Characterization of sol gel materials with a quartz resonator

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Abstract
The Sol-Gel (SG) process leads to an oxide macromolecular network through a sol to gel transition. To optimize this process, the control of the very strong increase of the bulk viscosity is required. Up to date any complete investigation during the SG formation cannot be achieved by a unique non destructive technique. In this paper, we propose an ultrasonic technique using AT cut quartz. This method is singularly effective to ensure a complete and reliable follow up of the viscoelastic parameters of SG. In order to increase the accuracy a more complete model of quartz loaded by gel is used to take into account the mass effect.

Introduction

The development of SG materials requires a tight control of the viscoelastic parameters during the sol to gel transition. Rheological method at low frequency is commonly used. This technique gives the access to the gelation time (t_g) using the winter criterion near the strong increase of the bulk viscosity [1]. However, because of its narrow sensitivity range, this method cannot afford a complete study from the sol state to gel state with a unique experimental setup. To investigate mechanical parameters of materials, an ultrasonic method using thickness shear mode quartz resonator sensors has been developed [2]. In addition with suitable model, this technique gives access to shear modulus G of viscoelastic layers from measured electrical impedance of quartz [3].

In this paper, this quartz crystal microbalance technique is used to follow the evolution of silica SG matrices. The viscoelastic parameters of these materials are deduced using a model taking into account the mass loading on the surface [4]. In order to study the efficiency of this technique, silica based gels from solution phase for different initial hydrolysis molar ratio are used in this work. From the temporal evolution of the elastic G' and viscous G'' moduli, a gelation time t_{gs} is estimated. This time is therefore compared to the gelation time t_g determined by a rheological method at low frequency using the winter's criterion [5,6].

Experimental setup

Sol gel matrices

For this work, the SG process is based on the inorganic polymerization of $Si(OCH_3)_4$ for which the hydrolysis and condensation reactions are known to be particularly slow. DiMethylAminoPyridin (DMAP) is chosen as catalyst. The elaboration mode has already been detailed in a previous paper [7]. The aggregated structure of this type of gel has been described by Nair [8].

A study on the influence of the initial hydrolysis ratio ($h=[H_2O]/[$ $Si(OCH_3)_4]$) with a constant $Si(OCH_3)_4$ concentration and temperature (25 °C) has been performed.

Quartz crystal microbalance device

The experimental set-up is presented Figure 1. A 6 MHz AT-cut quartz crystal is loaded on one side by the sol-gel material. The other side is loaded by air. The SG matrix is placed on the quartz surface in a thermostated cell. The admittance is measured within a 50 kHz bandwidth near the resonance frequency using the HP4195A network analyzer.
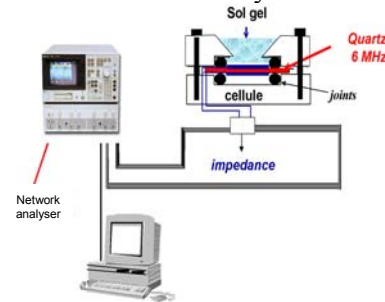

Figure 1 :   Experimental setup

Extraction of G' G"

The measurement of the modified Butterworth-Van Dyke (BVD) equivalent circuit parameters (figure 2) is necessary to characterize the shear modulus G [9]. When a layer of material is deposited on the surface of the quartz the lumped element model can be represented by the circuit in Figure (2).
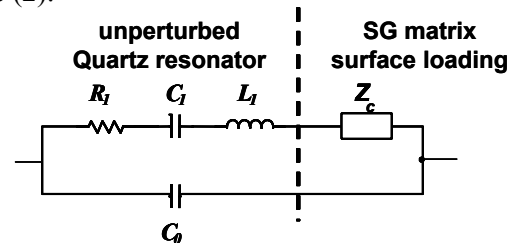

Figure 2 :   modified lumped element model.

The motional impedance of unperturbed crystal is described by a serial capacitance C_1, inductance L_1 and resistance R_1 circuit. The motional electrical impedance representative of the SG matrix viscoelastic parameters on the surface of the quartz is given by Z_c. Finally, the electrical quartz impedance

can be represented as a static capacitance C_0 in parallel with the total motional impedance.

For the first harmonic the mechanical impedance can be deduced from electrical impedance as follow:

$$Z_c = \frac{1}{8 K^2 f_0 C_0} \frac{Z_S}{Z_q} \qquad (1)$$

where Z_q is the mechanical impedance of quartz, f_0 is the motional resonance frequency, and K^2 is the complex electromechanical coupling factor for lossy quartz. The surface mechanical impedance contributed by a semi infinite layer Z_s is obtained by [3]:

$$Z_S = \sqrt{\rho G} \qquad (2)$$

where ρ is the layer density and G the shear modulus $(G=G'+ j G'')$.

