

## INTRODUCTION

Passive microrheology studies the viscoelastic properties of samples by studying the nanometric movement of particles due to Brownian motion. The movement or more precisely the displacement of the particles is directly related to the viscoelastic properties, such as elasticity and viscosity. This work shows that under controlled conditions (known particle size and size distribution, equilibrium & homogeneity) viscosity and elasticity measured with passive microrheology are in good agreement with those measured with conventional rheology.

Rheology

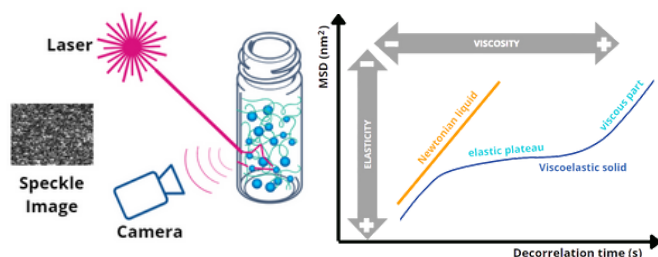
Viscoelasticity

Microrheology



## HOW IT WORKS

Rheolaser Master is based on Diffusing Wave Spectroscopy (DWS), a multiple light scattering technique. Light is backscattered by scatterers in the sample. The microstructure motion inside the sample (droplets, crystallites, etc.), creates an interference pattern (Speckle Image). Variation of this image in time is directly related to the mobility of the scatterers. (Figure 1-left). The faster the Speckle Image changes in time, the higher the mobility of the microstructure.



**Figure 1. Schematic representation of the measurement setup (left) and typical MSD curves (right).**

By mathematical treatment, Mean Square Displacement (MSD) curves are obtained (Figure 1-right), which contain the viscoelastic information. Straight lines (orange) indicate a purely viscous behavior of the sample. The viscosity can be calculated as the Macroscopic Viscosity Index related to the slope in a double-linear scale. Curves with a plateau (blue) indicate gel-like or solid-like behavior. The Elasticity Index is calculated at the elastic plateau. The lower the plateau, the higher the elasticity.

## REMINDER

Controlled conditions are required to convert the results into "absolute" macroscopic viscosity values (in Pa.s, or cP):

- Known particle size, and size distribution
- Homogeneity at the micro-scale
- Equilibrium of the sample

## VISCOSITY MEASUREMENTS

### A) Samples

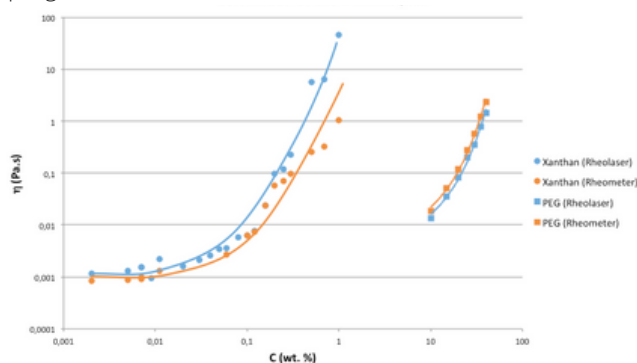
**Xanthan** was dispersed at 60°C in concentrations between 2.10-3% and 1% (w/w) until complete dissolution. The mixtures were seeded with 0.1% (w/w) polystyrene particles (1 μm) and cooled down to 25°C. When reached equilibrium, the samples were measured with Rheolaser Master and the rheometers at 25°C.

**PEG (35 kDa)** was prepared under slight heating (50°C). After the complete dissolution of the polymer, 0.1 % (w/w) polystyrene particles (1 μm) were added. The samples were sonicated for 1 hour to release all air bubbles. The dispersions were stored at 25°C for 3 days before the experiment. Concentrations from 10 to 40 % (w/w) were prepared.

### B) Results

Figure 2 shows the viscosities obtained with microrheology (blue) and with conventional rheology (orange). The values are in good correlation.

**Note:** At higher concentrations (> 0.3%) of xanthan, the viscosities measured with the rheometer are lower than those measured with the Rheolaser Master. The reasons for the differences can be attributed to the differences in method. Rheolaser Master measures under zero shear and without contact (optical), hence the sample is not disturbed. On the other hand, the rheometer is a contact method and the sample is highly compressed during sampling, which can disturb the network.



**Figure 2. Viscosity of xanthan and PEG dispersions tested with a conventional rheometer (orange) and Rheolaser Master (blue)**

**ELASTICITY (G') MEASUREMENTS**

**A) Samples**

Milk samples were acidified with different concentrations of glucono- $\delta$ -lactone (GDL). This cyclic lactone is hydrolyzed in contact with water and lowers the pH of the sample. Milk will coagulate when reaches a pH lower than pH 5. The acidification kinetic is highly dependent on the GDL concentration. Samples were continuously measured at 42°C.

