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Rheological investigation of the sol–gel transition: effect of hydrolysis variation in silicon oxide and titanium oxide based matrices

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The gelation of silicon oxide and titanium oxide based materials obtained from the sol–gel process at room temperature was studied through rheological measurements. The determination of the gelation time t_g was investigated by the variation of the storage and loss shear moduli as a function of time at several frequencies using Winter's criterion. The effect of hydrolysis ratio on gelation was studied for both materials. It was found that the decrease of the gelation time as a function of hydrolysis molar ratio is well described by a power law with different exponent values for the two systems. Moreover a fractal dimension at the gelation time can be deduced from the rheological measurements due to the structural self-similarity of the sol–gel matrices. This fractal dimension d_f seems to be independent of the hydrolysis molar ratio for each system. The higher value of d_f for silicon oxide based gels shows that they possess a more dense structure than titanium oxide based gels.

Introduction

The sol–gel process has been developed over the last two decades leading to new materials in various areas.[1,2]

A great variety of inorganic networks from silicon or metal alkoxide monomer precursors can be produced through this process at low temperature, as opposed to the much higher melting temperatures required in the production of conventional inorganic glasses. Consequently homogeneous inorganic oxide materials with desirable properties of hardness, optical transparency, tailored porosity and thermal resistance can be obtained.

Because of the room temperature process, the entrapment of organic molecules associated with optical transparency within the matrices provides optical properties (fluorescence, laser emission, photochromism, non-linear optics) which are very suitable in sol–gel optics.[3]

In the field of biotechnology, it has been shown that enzymes can be encapsulated within silicon oxide matrices.[4] The trapped biomolecules retain their biological activity and are protected against denaturation. The encapsulation can be extended to a wide range of biological species such as antibodies, proteins, whole cells.[5]

The versatility of this process allows various shapings of sol–gel matrices (monoliths, films, fibers and monosized powders[2]) for which the knowledge of the rheological properties such as viscosity and/or gelation time is essential. For example the deposition of ridge waveguides on silicon using photosensitive sol–gel derived glasses requires the measurement of the viscosity which must be low enough to allow embossing.[6]

Based on inorganic polymerization of molecular precursors, the sol–gel process involves the evolution of a polymer from a colloidal suspension (sol) to the formation of a network enclosing a continuous liquid phase (gel).

The molecular precursors used in the sol–gel process are essentially alkoxide $M(OR)_z$, where M is silicon or a transition metal, R is an alkyl group and z is the oxidation number of M.

The polymerization occurs in two steps. The first one is a hydrolysis reaction which creates the reactive group M–OH:

$$\text{M–OR} + \text{H}_2\text{O} \rightleftharpoons \text{M–OH} + \text{R–OH} \qquad (1)$$

The second one is a condensation reaction leading to the formation of oxo-bridges M–O–M with water or alcohol as by-products:

$$\text{M–OH} + \text{M–OH} \rightleftharpoons \text{M–O–M} + \text{H}_2\text{O} \qquad (2a)$$

$$\text{M–OH} + \text{M–OR} \rightleftharpoons \text{M–O–M} + \text{R–OH} \qquad (2b)$$

It has been shown[7] that hydrolysis and condensation reactions occur in the first few minutes after the addition of water and then slow down. Moreover the consumption of water is never complete.

The reactivity of alkoxide ($M(OR)_z$) strongly depends on the nature of M. Two molecular precursors are used in this study: $Si(OCH_3)_4$ and $Ti(OBu^n)_4$. In the case of the silicon oxide precursor, the coordination of silicon is equal to its oxidation number ($z = 4$). Therefore silicon alkoxides are not very reactive. The gelation time can be several days or weeks. It is then necessary to accelerate the polymerization by the use of catalysts. The hydrolysis reaction is promoted by acid catalysis while the condensation reaction is favoured by basic catalysis.[8]

It should be noted that the catalyst not only has a kinetic effect on the hydrolysis and condensation reactions but also modifies the network structure. In acidic conditions, low branched species are formed leading to opened structures. In contrast, high branched species with more compact structures are produced under basic conditions.[9] The silicon oxide gelation process will depend on the catalyst nature and the amount of added water.

