Non contact measurement of viscoelastic properties of biopolymers

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ABSTRACT

We present a new technique of passive microrheology for the study of the microstructure properties of materials such as colloids, gels, foams, ceramics, cements, semi-crystalline polymers and composite materials. Microrheology based on the Multi-Speckle Diffusing Wave Spectroscopy (MS-DWS) technique relates the particles thermal motion which is linked to the visco-elasticity of the product. It also allows a smart and easy to handle structural analysis.

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 cristallites… 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 beeing 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 scaterrers (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_bT 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.
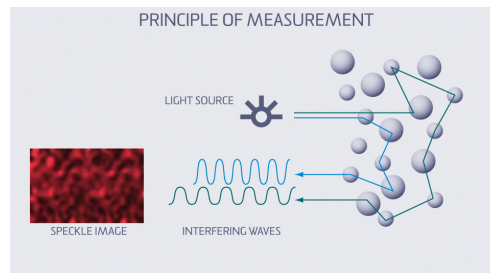

Figure1. Measurement principle – Multi Speckle Diffusing Wave Spectroscopy

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 ($\sim k_bT$). 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

Solid-like   Liquid-like

(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.
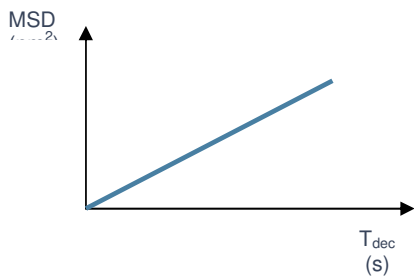
MSD
(nm²)

T$_{dec}$
(s)

Figure 3a. MSD of a purely viscous product
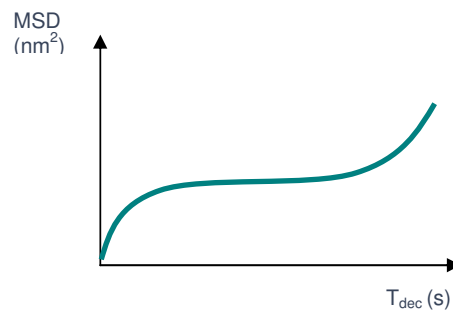
MSD
(nm²)

T$_{dec}$ (s)

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.
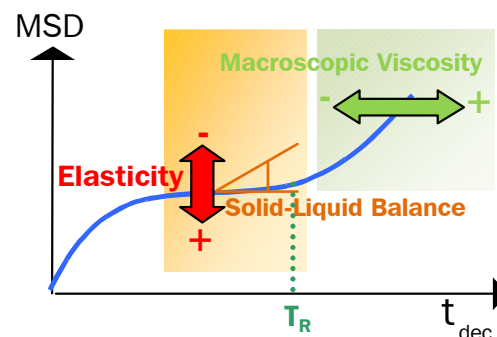
MSD

Macroscopic Viscosity

Elasticity

Solid-Liquid Balance

T$_R$

t$_{dec}$

Figure 4. MSD as a viscoelastic fingerprint of a material

4 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 control over end-use properties such as 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.

In this example, two different kinds of gelatins are used, of differing strengths (different blooms: the more blooms, the stronger the gel structure). Samples are prepared by adding gelatin to hot water containing dispersed TiO_2 particles (0.1% wt) gelatin. Measurements are launched while the samples are still warm, and the increase of the structure during cooling is monitored using Rheolaser LAB (Formulaction).
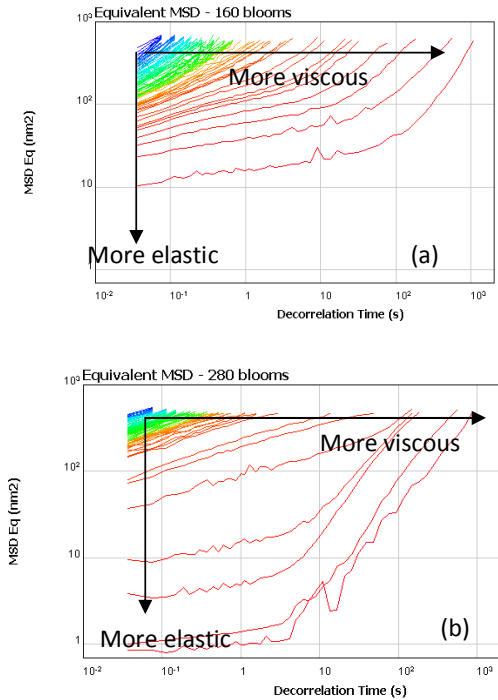

Figure 5. MSD curves (a = gelatin 160 blooms, b= gelatin 280 blooms)

MSD curves (Figure 5) give a first indication about the products viscoelastic properties and their evolution during cooling. Indeed, the MSD curves evolve (the first curves are in blue, then green, and lastly in red) versus gelation time. The displacement of the curves to the right indicates increasing viscosity, and the shift to the bottom indicates increasing elasticity.

