Preparation of Low Density Water Glass Based Silica Gels by Conventional Drying

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(Received September 23, 1998)

To reduce shrinkage and the possibility of fracture during ambient pressure drying, it is of great importance to increase the strength and stiffness of the wet gels. In this paper is presented the strengthening and stiffening of wet silica gels prepared from sodium silicate (water glass) as well as properties of the corresponding xerogels. By washing gels containing different initial silica contents in water solutions at elevated pH, a maximum in shear modulus of ~4 MPa was obtained. The maximum stiffness enabled xerogels with bulk density of 0.28 g/cm^3 to be made regardless of silica content and washing conditions. However, by aging the wet gels in a solution providing fresh monomers to the gel network, a shear modulus of 20 MPa was obtained after 27 h. By this method monolithic xerogels with a density down to ~0.2 g/cm^3 was prepared. The results are compared to alkoxide based gels.

Key words: Silica gel, Drying, Water glass

I. Introduction

Supercritical drying which is the normal preparation route for aerogels gives high quality materials and very low density, however the process is risky and costly. A cheaper, simpler, and safer process is obtained by drying at ambient pressure (subcritical drying), giving a xerogel. However, during drying of a gel under ambient pressure evaporation, capillary pressure causes shrinkage of the gel network and cracking frequently occurs. Since shrinkage is resisted by the bulk modulus of the wet gel,[1] it is of importance to reduce the capillary pressure and to increase the stiffness and strength of the wet gel.

The chemical reactions that are responsible for gelation, continue after the gel point causing stiffening, strengthening and sometimes shrinkage of the gel network.[2] Hence, after gel formation, the properties of the wet gel can be altered by washing or aging the gel either in mother liquor or in another liquid. A number of papers show how the properties including the mechanical strength and stiffness of the wet gel are changed by performing a washing or aging procedure.[3-18] During this step, strength and stiffness of the wet gel increase due to (a) an increased degree of condensation reactions,[9] (b) dissolution and reprecipitation of silica from the primary particle surfaces onto the points of contact,[8,10,13,14] (c) dissolution of silica from the smaller particles and precipitation onto the larger ones[8] and/or (d) attachment of unreacted oligomers from the gelation process[3] or addition of new monomers after the original gel formation.[7,15-19] The changes in the wet gel structure and properties have a profound effect on the subsequent drying process, *i.e.* reduc-

ing cracking and shrinkage.

To further enhance the strength and stiffness of wet gels, we have previously introduced an efficient step by aging the gels in a silane (*i.e.* tetraethoxysilane (TEOS)) solution.[7,15-19] New monomers are added to the already formed network and hydrolysis, polycondensation, and specific precipitation of these monomers favorably increase the strength and stiffness of the wet gel without increasing the pore size drastically. The increase in stiffness eliminates the shrinkage during drying especially when using a low surface tension liquid (*i.e.* n-heptane), and light xerogels are obtained.

The present work places emphases on strengthening and stiffening of wet gels prepared from water glass (water soluble sodium silicate) which is a cheap precursor for low density silica gels. The effect of washing wet gels with different silica content in water solutions at different pH is investigated along with the effect of increasing the initial density of the gels by aging in a TEOS solution. An analysis of the properties of the wet gels as well as the corresponding xerogels is given. A comparison to alkoxide based gels is also given.

II. Experimental

The TEOS based gels were prepared by a 2-step process previously described by Brinker *et al.*[20] The gels were cast into Teflon® tubes with an inner diameter of 8.6 mm and kept at 40°C for 1 h for gelation. After gelation, one part of the gels were soaked in a solution of 20 vol% water/ethanol at either pH=7.0 or 9.0 (pH adjusted by adding NH$_4$OH) for different time intervals at 50, 60 and

70°C. The other part of the gels were aged in a water solution at pH=9.0 at 50, 60 and 70°C for different times.