In the case of the titanium alkoxide precursor, the titanium metal tends to increase its coordination to reach the oxide coordination. Titanium alkoxides are very reactive and direct hydrolysis leads to the formation of precipitates. In order to

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avoid precipitation, the hydrolysis and condensation reactions must be slowed. Hydroxylated complexing ligands can be added to titanium precursors.[10] For example, acetylacetone (acacH) is a strong chelating ligand which replaces the very easily hydrolysable OR group. It should be noted that the acetylacetone ligand does not participate in the network formation but only reduces the number of active sites for condensation reactions. The amount of water and/or acetylacetone allows chemical control of the gelation process.

The silicon oxide based gels were synthesized under basic conditions with a nucleophilic activator (dimethylaminopyridine, DMAP). Acetylacetone (acacH) was used to control the inorganic polymerization of titanium alkoxide.

The sol–gel transition is characterized by an abrupt change of the steady state mechanical properties. For instance the shear viscosity increases and the modulus of the fully crosslinked material grows with time from the gelation time. The measurement of these two parameters is difficult in steady state conditions. An alternative approach is to measure the small amplitude oscillatory behaviour of the material.[11] Indeed the strains in oscillatory measurements are very small compared to steady shear measurements and are considered to preserve the weak structure of the gel.

The objective of this paper is to investigate by a rheological analysis the effect of the hydrolysis molar ratio on the gelation time of titanium butoxide and silicon methoxide.

Theoretical

Chambon and Winter[12] suggested a basic equation for the stress in crosslinking polymers at their transition from the liquid to the solid state leading to a new mechanical definition of the sol–gel transition. Because of the self-similarity of the rheological behaviour of the gel, the relaxation time spectrum is also self-similar and the time evolution of the complex modulus is:

$$G(t)=St^{-\Delta} \qquad t>\lambda_c \tag{3}$$

The gel strength S depends on the molecular structure of the gel. The relaxation exponent Δ depends in general on several parameters (stoichiometry, composition, *etc.*) and ranges between 0 and 1. λ_c is the lower cutoff of the self-similarity on very small distance scales.[13]

The frequency dependence of the elastic G' and viscous G'' moduli is then characterized by a power law in the linear response domain:

$$G'(\omega)\sim G''(\omega)\sim\omega^{\Delta} \qquad \omega<1/\lambda_c \tag{4}$$

It can be shown with eqn. (4) and the Kramers–Kronig relation that the ratio G''/G' is independent of frequency at the gelation time:

$$G''/G'=\tan(\Delta\pi/2) \tag{5}$$

As a consequence, the gelation time t_g is determined by the intersection of the curves G''/G' *versus* time at several frequencies.

Because of the structural self-similarity, the relaxation exponent Δ can be related to a cluster fractal dimension. Indeed, the theory of gelation describes the cluster growth process and the cluster radius R_H is expected to behave as follows:

$$R_H\sim M^{1/d_f} \tag{6}$$

with M the mass of the cluster and d_f the fractal dimension.

An expression for the relaxation exponent in terms of the fractal dimension has been derived. In the case where the excluded volume is screened, the expression is:

$$d_f=(d+2)(2\Delta-d)/2(\Delta-d) \tag{7}$$

where d is the space dimension.[14]

The d_f values can also be compared to the theoretical ones obtained by numerical simulations.

Experimental

Sample preparation

Due to the difference of reactivity of the titanium and silicon precursors, the preparations of both gels were different so as to obtain the same range of gelation times.

Titanium oxide based gels were prepared using titanium butoxide $Ti(OBu^n)_4$, n-butanol, and de-ionized water. Acetylacetone (acacH) diluted in n-butanol was added dropwise to a solution of $Ti(OBu^n)_4$/n-butanol at a constant complexation molar ratio $a=[acacH]/[Ti]=0.35$. Hydrolysis was then performed by the addition of a solution of water/n-butanol (19 wt% of water). The parent alcohol was used in order to avoid alcohol exchange. In all samples the concentration of titanium was kept constant to 0.47 mol L^{-1}.

