Soft matters end use properties analysis thanks to Microrheology

Formulaction, 10 impasse Borde Basse, 31240 L’Union, France, www.formulaction.com

Abstract. We present a new technique of passive microrheology for studying the end use properties of materials such as emulsions, suspensions, gels, foams, used in different industries: cosmetic, pharmaceutical, food, paints… End use properties like texture, shape stability, gelation, spreadability…, are directly related to the viscoelastic behavior of the samples. Rheolaser LAB measures the viscoelastic behavior of products at rest thanks to Diffusing Wave Spectroscopy.

In this paper several application examples are presented:
- Real time gelation monitoring of food gelatin;
- Gelation of Yogurt;
- Decrease of fat content in an emulsion by polymer addition;
- Shape stability analysis of tooth paste;

I. INTRODUCTION

Viscoelastic properties are key rheological parameters as they control 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 cristallites… contained in the material) which gives an insight into the elastic and viscous properties of the material. This technique enables to analyze a product at rest (with zero shear), it is a non contact measurement (the product is not denaturated), the same sample can be monitored versus ageing time.

II. EXPERIMENTAL SET-UP

The instrument Rheolaser LAB 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. Interferences between the photons are then monitored, using a correlation function. This accurate technique enables detection of particles mobility due to the thermal energy which is directly related to the viscoelastic behavior.
III. MICRORHEOLOGY

Microrheology consists in measuring the particle displacement resulting from an applied stress (active method) or due to the thermal energy which leads to particles thermal motion (passive method). Rheolaser LAB uses the passive approach.

The instrument measures the particle Mean Square Displacement (MSD) versus decorrelation time. Decorrelation time 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 1):

![Figure 1. Viscoelastic behavior over time](image)

IV. MEAN SQUARE DISPLACEMENT

Figure 2 gives the typical shapes of the MSD for a purely viscous or viscoelastic product.

**In the case of a purely viscous sample**, the MSD grows linearly with decorrelation time as the particles are completely free to move in the sample (cf. Fick law).

**In the case of a viscoelastic sample**, the typical shape for the MSD is not linear as the particles are not free to move due to the polymer network interaction or particles neighbours (concentrated system). At the beginning the particles are free to move in the continuous phase. They are then blocked by their neighbours (or by polymers network “cage”), and the MSD function reaches a plateau. This is characteristic of the elasticity in the product. The lower is the plateau, the stronger is the elasticity. Then, at longer time scale, the scatterers are able to find a way to escape from the “cages” 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, for long displacement.

![Figure 2. MSD curves of purely viscous and viscoelastic sample](image)

The MSD is the viscoelastic fingerprint of the analysed product (Figure 3).

![Figure 3. MSD as a viscoelastic fingerprint of a material](image)

Different data are computed from the MSD curve such as Elasticity Index, Solid-Liquid Balance, Macroscopic Viscosity Index.

- Elasticity Index (EI) is computed from the elastic plateau level. 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 behaviour dominates (gel behavior).
- The Macroscopic Viscosity Index (MVI) is a global computation and corresponds to a viscosity index at zero shear. The longer time the particles need to do a same displacement, the higher is the macroscopic viscosity.
These parameters enable to characterize and compare easily end use properties of samples:
- The Elasticity Index (EI) enables to monitor gelation process, recovery, network strength…
- The Solid-Liquid Balance (SLB) enables to study gelation, shape stability, stiffness…
- The Macroscopic viscosity Index (MVI) reports the texture behavior, the physical stability…

It is possible to acquire MSD curves and characteristic parameters like EI, SLB, MVI… versus time to monitor the evolution of the viscoelasticity: gelation, recovery, stability… as shown in the next application examples.

V. APPLICATION EXAMPLES

1. Gelation process

Gel structures are becoming more and more important in various application fields such as food, pharmaceuticals, cosmetics, paints, etc… Indeed, it allows to control end-use properties such as controlled ingredient release, shape stability, texture, spreadability, etc… 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 (non-drip paint for example). Thus, it is important to monitor gelation processes in real time.

a) Food Gelatin

In this example, two different grades of gelatins are used, of differing strengths (gelatin A of low level of gel and gelatin B of high level of gel). Samples are prepared by adding gelatin to hot water containing dispersed TiO₂ particles (0.1% wt). Measurements are started while the samples are still warm, and the increase of the structure during cooling is monitored using Rheolaser LAB.

MSD curves give a first indication about the products viscoelastic properties and their evolution during cooling. Indeed, the MSD curves evolve (Figures 4 and 5, the first curves are in blue, then green, and lastly in red) versus gelation time. The displacement of the curves from top to bottom indicates an increasing elasticity. Initially the MSD versus decorrelation time increases linearly corresponding to a liquid-like behavior (gel is not formed). Then at longer ageing time, for both samples, the slope decreases and the MSD forms a plateau, the solid like behaviour dominates (gel is formed).

![Figure 4. MSD curves of Gelatin A](image)

![Figure 5. MSD curves of Gelatin B](image)

Gel formation

The solid-liquid balance (figure 6) gives the ratio between liquid and solid behaviour. The gelation time corresponds to an SLB value equal to 0.5, the solid and liquid behavior being equal in the material.
Table 1. Gelation time (SLB = 0.5)

<table>
<thead>
<tr>
<th>Gelatin</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>33 min</td>
</tr>
<tr>
<td>B</td>
<td>13 min</td>
</tr>
</tbody>
</table>

The gelatin B forms faster than A: the time at which the structure becomes more solid than liquid is shorter for B than A.

