

SOL – GEL MODELLING ASSOCIATED WITH THE RHEOLOGY OF POLYMERIC PRECURSORS OF CERAMIC MATERIALS

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ABSTRACT:

A general constitutive relation describing the change of viscoelastic behavior during the liquid - solid (sol - gel) transition which takes place in preceramic polymers is derived on the basis of Jeffrey's 3-constants model with time dependent viscosities and elasticity. It is postulated that the sol - gel - transition can be analyzed analogous to the solutions of the Avrami equation used for modeling crystallization processes. Two different polymer systems used as precursor for the production of ceramic materials are investigated here: i) a mixture based on polysiloxane, alumatrane and isopropanol; ii) a non-oxidic carbodiimide gel based on the reaction of chlorosilanes with bis(trimethylsilyl)carbodiimide. Continuous measurements of the dynamic moduli versus reaction time, as well as creep tests at constant shear stress, evidenced both qualitative similarities and quantitative differences associated with the sol - gel transition of the two polymer systems. The shear rate and viscosity dependence of reaction time in creep tests, respectively the evolution of Lissajous figures associated with oscillatory experiments, are found to be consistent with the numerical simulations of the proposed constitutive relation.

ZUSAMMENFASSUNG:

Eine allgemeine konstitutive Beziehung zur Beschreibung der Änderung des viskoelastischen Verhaltens während des flüssig-fest Sol-Gel-Übergangs präkeramischer Polymere wird auf der Basis des 3-Konstanten-Modells von Jeffrey unter Berücksichtigung der zeitabhängigen Viskosität und Elastizität abgeleitet. Lösungen der Avrami-Gleichung zur Modellierung von Kristallisationsprozessen werden hier zur Beschreibung des Sol-Gel-Prozesses herangezogen. Untersucht wurden zwei unterschiedliche Polymersysteme, die zur Herstellung keramischer Materialien verwendet werden: i) eine Mischung aus Polysiloxan, Alumatran and Isopropanol und ii) ein nicht-oxidisches Carbodiimid-Gel, hergestellt durch Reaktion von Chlorsilanen und Bis(trimethylsilyl)carbodiimid. Die hier untersuchten Phasenübergängen der beiden Sol-Gel Prozesse sind qualitativ ähnlich, zeigen jedoch quantitative Unterschiede wie kontinuierliche Messungen der dynamischen Moduli in Abhängigkeit der Zeit sowie Kriechtests bei konstanter Scherbeanspruchung ergeben haben. Die Abhängigkeit der Reaktionszeit von der Scherrate und der Viskosität in Kriechtests sowie das Auftreten von Lissajous Figuren in oszillatorischen Experimenten stehen im Einklang mit den numerischen Simulationen der hier vorgeschlagenen konstitutiven Beziehung.

RÉSUMÉ:

Une relation constitutive générale qui présente le changement du comportement viscoélastique qui se produit pendant la transition liquide-solide (sol-gel) des polymères céramiques est décrite avec le modèle Jeffrey avec 3-constantes, modèle dans lequel la viscosité et l'élasticité dépendent du temps. On postule que la transition sol-gel peut-être analysée comme la solution donnée par les équations de Avrami, équations qui sont utilisées pour modéliser la cristallisation. Dans cet article sont analysés deux systèmes différents de polymères qui sont utilisés comme précurseurs pour la production des matériaux céramiques: i) une mixture de polysiloxane, alumatrane et isopropanol; ii) un gel non-oxidique carbodiimide basé sur une réaction du chlorosilanes avec bis(trimethylsilyl) carbodiimide. Les mesures continues du module dynamique qui dépend du temps de réponse, mesures qui ont été réalisées avec des tests viscométriques à contraintes tangentielles constantes, mettent en évidence des similarités qualitatives et aussi des différences quantitatives qui sont associées avec la transition sol-gel pour les deux systèmes de polymères. La dépendance de la vitesse de cisaillement et de la viscosité en fonction du temps de réponse qui est relevée dans les tests viscométriques, et aussi l'évolution des figures de Lissajous associées avec les expériences oscillatoires sont en concordance avec les simulations numériques de la relation constitutive proposée.