Initially the MSD versus decorrelation time increases linearly corresponding to fluid samples as no plateau are observed. Then, for both samples, a plateau is observed between 10^{-1} and 10 s (decorrelation time). This plateau appears after 25 mins for sample a and 12 mins for sample b. The length of the plateau increases (width of the plateau) indicating that the gelatin is solid over a longer time range (frequency range), and the plateau lowers during the ageing time indicating that the gel is getting stronger.

Note that the final plateau is lower for the stronger gelatin (0.8 nm^2 vs. 10 nm^2), indicating a stronger elasticity (the lower the plateau, the tighter the network of polymers).

Elasticity

The kinetics of gelation are monitored by measuring the elasticity index (see figure 6). The elasticity increases earlier in the stronger gelatin (after only 6 minutes of cooling, while it takes 15 minutes in the other sample). The Elasticity index is 15 times greater in the stronger gelatin at any given time during the cooling of the samples until equilibrium is reached.
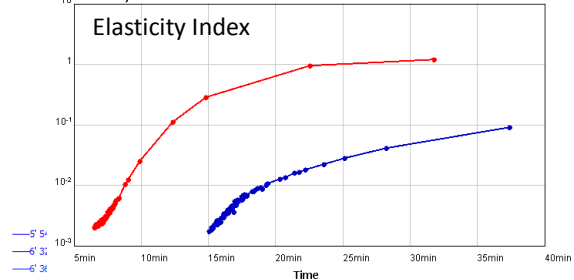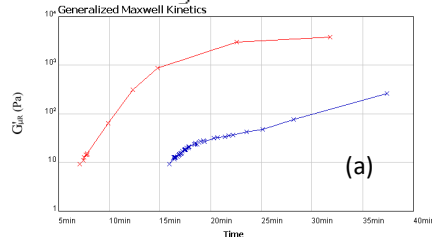

Figure 6. Elasticity index for both samples during cooling

Elasticity and mesh 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 ξ (see Figure 7).

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

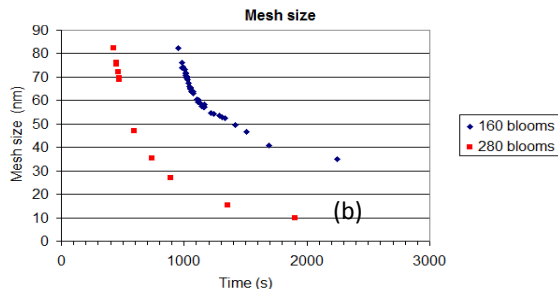$$G'_p = \frac{k_b.T}{\xi^3} \quad \rightarrow \quad \xi = \sqrt[3]{\frac{k_b.T}{G'_p}}$$

Figure 7. Elasticity at the plateau (a) and mesh size (b) during cooling

Thanks to these parameters, it is possible to compare the processes at various times during the formation of the gel. While the strong gel reaches its final elasticity value (3.800 Pa) after 25 minutes of cooling, the weak gel reaches a value 15 times lower (258 Pa) after a longer cooling time (40 minutes). These values allow the computation of the mesh size, which is lower (network is tighter) in the stronger gel (10 nm vs. 35 nm at the final state of the gel).

2. Effect of adding a polymer in an emulsion

Food stabilizers, thickeners and gelling agents are obtained from a wide range of natural raw materials including microorganisms, land and sea plants…They control moisture and provide structure, flow, stability to cosmetic and food products… The following example compare one emulsion (volume fraction=50%) with emulsions at the same volume fraction (50%) with same amount (0.3% w/w) but different common polymers: alginate, xanthan, carraghenan.
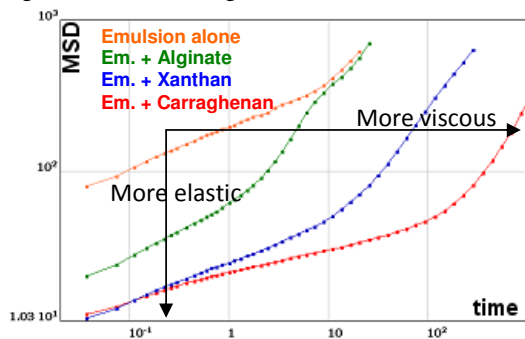

Figure 8. MSD of emulsion alone and with polymer

The samples can be ranked from the least to the most elastic and viscous: emulsion < emulsion+alginate < emulsion+xanthan < emulsion+carraghenan. For the same amount, the three polymers do not provide same viscoelastic properties to the emulsion.

