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An acoustic technique for investigating the sol–gel transition

S. Serfaty,[a] P. Griesmar,*[b] M. Gindre,[a] G. Gouedard[c] and P. Figuière[b]

[a] Laboratoire de Modélisation et Optimisation des Systèmes en Electronique, [b] Laboratoire de Physico-chimie des Matériaux Organiques (E-mail: griesmar@paris.u-cergy.fr) and [c] Laboratoire de Physique des Materiaux et Surfaces, Université de Cergy Pontoise, 5 mail Gay-Lussac, F-95 031 Cergy Cedex, France

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The sol–gel synthesis of glasses and ceramics has received a great amount of scientific and technological interest. The close control of the evolution between the sol and gel states allows the elaboration of highly appropriate materials for technical purposes. The sol–gel transition can be characterized by a very rapid increase of the bulk viscosity of the medium. This work presents a non invasive technique of investigation based on acoustic resonance which can trace sol–gel evolution. Two different sol–gel matrices have been prepared from silica gels in the presence of either acidic and basic reagents. The study of the evolution of these sol–gel matrices, shows that in the gel phase, several resonance frequencies appear and increase as a function of time. In both types of matrices the evolution of these resonance frequencies follow an exponential law according to percolation models for a cross-linked polymeric network. In addition, this technique is particularly well suited to investigate SG matrices with short gelation times.

Introduction

For more than 10 years, new methods of synthesis of glasses and ceramics by a method known as the sol–gel (SG) process have attracted a great deal of scientific and technological interest. This process is based on hydrolysis together with a condensation reaction and leads to a macromolecular oxide network.[1] Several days or even several weeks may be required to obtain a stable gel. This state can be obtained more rapidly by changing the pH of water added to promote the hydrolysis–condensation reactions. The chemical nature of the additive used to change the pH modifies the kinetic reaction and therefore the SG matrix structure. The tight control of SG evolution permits the elaboration of highly appropriate materials for technical purposes.[2,3]

Hydrolysis condensation reactions can be described by theoretical models such as percolation.[4,5] The ‘sol’ to ‘gel’ transition is characterized by a very rapid increase of the bulk viscosity during the gelation time, designated t_g. The SG transition is therefore a transition which implies a critical evolution of the mechanical properties of the material. By dynamic rheological measurements, the evolution of SG matrices can be followed by measuring the complex shear modulus G, which corresponds to the normalized stress after a sudden imposed strain beyond t_g.[6] Such transitions can be studied by changing the oscillation frequency. Several experimental techniques for a wide array of frequency ranges can be used:[7,8] thus, at low frequencies (10^{-6}–10^{-1} Hz) flow-relaxation techniques are required. In the range of 10^{-2}–10^{3} Hz frequencies resonance oscillation or thermodynamic analysis techniques are used. Between 10^{6} and 10^{9} Hz ultrasonic techniques are used.

To the best of our knowledge, only one investigation technique using the audible range (10–10^{4} Hz) has so far been published.[9] However acoustic spectroscopy seems particularly adapted to SG matrices displaying resonance frequencies in this frequency range. After striking their containers, some SG matrices provide an audible acoustic resonance that changes with time and Pucetti and Leblanc describe a system emphasizing this observation.[9] Their experiment is based on the photo-acoustic resonance provided by a YAG laser, the sound of which can be measured with a microphone. The spectrum obtained by Fourier transformation shows several resonance frequencies which diminish with time. Our paper presents a technique of investigation in the audible range which is quite simple to perform and more precise than the previously reported technique.[9] The high dynamic of the system allows precise measurement of the evolution of the resonance frequencies. An interpretation of this phenomenon will also be proposed.

Experimental

Our experimental device is shown in Fig. 1. It is constructed of two identical cylindrical cells which can be connected together, allowing an increase of the SG volume matrix, into which the SG matrix is poured. Each cell has a radius of 10 mm and a length of 20 mm. The cell is waterproofed to alleviate matrix loss by placing a thin plastic foil (10 µm) at both ends.

In order to follow the SG matrix evolution as a function of time, we applied an electrical sinusoidal signal $V_e(t)$ to a transducer placed at one end of the cell. This transducer converts this electrical signal into an acoustic wave. A microphone placed at the other end collects the waves transmitted through the SG matrix and converts the acoustic wave into an electrical signal. Finally, this signal is amplified by a linear amplifier (bandwidth 0.3–30 kHz; gain 25) and produces a signal $V_s(t)$. Then both signals [$V_e(t)$ and $V_s(t)$] are trans-

