

# A new interpretation for the dynamic behaviour of complex fluids at the sol–gel transition using the fractional calculus

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**Abstract** We propose to analyse power law shear stress relaxation modulus observed at the sol–gel transition (SGT) in many gelling systems in terms of fractional calculus. We show that the critical gel (gel at SGT) can be associated to a single fractional element and the gel in the post-SGT state to a fractional Kelvin–Voigt model. In this case, it is possible to give a physical interpretation to the fractional derivative order. It is associated to the power law exponent of the shear modulus related to the fractal dimension of the critical gel. A preliminary experimental application to silica alkoxide-based systems is given.

**Keywords** Stress relaxation · Small amplitude oscillatory shear · Fractional calculus · Gel · Power law

## Introduction

In recent years, much attention has been focused on the relationship between structure and dynamic properties of complex materials. In particular, relaxation processes in disordered systems have attracted much attention because the observed relaxation present some general characteristics which are independent of the studied materials and deviate from an exponential relaxation behaviour.

A shear stress power law relaxation with non-entire exponent over a wide time window has been observed by rheological investigations in critical gel near the sol–gel transition (SGT; Winter and Chambon 1986; Chambon and Winter 1987; Mours and Winter 1996), gelling Laponite clay suspensions (Cocard et al. 2000), micro-gels (English et al. 1999), polymers melts (Larson 1985), bio-polymer gel network (Rodd et al. 2001) and cross-linked actin networks (Tempel et al. 1996). Dynamic light scattering (DLS) in gelling solutions of polymers (Martin and Wilcoxon 1988; Martin et al. 1991) and X-ray scattering in colloidal aggregates (Schaefer and Keefer 1984), measurements also, show a power law relaxation of the dynamic structure factor. Diffusing wave spectroscopy was used to measure a power law frequency dependence in concentrated dispersed suspensions (Mason et al. 1997), in actin filament networks (Palmer et al. 1999) and critical power law behaviour in sol–gel transition of concentrated colloidal suspensions (Romer et al. 2000).

Power law behaviours are also observed at various levels of organisation in biological phenomena with different techniques: micro-rheology in living cells by magnetic twisting cytometry (Puig-de-Morales et al. 2001; Fabry et al. 2001), magnetic bead micro-rheometry (Bausch et al. 1998) and atomic force microscopy (Alcaraz et al. 2003). This frequency (or time) dependence of dynamic properties is difficult to describe with classical viscoelasticity. The behaviour of viscoelastic materials is intermediate between classical Hookean solids and Newtonian fluids. They show damping (or energy dissipation) properties for which the actual stress depend both on the actual strain and the entire strain history. Viscoelastic materials are said to possess memory. Classical viscoelastic models based

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on integer derivative operators are inadequate to describe such behaviour at least without a large number of material parameters (Ferry 1980).

On the contrary, fractional order parameters used in the viscoelastic constitutive laws allow reducing significantly the number of parameters and then to describe the material behaviour that conforms to a power law. The early observations of Nutting (1921) could be considered as the first step for the use of fractional calculus in modelling the stress relaxation phenomena by fractional powers of time in contrast with the usual stress relaxation described by decaying exponential function (Debye–Maxwell behaviour).

In 1936, Gemant (1936) observed that the properties of viscoelastic materials were proportional to fractional order of frequency. This author (Gemant 1938) then suggested to use fractional time derivatives to analyse these observations.

Later, Caputo and Mainardi used the concept of fractional calculus to describe the mechanical properties of metals and glasses (Caputo and Mainardi 1966) and viscoelastic solids (Caputo and Mainardi 1971). They first established a connection between fractional derivatives and the theory of linear viscoelasticity. It was only in the beginning of the 1980s that Bagley and Torvik (1983) gave a physical interpretation for this concept by linking molecular theory that described the viscoelastic properties of polymer solutions and polymer solids without cross-linking and fractional derivative relationships between stress and strain up to now used empirically to viscoelasticity.

