Soft Matter Analysis by Means of Microrheology

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Viscoelastic behavior drives end-use properties of soft matter such as the spreadability, flowability, shape stability, and physical stability. This article deals with a new domain of rheology, called microrheology, for the measurement of the viscosity and elasticity of materials such as suspensions, gels, and emulsions used in different industries like cosmetic, pharmaceutical, food, and paints. The device presented here enables the measurement of the viscoelastic behavior at rest as a result of multi-speckle diffusing wave spectroscopy. Several application examples are presented, such as real time monitoring of gelatin, shape stability analysis of toothpaste, the effect of polymer addition in an emulsion, and paint stability. The rheological properties, particularly at the microscopic scale, need to be characterized for soft matter before being applied as a rubber, layer, thin film, or coating.

INTRODUCTION

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

Microrheology is a new domain of rheology methods that studies 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, etc.,

contained in the material) which gives an insight into the elastic and viscous properties of the material. This technique enables the analysis of a product at rest (with zero shear). It is a non-contact, non-invasive measurement and various properties of the same sample can be studied over a considerable time range.

EXPERIMENTAL SET-UP

The instrument used for this work (the Rheolaser LAB, from Formulaction, France) is based on diffusing wave spectroscopy.[1] It consists of dynamic light scattering (DLS) extended to an opaque or concentrated media. DLS is a well known method of monitoring Brownian motion of particles in a diluted media to determine the particle size. In a DWS experiment (more precisely, multi speckle-DWS, in this case), a coherent laser beam is applied to the sample containing scatterers (particles, droplets, fibers, etc.). The light is multi-scattered by these particles, which leads to interfering backscattering waves (*Figure* 1). An interference image, called a speckle image, is detected by a multi-pixel detector. This image is composed of bright and dark spots corresponding to constructive and destructive interferences, respectively. The particle's motion induces spot movements of the speckle image.[2] A patented algorithm[3] using a correlation function enables the determination of the scatterers' mobility in terms of speed and displacement. The particle's mobility due to the thermal energy is directly related to the viscoelastic behavior of the material. The optical technique enables the detection of displacements between 1 and 100 nanometers.
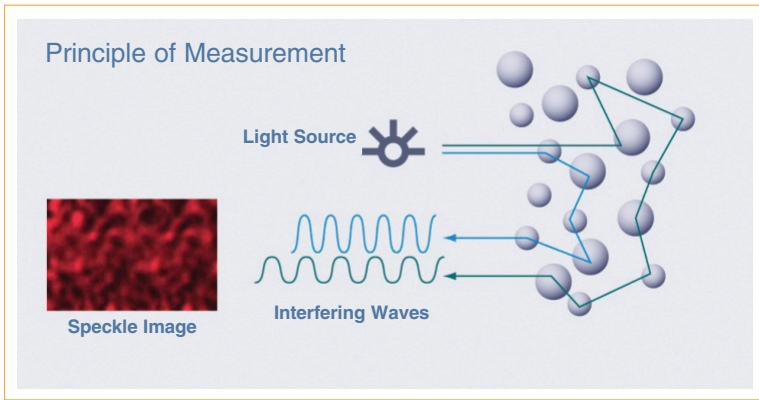
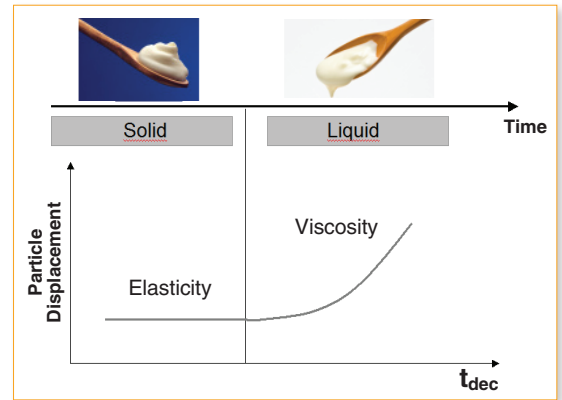**Figure 1**—Measurement principle–multi-speckle DWS.