In many cases, the thickening effect of polymers may be probed directly, just by varying the polymer concentration and without any added particles. As far as the polymer solution is slightly diffusive because of the presence of polymeric clusters, the increase of elasticity and viscosity with increasing polymer concentration can be revealed (see Figure 9):
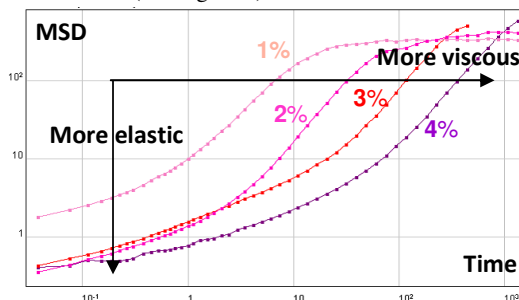

Figure 9. Study of the concentration effect of PAM (average M = 5-6.10^6 g/mol) aqueous solutions (PAM concentration from 1% to 4%)

Figure 9 shows clearly a shift from left to right of the Mean Square Displacement (MSD) curves when increasing polymer concentration and as a consequence, the solution viscosity. Moreover, the elastic plateau of the MSD curves (at about 0,1s) is decreasing significantly when polymer concentration is increased from 1% to 2% accounting on greater elasticity of the 2% solution. A further increase in PAM concentration up to 4% causes only a very slight decrease of the MSD curve elastic plateau. Indeed, PAM aqueous gel is formed at a polymer concentration in between 2% and 3% in water. Obviously, the macromolecular entanglement determines the existence of such a gel. In turn, that gel is responsible for the jamming of the polymer clusters that scatter the laser beam. Finally, a jammed scatterer has a low MSD in microrheology (see Figure 4). The entanglement concentration of aqueous PAM is measured by mechanical rheology using cone-plane geometry. For this, the elastic and viscous moduli of the polymer solutions are compared. In the case of 2% PAM solution, the rheometer gives G'(2%) < G''(2%) at 1Hz. On the other hand, the 3% PAM solution shows G'(3%) > G''(3%) at 1Hz. From a rheological point of view, PAM aqueous gel is formed between 2% and 3% wt. of polymer in water.

3. Temperature dependant gel formation

The gel formation in aqueous solution of methyl cellulose upon heating is a standard example for such a process. Indeed, gel formation in the case of aqueous methyl cellulose is based on the existence of a Lower

Critical Solubility Temperature (LCST) of this polymer in water. The heating causes the aggregation of some portions of different macromolecular chains leading to the formation of a macroscopic gel. Figure 13 shows the typical evolution of the MSD curves of 1% aqueous solutions of methyl cellulose upon heating from from 25°C to 55°C. The solution contains 0.2% wt of TiO_2 particles (average diameter = 1µm) as the scatterers. We can clearly see the formation and the lowering of the MSD elastic plateau at short time-scale (between 0.1 and 10s) indicating the increase of the elasticity (or the stiffness) of the gel. Also, the increase in viscosity is made visible accounting on the MSD shift from left to right corresponding to longer decorrelation times.
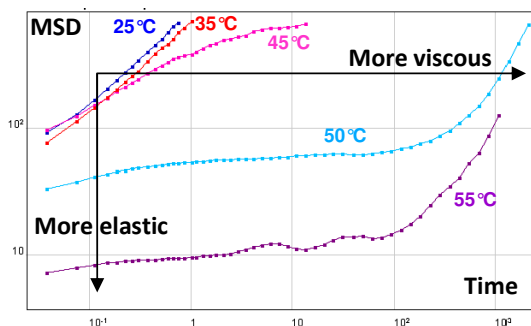

Figure 10**.** MSD of TiO_2 particles in aqueous methyl cellulose upon heating

The elastic and viscous evolution of the sample over time can be monitored in a very simple way. For example, one can plot the evolution of the elasticity index of the sample. Elasticity index is a number inversely proportional to the level of MSD elastic plateau: the higher the elasticity index, the higher the stiffness of the sample (see Figure 11):
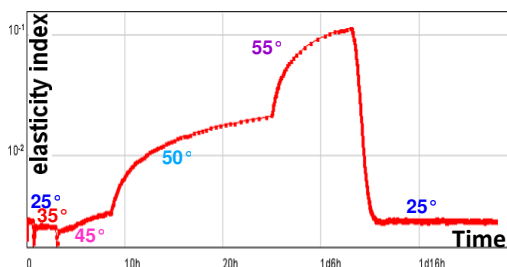

Figure 11.   Elasticity index of 1% aqueous methyl cellulose with TiO_2 particles

4 CONCLUSION

We present a **new instrument**, **Rheolaser Lab**, based on passive microrheology coupled with Multi-Speckle Diffusing Wave Spectroscopy (MS-DWS). The ability of this technique to follow the thermal motion of micro-particles within a material makes it perfectly **adapted in** **monitoring visco-elastic characteristics, in kinetics studies and in fast and easy structural analysis**. It can be applied on a wide variety of materials such as **emulsions, suspensions, gels, foams, ceramics, cements, semi-crystalline polymers, polymer-based composites and paintings**.

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