Tetramethylorthosilicate (TMOS), methanol, de-ionized water and a nucleophilic activator (DMAP) were used for silicon oxide based gels under basic conditions. Methanol and water were added successively to a solution of TMOS and DMAP. The molar ratio [DMAP]/[TMOS] was fixed to 0.003 with a silicon concentration of 1.6 mol L^{-1}.

It should be noted that silicon oxide based gels remain transparent even for times much longer than the gelation time. In contrast, titanium oxide based gels could become opalescent depending on the complexation and hydrolysis molar ratios.

For both systems the hydrolysis molar ratio $h=[H_2O]/[M]$ (with $[M]=[Ti]$ or $[M]=[Si]$) was varied from 8 to 12.

Experimental procedure

Oscillatory shear measurements were carried out with a rheometer Haake RS 150 working in the constant shear stress mode. The used geometry was a double cylinder cell topped with a trap in order to avoid solvent evaporation. This sensor was very suitable for low viscous fluids (viscosity lower than 1000 Pa s) and then to obtain information from the sol state to the gel state.

The determination of the elastic G' and viscous G'' moduli was performed by successive frequency sweeps at seven frequencies between 0.55 and 10 Hz followed by a rest time (30 s). The amplitude of the applied stress was fixed to 0.04 Pa in the linear viscoelastic domain.

The temperature, controlled by water circulation from a thermostatted bath, was maintained constant at 20.0 ± 0.2 °C.

Results and discussion

Gelation time

Fig. 1 shows the evolution of G''/G' as a function of time at different frequencies for a titanium oxide based gel ($a=0.35$, $h=12$). The gelation time ($t_g=675$ s) is defined by the intersection of the different curves as mentioned in the theoretical section. The same type of curve is observed for all silicon oxide and titanium oxide based samples and t_g values were obtained in the same way. Before the gel point ($t<t_g$), the ratio G''/G' is higher than unity for almost all frequencies which indicates a more viscous behaviour. After the gel point, ($t>t_g$), G''/G' is lower than unity characteristic of a predominant elastic behaviour as the network grows.

The values of the gelation times as a function of hydrolysis molar ratio for both systems are given in Table 1.

For both systems, t_g decreases as h increases. However the hydrolysis dependence of t_g is well described by a power law

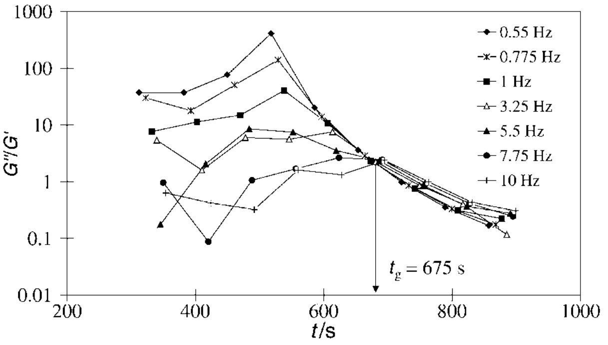

Fig. 1 Evolution of G''/G' with time at several frequencies for a titanium oxide based gel (titanium concentration $[\mathrm{Ti}] = 0.47\ \mathrm{mol\ L^{-1}}$, complexation molar ratio $a = 0.35$, hydrolysis molar ratio $h = 12$).

Table 1 Values of gelation time t_g as a function of hydrolysis molar ratio h for titanium oxide and silicon oxide based systems

h	8	9	10	11	12
t_g Si/s	1980	1720	1530	1300	1190
t_g Ti/s	6400	2830	1870	1435	675

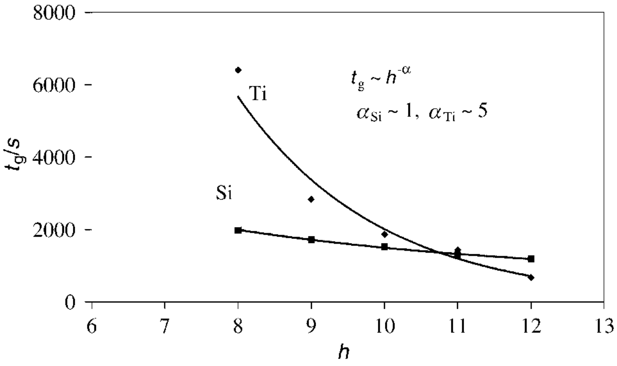

Fig. 2 Dependence of the gelation time t_g on the hydrolysis molar ratio h for titaniaum oxide and silicon oxide based systems.