Figure 2—Viscoelastic behavior over decorrelation time (t_{dec}) (between 0 and 10^5 sec).

MICRORHEOLOGY

Microrheology[4] measures the particle displacement resulting from an applied stress (active method) or due to the thermal energy (passive method).[5] In this work, only the passive approach is used (Rheolaser LAB). The instrument measures the particle mean square displacement (MSD) against decorrelation time. Decorrelation time (t_{dec}) is the time scale of observation: at the beginning (short time scale) the particle probes the solid-like behavior of the sample (elasticity) and then (longer time scale) the liquid-like behavior (viscosity) (*Figure* 2).

MEAN SQUARE DISPLACEMENT

Figure 3 gives the typical shapes of the MSD for a purely viscous or viscoelastic product. In the case of a purely viscous material, the MSD grows linearly with decorrelation time as the particles are completely free to move in the sample (cf. Fick's law). In the case of a viscoelastic material, the typical shape for the MSD is not linear as the particles are not free to move due to interaction with the polymer network, or neighboring particles (concentrated system). At the beginning, the particles are free to move in the continuous phase. They are then blocked by their neighbors, or by polymer networks, which form a "cage," and the MSD function reaches a plateau. This is characteristic of the elasticity in the product. The lower the plateau, the tighter is the network, and the stronger the elasticity. Then, at longer time scales, the particles are able to find a way to escape from the "cages" and the MSD grows again 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 over long displacements.

The MSD is the viscoelastic fingerprint of the analyzed product (*Figure* 4). Various data can be computed from the MSD curve, such as the Elasticity Index (EI), the Solid–Liquid Balance (SLB), and the Macroscopic Viscosity Index (MVI).

- EI is computed from the elastic plateau level. The lower the elastic plateau, the stronger the elasticity.

- SLB corresponds to the MSD slope at short decorrelation times: SLB = 0.5 means that the liquid and solid components are equal, 0.5 < SLB < 1 means that the liquid behavior dominates, 0 < SLB < 0.5 means that the solid behavior dominates (gel-like behavior).
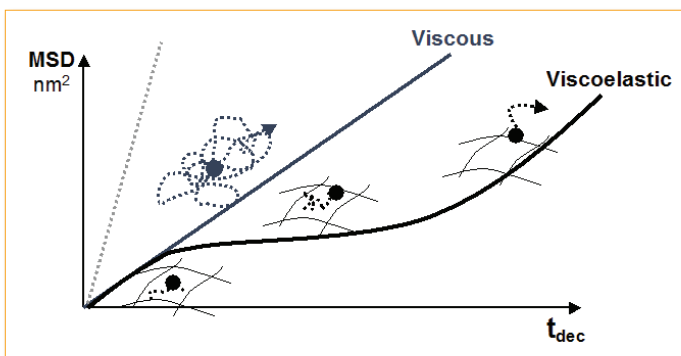

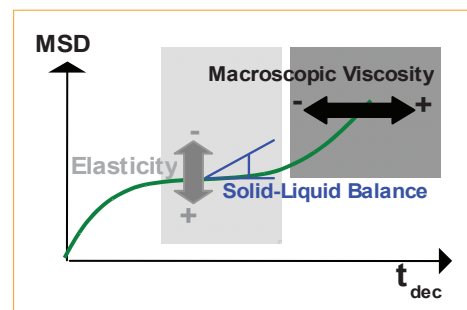**Figure 3**—MSD curves of purely viscous and viscoelastic product.

