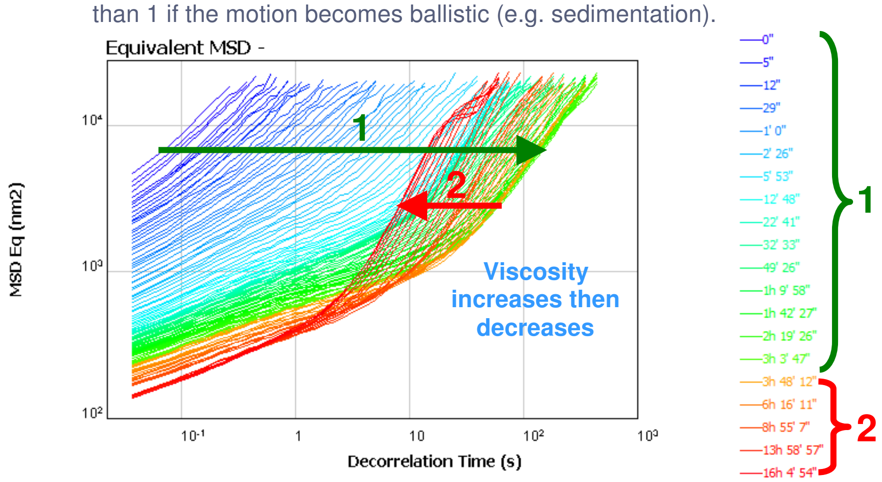


Figure 12. MSD curves evolution over ageing time during a physical destabilization

In the example above, a drilling mud is studied after an initial shear. The first evolution (1) is an increase of viscosity and elasticity (corresponding to structure recovery), then a second evolution (2) is a decrease of the viscosity (corresponding to the physical destabilization).

3. What can you compute?

In order to monitor the stability of a product, the interesting parameters to compute are:

- ➢ **Elasticity Factor** (EF) and **Viscosity Factor** (VF) versus ageing time ;
- ➢ **Relaxation time** (t_R) versus ageing time ;
- ➢ **MSD slope** at long decorrelation times versus ageing time.

The strong decrease of viscosity after a given time is characteristic of the destabilization of the product.
This method allows a quick comparison of the microscopic stability of any product (viscosity monitoring is a classic tool for formulators)

The strong decrease of relaxation time during ageing time is characteristic of the destabilization of a product.
The relaxation time is even more pertinent than the viscosity, because it depends directly on both viscosity and elasticity of the product.

The MSD slope for long decorrelation times is characteristic of the motion type:
- Slope ≈ 1, Brownian motion ;
- Slope > 1, Ballistic motion.
A ballistic motion corresponds to a specific motion of the particles which is not purely Brownian. Very often, this ballistic motion corresponds to a sedimentation or a creaming phenomenon.

In the below example, the stability of 3 drilling muds is compared. It is possible to observe a drop in the Viscosity Factor, but also in the Relaxation Time during the ageing of the products 2 and 3, meaning a destabilization.
This drop is observed on the Viscosity Factor after 3 hours of analysis for the product 3, and 22 hours after the beginning for the product 2. If the user observes the Relaxation Time, it happens after respectively 2 hours and 5 hours.

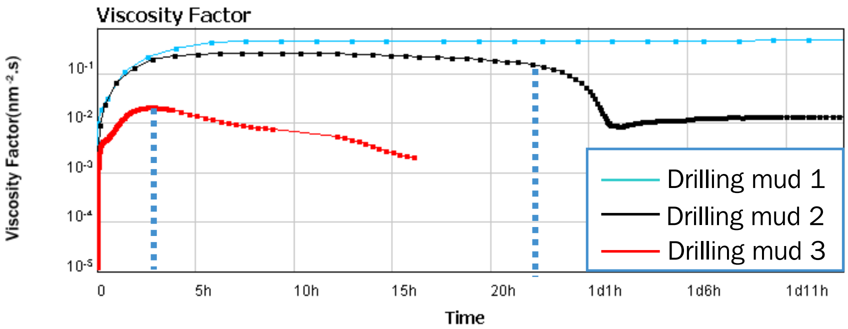


Figure 13. Evolution of the Viscosity Factor versus ageing time for 3 drilling muds