KEY WORDS: constitutive relation, viscoelasticity, rheometry, Lissajous figures, sol - gel process, phase transition, ceramic precursors

1 INTRODUCTION

The conversion of polymeric precursors into amorphous ceramic starts with the process of increasing the average molecular weight of the precursor during a sol - gel transition (for chemical details of the process see Trassl et al. [1], Gonon et al. [2], Tsai [3]). A gel is defined as a multi-component system, rich in liquid and consisting of continuous fluid and solid phases of colloidal dimensions. The network structure of the gel is formed by chemical or physical processes, Brinker and Scherer [4]. During chemical sol - gel process the material undergoing a liquid - solid transition due to the developing of a branched structure based on covalent bonds within the solvent, as the extent of reaction p is progressing from 0 (fluid) to 1 (solid). Therefore, from a rheological point of view, a chemical gel is a viscoelastic material with time dependent internal network structure.

The sol - gel process is dominated by the existence of a critical gel point. In this particular state, the reaction reaches a critical value, $p = p_c$, where the liquid and solid phases of the material are coexisting and contribute equally to the viscoelastic properties of the material. For some sol - gel processes p has a high gradient in the vicinity of the critical gel point, which means that the mutation of the sample is too rapid close to p_c that the rheology is difficult to be investigated without stopping the reaction. In this case, the classical procedure to determine the critical gel point, e.g. where G' (elastic modulus) and G'' (viscous modulus) are proportional to ω^n (ω = oscillatory frequency, n = relaxation exponent), becomes relative since the material structure undergoes a relevant evolution during the frequency sweep test (see for details the review by Winter and Mours [5]).

Another procedure to characterize the rheological behavior at the critical gel point has been proposed by Balan et al. [6]. Instead of freezing the material at different extents of the reaction around p_c and applying for each obtained sample a sweep test in frequency, in order to detect which one discloses parallel dynamic moduli, the authors measured continuously the time evolution of dynamic moduli at different constant frequencies and established the region where the values of the moduli are fitted by the power relaxation function $G(t) = St^{-n}$ (we have to remark that the above expression of the relax-

ation function is limited to the region where the moduli are parallel). For the analyzed materials (carbodiimide non-oxide gels), the critical gel point was located in vicinity of the cross point (i.e. $G' = G''$). The obtained values for the gel exponent and the gel strength were: $n = 0.65$ and $S = 0.25$, respectively. It is important to remark that the cross point was reached at the same reaction time, independent of frequencies.

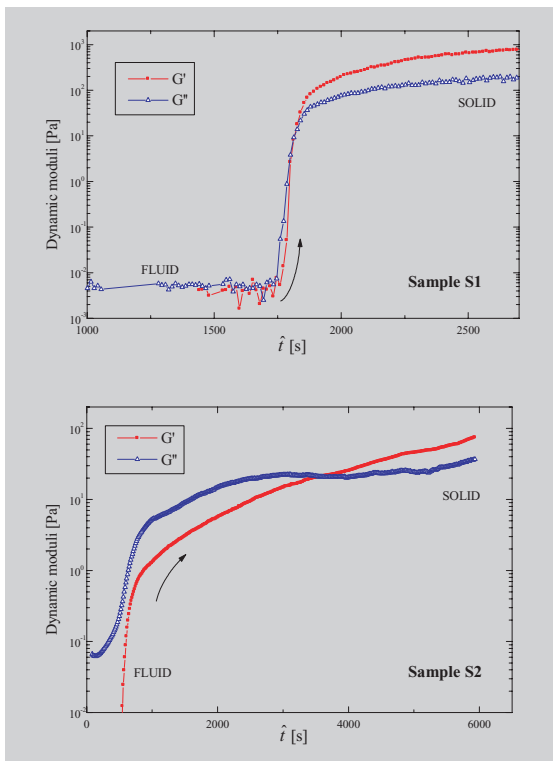
The present paper is focused on the rheological modeling of the liquid - solid transition in chemical sol - gel processes. The aim of the study is to establish a general phenomenological model describing the rheology of materials during gelation process under viscometric flows, simple shear and oscillatory motions, respectively.

2 RHEOLOGICAL MEASUREMENTS

The samples under experimental investigation are the following: i) a mixture based on polysiloxane, alumatrane and isopropanol (sample S1), ii) a non-oxidic carbodiimide gel based on the reaction of chlorosilanes with bis(trimethylsilyl)carbodiimide (sample S2). Both materials are considered as possible precursors in processing of ceramic materials, see for details Riedel et al. [7], Gabriel [8] and Völger [9].

