

INTRODUCTION

Gels have become omnipresent over the last decades due to their unique viscoelastic properties, which can be used to stabilize and texturize in all kinds of applications (food, cosmetics, pharmaceuticals, paints, etc.). A gel is usually defined as a dispersion of one phase (water, oil, air) in a 3-dimensional solid continuous phase of fibers or particles bound physically or chemically (Ferry et al., 1980, Wiley). The gel formation is influenced by a whole range of parameters, including the type and quantity of the solvent, the network-forming component, or of the gelling agent, as well as temperature, pH, etc. An important parameter of gel analysis is the gel point, i.e. the transition point between the liquid phase and the solid-like jelly phase.

Fast

Accurate

Multi-Sample



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). The faster the Speckle Image changes in time, the higher the mobility of the microstructure. By mathematical treatment, Mean Square Displacement (MSD) curves are obtained (Figure 2), which contain the viscoelastic information. Short straight lines (red curve) indicate the liquid behavior of the sample, whereas curves with a plateau, the so-called elastic plateau (pink curve), indicate gel-like or solid-like behavior.

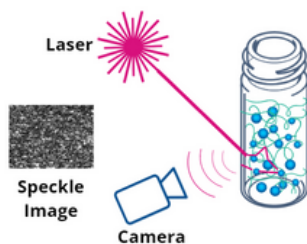


Figure 1. DWS experiment.

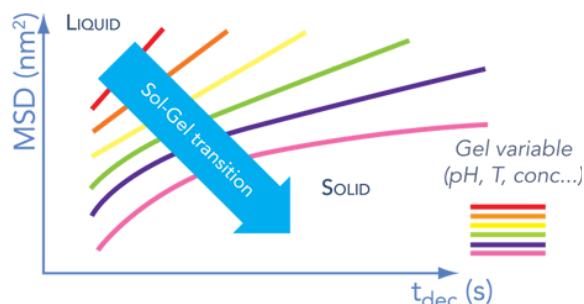


Figure 2. Typical result of MSD curves during gelation.

RESULTS AND DISCUSSION

Several definitions of the gel point are applied in conventional rheology. The Winter-Chambon-Criterion, the most complete definition of the gel point, defines the gel point as the point at which $\tan \delta$, and therefore the relation between G' and G'' , is constant over a wide range of frequencies.

Figure 3 shows the schematic representation of G' , G'' , and $\tan \delta$ at the gel point. It has to be noted, that G' is not necessarily equal to G'' at the gel point (Winter et al. 1986, J. Rheology).

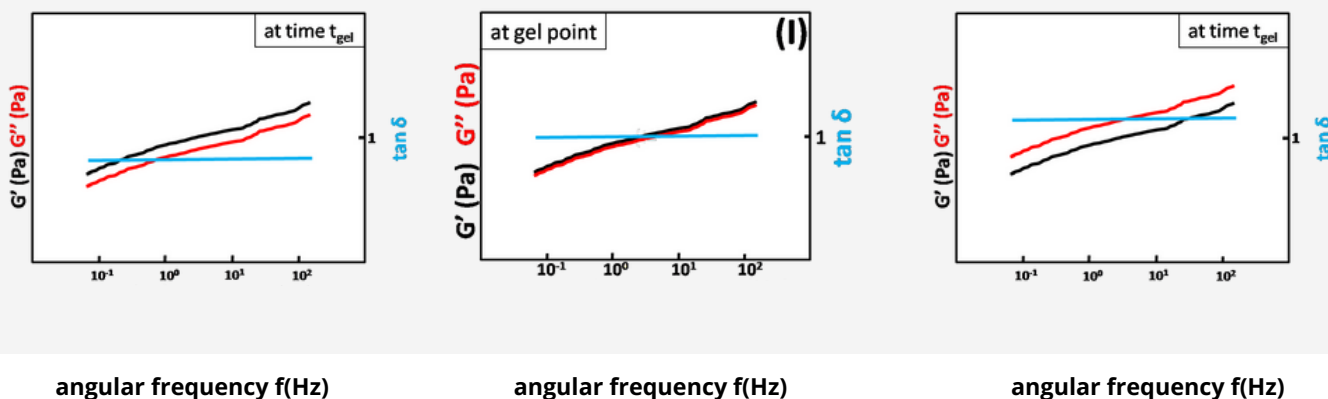


Figure 3. Elastic Index of pasteurized milk at 70°C and at 85°C (33°C, no CaCl₂ addition, 20 mL/L).

Why is the TCS-treatment correct?

