

Passive microrheology : Non intrusive measurement of emulsion and suspension stability

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ABSTRACT

This work presents a new technique of the passive microrheology for the study of the microstructure properties of soft materials like emulsions. Our technology uses Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. It allows to measure the mean displacement of the microstructure particles in a spatial range between 0,1 and 100 nm and a time scale between 10^{-1} and 10^5 seconds. Different parameters can be measured or obtained directly from the Mean Square Displacement (MSD) curve like, an elasticity index, a solid-liquid balance, a viscosity index, a MSD slope at long observation time.

This technique allows to monitor the evolution of the microstructure, the restructuration after shearing, the variation of the viscoelastic properties versus temperature, pH, the physical stability of emulsion or suspension...

This work focuses on the measurement of viscoelastic properties evolution of emulsions and paints to follow their stability. The results will show the advantages of using a non intrusive method to detect nascent destabilisation of the microstructure before rheology or visual method.

1 INTRODUCTION

Viscoelastic properties are key rheological parameters as they shape several properties of soft materials such as the consistency, spreadability, shape stability, workability or physical stability. Thus, it is crucial to characterize the rheological behavior using properly adapted techniques.

Microrheology is a new domain of rheology methods studying the viscoelastic behavior of several products such as emulsions, suspensions, gels or colloidal dispersions at the micron length scale. The optical technique used in microrheology consists of measuring the mean displacement of particles (or droplets or fibers or crystallites... contained in the material) which gives an insight into the elastic and viscous properties of the material. This technique enables to measure a product at rest (with zero shear), it is a non contact measurement

(the product is not denaturated), the sample being monitored versus ageing time.

2 EXPERIMENTAL SET-UP

The instrument *Rheolaser Lab* presented in this work is based on Diffusing Wave Spectroscopy. It consists of Dynamic Light Scattering (DLS) extended to an opaque media. DLS is a well known method of monitoring Brownian motion of particles in a diluted media in order to determine the particle size. In a DWS experiment (more precisely Multi Speckle-DWS in our case), a coherent laser beam is applied to the sample containing scatterers (particles, droplets, fibers...). The light is multi-scattered by these scatterers, which leads to interfering backscattering waves (Figure 1). An interference image called a "Speckle image" is detected by a multi-pixel detector. In dynamic mode, the scatterers motion (resulting from thermal energy $k_b T$ with k_b being the Boltzman constant, and T the temperature) induces spot movements of the speckle image. A patented algorithm enables the treatment of this speckle image in order to determine the scatterers mobility in terms of speed and displacement which are directly related to the samples viscoelastic properties. The MS-DWS technique enables the measurement of the viscoelasticity of samples by microrheology method presented in the following chapter.

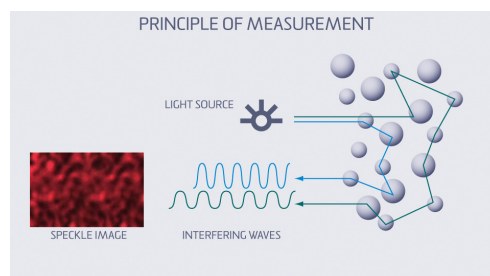


Figure1. Measurement principle – Multi Speckle Diffusing Wave Spectroscopy

3 MICRORHEOLOGY

Microrheology consists of using micron sized particles to measure the local deformation of a sample resulting from an applied stress or thermal energy ($\sim k_b T$). When microrheology measurements are performed using an applied stress to displace the particles (optical tweezers, magnetic field), the method is called active microrheology. When microrheology measurements are performed by measuring the displacement of particles due to the thermal energy, that is to say the Brownian motion, the method is called passive microrheology. The instrument used to perform this work uses the PASSIVE approach. The measurement is done at rest as no mechanical or external stress is applied. The unique force used to displace the particles is thermal energy which may be 10^{12} times lower than macroscopic mechanical stress.

The treatment of the speckle pattern with a patented algorithm, enables the plotting of the Mean Square Displacement (MSD) of the particles versus decorrelation time. Decorrelation time is the time scale observation: at the beginning (short time scale) the particle probes the solid part of the sample (elasticity) and then (longer time scales) the liquid part of it



(viscosity) (Figure 2):

Figure 2. Visco-elastic behavior over time

Brownian motion is diffusive and not ballistic; this means that the particles do not move in any particular direction but randomly everywhere within the available space. Thus the displacement is measured as a squared distance (in nm^2). It is a “Mean” displacement because the displacement of many particles is tracked with just one measurement.

Figure 3a gives the typical shape of the MSD for a purely viscous product : the MSD grows linearly with decorrelation time as the particles are completely free to move in the sample.