The experiments have been performed with controlled stress rheometers, simple and double Couette cylinders geometry, at constant temperature. A dynamic stress rheometer DSR 200 (Rheometric Scientific) or an universal dynamic spectrometer UDS 200 (Paar Physica) coupled with a thermostat TEK 350 were used. The liquid samples were filled into the cup under inert gas. After moving down the inner cylinder the sol was covered by a low viscosity silicone oil to protect it from the air and evaporation of volatiles. A slight argon flow during the measurements was also applied. After the measurements a gel body was obtained in the gap between cylinders which appeared like the product of a standard reaction in a flask. Two different viscometric tests are used to characterize the rheology of the sol - gel transition:

- dynamic controlled stress at constant frequency (the dynamic moduli are measured continuously during the gelation process)



■ creep tests (the evolution of strain and viscosity is measured during the process, at constant shear stress)

In viscometric controlled stress experiments the shear stress is applied and the strain is measured. At the beginning of reaction the sample disclose small viscosity and no elasticity, therefore the measured strain will be large. In dynamic tests, the strain amplitude γ_0 starts to decrease dramatically at the onset of reaction from the level of 10 to very small values, 10^{-3} and less, at the end of gelation. Were not observed qualitatively modification in the sol - gel process due the large amplitudes of strain oscillations, only a delay in the onset of phase transition (same conclusion has been obtained recently by Rimdusit and Ishida [10], and by Daniel et al. [11]). Even if there is no control of the strain magnitude during the rheological experiments, the stress controlled experiment has the advantage that the input becomes homogeneous in the gap almost instantaneously. The high rate dynamics of structure formation in liquid - solid transition might determine inhomogenities of the deformation in the gap, therefore the strain controlled experiments are in this particular case less adequate (see also Balzer et al. [12], in relation to the applied experimental procedure). The change of rheological properties, as a function of reaction time, for the samples under investigations are presented in Fig. 1 and in Fig. 2.

3 RHEOLOGICAL MODEL

The gelation models have their origin in kinetic theories of the structure growth in a continuous

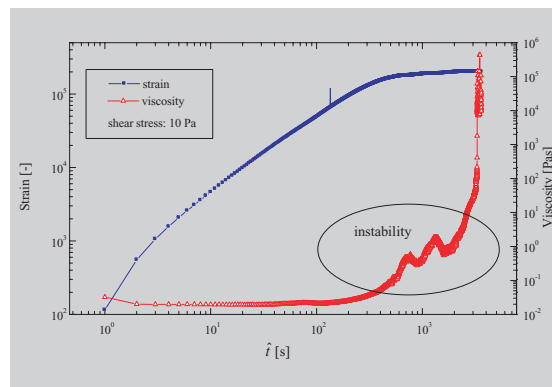


Figure 1 (left): Evolution in time of the dynamic moduli at constant frequency $\omega = 1 \text{ s}^{-1}$ in a gelation process for the samples under investigation (stress amplitude: $\tau_a = 0.5 \text{ Pa}$ for sample S1, and $\tau_a = 10 \text{ Pa}$ for sample S2, respectively). Sample S1 discloses a more sharp transition to the “solid” rheological behaviour.

Figure 2 (right): Experimental creep test for sample S2 (a region of “instability” is observed in vicinity of the critical gel point).

phase. In the most simple approach, the process is described by the first order non-linear differential equation

$$\dot{u} + A(\hat{t})u = B(\hat{t}, u) \quad (1)$$

where $u(\hat{t})$ is assumed to be a continuous function of reaction time \hat{t} , i.e. the relative time with origin at the onset of chemical process in sol - gel transition. Here \hat{t} is considered the internal variable of the process, playing a similar qualitative role as the extent of reaction p .