Mechanical ladder models with springs and dashpots have been proposed to describe the relaxation patterns found during the sol–gel transition of chemical systems (Schiessel and Blumen 1995). However, the ladder arrangements with equal spring constants and viscosities lead to a constant value (1/2) of the exponent for the power law behaviour of the complex modulus. In order to take account for the dependence of this exponent on structural properties of the system, it is necessary to use infinite fractal network and numerical simulation to relate this exponent to a spectral dimension of the fractal. The connection between fractal rheological models and integrodifferential equations of fractional order has also been shown to describe the deformation mechanism of a polymer chain (Heymans and Bauwens 1994).

In this paper, we use the fractional calculus approach to express the power law relaxation modulus of both critical gel near the sol–gel transition and the gel state after the transition. Mechanical models based on fractional elements for viscoelastic gels are then given.

## Theoretical background

Exponential function named as Maxwell–Debye relaxation is classically used to describe relaxation processes with a characteristic time constant  $\lambda$  (Maxwell 1867):

$$f_{\text{MD}}(t) \sim \exp - (t/\lambda). \quad (1)$$

This exponential relaxation was observed for the correlation function of the light scattered from thermally excited density fluctuations in gels (Tanaka 1999). In this earlier work, only this so called gel mode was measured. Many more recent DLS measurements have shown power law relaxation after the gel mode (Martin et al. 1988, 1991; Lang and Burchard 1991; Ren et al. 1992).

Experimental data are then often fitted empirically by a stretched exponential or Kohlrausch–Williams–Watts function (KWS; Williams and Watts 1970)

$$f_{\text{KWS}}(t) \sim \exp - (t/\lambda)^\beta \quad 0 < \lambda < 1 \quad (2)$$

with  $\beta$  as an exponent inversely proportional to the width of the relaxation time distribution and  $\lambda$  as a time constant.

By supposing that  $f_{\text{KWS}}$  could be decomposed as a superposition of independent single relaxation states, the distribution of relaxation times can be obtained by means of inverse Laplace transformation (Alvarez et al. 1991). The application of KWS function to mechanical, enthalpic and dielectric relaxation of single crystals in both time and frequency domains was demonstrated (Cumbrera et al. 1993).

Berry and Plazek (1997) discussed the possibility to use KWS function in linear viscoelasticity. Continuous fluorescence lifetime distributions in biological tissues (collagen and elastin) were also shown well represented by stretched exponential decay function (Benny Lee et al. 2001). In this empirical fitting method, the function  $f_{\text{KWS}}$  is supposed to be decomposed as a superposition of single relaxation (discrete relaxation time distribution) and a large number of parameters are necessary to obtain a good fitting data.

Anomalous shear stress relaxation pattern is also observed near the sol–gel transition. During a SGT, the mechanical properties of the system evolve from a viscoelastic fluid before the gelation time  $t_g$  (sol state or pre-SGT state) toward a viscoelastic solid above  $t_g$  (gel state or post-SGT state). The relaxation pattern is strongly affected by the gelation kinetic extent  $p$  defined in polymeric systems by the ratio of the number of formed bonds by the total number available bonds. Near the gelation threshold, the system exhibits a drastic change in these viscoelastic properties: a strong

increase of the shear viscosity in the pre-SGT state near  $t_g$  and an onset of the elastic behaviour just after  $t_g$  in the post-SGT state. This transition is typical of polymer gelation phenomenology and is observed for organic and inorganic chemical gel (de Rosa and Winter 1994; Rosa et al. 1997; Hess et al. 1988; Koike et al. 1996; Mours and Winter 1996; Ponton et al. 1999; Venkataramann and Winter 1990; Vlassopoulos et al. 1998; Winter and Chambon 1986; Chambon and Winter 1987), physical gel (Chenite et al. 2001; Hsu and Jamieson 1993; Lin et al. 1991; Michon et al. 1993; Ming et al. 1997; Nijenhuis et al. 1989; Power et al. 1998; Richtering et al. 1992; Sato et al. 2000; Takenata et al. 2002) and colloidal gels (Cocard et al. 2000).