($t_g \sim h^{-\alpha}$) with $\alpha \sim 1$ for silicon oxide and $\alpha \sim 5$ for titanium oxide based gels as shown in Fig. 2. In the investigated range of high hydrolysis molar ratio, the gelation time varies only a little for silicon, in contrast to titanium. In fact, measurements performed for lower hydrolysis molar ratios ($2 < h < 8$) have shown that this study corresponds to the final linear part of a power law which is also observed for silicon oxide with the same exponent ($\alpha \sim 1$). In the case of titanium oxide systems the same lower hydrolysis molar ratios were not investigated because only sols are formed.[7]

These results can be explained by the different reactivity of the two systems. In the case of silicon oxide based gels with a basic catalyst, hydrolysis is the limiting reaction. All samples have a high hydrolysis molar ratio and a simple kinetic effect can be assumed. For titanium oxide based gels, the addition of acacH to titanium oxide reduces the titanium reactivity. However the molar ratio [acacH]/[Ti] is less than unity in our samples, limiting this effect. Consequently the function of water is twofold: the formation of hydrolyzed groups (Ti–OH) and the increase of the titanium coordination by the creation of oxo bridges (Ti–O–Ti) leading to the network growth.

Evolution of moduli during the gelation process

The variation of log G' *versus* time for both systems at different hydrolysis molar ratios and the smallest studied frequency (0.55 Hz) is shown in Fig. 3 and 4.

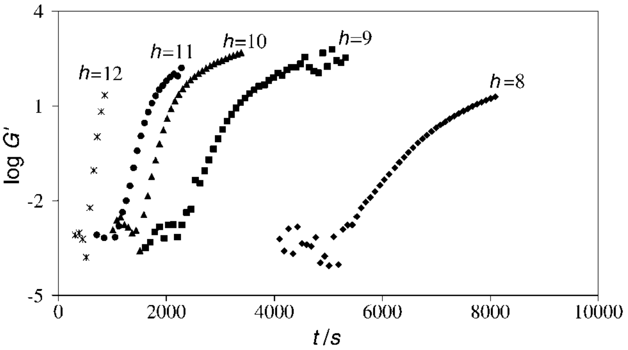

Fig. 3 Evolution of elastic modulus G' with time at different hydrolysis molar ratios ($8 < h < 12$) for the titanium oxide based system (titanium concentration $[\mathrm{Ti}] = 0.47\ \mathrm{mol\ L^{-1}}$, complexation molar ratio $a = 0.35$).

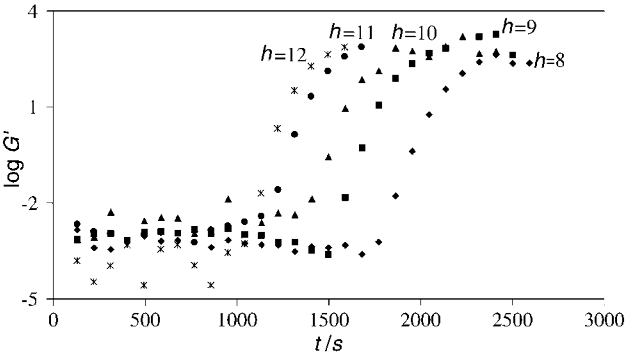

Fig. 4 Evolution of elastic modulus G' with time at different hydrolysis molar ratios ($8 < h < 12$) for the silicon oxide based system (silicon concentration $[\mathrm{Si}] = 1.6\ \mathrm{mol\ L^{-1}}$).