Figure 3b gives the typical shape for the MSD of a viscoelastic product (concentrated emulsion, polymer solution with particles). Over very short observation times, the scatterers (particles, ...) are free to move in the continuous phase. They are then blocked by their neighbours (or by polymers), and the MSD reaches a plateau. This is characteristic of the elasticity of the product, as the lower is the plateau, the tighter is the network, and the stronger is the elasticity. Then, at

longer time scales, the scatterers are able to find a way to escape from the “cages” formed by neighbouring particles or polymers and the MSD grows as it would for a viscous fluid. This is characteristic of the macroscopic viscosity, as it corresponds to the speed of the particles in the sample.

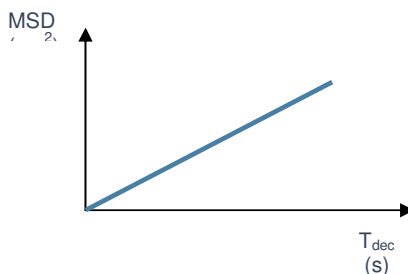


Figure 3a. MSD of a purely viscous product

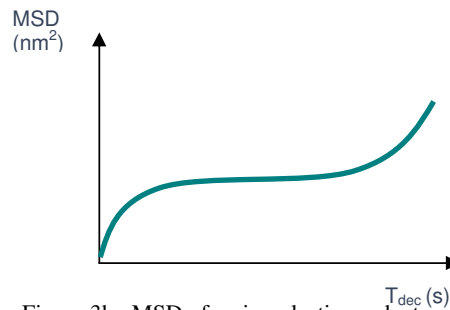


Figure 3b. MSD of a viscoelastic product

In summary, the MSD is the viscoelastic fingerprint of the analysed product (Figure 4):

- The lower is the elastic plateau, the stronger is the elasticity ;
- The solid-liquid balance (SLB) corresponds to the MSD slope at short decorrelation time: $SLB = 0.5$ means that the liquid and solid parts are equal, $0.5 < SLB < 1$ means that the liquid behaviour dominates, $0 < SLB < 0.5$ means that the solid behavior dominates (gel behavior).
- The longer time the particles need to do a same displacement, so the lower is the particle speed, the higher is the macroscopic viscosity.

From the MSD curve can be measured :

- The viscosity and elasticity indexes which are a simple way of comparing the viscous and elastic behavior of similar products.
- Other parameters such as relaxation time or macroscopic viscosity can be measured.
- The elastic and viscous moduli G' and G'' using the Generalized Stokes Einstein relation by knowing precisely the particle size and being in the microrheology conditions.

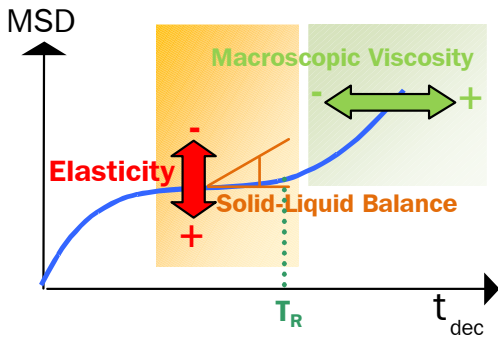


Figure 4. MSD as a viscoelastic fingerprint of a material

4 APPLICATION EXAMPLES

1. Emulsion stability

Emulsions are commonly used in food, cosmetic ...industries. Their shelf life is very important for the supplier and also for the customer. Polymers are used to stabilize emulsions and provide them particular viscoelastic properties. These properties drive several end use properties such as physical stability or efficiency during the use.

In this example, four emulsions with xanthan polymer are analysed and the goal is to determine their physical stability to rank them depending on this criteria. Xanthan is known as a non-absorbing polymer, will play the role of depletion flocculant and will create a transient gel with the emulsion. The integrity of the gel persists for a finite period of time, then the structure collapses suddenly, local crackings appear, a percolation network is forming then a denser creamed phase is forming. This phenomenon is called delayed creaming.

Studied Emulsions are oil in water emulsions (palm oil) (volume fraction 20%) with tween 20 stabilised with xanthan at different concentrations (between 0 and 0,1% wt). The figure 5 gives the MSD curves at different ageing times for one of the samples. The analysis is started just after preparation.

- 1) The MSD curves first move from high to small displacement meaning an increase of elasticity and from short to long decorrelation time (meaning an increase of viscosity) (**step 1**). This step monitors the network flocculation and then stabilisation.
- 2) Then at one moment, the curves move towards to the left, linked to the sample destabilisation, the structure is breaking (**step 2**). This is the beginning of microstructure evolution.