For preparation of sodium silicate (water glass) based gels, water glass (Akzo, PQ, $SiO_2:Na_2O=3.4$) with silica content of 13 or 18.3 wt% was exchanged using an ion exchanger (Amberlite IR-120, pH 2.3). To avoid air bubbles, the sol was placed in an ultrasonic bath several minutes before adding 1 M NH_4OH until pH reached 4.6. The gels were cast into Teflon® tubes and kept at 50°C for 1 h for gelation. After the gel formation, the gels with different silica content were soaked in a water solution at either pH=8.0 or 9.0 for 6, 12 or 24 h at 70°C. Following the first soaking, these gels were soaked again in a solution of 20 vol% water/ethanol for 24 h at 60°C to avoid cracking of the gels during the subsequent procedure. For comparison some of the gels with the lowest silica content were soaked in a washing solution of 20 vol% water/ethanol for 24 h at 60°C to increase the water content in the pore liquid[17] followed by aging in a solution of 70 vol% TEOS/ethanol for various durations (6, 13, 18, 24 and 27 h) at 70°C. By this procedure the initial density of the gels was increased.

The following treatment of all the gels consisted of washing 4 times in ethanol within 24 h at 50°C before measurement of mechanical properties. The modulus of rupture, MOR, was determined by using a three-point beam bending apparatus (ASTM C674-81). Load-relaxation experiments were done as described by Scherer[21] to measure the shear modulus, G, as well as the permeability, D.

Samples were washed in n-heptane 4 times within 24 h at 50°C before drying at ambient pressure. During the drying performed in 24 h intervals at 90, 120 and 180°C, the gels were partly covered. The xerogel densities were calculated from the mass and the volume of the samples. The initial density was calculated from the volume of the wet gel and the gravimetric measurements of the dried gel and is the bulk density of the gel if there was no shrinkage during drying. The linear shrinkage during drying was calculated from the diameter of the wet gel rod after aging and after drying, respectively.

III. Results and Discussion

When a silica gel is soaked in a solution where silica is partly soluble, silica will be transported from the surface of the particles onto the necks between them due to the difference in chemical potential. Both the modulus and the stiffness of the gel depend on the load-bearing fraction of the cross-sectional area between the particles[2] and is therefore dependent on the particle size, particle size distribution, particle-particle bonding (contact area) and the spatial particle arrangement. Hence, the transport of silica will increase the strength and stiffness of the gel network as the contact area between the particles is increasing. However, at the same time, if the particle size
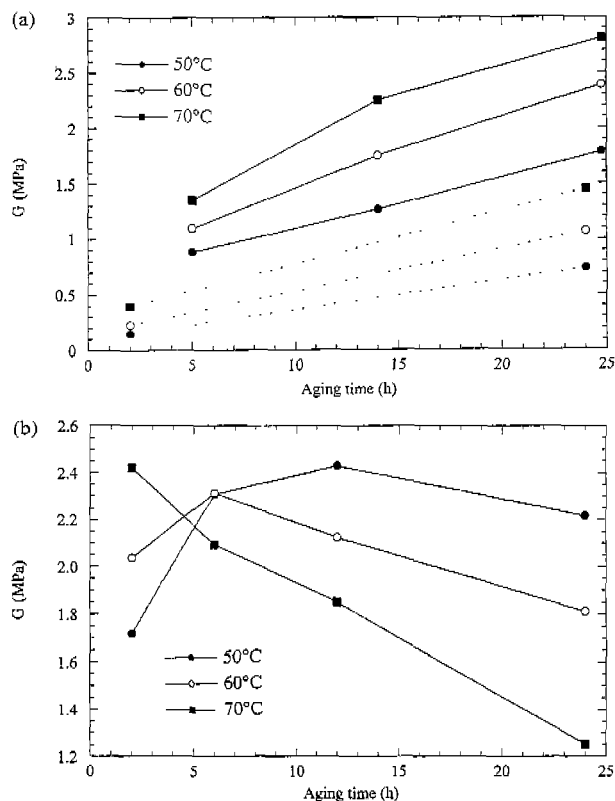

Fig. 1. G modulus of TEOS-based gels aged in a) 20 vol% water/ethanol solution at pH=7.0 (broken lines) and 9.0 (solid lines) for 50, 60 and 70°C and b) water solution at pH=9.0 at 50 (filled circles), 60 (open circles) and 70°C (filled squares) as a function of time. The uncertainty in G modulus is ±0.08 MPa.

of the gel network is not homogeneous, there will be a dissolution of the smaller particles in the gel network and growth of the larger ones, i.e. Ostwald ripening. This process might lead to a reduction of both the modulus and stiffness of the gel network as the number of contact points between the particles is reduced and the particle size is increased. Such a behavior has previously been observed by Hæreid et al.[8] by washing tetramethoxysilane (TMOS) based gels in water. Hence, there will be a competition between the strengthening and a weakening of the gel network depending on the washing parameters like pH, water content and temperature as well as particle size and distribution of the gel network.