**B) RESULTS**

Rheolaser Master uses Multi Speckle-Diffusing Wave Spectroscopy (MS-DWS) to measure particle displacement in a sample. This is an optical method, which uses the backscattering of laser light. As shown in the literature (Pine & Weitz, 1993), this is a powerful technique to study the rheological behavior of a sample. However, as it is an indirect measurement, several approximations need to be taken into account.

Respecting the general conditions, i.e. knowing particle size and size distribution, equilibrium, and homogeneity, it is possible to access viscoelastic properties. Figure 3 shows the evolution of G' (Rheo) and Elasticity Index measured with a rheometer and Rheolaser Master, respectively. The G' ( $\mu$ -Rheo) are calculated from the original MSD curves.

The absolute values of G' (Rheo) and G' ( $\mu$ -Rheo) are in good correlation for this system, however, as it can be seen, due to the approximation needed in the calculations, the G' ( $\mu$ -Rheo) can be calculated only at an advanced state of the gelation. Contrarily, the EI values are available as the G' (Rheo) values, all along the gelifications.

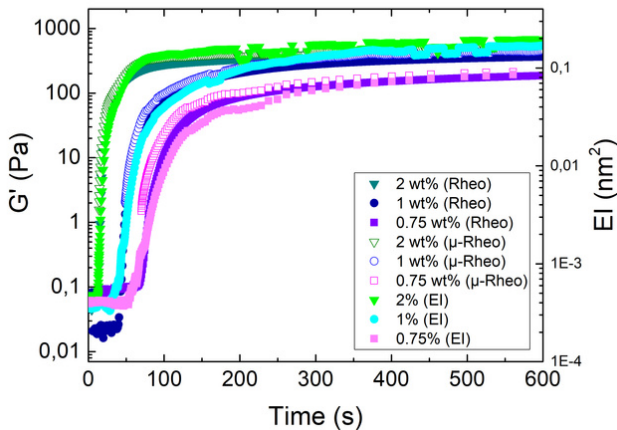


Figure 3: G' (Rheo), G' ( $\mu$ -Rheo) and EI (Rheolaser Master) as function of time for three different concentrations of GDL.

Figure 4 shows the G' (Rheo) obtained with a conventional rheometer plotted against the Elasticity Index measured with Rheolaser Master for different milk/GDL systems. There is a good correlation between both measurements. Similar results have been stated by Raak et al. 2016 and Rohart et al. 2016).

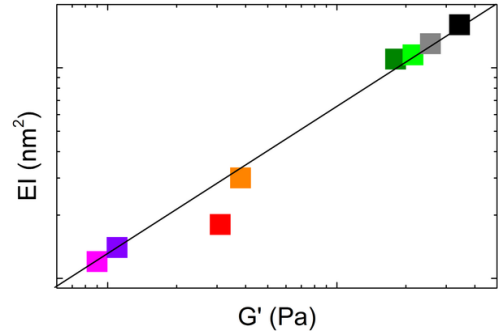


Figure 4: SLB values versus EI values of emulsions stabilized with different biopolymers.

**REFERENCES**

Weitz, D. A.; Pine, D. J. Diffusing-Wave Spectroscopy. In Dynamic light scattering; Oxford University Press: New York, 1993; p 652.

Rohart, A.; Michon, C.; Confac, J.; Bosc, V. Evaluation of Ready-to-Use SMLS and DWS Devices to Study Acid-Induced Milk Gel Changes and Syneresis. Dairy Science & Technology 2016, 96 (4), 459-475. <https://doi.org/10.1007/s13594-016-0281-6>.

Raak, N.; Leidner, R.; Rohm, H.; Jaros, D. Potential of Thromboelastometry and Multispeckle Diffusing Wave Spectroscopy for Monitoring Acid-Induced Casein Gelation. In Annual Transactions of the Nordic Rheology Society; 2016; Vol. 24, pp 81-85.

**CONCLUSION**

Rheolaser Master uses Multi Speckle-Diffusing Wave Spectroscopy (MS-DWS), which uses the backscattered light to measure particle displacement. Particle displacement is directly related to the viscoelastic properties of a sample. As a non-destructive, non-invasive technology, MS-DWS is a highly accurate and sensitive way to study the gelation and viscoelastic properties of complex systems. Even if it is theoretically possible, the needed conditions and approximations are restrictive and render it very complicated. Contrarily, the use of Elasticity and Viscosity indices is straightforward, easy, and correlates perfectly with standard rheological parameters. Rheolaser Master is therefore a useful, simple, and user-friendly instrument to study the viscoelasticity of many samples.