Based on rheological measurements on cross-linking polydimethylsiloxane with balanced (Winter and Chambon 1986) and imbalanced (Chambon and Winter 1987) stoichiometry, Winter and Chambon were the first to propose a new determination of the gelation time for network polymer near the SGT from the frequency independent ratio of loss modulus ( $G''$ ) by elastic modulus ( $G'$ ). This SGT study by mechanical spectroscopy represented a significant progress if it is recalled that until this work, the gelation time was determined by extrapolation of equilibrium quantities difficult to measure such as the low shear viscosity  $\eta_0$  or the equilibrium modulus  $G_e$  (Adam et al. 1985).

H. H. Winter proposed to define a new state of the matter at the gelation threshold ( $p = p_c$ ) named the critical gel state CG and characterised by a power law shear stress relaxation modulus:

$$G(t, p_c) = S_{p_c} t^{-\Delta_{p_c}} \text{ for } t > \lambda_0 \quad (3)$$

where  $S_{p_c}$  is the “strength” of the critical network so called the gel stiffness,  $\Delta_{p_c}$  is the relaxation exponent and  $\lambda_0$  is a lower cutoff time due to the glassy response or entanglement relaxation at small scales (de Rosa and Winter 1994). Only two material parameters are then necessary to completely characterise the linear viscoelastic properties of the CG at  $t_g$ . The possible limit values of  $\Delta_{p_c}$  lies between 0 and 1, respectively, associated to Hookean solid or Newtonian fluid-like behaviour.

The viscoelastic solid-like behaviour experimentally observed in the post-SGT state presents a shear stress relaxation modulus described by means of a power law time decay added to a non-zero shear equilibrium modulus  $G_{ep}$

$$G(t, p) = S_p t^{-\Delta_p} + G_{ep}. \quad (4)$$

All these power law shear stress relaxation patterns are not easily described by means of linear constitutive

equation of classic viscoelasticity that only contains integer derivative operators. An alternative is a combination of linear viscoelasticity and fractional order operator.

In the linear viscoelastic domain, it is generally assumed that the relation between the deformation and the stress tensors for a viscoelastic material with damping properties is described through the constitutive equation introduced by Boltzmann (Ferry 1980):

$$\sigma(p, t) = \int_{-\infty}^t G(t-t', p) \dot{\gamma}(t') dt' \quad (5)$$

where  $\sigma(p, t)$  is the extra tangential stress tensor,  $\dot{\gamma}$  is the rate of deformation tensor and  $G(p, t)$  is the shear relaxation modulus. It should be noted that in the case of a SGT, all these quantities depend on the extent of reaction  $p$ .

If a power law time decay shear relaxation modulus is introduced in Eq. 5, the constitutive equation is:

$$\sigma(p_c, t) = S_{p_c} \int_{-\infty}^t (t-t')^{-\Delta_{p_c}} \dot{\gamma}(t') dt'. \quad (6)$$

This integral named gel equation was initially proposed by Chambon and Winter (1987) and can be only solved numerically in the entire time derivative domain. On the contrary, analytical solution is found by using non-entire time derivative operator and fractional relation.

Starting from the Riemann–Liouville (RL) integral operator of order  $\Delta$ ,

$$D^{-\Delta} [f(t)] = \frac{1}{\Gamma(\Delta)} \int_0^t \frac{f(t')}{(t-t')^{1-\Delta}} dt' \quad (7)$$

Eq. 6 reads:

$$\begin{aligned} \sigma(p_c, t) &= S_{p_c} \Gamma(1 - \Delta_{p_c}) \frac{d^{\Delta_{p_c}-1} \dot{\gamma}(t)}{dt^{\Delta_{p_c}-1}} \\ &= S_{p_c} \Gamma(1 - \Delta_{p_c}) \frac{d^{\Delta_{p_c}-1} \gamma(t)}{dt^{\Delta_{p_c}}} \end{aligned} \quad (8)$$

where  $\Gamma$  is the complete Euler gamma function,  $\Delta$  is the fractional derivative order defined between 0 and 1 and the symbolic notation  $D^{-\Delta} f(t) \equiv \frac{d^{\Delta} f(t)}{dt^{\Delta}}$ .