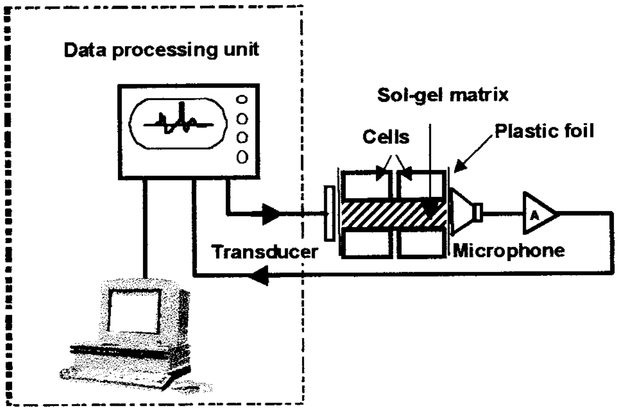

Fig. 1 Acoustic analysis system of sol–gel matrices.

mitted to the data processing unit to calculate the ratio $V_s(t)/V_e(t)$ denoted the complex transfer function. By a synchronous detection we extract the magnitude and the phase of the SG matrix response for a given frequency. By sweeping the signal frequency of the transducer, we obtain the complete transfer function of the transducer–SG matrix–microphone. To preserve a high signal to noise ratio, we applied 30 periods of a sinusoidal signal of frequency f to the transducer. To take into account the large variation of the resonance frequency magnitude an automatic regulation of the transmitted magnitude signal is performed to avoid an overload of the outgoing signal.

Because the transducer and the microphone response depend on the signal frequency, the transfer function of the SG matrix is extracted by using a compensation operation. The measurement obtained just after pouring the liquid phase SG matrix into the container gives us a reference for the transfer function. In addition, we apply the Savitzky–Golay[10] smoothing filter in order to locate resonance frequencies of the SG matrix.

During our experimentation, two SG matrices were studied.[11] The first matrix (denoted gel A) is a silica oxide network in a solution of tetramethoxysilane under acidic conditions (hydrochloric acid + sorbitol) and a monolithic gel was obtained within 20 min. The second matrix (gel B), is made from the same molecular precursor in the presence of a nucleophilic agent [dimethylaminopyridine (DMAP)] which gives a monolithic gel within 10 min.

Results and discussion

To study the sol–gel matrix evolution as a function of time, the transfer function was measured every 2 min during 2 h. This timing was chosen mainly based on experimental considerations (number of sample points, data), and takes into account the characteristic evolution time of the matrix. Each frequency scan is assumed to be fast enough to prevent a noticeable evolution of the matrix during the scan. Fig. 2 shows the acoustic transfer function measured for gel B at two different times in its evolution. In the liquid phase, the transfer function has clearly a smaller modulus than the value observed in the gel phase. A large variation of the transfer function modulus, as reflected by the observed resonance frequencies (for example the variation is +50 dB near $f = 400$ Hz), is clearly seen and analogous variations were observed for gel A.

Fig. 3 shows the evolution of the resonant frequencies which shows an exponental rate-law behaviour. In condensed matter, two types of pressure waves may propagate: transversal (shear) waves and longitudinal waves. It is well known that the transversal wave has a velocity depending on the shear modulus G, and the longitudinal wave has a velocity depending on the longitudinal modulus M.[12,13] The measured transfer function is then affected by the variation of G and M. Percolation models,[14] describe this variation of the shear modulus in terms of exponential rate-law behavior. In addition, according to Navier–Stokes theory, the moduli M and G are linked to the bulk modulus K by eqn. (1):

$$M = K + \frac{4}{3}G \tag{1}$$

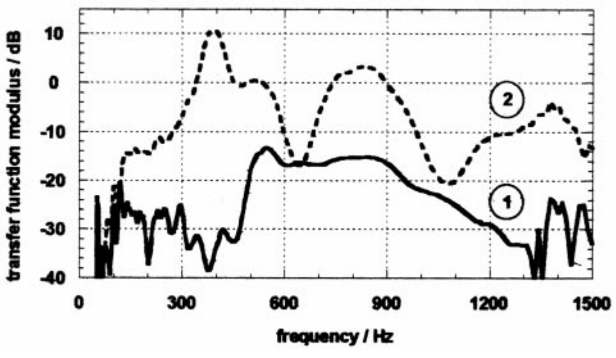

Fig. 2 Transfer function for gel B: (1) in the liquid phase ($t \approx 0$) and (2) in the gel phase ($t = 120$ min).

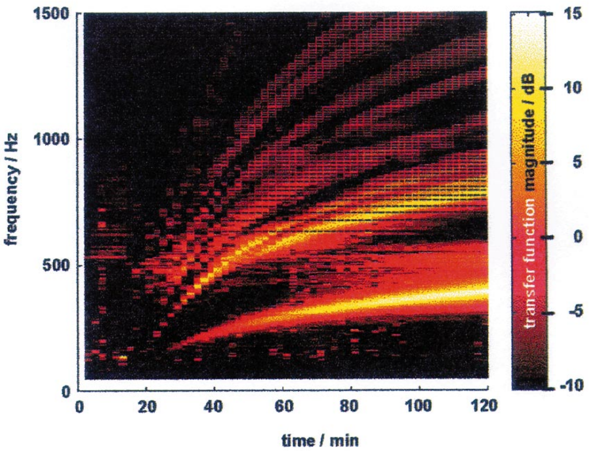

Fig. 3 Evolution of the resonance frequencies and their transfer function magnitude *vs.* time for gel B.