All the curves present three domains: low and nearly constant values of log G' ($G' \sim 1$ mPa) corresponding to the sol state, a sharp increase around the gelation time and a last domain with a tendency to a plateau value of log G'. The sharp increase of G' from 1 mPa to 100 Pa observed on each curve is linked to the gelation process.

It is clearly observed, especially for the titanium oxide based gels, that the slope of the curve in the second domain increases as the hydrolysis molar ratio increases. This result could be explained by the effect of the hydrolysis molar ratio on the gelation kinetics. In order to verify if another effect could be involved, it is suitable to use a reduced time variable t/t_g instead of time t to follow the evolution of the elastic modulus. The results are shown in Fig. 5 for both systems. A master curve is obtained for each system. Therefore the variation of the hydolysis molar ratio ($8 < h < 12$) has an effect on the gelation time but not on the evolution of the elasticity. Nevertheless the slope of the master curve near the sol–gel transition ($t/t_g \sim 1$) and the plateau value of G' are higher for silicon oxide based gels than for titanium oxide based gels.

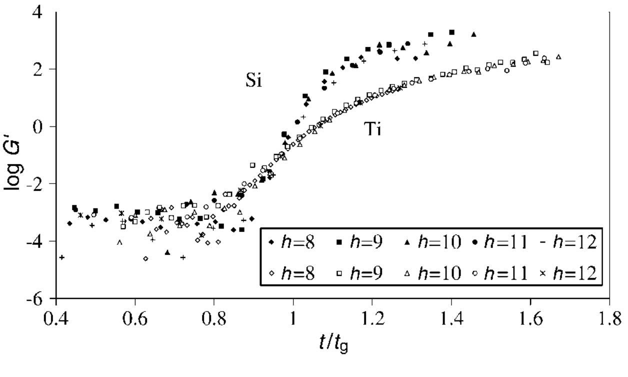

Fig. 5 Evolution of elastic modulus G' with reduced time t/t_g for titanium oxide (open symbols) and silicon oxide based (filled symbols) systems.

Moreover the behaviour near the sol–gel transition gives further information on the structure of the two systems as described in the next section.

Behaviour at gelation time

For titanium oxide based systems, the elastic modulus G' for the lowest studied frequency (0.55 Hz) at the gelation time (ranging from 100 mPa to 390 mPa) is always lower than the viscous modulus G'' (from 340 mPa to 540 mPa). In contrast, for silicon oxide based systems G' (from 1200 mPa to 5300 mPa) is greater than G'' (from 980 mPa to 3100 mPa).

Silicon oxide based gels are then more elastic than viscous, in contrast to titanium oxide based gels. This could be explained by the different structures of the systems. More precisely the use in titanium oxide based gels of acacH, which decreases the number of active sites for the condensation reactions, leads to a decrease of the network elasticity.

This difference of structure can be evaluated by the determination of the fractal dimension.

In fact, structural information near the sol–gel transition is obtained from the relaxation exponent Δ and the fractal dimension d_f as described in the theoretical section. These two parameters are computed for each frequency from eqn. 5 and 7 and the mean values $\langle d_f \rangle$ are given in Table 2 as a function of the hydrolysis molar ratio.

The fractal dimension $\langle d_f \rangle$ is nearly constant for each system as h is varied ($8 < h < 12$). Consequently the hydrolysis molar ratio seems to have no effect on the gel structure in the investigated range of h.

This result is in good agreement with the master curve for the evolution of elasticity with time for these different hydrolysis molar ratios (Fig. 5).

However the fractal dimensions for the titanium oxide and silicon oxide based gels are different for a given hydrolysis molar ratio. The value obtained for titanium oxide based gels ($\langle d_f \rangle = 1.74$) is lower than the one for silicon oxide based gels ($\langle d_f \rangle = 2.02$) showing that the titanium network is less dense than the silicon network. Indeed, the presence of Ti complexed acacH inhibits the condensation process and leads to a more open gel structure. Moreover the titanium concentration is higher than the silicon concentration.

In the case of silicon oxide based systems, Jokinen *et al.*[15] have found from rheological measurements a fractal dimension $d_f = 2.06$ for a gel coagulated from a basic sol by adding a salt ($NaNO_3$). This value is very close to our value for silicon oxide based gel also synthesized in basic conditions.