The lower limit in the Boltzmann's equation is  $-\infty$ . We have supposed that the shear stress and the shear strain are equal to zero for negative time in order to use RL integral.<sup>1</sup>

A generalisation of Hooke's law

$$\sigma(p, t) = G_{ep} \frac{d^0 \gamma(t)}{dt^0} \quad (9)$$

<sup>1</sup>When the lower limit is  $-\infty$  in Eq. 7, the equation is named Weyl integral.

and Newton's law

$$\sigma(p, t) = \eta_p \frac{d^1 \gamma(t)}{dt^1} \quad (10)$$

where the constant elasticity  $G_{ep}$  and the shear viscosity  $\eta_p$  are associated to spring and dashpot that can be obtained by rewriting Eq. 8 as follows:

$$\sigma_{FE}(p, t) = \Lambda_{p_c, \Delta_{p_c}} \frac{d^{\Delta_{p_c}} \gamma(t)}{dt^{\Delta_{p_c}}} \quad (11)$$

with

$$\Lambda_{p_c, \Delta_{p_c}} = S_{p_c} \Gamma(1 - \Delta_{p_c}). \quad (12)$$

This stress–strain law (Eq. 11) is characteristic to a novel mechanical element named single fractional element (FE) or spring–pot intermediate between a purely elastic and viscous element. This new viscoelastic element is characterised by its fractional time dependence (derivative order— $\Delta_p$ ) and by a fractional physical property up to now not clearly identified ( $\Lambda_p$ ).

The resolution of the Fourier transform of Eq. 11 leads to:

$$G_{FE}(p, t) = \frac{\Lambda_{p, \Delta_p}}{\Gamma(1 - \Delta_p)} t^{-\Delta_p}. \quad (13)$$

A power law shear stress relaxation modulus can then be deduced from the single fractional element. The mechanical response of the post-SGT state is characterised by a power law kernel of relaxation added with an equilibrium quantities ( $G_{e, p > p_c} \neq 0$ ).

In the framework of fractional approach, this anomalous viscoelastic solid behaviour could be represented by the addition in parallel of a spring and a fractional element. This fractional Kelvin–Voigt (KVF) model is a generalisation of the standard Kelvin–Voigt model by replacing the dashpot by the fractional element. The conservation of the total stress leads to the following fractional shear–stress relationship:

$$\sigma_{KVF}(p, t) = \Lambda_{p, \Delta_p} \frac{d^{\Delta_p} \gamma(t)}{dt^{\Delta_p}} + G_{ep} \gamma(t) \quad (14)$$

The corresponding shear stress relaxation modulus is found by the resolution of the Fourier transform of Eq. 13:

$$G_{KVF}(p, t) = \frac{\Lambda_{p, \Delta_p}}{\Gamma(1 - \Delta_p)} t^{-\Delta_p} + G_{ep}. \quad (15)$$

The application of fractional element and fractional Kelvin–Voigt model to the description of the critical gel and the post-SGT state near a SGT transition will be discussed in the next paragraph.

## Discussion

The fractional parameter:  $\Delta$

The power law shear stress relaxation modulus observed for a critical gel (Eq. 3) is identical to the solution (Eq. 13) of the linear constitutive equation of viscoelasticity in the time domain fractal operator form (Eq. 11). The mechanical element associated to the critical gel is the spring pot. In the same manner, the fractional Kelvin–Voigt model gives a good description of the post-SGT state by identification of Eqs. 4 and 15.