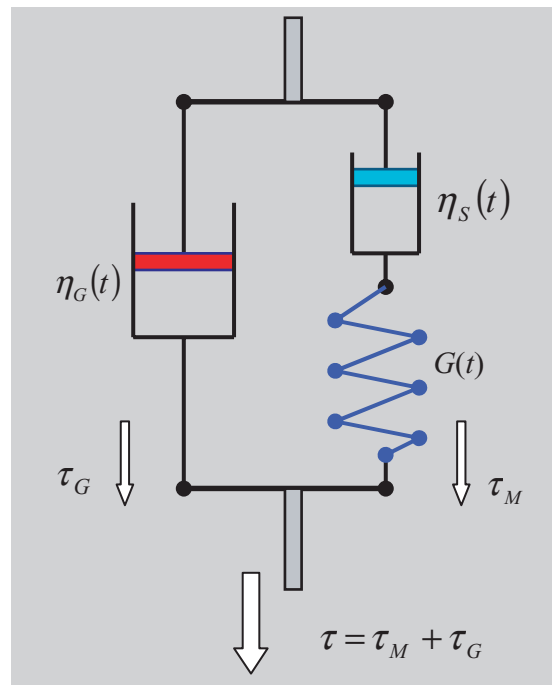
The function $u(\hat{t})$ represents the evolution of some parameter related with the microscopic growing of the network structure: number of clusters [5], particle size distribution or/and cluster growth (Amann [13], Yang and Sigmund [14]), mass fraction of material transformed (Maldelkern [15]), height of growing interface (Kardar et al. [16]). In Eq. 1, $A(\hat{t})$ and $B(\hat{t}, u)$ are material functions which individualize the process under investigation (for details see the examples from Chapter I in Braun [17]).

The dynamics of u determine the macroscopic rheological properties of the material, i.e. the evolution of viscosity and elasticity during the process. Assuming the proportionality of the macroscopic continuum properties on the average of values of u one obtains that the evolution of elasticity and viscosity are given by combinations of time dependent functions which are in form similar to the solutions of Eq. 1. Therefore, we are looking for functions of the generic form

$$\psi(\hat{t}) = \psi_1 e^{a\hat{t}^m} + \psi_2 (1 - e^{-b\hat{t}}) \quad (2)$$

to model the evolution of elasticity and viscosity during the rheological transition within the material. In Eq. 2, Ψ_1 and Ψ_2 are particular values of the material property Ψ (i.e. viscosity or elasticity), a and b are positive constants and n, m are the growing exponents (related to the microstructure of network [14]). In particular, Eq. 2 with $\Psi_1 = 0$ belongs to the family of Avrami's equations which models the growth of crys-

Figure 3: Rheological model of the gels structure in simple shear motion.



talline phases where $\Psi(\hat{t})$ represents in this case the mass fraction of the solid phase, see for details Rao and Rajagopal [18] and [19].

For modeling the viscometric flow associated with the gelation process, respectively with liquid - solid transition, we proposed a phenomenological one-dimensional differential model, similar in form with Jeffrey's model. The proposed model is obtained by formally connecting in parallel a viscous element of viscosity $\eta_G(\hat{t})$ with a Maxwell model of viscosity $\eta_S(\hat{t})$ and elastic modulus $G(\hat{t})$ see Fig. 3 (in Balan and Riedel [20] and [21] was investigated the model obtained by connecting in series a viscous element with a Kelvin-Voigt element). The final expression of the constitutive relation is:

$$\eta_S(\hat{t})\dot{\tau} + G(\hat{t})\tau = \left[(\eta_S(\hat{t}) + \eta_G(\hat{t}))G(\hat{t}) + \eta_S(\hat{t})\dot{G}(\hat{t}) \right] \dot{\gamma} + \eta_S(\hat{t})\eta_G(\hat{t})\ddot{\gamma} \quad (3)$$

where

$$\tau = \tau_G + \tau_M \quad (4)$$

represents the total shear stress, with τ_G and τ_M given by

$$\tau_G = \eta_G(\hat{t})\dot{\gamma} \quad (5)$$

respectively

$$\eta_S(\hat{t})\dot{\tau}_M + G(\hat{t})\tau_M = \eta_S(\hat{t})G(\hat{t})\dot{\gamma} \quad (6)$$

Accordingly to Eq. 2, the material functions from Eq. 3 are postulated to have the following expressions:

$$\eta_S(\hat{t}) = \eta_S(0)e^{c_1\hat{t}^m} \quad (7)$$

$$\eta_G(\hat{t}) = \eta_G(0) + \eta_\infty(1 - e^{-c_2\hat{t}^n}) \quad (8)$$

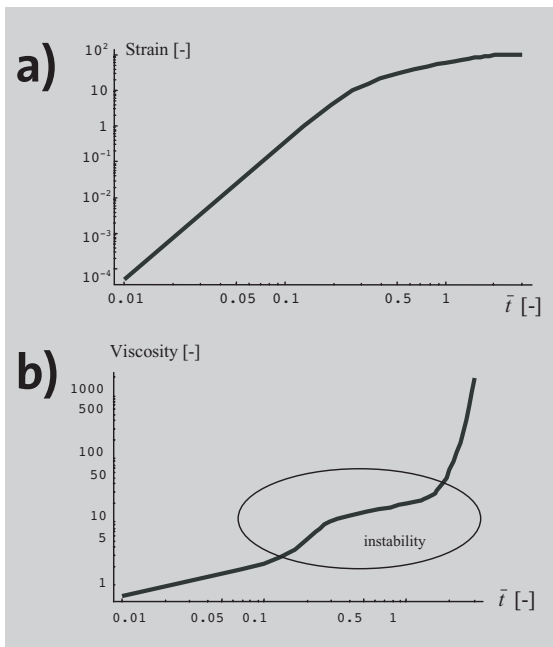
$$G(\hat{t}) = G_\infty(1 - e^{-c_3\hat{t}^r}) \quad (9)$$

In Eqs. 7 - 9, $\eta_S(0)$ and $\eta_G(0)$ are the initial viscosities of the elements (the material is initially a pure fluid with viscosity $\eta(0) = \eta_S(0) + \eta_G(0)$) and η_∞ ($\eta_\infty \gg \eta_G(0)$), respectively G_∞ , are the final viscosity and final elastic modulus of the gel. At the end of reaction the proposed Jeffreys model becomes a Kelvin-Voigt model due the asymptotic increasing to infinity of the Maxwell's viscosity $\eta_S(\hat{t})$, see also [20]. Equation 3 has an identical expression in non-dimensional form if the following scale values $G_O = \langle G \rangle$, $\eta_O = \langle \eta \rangle$, $\tau_O = G_O = \langle \tau \rangle$, $t_O = k\langle \eta_O / G_O \rangle$, respectively, are used.

$$\bar{\eta}_S(\bar{t})\dot{\bar{\tau}} + \bar{G}(\bar{t})\bar{\tau} = \left[(\bar{\eta}_S(\bar{t}) + \bar{\eta}_G(\bar{t}))\bar{G}(\bar{t}) + \bar{\eta}_S(\bar{t})\dot{\bar{G}}(\bar{t}) \right] \dot{\bar{\gamma}} + \bar{\eta}_S(\bar{t})\bar{\eta}_G(\bar{t})\ddot{\bar{\gamma}} \quad (10)$$

where $\bar{G} = G/G_O$, $\bar{\eta}_S = \eta_S/\eta_O$, $\bar{\eta}_G = \eta_G/\eta_O$, $\bar{\tau} = \tau/G_O$, $\bar{t} = t/t_O$, and the corresponding time derivatives are the non-dimensional quantities. The reference values for viscosity η_O , elastic modulus G_O , and time non-dimensional constant k are scaling the results of numerical simulations accordingly to the considered gelation process.

The numerical simulations using Eq. 10 have been performed with the following values: $\bar{\eta}_S(0) = \bar{\eta}_G(0) = 0.01$, $\bar{G}_\infty = 10^4$, $\bar{\eta}_\infty = 10^3$, $c_1 = 1$, $c_2 = 0.02$, $c_3 = 0.001$; $m = 6.5$, $n = 1$, $r = 5.5$ for sample S1; $m = 4.5$, $n = 0.5$, $r = 2.5$ for sample S2 (the magnitude of growing exponents are determined by the rate of transition specific to each of the samples (see Fig. 1). We have performed numerical simulations of Eq. 10 for two controlled stress viscometric motions: i) creep flow (the deformation process under constant applied shear stress $\bar{\tau} = \bar{\tau}_O = \text{constant}$), and ii) oscillatory motion (the deformation process under oscillatory shear stress with constant amplitude, $\bar{\tau}_a$



= constant, and constant frequency, $\omega = \text{constant}$).