Several theories have been proposed to describe the changes in properties that occur during the sol–gel transition. For example percolation theory predicts the critical behavior of several properties (shear viscosity, shear modulus, *etc.*) but does not take into account the kinetics of gelation. Thus kinetic theories have been developed to describe the sol–gel process for which the hydrolysis and condensation reactions lead to the growth of clusters that collide and link together into a three dimensional network.

The aggregation between clusters can occur under diffusion or reaction limited conditions.[15] Under diffusion limited cluster–cluster aggregation (DLCCA), clusters stick irreversibly on first contact and predominate when no barrier exists. The predicted fractal dimension is $d_{f,DLCCA} = 1.8$. Under reaction limited cluster–cluster aggregation (RLCCA) the sticking probability is less than unity. Many collisions are required to form contacts between clusters. These later may interpenetrate and the resulting clusters are more compact with a higher fractal dimension ($d_{f,RLCCA} = 1.98$ for monodispersed clusters and $d_{f,RLCCA} = 2.11$ for polydispersed clusters).

Table 2 Values of fractal dimensions $\langle d_f \rangle$ determined at gelation time as a function of hydrolysis molar ratio h for the titanium oxide and silicon oxide based systems

h	8	9	10	11	12
$\langle d_f \rangle$ Si	1.96	2.07	1.94	2.05	2.09
$\langle d_f \rangle$ Ti	1.73	1.78	1.85	1.74	1.73

In this study reaction limitations should be dominant because of the relatively high concentrations of the samples ($[Si] = 1.6\ mol\ L^{-1}$). The good agreement between the experimental fractal dimension ($\langle d_f \rangle = 2.02$) and $d_{f,RLCCA} = 1.98$ corroborates this assumption.

To our knowledge, there has been no study on the determination of fractal dimensions from rheological measurements for titanium oxide based systems. However Blanchard *et al.*[16] have studied the effect of hydrolysis molar ratio on the structure of titanium oxopolymers in the presence of acetylacetone. SAXS experiments performed on different systems ($[Ti] = 0.4\ mol\ L^{-1}$, $a = 0.4$, $6 < h < 10$) show a nearly constant fractal dimension around 2.4. This value is higher than our value obtained by rheology. This difference could be explained by the time at which the measurements were performed. Rheological measurements give a fractal dimension at $t \sim t_g$. In contrast, the SAXS fractal dimensions are obtained at $t \gg t_g$ for which the gels are aged and do not evolve any more. It could be then assumed that the gels formed at $t \sim t_g$ would become more dense during aging.

Conclusion

A rheological study of the sol–gel transition of titanium oxide and silicon oxide based materials has been presented in this paper.

These two molecular precursors have different reactivities and need two types of synthesis. A nucleophilic activator (DMAP) was used for the silicon oxide based system because of its low reactivity. In contrast, the high reactivity of the titanium oxide based system was reduced by the addition of a chemical inhibitor (acetylacetone, acacH).

However the two systems were studied at the same temperature ($T = 20\ °C$) and for the same range of hydrolysis molar ratios ($8 < h < 12$).

The gelation times t_g were determined from the variation of G' and G'' *versus* time at several frequencies according to Winter's criterion. The variation of t_g as a function of hydrolysis molar ratio is well described by a power law with an exponent higher for the titanium oxide based system than for the silicon oxide based system in the studied range of hydrolysis molar ratios.

A master curve for the evolution of the elastic modulus as a function of the reduced time t/t_g was found. This result shows that the hydrolysis molar ratio only has an effect on the gelation process. However the master curve does not superimpose for the two systems. This could be explained by the different structures of the silicon oxide and titanium oxide based matrices.

Finally, fractal dimensions were estimated near the sol–gel transition giving some information on the gel structure. The fractal dimension was found to be independent of the hydrolysis molar ratio for each system ($d_f \sim 2.02$ for silicon oxide and $d_f \sim 1.74$ for titanium oxide). The lower values for the titanium oxide based system indicate a more open structure than that of the silicon oxide based system.

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