The new viscoelastic parameter  $\Lambda_{p, \Delta_p}$  is then proportional to the gel stiffness (Eq. 12) which depends on several physicochemical parameters. A dimension analysis shows that the gel stiffness is composed of a modulus and a time constant. From experimental studies on end-linked polydimethylsiloxane, it was proposed (Scanlan and Winter 1991) the following relationship:

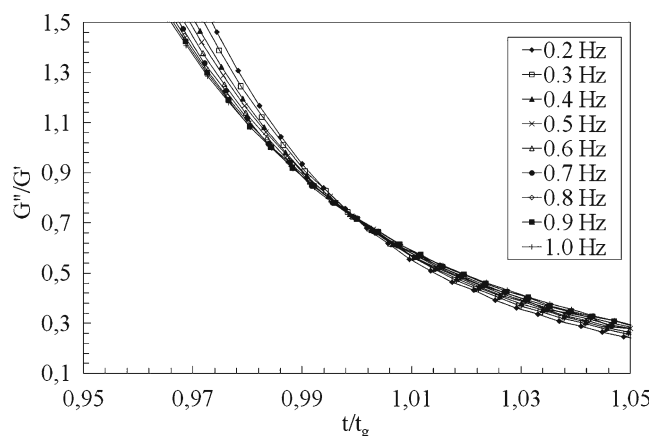
$$S = G_0 \lambda_0^\Delta \quad (16)$$

where  $G_0$  and  $\eta_0 = G_0 \lambda_0$  were very close to the modulus of the fully cross-linked material and the zero shear viscosity of the pre-polymer, respectively.

The gel stiffness at SGT was found to increase with the precursor molecular weight for polybutadiene (de Rosa and Winter 1994) and for polycaprolactone critical gels (Izuka et al. 1992). It has also strong concentration dependence for end-linked polydimethylsiloxane (Scanlan and Winter 1991), chemically cross-linked polyvinylalcohol (Kjoniksen and Nyström 1996) and gelatin (Hsu and Jamieson 1993). As the relaxation exponent (or the fractional derivative order), the gel stiffness is also defined in the post-SGT state.

In a previous study (Warlus et al. 2003), dynamic viscoelastic properties of silica alkoxide during the sol–gel transition have been analysed using an extended shear relaxation modulus expression with a functional form based on a product of power law and Debye–Maxwell relaxation kernels. The dynamic properties were probed by small amplitude oscillatory shear measurements in three viscoelastic domains (pre-SGT, SGT, post-SGT). An example of result of the reduced time evolution of the dynamic moduli around the SGT is given in Fig. 1.

Using analytical expressions for the storage  $G'$  and loss  $G''$  moduli in these three domains, the amplitude  $S_p$  and the critical exponent  $\Delta_p$  of the power law relaxation at the gelation time first introduced by Winter and Chambon are estimated in the pre- and post-SGT domains. It is then possible to deduce the reduced time evolution of the fractional parameter (Fig. 2) related



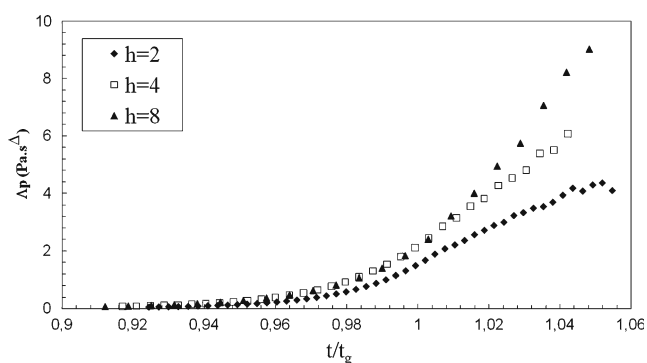
**Fig. 1** Variation of the ratio of loss moduli by the elastic moduli as a function of the reduced time ( $t/t_g$ ) for the different tested frequencies for silica alkoxide-based materials at the stoichiometric hydrolysis molar ratio  $h = 4$  (Warlus et al. 2003)

to the relaxation exponent  $\Delta_p$  and the gel stiffness  $S_p$  through Eq. 12.

These experimental set of data link the fractional formalism without evident physical support and the phenomenological description of the SGT parameter such as the gel stiffness. In the same way, the CG and the post-SGT state is also described by the time evolution of the relaxation exponent  $\Delta$ .