In liquid phase the SG matrix is quite equivalent to a Newtonian fluid. Theoretically $G'=0$ and the real part (R) and imaginary part (X) of Z_C are equal.

In gel phase, the SG matrix is a viscoelastic material so the real and imaginary part of Z_C depend on viscoelastic parameters with the following equations [3] :

$$R \propto \sqrt{\frac{\rho(|G|+G')}{2}} \qquad (3)$$

$$X \propto \sqrt{\frac{\rho(|G|-G')}{2}} \qquad (4)$$

Note that in a pure solid phase $G''=0$ and the imaginary part is equal to 0.

Results and discussion

To observe the viscoelastic evolution during the sol to gel state, the real and imaginary parts of the electrical admittance of the quartz are stored every 10 seconds. The figure 3 shows some of typical plots in complex plan of this admittance for the unperturbed quartz and the loaded by SG matrix.
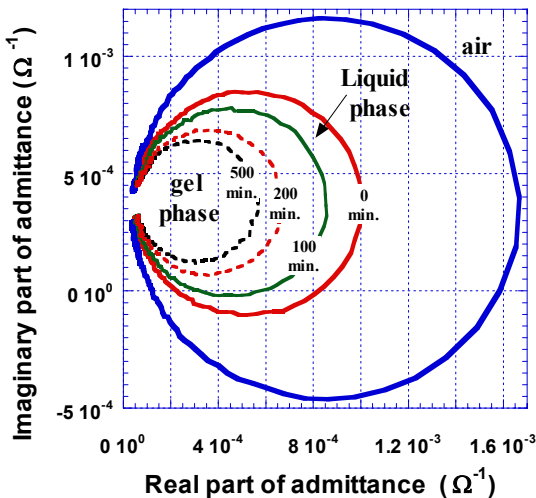
Figure 3 : Ttypical variation of electrical admittance during gel process.

On this figure we mainly observe the damping effect due to the matrix loading. The circle shape

drops following SG matrix evolution. However the presence of SG matrix on the surface of the quartz also induces a resonance frequency shift. The real part of the electrical admittance versus frequency for different states of SG matrix pinpoints this effect (figure 4).
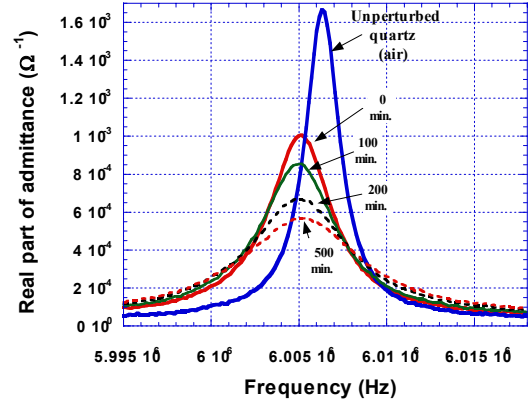
Figure 4 : Real part of electrical admittance versus frequency.

This figure shows clearly that both resonance frequency and damping are modified by the SG matrix evolution. On one hand, the viscoelastic parameters and the mass effect modify the frequency shift [10]. On the other hand, the magnitude of the real part only depends on the viscoelastic parameters [11, 12].

To deduce with accuracy G' and G'', the electrical model must be modified to separate the mass effect from the viscoelastic one. The figure 5 presents the equivalent Z_c model used.
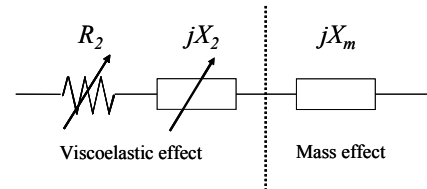
Figure 5 : Equivalent circuit of Z_c separating Viscoelastic and mass effects.

Assuming that for our setup the evaporation during the SG process is negligible, we can assume that the SG density remains constant. As a consequence, the mass effect term X_m is considered constant. R_2, X_2 only take account of the viscoelastic effects during the gelation process.