To study the washing conditions which increase/decrease the modulus and stiffness of the wet gels, the first part of this paper is dealing with the change in strength and stiffness of 2-step TEOS based gels during washing in water solutions at different pH, temperatures, and time intervals. Fig. 1. A displays the increase in G modulus of the displays TEOS based gels as a function of aging time in 20 vol% water/ethanol solution at pH=7.0 and 9.0 at three different temperatures. It is evident that there is an increase in G modulus with increasing pH, time, and temperature which can be attributed to a solution/precipitation

process where silica is transferred from the surface of the particles to the necks between them. The silica solubility is likely to increase by increasing pH and temperature.[2] In Fig. 1b, the TEOS based gels are washed in water solution at pH=9.0 for three different temperatures and it is clear that the G modulus of the gels are first increased and then decreased as the washing time is increased. The time where the maximum G modulus is obtained, is decreasing with increasing temperature, and for the gels washed at 70 °C the maximum can be obtained within less than 2 h of washing. Hence, by washing the wet gels at elevated pH, a maximum in G modulus is obtained, and for the present 2-step TEOS-based gels this maximum is ~3 MPa (Fig. 1a and b). This can be compared to the results by Hæreid et al.[8] in which a maximum of ~1.6 MPa was obtained by 1 step TMOS based gels. However, maximum in G modulus will depend on several parameters such as preparation route and the initial density of the gels.

In addition, we prepared two sets of gels based on water glass with different silica contents giving initial densities of 0.118 and 0.131 g/cm³. With the present preparation technique, an initial density of 0.131 g/cm³ was the maximum obtainable. These two sets of gels were washed in water solutions at pH=8.0 or 9.0 at 70°C for different time intervals. Fig. 2 displays the change in initial density, G modulus, MOR, and permeability of these gels as a function of washing time. Fig. 2 shows an increase in initial density with increasing washing time for the first 5 to 10 h which is due to a shrinkage of the wet gels. This shrinkage is caused by continued condensation reactions due to the increased pH of the solvent. At pH=9.0, the initial density tends to decrease after about 12 h of washing for both types of gel. This decrease arises from a swelling of the wet gels which was confirmed by measuring the diameter of the wet gels.

The G modulus given in Fig. 2 shows a similar behavior for both types of gel. For pH=8.0 a maximum in G modulus is obtained whereas for pH=9.0 there is a decrease in G modulus with increasing washing time. The continued condensation reactions as well as neck growth by dissolution/precipitation occurring during washing at pH=8.0 caused the increase in G modulus. However, after about 12 h of washing a reduction in G modulus begins due to dissolution of smaller particles and precipitation onto the larger ones, which will decrease the connectivity. The dissolution of the smaller particles will increase the pore size as well as particle size as can also be seen from the slight increase in permeability (Fig. 2). However, the increase in permeability is within the uncertainty of the measurements. At pH=8.0, the MOR shows a slightly different behavior than the G modulus because the maximum is observed at a shorter washing time.