The fractional derivative order:  $\Delta$

The fractional derivative order is identical to the relaxation exponent introduced by Winter and Chambon (1986) and Chambon and Winter (1987). This parameter takes a peculiar value ( $\Delta_{pc} = 1/2$ ) for cross-linking



**Fig. 2** Variation of the fractional parameter ( $\Delta_p$ ) as a function of the reduced time ( $t/t_g$ ) for the different hydrolysis molar ratios  $h$

polymers with balanced stoichiometry. In general, many experimental studies have shown that  $\Delta_{pc}$  takes different values depending on molecular weight (Izuka et al. 1992), cross-linker concentration (Winter et al. 1988; Scanlan and Winter 1991), ratio functionality/molecular weight of the cross-linker (Tixier and Tordjeman 2003), concentration of cross-linkable polymer (Isuka et al. 1997; Kjoniksen and Nyström 1996) or concentration of the species which constitute the gel network (Power et al. 1998), thermal history (Michon et al. 1993) or temperature (Bu et al. 2004). Because of this dependence on structural properties of the critical gel, the relaxation exponent  $\Delta$  (or the fractional derivative order) is related to the connectivity of the network.

Many theoretical approaches have been proposed in order to predict the value of  $\Delta$ . Based on percolation model and assuming a single time scale for a single fractal object, Martin et al. (1988) derived a relation between  $\Delta$  and the critical exponents of the viscosity ( $k$ ) and the zero frequency elastic modulus ( $z$ ) near the sol-gel transition:

$$\Delta = z/(z + k). \quad (17)$$

Depending on the type of interactions between species which constitute the gel, several values of  $z$  and  $k$  are found. Flory (1942) developed methods for calculating the distribution of molecular sizes during the course of polycondensation of bi-functional monomers with tri- or tetra-functional branch points. An extension for chains of any length and branch units of any functionality was added by Stockmayer (1943). In this equilibrium, model bonds are randomly formed on an infinite Cayley tree or Bethe lattice neglecting the formation of loops within the growing clusters leading to  $z \sim 3$ , no divergence of the steady state viscosity ( $k = 0$ ) and therefore to  $\Delta \sim 1$ .

The analogy between mechanical properties of gels and electrical properties of random percolation networks predicts  $k = 0.75$  and  $z = 1.94$  (de Gennes 1979) leading to  $\Delta = 0.72$ . On the other hand, Adolf et al. (1990) have shown that the critical exponents describing the evolution of static structure near the sol-gel transition were found to be significantly different from the predictions of mean field theory. The authors (Martin et al. 1988) proposed a model based on length-scale dependent viscosity of percolating clusters with no hydrodynamic interactions and screened excluded volume effect. In three dimensions, the bounded value  $0 \leq k \leq 1.35$  and  $1 \leq z \leq 2.67$  give  $0.66 \leq \Delta \leq 1$ .

As stated above, many experimental values are found to be related to the polymer conformational



changes which are not taken account in the percolation model. de Arcangelis et al. (2002) proposed a minimal statistical-mechanics model based on the bond-fluctuation dynamics to study the viscoelastic behaviour of a polymer solution at SGT. Numerical simulations of the model, where randomly distributed monomers with a functionality  $f = 4$  are free to diffuse, are performed on two- and three-dimensional cubic lattices. From the diffusion properties of the clusters in the sol and independently from the distribution of relaxation times in the system, the value 1.3 has been found for the critical exponent  $k$ . For the critical behaviour of the zero frequency elastic modulus, the authors have calculated the mean square displacement of the centre of mass of the percolating cluster considered as a Brownian particle as a function of time and determined  $z \sim 2.6$  in  $d = 3$  and  $z \sim 2.7$  in  $d = 2$ . This model presents the advantage to propose the same approach for chemical and colloidal gels (Del Gado et al. 2003) for which power law shear stress relaxation modulus is observed.

Many small angle scattering investigations (neutrons SANS, X-ray, visible light) have shown that the growing clusters are not uniform objects but tenuous structures characterised by a power law molecular mass  $M$  in terms of radius  $R$  with an exponent  $d_f$  called the fractal Hausdorff dimension ( $M \sim R^{d_f}$ ).