The results of the creep simulation associated to Fig. 2 are shown in Fig. 4. The obtained evolutions of strain and viscosity are identically from qualitative point of view with the experiments (it is important to remark the presence of the “instability” region both in experiments and numerical simulation). In the oscillatory motion (i.e. dynamic test) the input is given by the function

$$\bar{\tau}(\bar{t}) = \bar{\tau}_0 e^{i\omega\bar{t}} \quad (11)$$

and the answer in strain variation of Eq. 10 is assumed to have the form

$$\gamma(\bar{t}) = \gamma_0(\bar{t}) e^{i(\omega\bar{t} + \bar{\delta}(\bar{t}))} \quad (12)$$

(here $\bar{\omega}$ is the frequency of the input signal and $\bar{\delta}$ is the time dependent phase angle of the output, see for details Findley et al. [22]). Equations 7 - 9 are introduced with Eq. 11 into Eq. 10, where the strain is considered the unknown function. The solution $\gamma(\bar{t})$ is obtained using the specialized subroutine of the commercial *Mathematica* code. The direct simulation of Eq. 10 discloses the change of the phase angle $\bar{\delta}$ with reaction time \bar{t} : from 90° at the onset of the test (i.e. material is a pure fluid) to the vicinity of 0° , at the end of gelation process (i.e. the material is almost a solid), see Fig. 5.

A suggestive evolution of liquid - solid transition associated with the sol - gel process is given by the Lissajous figures, respectively by solution $\bar{\tau}(\gamma)$ of Eq. 10 in the oscillatory test. The Lissajous figure is the time parametric representation of the solution of a differential equation, where both the input variable and the unknown

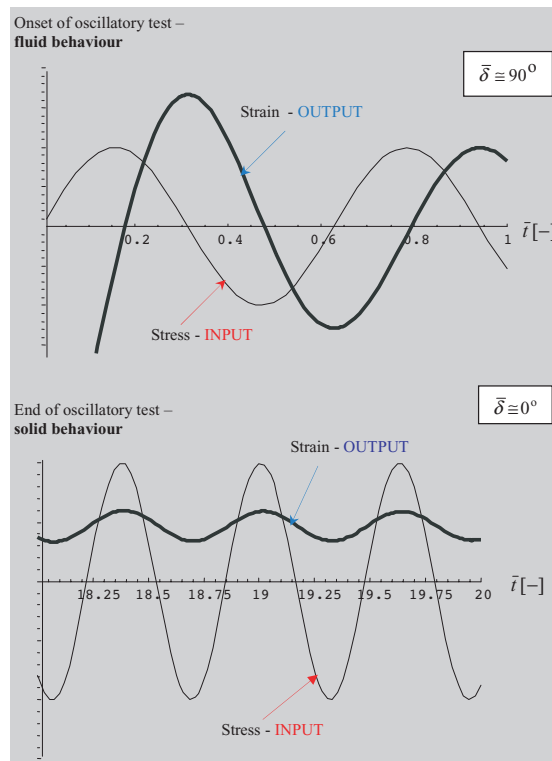
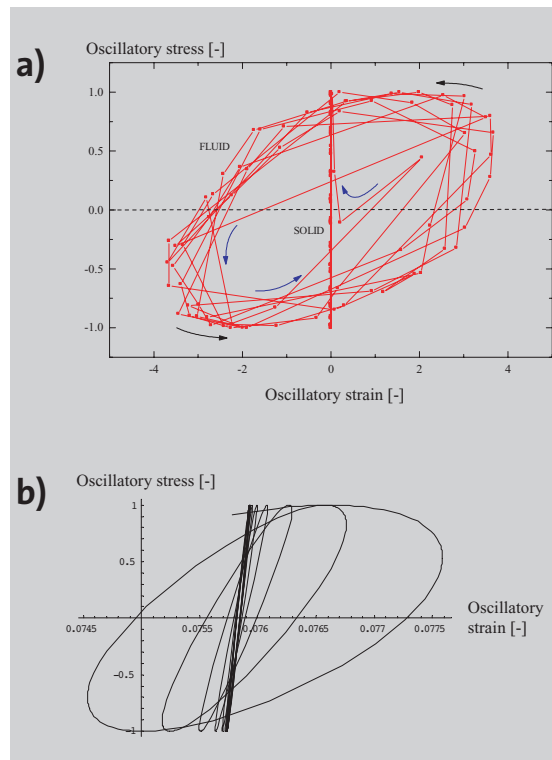


Figure 4 (left above): Numerical simulation of the creep test in sol - gel process: a) strain evolution in time; b) viscosity evolution in time (the instability region is remarked by the presence of inflexion points in the time variation of viscosity function, see also Fig. 2).

Figure 5 (right above): Direct simulation of constitutive Eq. 10 in oscillatory test (onset and end of the process).