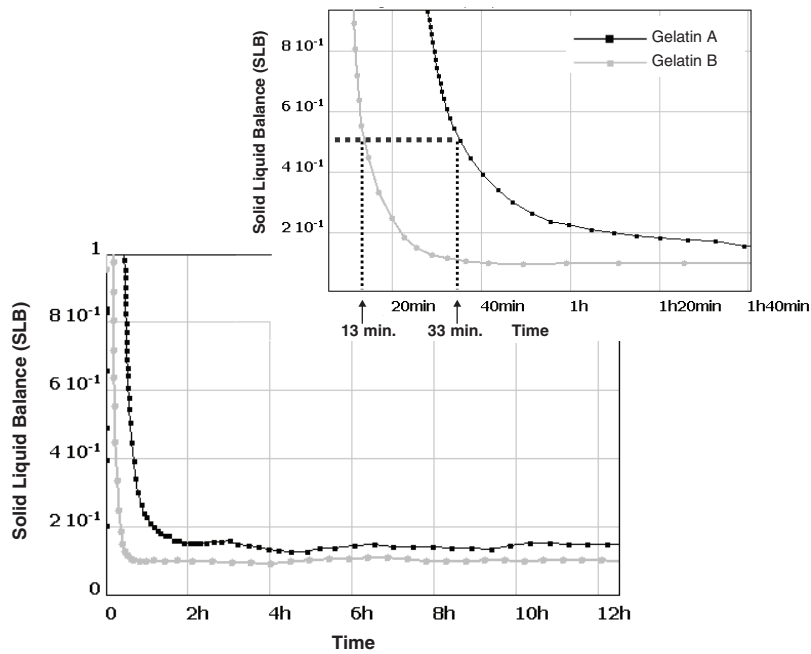**Figure 4**—MSD as a viscoelastic fingerprint of a material.

Figure 5—SLB against aging time.

Figure 6—EI for both gelatins during cooling.

- MVI is a global computation and corresponds to a viscosity index at zero shear. The more time needed by the particles to do a given displacement, the higher the macroscopic viscosity.

These parameters enable the easy characterization and comparison of the end-use properties of samples:

- EI enables the monitoring of the gelation process, recovery, network strength, etc.
- SLB enables the study of gelation, shape stability, stiffness, firmness, etc.
- MVI provides an insight into the textural behavior, the physical stability, etc.

It is possible to acquire MSD curves and characteristic parameters like EI, SLB, and MVI and plot them against aging time to monitor the evolution of

Table 1—Gelation time (minutes) (SLB = 0.5)

Gelatin A	Gelatin B
33 min	13 min

Table 2—Elasticity Index and Gel Formation Time

Sample	Elasticity Index (nm⁻²)	Gel Formation Time (hr) 80%
Gelatin A	2.0	7
Gelatin B	8.1	4.5

the viscoelasticity: gelation, recovery, stability, and so on, as shown in the following application examples.

RESULTS

Real-Time Analysis of Gelation Process

Gel structures are becoming increasingly important in various application fields such as food, pharmaceuticals, cosmetics, and paints. Indeed, they allow the user to manage end-use properties such as controlled ingredient release, shape stability, texture, and spreadability. Gel strengths can vary widely depending upon the application. For instance, weak gels are used as stabilizers in the beverage industry, while strong gels can be used in the paint industry (in non-drip paint, for example).

In this example,[6] two different grades of gelatins of differing strengths are used (gelatin A of a low level of gel and gelatin B of a high level of gel). Samples are prepared by adding gelatin to hot water containing dispersed TiO_2 particles (0.1 wt%). Measurements are started while the samples are still warm, and the increase of the structure during cooling is monitored using the Rheolaser LAB.

The Solid–Liquid Balance (*Figure* 5) gives the ratio between liquid and solid behavior. The gelation time corresponds to an SLB value equal to 0.5, where the solid and liquid behavior are equal in the material (*Table* 1).

Gelatin B forms faster than A, since the time at which the structure becomes more solid than liquid is shorter for B than for A. The kinetics of gelation are also monitored by measuring the EI (*Figure* 6) which gives an indication of the gel strength. Gelatin B forms faster than A and forms a stronger gel (*Table* 2).