With the help of these fractal concept, a relation for polydisperse polymeric fractals with full screening of excluded volume has been derived (Muthukumar 1989):

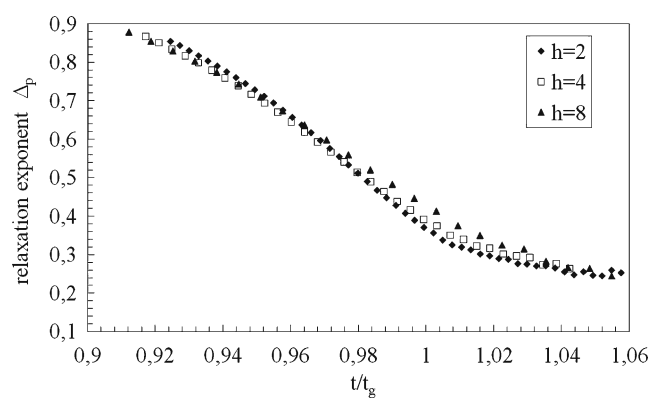
$$\Delta = d(d + 2 - 2d_f)/2(d + 2 - d_f) \quad (18)$$

where  $d = 3$  for a three-dimensional space.

The relaxation exponent (or the fractional derivative order) is not only defined in the CG state but also in the post-SGT state (see Eqs. 4 and 14). It is then possible to obtain this parameter at different stages of the SGT.

By using Eqs. 3 and 4, we have analysed our previous experimental data on viscoelastic properties of silica alkoxide-based systems during SGT (Warlus et al. 2003). We have then obtained a continuous evolution of relaxation exponent from the CG state to the post-SGT state with no significant dependence on the amount of water which is the initiator of the gelation process in the studied silica alkoxide-based materials (Fig. 3).

However, if a basic dimension analysis allow us to identify the so-called gel stiffness  $S_p$  with the fractional viscoelastic parameter  $\Lambda_{p,\Delta_p}$ , the understanding of the fractional derivative orders is not so easy in the post-SGT state. Indeed, the relation between the



**Fig. 3** Variation of the fractional derivative order  $\Delta_p$  as a function of the reduced time ( $t/t_g$ ) for different hydrolysis molar ratios  $h$

relaxation exponent and the fractal dimension (Eq. 18) is strictly valid at the sol–gel transition. The shear stress relaxation modulus of the post-SGT state (Eq. 15) is composed of two terms: a constant one corresponding to the equilibrium elasticity of the percolating network and a power law kernel describing the relaxation of fractal polymeric clusters not linked to the percolating network. By continuity, it seems reasonable to connect the relaxation exponent or the fractional derivative to geometrical features in the post-SGT state in the same manner as at the sol–gel transition.

## Conclusion

In this work, the anomalous shear stress relaxation pattern first highlighted by Chambon and Winter (1987) and predicted by the percolation theory for critical gel CG has been analysed in terms of fractional calculus by the introduction of a novel viscoelastic element: the spring pot. The power law time decay associated to the fractional viscoelastic element relaxation pattern is the exact phenomenological description of a CG shear relaxation modulus pattern displayed by a sol–gel system at the transition. Moreover, the unusual physical sense attribute to the pre-factor  $S_p$  so-called gel stiffness and to the relaxation exponent  $\Delta_p$  is then more clearly defined.  $S_p$  is defined through the fractional physical property  $\Lambda_p$  associated to spring pot as the constant elasticity  $G_{ep}$  and the viscosity  $\eta_p$  are respectively associated to the spring and dashpot. The relaxation exponent is identified to the fractional derivative order.

The shear stress power law associated to this new fractional viscoelastic element is obtained by the resolution of a fractional derivative equation intermediate

between the classical equations of Hooke's law and Newton's law allowing a theoretical description of the shear stress relaxation modulus pattern displayed by many systems at the sol–gel transition.

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