R_2 and X_2 values are estimated for each measurement using this model. According to equations 3 and 4, we can extract G' and G'' from these values. In order to follow the kinetic of matrix formation, the temporal evolution of R_2, X_2 and consequently G', G'' is then studied. This procedure has been applied for different hydrolysis ratio h=2, 4, 6, 8. A typical result of $G'(t)$ and $G''(t)$ observed for a SG matrix is presented figure 6.
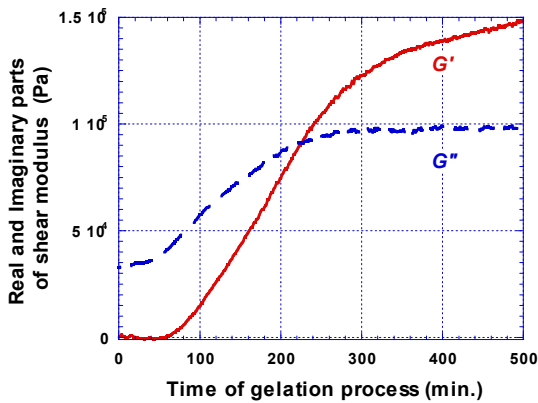
Figure 6 :   Temporal evolution of G' and G" for the $Si(OCH_3)_4$ gel (h=2).

We can observe a very strong variation of viscoelastic parameters. At the beginning the SG matrix is in liquid phase and $G'=0$. The matrix has only viscous properties and the shear modulus only depends on G'' value. This result is in good agreement with the known viscoelastic parameters for this phase. When the matrix becomes a gel, G' and G'' increase significantly and seem to reach a plateau. At this relatively high frequency (~6MHz), we can observe that G' is bigger than G'' for these gels. This result shows that these gels stay more elastic than viscous. Between the liquid and gel phases, the viscoelastic parameters increase continuously. To determine the beginning of the significant sol to gel state transition, we determine the time when the matrix can not be considered as a Newtonian fluid. According to equations 3 and 4, this time noted t_{gs} occurs when $R_2 \neq X_2$. Figure 7 shows the typical time evolution of R_2 and X_2.
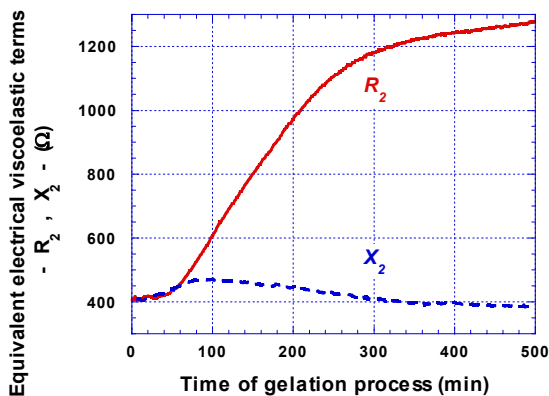

Figure 7 :   Time evolution of R_2 and X_2 for h=2.

As shown in this figure, this time can clearly be detected. This time noted t_{gs} depends on h as shown in the following table.

h	2	4	6	8
t_{gs} (min.)	75	30	17	14

Comparison of gelation time with classic method

We compared these values with the gelation time obtained by rheological method at low frequency. The figure 8 shows a comparison between t_{gs} and t_g measured by rheological Couette method using Winter's criterion [13].
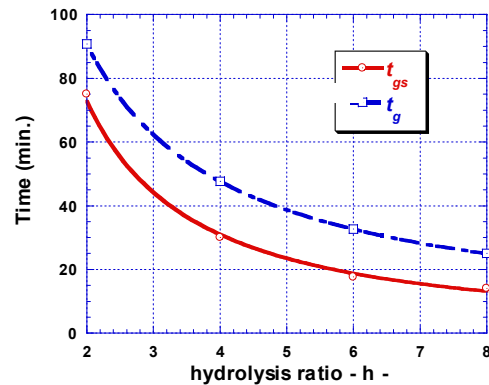

Figure 8 :   Comparison between gelation time and rheological method.

In this figure, we can see that t_{gs} is always lower than t_g. We can also see that the shape of time versus hydrolysis ratio curves follows the similar power law. This last result proves that t_{gs} is a good criterion to characterize earlier the SG matrix evolution.

Conclusion

The microbalance quartz device allows the measurement of viscoelastic parameters in a large dynamical range (500-200,000 Pa). Compared with the rheological method, the quartz microbalance device makes it possible to completely follow the viscoelastic parameters evolution with a unique device. The SG matrix can be optimized during its process. Taking into account the frequency range used (wavelength around 1μm) our system gives us access to the formation of the gel on the surface. Our results thus confirm that the gel has an isotropic formation during the gelation process: no direction of growth is privileged for this type of gel.

By its nondestructive character and its simplicity of measurement, this technique is a first step to make an online rheometer.

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