Elasticity and mesh (pore) size: Using the Maxwell model, it is possible to compute the elasticity at the plateau (G'_p), and to measure the mesh
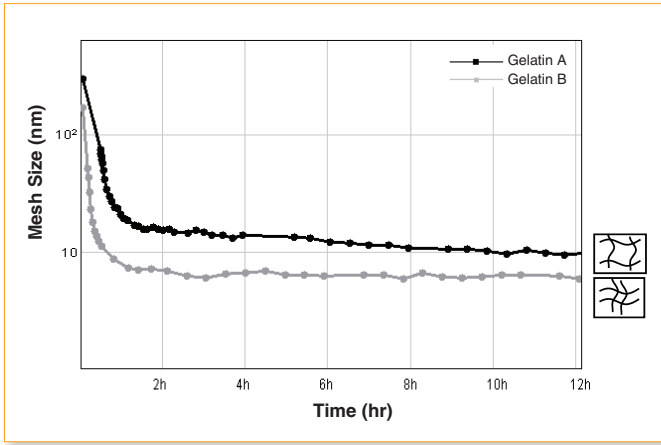
Figure 7—Mesh size during cooling.

Figure 8—MSD of the original emulsion (A), the diluted emulsion (B), the diluted emulsion + 0.4% of alginate (C), and the diluted emulsion + 0.8% of alginate (D).

size of the network ξ (see *Figure 7*). For this kind of polymer structure, the equation linking these two parameters follows:

$$G'_p = \frac{k_b.T}{\xi^3} \rightarrow \xi = \sqrt[3]{\frac{k_b.T}{G'_p}} \qquad (1)$$

As a result of these parameters, it is possible to compare the processes at various times during the formation of the gel.

Mesh (or pore) size is lower (the network is tighter) in the stronger gelatin B (6 nm vs. 10 nm for gelatin A).

Effect of Polymer Addition in an Emulsion

Stabilizers, thickeners, and gelling agents are obtained from a wide range of natural raw materials including microorganisms, land and sea structures, etc. They are used to control flow, texture, and stability in cosmetics, pharmaceuticals, and food products.

The goal of the following study was to decrease the oil content in an emulsion (from 75% v/v to 40% v/v), by using a given thickener (alginate) at various concentrations in order to match the textural properties of the original emulsion.

Figure 8 shows the MSD of four kinds of emulsions: the concentrated emulsion A at 75% v/v, the emulsion B at 40% v/v, and the 40% emulsion v/v with different polymer (alginate) concentrations C and D (0.4 and 0.8% w/w) as a thickening agent.

The original emulsion (75% v/v) has a low MSD curve, meaning that the elasticity of the product is important. When diluting the emulsion, the effect on the MSD is very significant (the MSD curve is higher by more than one decade, meaning that the elasticity has decreased drastically). By adding polymer, it is possible to observe the MSD getting lower, first in an intermediary height (emulsion C 40% v/v with 0.40% alginate) then at a similar
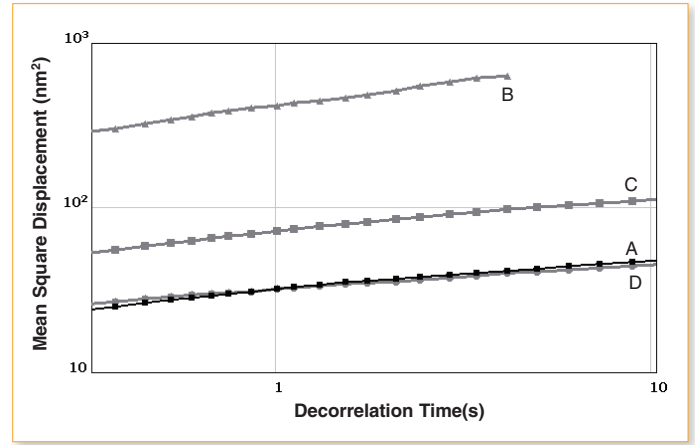
level (emulsion D 40% v/v with 0.8% alginate) to the original emulsion, meaning that the elasticity increases and reaches the same value as the reference emulsion A.

The other interesting visual observation is that the slopes of the MSD curves are also changing. Emulsion A (concentrated) and D (diluted with 0.8% polymer) have a lower slope value, which corresponds to a more solid-like behavior.

These characteristics can be quantified using the microrheological parameters EI and SLB, as shown in *Table 3*.