From the results of Fig. 3, the positions of the relative maxima of the transfer function have been extracted for each measurement time and the results are presented in Fig. 4.

The fit of experimental points performed with eqn. (2) confirms that the evolution of pressure waves in the SG matrix are in good agreement with percolation models.

$$f_n(t) = f_n(\infty)[1 - \exp(-t - t_g/\tau)] \tag{2}$$

Here, $f_n(t)$ is the nth resonance frequency *vs.* time in the model, $f_n(\infty)$ is its long time limit, and τ is a characteristic constant evolution time. The frequencies are then numbered in increasing order.

It is easy to show that there are two families of curves in each of 4(a) and (b). The first (lower) curve differs from the others because it nearly reaches its asymptotic value after 2 h. This is the lowest resonant frequency and exhibits the propagation of a purely transversal wave inside the transducer–material–microphone cavity. Taking into account the sample dimensions and the measured value of the resonance frequency, we deduce a velocity for this acoustic wave of *ca.* 20 m s^{-1} in the gel phase. It is well known that the gelation process induces the formation of a connected array of polymeric species. This array, which is very similar to a loose three dimensional grid, may have vibrational modes that are largely decoupled (expected perhaps for attenuation) from the surrounding liquid. We can then observe the acoustic standing waves of this grid in the container. This is a rather surprising result that has already been observed and explained for aerogels.[15,16]

The different curves belonging to the second family are related to each other by a multiplication factor in the vertical scale. They thus correspond to various overtone modes for longitudinal waves propagating in the cavity.

The evolution of the resonance frequencies (longitudinal and transversal) is mainly due to the variation of the corresponding modulus with time induced by the structural modifications of the SG matrix.

The curves of the second family converge at a single point on the abscissa axis ($f = 0$). This point may be identified with the gelation time t_g, in good agreement with the visual observation of the gelation process.

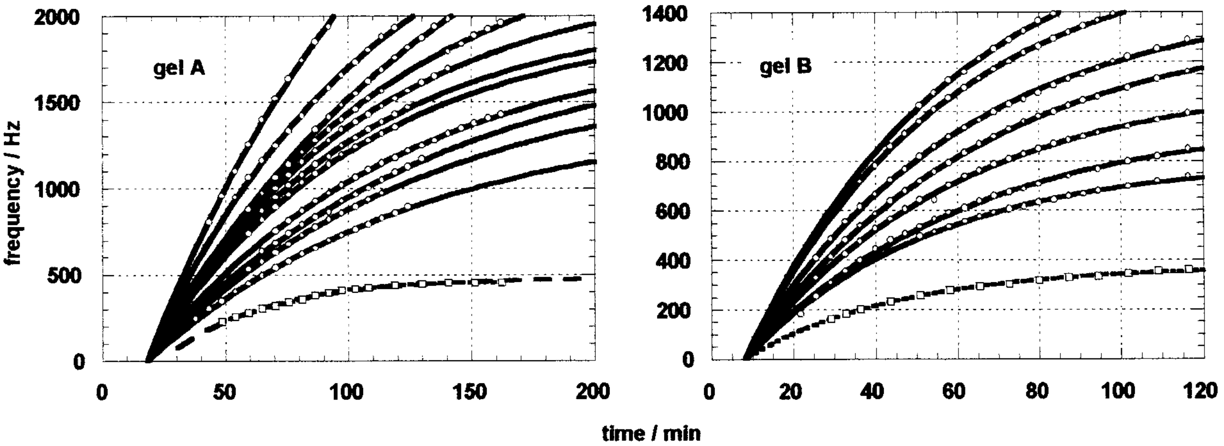

Fig. 4 Evolution of the resonance frequencies *vs.* time (a) for gel A and (b) for gel B.

Conclusion

Classical techniques used to characterize the first stages of the gelation process may interfere and modify its evolution. For example, viscosity measurements by a rheological technique may delay the gelation time by the mechanical constraints imposed on the material. Other techniques using optical second harmonic generation[17] or diffusion coefficient measurements of electro-active species,[18] may modify the SG matrix structure because they require additional chemical probes. Finally even with relaxation additives, ^{29}Si NMR measurement does not allow the study of the gelation process of SG matrices with short gelation times.

In contrast to these techniques, our method based on acoustic resonance tracking, does not require the addition of any probe. Furthermore, the weak signal level required to study the SG matrix evolution, does not modify the gelation time. Consequently, our technique which is very simple to carry out, does not affect the SG structure. Our first results show that it is particularly well suited to study the SG matrices with short gelation times. Moreover, to the best of knowledge, no other technique exists, which allows the study of sol–gel matrices with such a large dynamic range.

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