Figure 6 (right below): Experimental and theoretical Lissajous figures: Oscillatory stress as function of oscillatory strain (with time parameter) associated with the dynamic test (sample S1).



output are oscillatory functions in time. At a constant frequency and amplitude of the oscillatory stress, the frequency and amplitude of the strain oscillation is changing in time, accordingly with the evolution of the reaction. Consequently, the Lissajous figure $\bar{\tau}(\gamma)$ is transforming from a circle ($\bar{\delta} \approx 90^\circ$, respectively $p = 0$) to an ellipse ($\bar{\delta} \approx 0^\circ$, respectively $p = 1$).

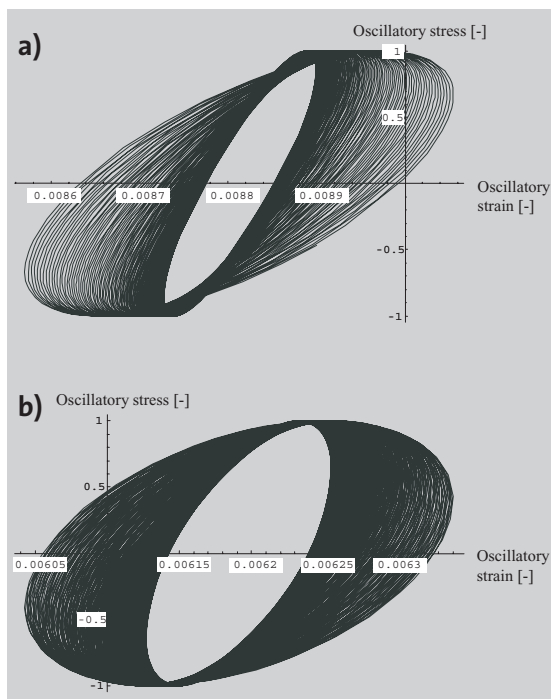
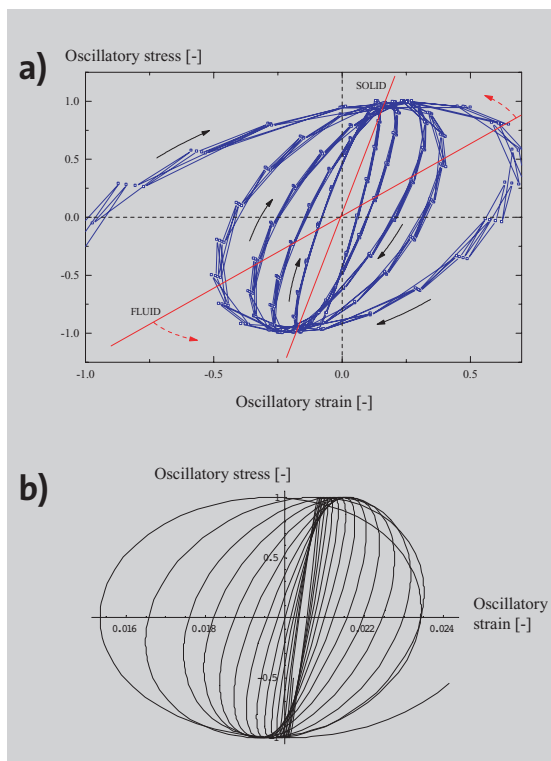
In Fig. 6 and Fig. 7 are compared the experiments with numerical simulation of the proposed model for the samples under investi-

Figure 7 (left above): Experimental and theoretical Lissajous figures: oscillatory stress as function of oscillatory strain (with time parameter) associated with the dynamic test (sample S2).