By plotting the samples' SLB values against the EI values (*Figure 9*), it is easy to visualize the differences and similarities in terms of textural

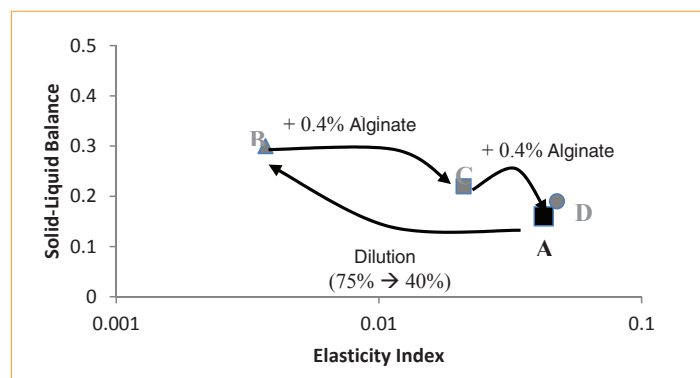| Table 3–Elasticity Index and Solid–Liquid Balance for All Emulsions		
Sample	**EI (10^{-3} nm^{-2})**	**SLB**
A : 75% v/v	42.4	0.16
B : 40% v/v	3.7	0.30
C : 40% v/v + 0.4% alginate	21.0	0.22
D : 40% v/v + 0.8% alginate	47.6	0.19

Figure 9—Solid–Liquid Balance vs. Elasticity Index (nm^{-2}).
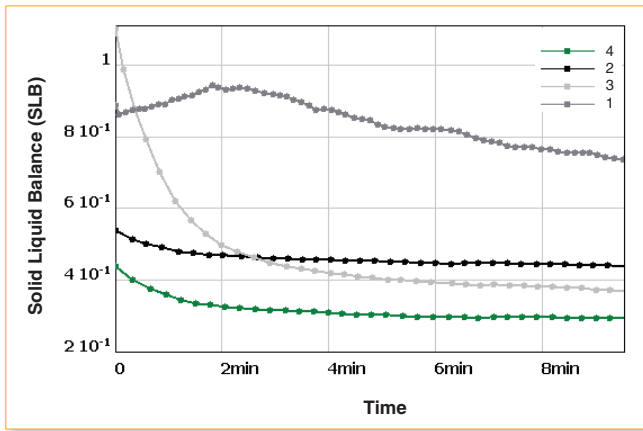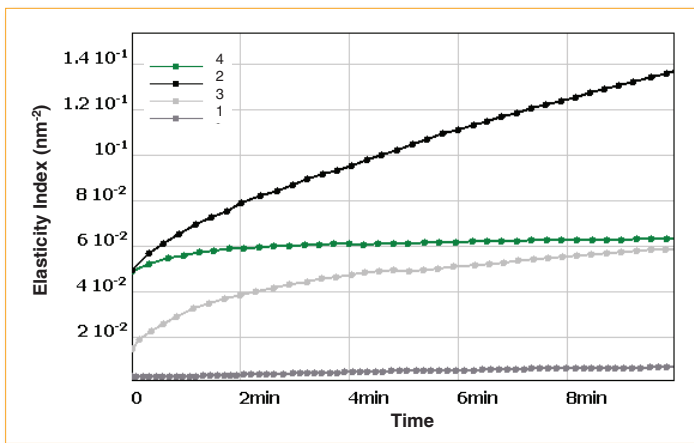
Figure 10—SLB of four toothpastes.

Figure 11—EI of four toothpastes.

Figure 12—MSD slope at long decorrelation time vs. aging time.

(strong solid-like behavior) meaning the best shape stability. Samples 2 and 3 have intermediate behavior. During the first two minutes, sample 2 has a better solid behavior than 3, as its SLB is lower. The oral texture of the toothpastes can be ranked thanks to the EI (*Figure* 11).

Sample 1 is the softest, sample 2 is the hardest, and samples 3 and 4 are intermediary. It is noticeable that the elasticity increases versus time for samples 2 and 3 meaning that the sample structure was affected by shearing during sampling, while the structures for samples 1 and 4 were not.

