

INTRODUCTION

Sol-gel processes are used to obtain tailored mesoporous materials with specific properties for a multitude of applications (building and insulating materials, captors, special glass or ceramics, etc.) These materials are prepared usually by a two-step process: first polymerization of a solution to become a gel (thanks to an initiator), and second gel drying to achieve the final hard material. The formulation (initiator concentration, nature of monomers) and process (temperature conditions) strongly impact the first step - gel formation. This study presents the impact of these parameters on the gel formation kinetics by a non-invasive and straightforward measurement by a Rheolaser Master. That directly links to the quality of the final mesoporous (silica-based) materials and their application.

Fast

No Dilution

Sensitive



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.), create 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. Mean Square Displacement (MSD) curves contain 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.

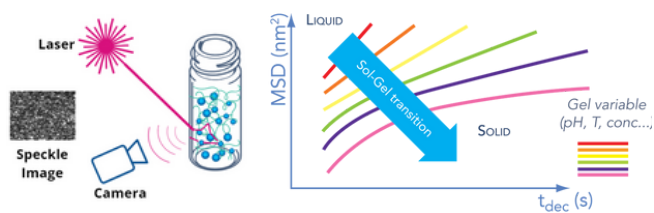


Figure 1. Schematical representation of the measurement set-up.

EXPERIMENT AND METHOD SET-UP

As a first step, four different formulations of silica were studied by varying the initiator concentration (sample 1 having the lower initiator concentration and sample 4 having the highest). Secondly, the influence of the temperature was also studied at 20°C and 30°C.

Aim: To study the impact of the initiator concentration and temperature on the sol-gel kinetic.

Once the samples are prepared*, they are directly transferred to a 20 ml glass vial and placed in the Rheolaser Master. Thanks to its 6 position, one-click analysis, and calibration-free measurement, the experiment can be performed with extreme ease and robustness compared to the method in place (1-day gelling time checked visually).

Gel point information was obtained by the Time-Cure Superposition data processing and according to the Winter-Chambon criterion, described in RHMAS-TN-01.

* for this study, and due to the absence of natural scatterers in the solution, samples were seeded with 1µm melamine resin particle at 0.1%wt

RESULTS AND DISCUSSION

Part 1 - Sol-Gel transition determination

This evolution can be studied by the calculation of the Elasticity Index (EI) which quantifies the elasticity of the sample network. The higher the EI, the higher the sample's elasticity.

Figure 2 Simultaneous comparison of Elasticity Index for Samples 1 through 4 measured at 30°C for 60 minutes.

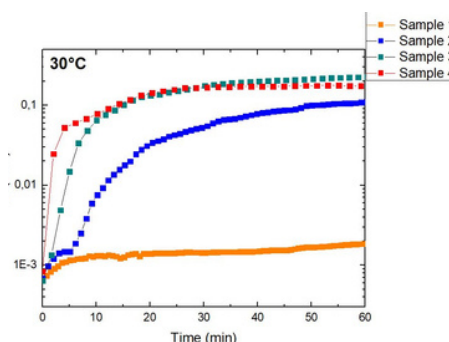


Figure 2. Evolution of Elasticity Index (EI) of 4 sol-gel reactions at 30°C.

A strong increase in the EI corresponds to a “rapid” elastic network formation due to gel formation. In the formulation with the lowest initiator concentration (Sample 1), gel formation is not observed. Whereas higher concentrations led to different gel formation kinetics.

Two characteristic times are determined:

- Gel point thanks to time-cure superposition data processing (TCS),
- End of gelation: time for EI to reach a plateau.

Latter time indicates when the sol-gel process is finished and the second step (drying, calcination, etc.) can be started. Table 1 shows the characteristic times and Elasticity Index for the different concentrations at the end of the experiment (t=60min).

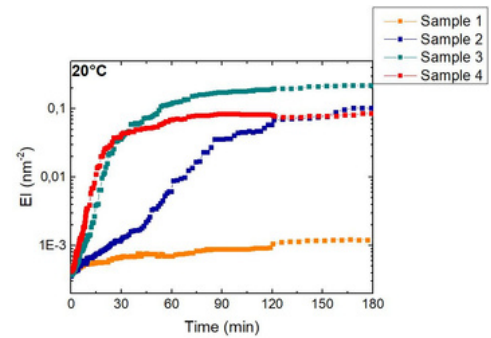


Figure 3. Evolution of Elasticity Index (EI) of 4 sol-gel reactions at 20°C.

Table 1. Gelation times and final gel strength of sol-gel samples at 30°C

Sample	Gelation by TCS (min)	End of gelation (min)	EI (nm ⁻²)
Sample 1	no gel	no gel	no gel
Sample 2	6	48	0.22
Sample 3	3	30	0.22
Sample 4	1	26	0.18

The gel time decreases with increasing initiator concentration. However, studies show that an excess of initiator may lead to weaker gel. For samples 2, 3, and 4, a gel is formed in less than an hour. However, for this specific application, gel time must be over one hour to adjust the final property of the materials (transparency).

Table 2. Gelation times and final gel strength of sol-gel samples at 20°C

Sample	Gelation by TCS (min)	End of gelation (min)	(nm ⁻²)
Sample 1	no gel	no gel	no gel
Sample 2	40	120	0.10
Sample 3	15	68	0.22
Sample 4	10	70	0.08

Thanks to Rheolaser Master, the sol-gel transition can be fine-tuned by adjusting the formulation and process conditions to reach the desired material properties. Measurements are performed without any stress or sample preparation and the 6 parallel tests can be crucial to quickly and effectively screen a large number of parameters

Part 2 - Gelling process optimization

To slow down the gelation kinetics, decreasing the amount of initiator is not an option (no sol-gel transition). Another method is to decrease the temperature of the reaction.

Figure 3 shows the evolution of the Elasticity Index of the sol-gel process of the same 4 samples at 20°C instead of 30°C. The resulting gelation times and Elasticity Index are listed in Table 2.

As expected, full gelation takes more time for all samples. The two samples with the highest concentrations of initiator (Sample 3 and 4) have seen their gelation time increase (TCS), but the end of gelation time remains too fast for the application. Sample 2 gel point increased significantly and is a good candidate for this specific material.

CONCLUSION

Rheolaser Master is a powerful tool for the analysis of gelation time in sol-gel processes. The instrument offers 6 measurement positions for fast and simultaneous screening of different formulations. As gelation time may take several hours, it is essential for accelerating the development time of new sol-gel materials, such as mesoporous silica, specialty glasses and other highly functional materials.