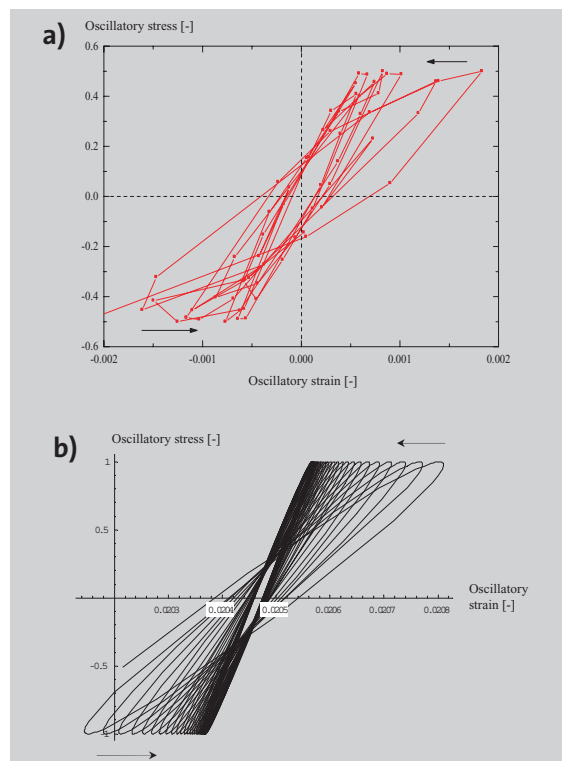
Figure 8 (right above): Experimental and theoretical Lissajous figures for sample S1: detail at small strain amplitudes.

Figure 9 (left below): Lissajous figures, oscillatory stress as function of oscillatory strain (with time parameter), associated with dynamic test; numerical simulation of Eq.10 with $\bar{\tau} = 1$: a) $\bar{\omega} = 10$; b) $\bar{\omega} = 50$.

Figure 10 (right below): Experimental non-dimensional Lissajous figure for sample S1 (It is observable the sharp rheological transition from “fluid” to “solid” like behaviour, see the associated Fig. 1).



gation. A detail for sample S1 at small strain amplitudes is shown in Fig. 8. The Fig. 9 represents the answer of the model at higher frequencies, beyond the frequencies used in the present experiments. As the gelation process is in progress, the Lissajous ellipse becomes more and more narrow, and finally the ellipse is degenerating in a line (which is associated with a solid rheological state). It is observed in Fig. 6 and Fig. 7 that transition from “fluid” to “solid” rheological behavior is more pronounced in sample S1 than in sample S2. This is more evident in the rep-



resentation of experimental Lissajous figures given in Fig. 10, respectively in Fig. 11.

4 CONCLUSIONS

The evolution of viscoelastic properties in sol-gel transition have been investigated in simple shear motions, oscillatory and creeping tests. The constitutive relation was built by analogy with the Jeffreys 3-constant model, based on the assumption that the viscosities and elasticity are time dependent accordingly with the solutions of Avrami’s equation. The consistency of the numerical simulations of the model with experiments proves the promising future of the proposed constitutive relation in modeling the phase transition phenomena.

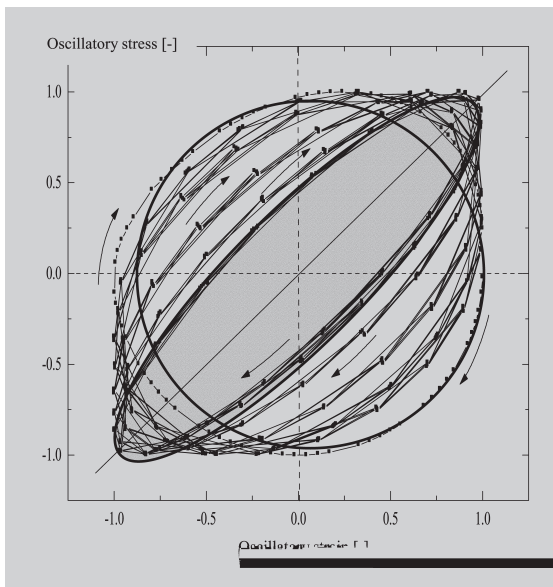


Figure 11: Experimental non-dimensional Lissajous figure for sample S2.

Structural characteristics and phenomenological properties define the sol - gel process. The correlation of the macroscopic changes during the liquid - solid transition with the evolution of chemical reaction is not completely understood and there is no comprehensive and complete model describing the change of viscoelastic properties. The main aim of our future research is to extend the rheological experimental investigations to the evolution of the normal stresses during gelation and to correlate the rheometry with a visualization technique of the growing network structure (Trappe et al. [23], Loren et al. [24]), and the evolution of diffusion coefficients (Romer et al. [25], Drabarek et al. [26]), respectively. We also intend to use other techniques like Small Angle X-ray Scattering to study structural changes in sol - gel transition and to correlate the results with the theoretical approach presented here, in order to gain a better understanding of liquid - solid transition in polymeric precursor in general, respectively to establish a correlation between the precursor properties and the structure of amorphous and crystalline ceramic, in particular.

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