Study of the Paint Stability

Paints are mainly dispersions of pigments and binders stabilized with a polymer. Depending on the formula and type of polymer, the paint will be more or less stable and a transparent layer may or may not appear on the top when the user opens the container. The following example studies the stability of two paints: one classic paint and one non-drip paint.

The MSD slope at long decorrelation time is characteristic of the type of particle motion: (1) Slope = 1: Brownian motion; (2) Slope > 1: Ballistic motion (like sedimentation). A ballistic motion corresponds to a specific motion of the particles, which is not purely Brownian. Very often, the ballistic motion corresponds to sedimentation or a creaming phenomenon. Thus, by examining the MSD slope versus aging time, it is possible to monitor the product's stability.

For the non-drip paint, the slope remains equal to 1 to 100 hours, meaning that the particle motion is purely Brownian (particles are completely stable in

properties between the products and the effect of the formulation changes.

By diluting emulsion A, the solid-like behavior of the sample is decreased, and it becomes very fluid-like and less elastic (increase of SLB, decrease of EI). Then, the successive additions of alginate give a structure which is closer to the original product. The final emulsion (D) has a behavior very similar to the original emulsion (A), except that its fat content has been decreased by almost 50%.

Study of the Shape Stability of Different Toothpastes

Shape stability of toothpaste on the top of a brush is one of the key parameters of toothpaste formulation. *Figure* 10 reports the SLB evolution of four toothpastes just after sampling (~loading paste on the brush). Sampling affects the viscosity and elasticity properties because of the sampling shear. Then the paste recovers to guarantee good shape stability.

Sample 1 has weak shape stability as the liquid behavior dominates during the first minutes the paste flows. Sample 4 has the lowest SLB
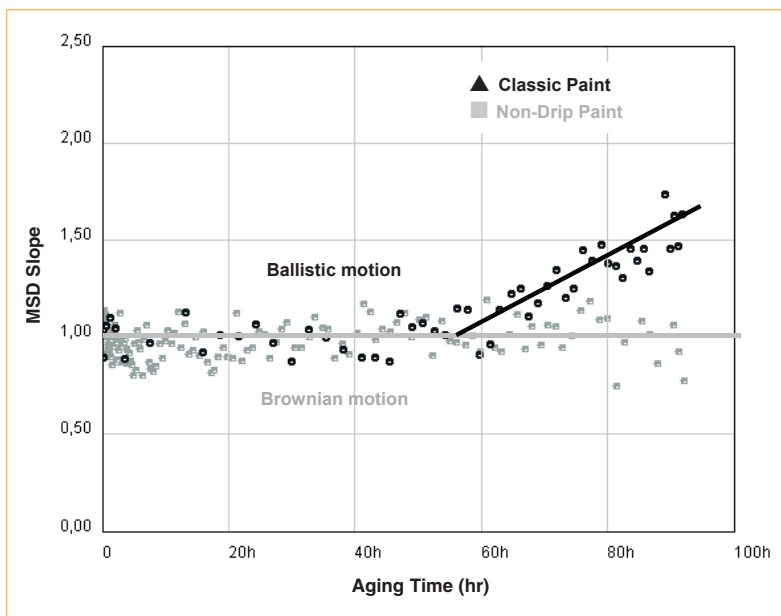
the paint). For the classic paint, we can observe an increase in the slope after 60 hours, meaning that ballistic motion is occurring in the sample (pigment particles are settling toward the bottom), thus indicating the initial time of destabilization of the paint.

CONCLUSION

The Rheolaser LAB instrument developed by Formulaction enables the study of end-use properties such as gelation, shape stability, thickening power of polymers, or microrheology phenomenon versus pH, temperature, etc., due to viscoelastic analysis. It quickly measures elasticity and solid-liquid ratio. In addition, the instrument can provide information on the zero shear viscosity behavior of samples at rest as well as versus aging time. It can be applied on a wide variety of materials such as emulsions, suspensions, gels, foams, ceramics, cements, polymer-based composites, and coatings. ⓒⓣ

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