Moreover, as shown in Figure 4, the results of conventional rheology, measured at different frequencies, might not be sufficiently precise to determine the gel point. In this example, we show the gelation of porcine gelatin during cooling, measured at different frequencies, which requires a considerable amount of sample and time. Due to experimental noise, no single cross-over is obtained as theoretically assumed. One can only determine a gelation zone between 24°C and 27°C. In contrast to that, we propose a new approach based on the Time-Cure-Superposition (TCS) method. This new data treatment allows the automatic and precise determination of the gel point according to the definition of Winter and Chambon by using microrheology data obtained in a single measurement. In Figure 2, the results of this method indicate precisely a gel point of 27°C.

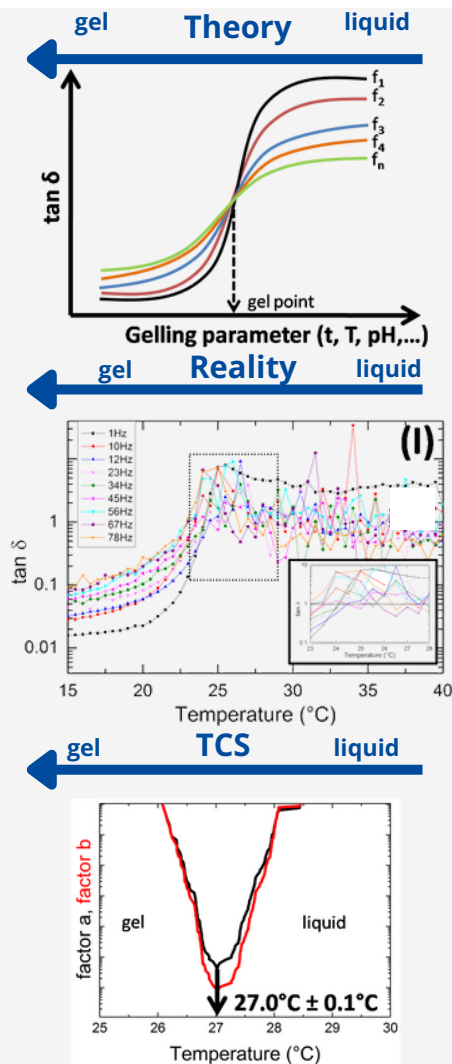


Figure 4. Theoretical and experimental $\tan \delta (f)$ vs. T (osc. rheology). Results of TCS method using a single Rheolaser Master measurement.

How does it work?

According to Winter & Chambon, at the gel point the ratio of G' and G'' is constant over a wide range of frequencies. Rheolaser Master uses microrheology for its analysis of viscoelastic systems. The particle Mean Square Displacement (MSD) is given as a function of decorrelation time, which is the reverse of the angular frequency (1/decorrelation time). Thus, each MSD curve is the viscoelastic response of the system at different frequencies. The MSD curves in the top left are those at high temperatures (red curves). They are linear, which indicates the liquid behavior of the gelatin dispersions. As the temperature decreases, a gel network is formed by the polymer chains and the characteristic MSD signature for viscoelasticity (plateau formation) is obtained (blue curves). A single MSD curve measured with Rheolaser Master is therefore sufficient to scan all frequencies. As particle displacement is proportional to the viscoelastic behavior (G' , G'') and MSD curves are scanned constantly, the gelation process can be observed directly in one measurement over all frequencies (Furst et al 2008, Phys. Rev. Letters).

The Time-Cure-Superposition (TCS) treatment consists of automatically superposing the MSD data to obtain two master curves – one describing the liquid behavior and one describing the gel-like behavior (as shown in Figure 5). These master curves were obtained by an automatic rescaling of each MSD curve by a factor a and b for the x - and y -axis, respectively. Plotting a and b calculated for each value of the control parameter (here: temperature) results in a peak-like signature, which “indicates” the gel point.

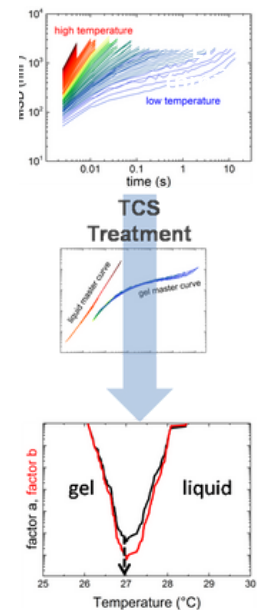


Figure 5. Gel point determination with TCS.

CONCLUSION

- Precise: According to the Winter-Chambon criterion
- Fast: Full-frequency gel point analysis
- Reliable: Non-intrusive measurement at rest
- Time-saving: 6 measurements in parallel