Elasticity level

The kinetics of gelation are also monitored by measuring the Elasticity Index (see figure 7).

Table 2. Elasticity index and gel formation time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Index (nm-2)</th>
<th>Gel formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.0</td>
<td>7 hours</td>
</tr>
<tr>
<td>B</td>
<td>8.1</td>
<td>4 hours 1/2</td>
</tr>
</tbody>
</table>

The gelatin B forms faster than A and forms a stronger gel.

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 size of the network $\xi$ (see Figure 8).

For this kind of polymer structure, the equation linking these 2 parameters is the following:

$$G'_p = \frac{\kappa T}{\xi^2} \Rightarrow \xi = \frac{\sqrt{\kappa T}}{G'_p}$$

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

b) Gelation of yoghurt

Gelation process in the dairy industry can be monitored with the chemical acidification of milk. In this example, two milks (skim and whole, different in terms of fatty content) were stirred with 1.5% of Gluco-Delta-Lactone then heated at 42°C.

Figure 8. Mesh size during cooling

Mesh (or pore) size is lower (network is tighter) in the stronger gelatin B (10 nm vs. 20 nm for gelatin A).

Figure 9. MSD curves (a = whole milk, b = skim milk)

The elasticity increases versus time. The MSD curve at the beginning is almost linear and during yoghurt formation, an elastic plateau appears and
become very flat meaning a dominant solid behaviour. The acidified milk is forming a gel structure.

![Elasticity factor versus gelation time](image)

**Figure 10.** Elasticity factor versus gelation time

As seen previously on the MSD curves, the elasticity increases during milk acidification, showing the structure formation. It goes on increasing for both samples until 14 hours after beginning, showing the importance of a long heating time. The elasticity is higher for yogurt done with skim milk, showing the different effect of the milk nature.

![Solid-Liquid Balance versus gelation time](image)

**Figure 11.** Solid-Liquid Balance versus gelation time

The Solid-Liquid Balance decreases versus time from values close to 0.7 to values between 0.15 and 0.25. The structure gets stronger (solid behavior > liquid behavior).

All these parameters show that viscoelastic properties and so structure texture depend on fatty content in the milk and heating time.

### 2. Effect of added polymer in an emulsion

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

The goal of the following study was to produce a low fat emulsion which has the same viscoelastic properties than the same emulsion at high oil concentration. This procedure is common to decrease the fat content of emulsions in food industry by addition of thickening polymers.

Figure 12 shows the MSD of 4 kinds of emulsions: the concentrated emulsion at 75% in volume, the same emulsion at 40% and the 40% emulsion with different polymer (Alginate) concentration (0.4 and 0.8% w/w) as thickening agent.

![Mean Square Displacement of emulsion at 75%, 40% and 40% + polymer](image)

**Figure 12.** Mean Square Displacement of emulsion at 75%, 40% and 40% + polymer

The polymer addition enables to improve the viscoelastic properties to match the concentrated emulsion at 75% in volume (reference emulsion). The graph below reports the Elasticity Index of the 4 samples.

![Elasticity Index versus polymer concentration](image)

**Figure 13.** Elasticity Index versus polymer concentration

The best formula which matches the reference emulsion at 75% is the emulsion at 40% with 0.8% of alginate.
4. Study of shape stability of different tooth pastes

Shape stability of tooth paste on the top of a brush is one of the key parameter of tooth paste.

Figure 14 reports the Solid-Liquid Balance evolution of 4 tooth pastes 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 guaranty a good shape stability.

Sample 1 has a weak shape stability as the liquid behavior dominates during the first minutes. The paste flows. Samples 4 has the lowest SLB (strong solid-like behavior) meaning the best shape stability. 2 and 3 have intermediate behavior. During the first 2 minutes sample 2 has a better solid behavior than 3 as SLB is lower.

Shape stability of the 4 tooth pastes can be ranked as follow:

The consistency of the tooth pastes can be ranked thanks the Elasticity Index (figure 15).

5. pH dependant gel formation

Along with temperature, pH is a key factor affecting the properties of polymer-based formulations in pharmaceutics for example. An example of the pH effect is the gel formation of a 1% gellan gum in acidified aqueous solution. Figure 16 presents the evolution of the MSD curve of such a solution containing 0.1% wt. of TiO$_2$ particles versus pH:

One can clearly see the shift downward of the MSD curves when changing pH from neutral to acidic.
The Elasticity Index evolution enables to monitor the gel formation. The pH is acidified 4 hours after the beginning of analysis (vertical dark blue line on Figure 17). The gel formation is complete 8 hours after the acid addition. Monitoring the gel formation and stiffness enables to optimize process.

**Figure 17.** Elasticity index evolution during the gel formation of 1% aqueous gellan gum with TiO$_2$ particles.

### VI. OUTLOOK

The instrument Rheolaser LAB enables to study end use properties such as gelation, shape stability, thickening power of polymers or evolution phenomenon versus pH, temperature... thanks to viscoelastic analysis. It measures quickly elasticity, solid-liquid ratio and can also provide zero shear viscosity behavior of samples at rest and 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 paintings.

### VII. REFERENCES