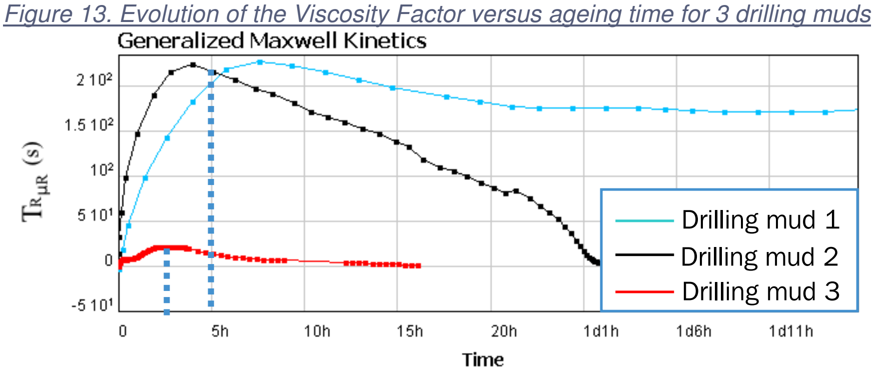


Figure 14. Evolution of the Relaxation time versus ageing time for 3 drilling muds

In the last example, below, the stability of 2 different paints is studied. Paint 1 is a so-called "non-drip" paint (strong gel structure), while Paint 2 is a classic architectural paint.

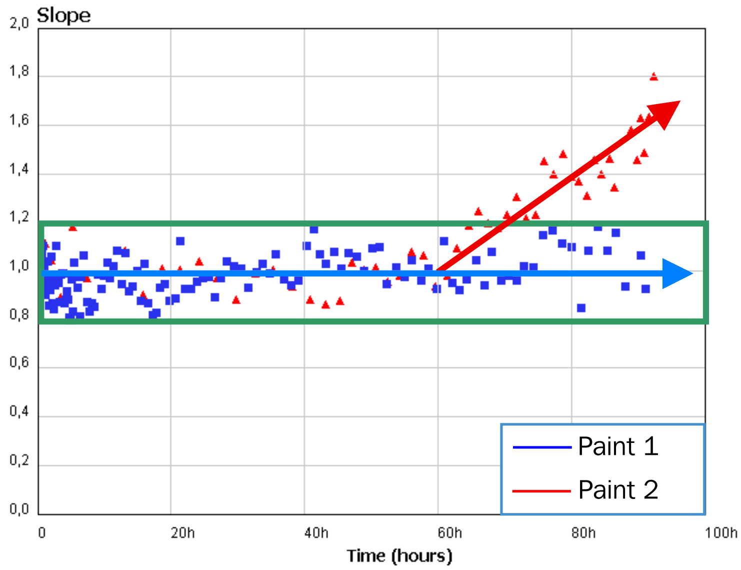


Figure 15. Evolution of the MSD slope versus ageing time

For the Paint 1, the slope remains equal to 1 for 100 hours, meaning that the particles motion is purely Brownian (particles are completely stable in the paint).
For the Paint 2, we can observe an increase of the slope after 60 hours, meaning that Ballistic motion is occurring in the sample (pigment particles are settling toward the bottom of the cell), thus indicating the initial time of destabilization of the paint.

Conclusions

Microrheology is a powerful measurement enabling to deeply characterize the rheological behavior of materials at different life times (structure recovery, viscoelastic equilibrium, physical destabilization).
This technique is easy to use as the sample is loaded in a closed glass measurement cell, and does not require any hardware or software configuration before the launch of analysis.

Several parameters can be measured, from Elasticity and Viscosity Factors, for a first level analysis and an easy comparison of samples, to rheological parameters such as Elastic and Viscous moduli (G' and G'').
This technique is well-adapted for both experts and non-experts in rheology.

References

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