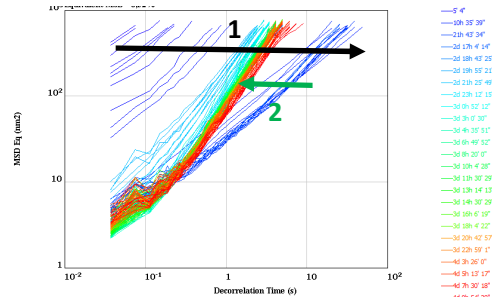


Figure 5. MSD curves at different ageing times

From the MSD curves is directly obtained the macroscopic viscosity index. Its evolution shows a first increase in step 1, then a drop corresponding to step 2. So when the viscosity becomes to decrease, the sample becomes unstable.

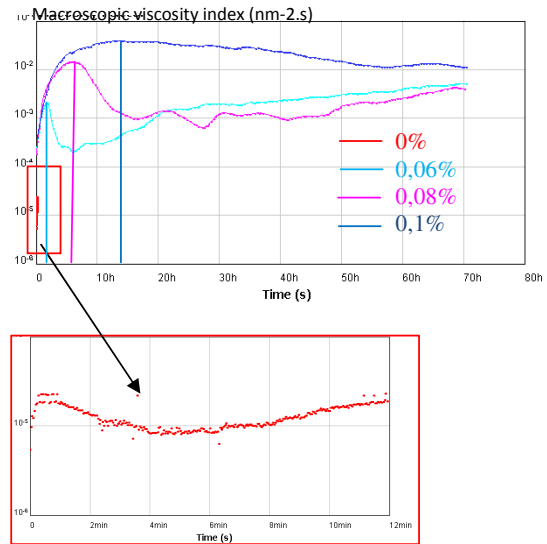


Figure 6. Macroscopic viscosity index versus ageing time

The drop of the viscosity index appears for longer time when the xanthan concentration increases. The more thickener is added to the sample, the more delayed is the creaming.

Xanthan concentration	Stability
0	1 minute
0,06%	2 hours
0,08%	6 hours
0,1%	13 hours

Table 1. Stability for all samples measured with microrheology (extracted from figure 6)

The more structured is the sample (the higher is the xanthan concentration), the more time is saved by microrheology (the longer is the viscosity drop time).

2. Paint stability

Paints are mainly dispersions of pigments and binders stabilized with a polymer. Depending on the formula and polymer kind, the paint will be more or less stable and a transparent layer will appear or not on the top when the user opens the container.

This example studies the stability of both paints : one classic paint and one called non-drip.

The figure 7 gives the MSD curves for one of the paint at different ageing times. The green square focuses on the part of MSD curves at long decorrelation times. The slope of the MSD at this part of the curve provides information on the nature of the motion :

- 1) Slope = 1 : Brownian motion
- 2) Slope > 1 : Ballistic motion

The MSD provides information on stability.

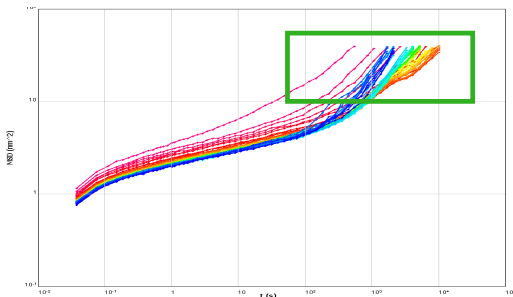


Figure 7. Mean Square Displacement at different ageing times

The figure 8 monitors the MSD slope versus ageing time for both paints.

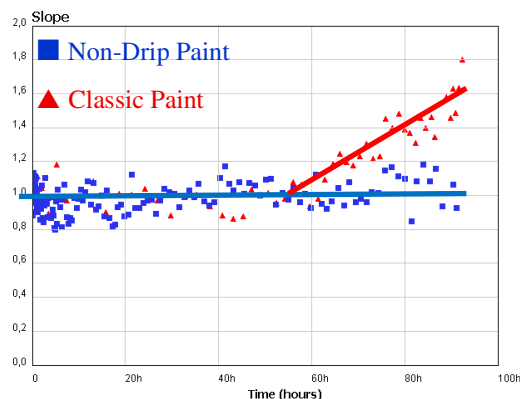


Figure 8. MSD slope at long decorrelation time versus ageing time

The slope becomes higher than 1 after 60 hours for classic paint, the motion becomes ballistic meaning the beginning of destabilization : sedimentation of the particles. So classic paint is less stable than non drip paint.

5 CONCLUSION

The microrheology methods using MS-DWS enables to characterize the viscoelasticity of soft matter in real time linked to the wish end use properties. The measurement is performed using a non-contact method which enables sample analysis without the application of an external stress. So it is perfectly **adapted in monitoring physical stability**. We have seen that it can be applied to emulsions, dispersions...