At pH=9.0 where the solubility of silica is significantly higher than at pH=8.0[22] there is a decrease in both G modulus and MOR as well as a significant increase in
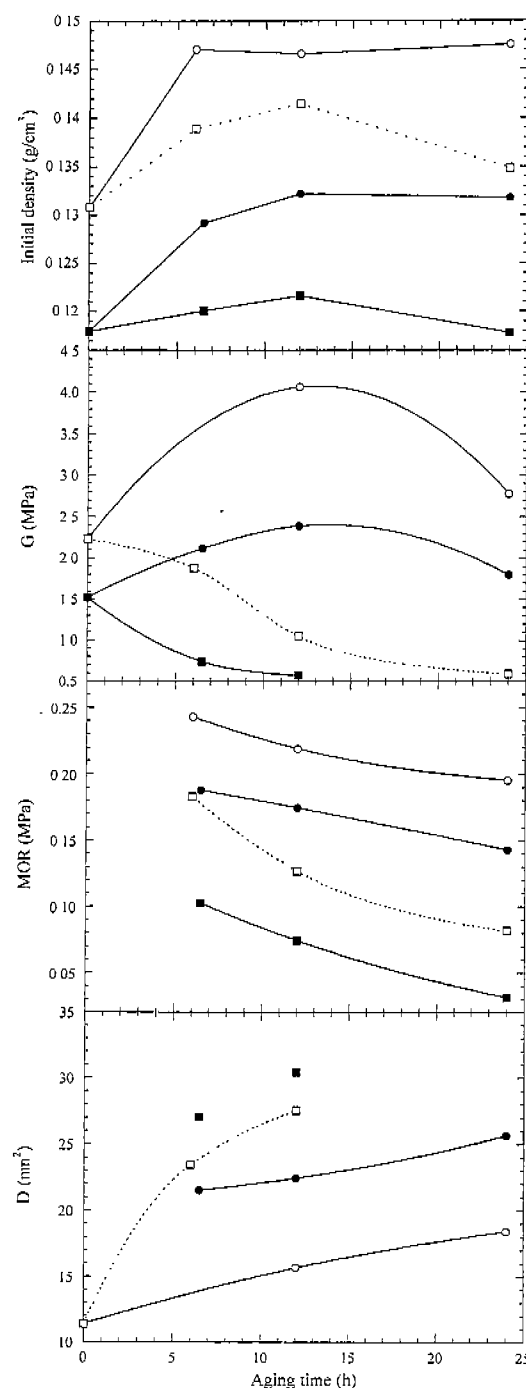

Fig. 2. Initial density, G modulus, MOR and permeability of water glass based gels aged in water solution at pH=8.0 (●) or 9.0 (■) at 70°C as a function of aging time. Open symbols represent gels with initial density 0.131 g/cm³ and filled symbols represent gels with initial density 0.118 g/cm³. Un-certainty is within ±0.009 g/cm³ for initial density, ±0.17 MPa for G modulus, ±0.05 MPa for MOR and ±4.0 nm² for permeability. Lines are drawn as a guide to better distinction.

permeability with increasing washing time as can be seen from Fig. 2. This behavior shows that Ostwald ripening takes place, confirming quite broad particle size distribution for this type of gels. In addition, it can be concluded
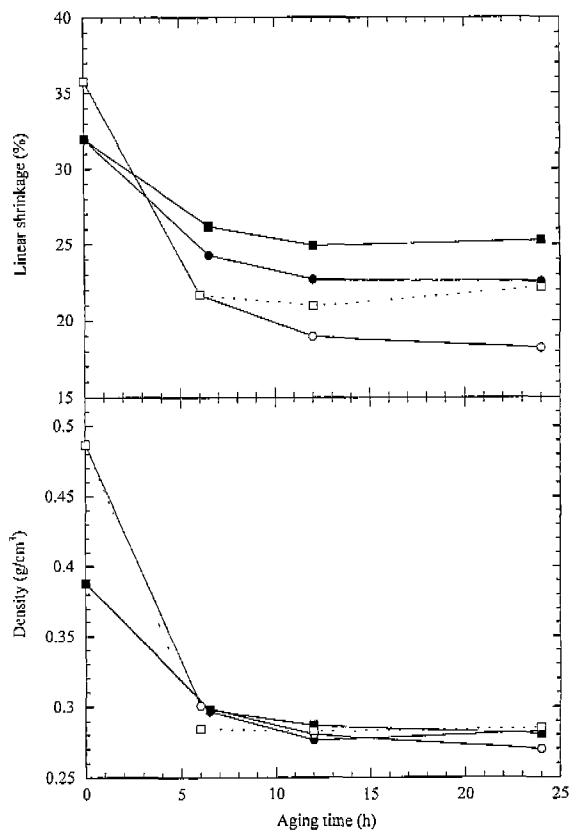
Fig. 3. Linear shrinkage during drying from n-heptane and xerogel density of water glass based gels aged in water at pH=8.0 (●) or 9.0 (■) at 70°C as a function of aging time. Open symbols represent gels with initial density 0.131 g/cm³ and filled symbols represent gels with initial density 0.118 g/cm³. Uncertainty is within ±1.26% for linear shrinkage and ±0.03 g/cm³ for xerogel density. Lines are drawn as a guide to better distinction.

the wet gels with the highest initial density show the highest shrinkage and xerogel density most probably due to the low permeability of these gels. The xerogel densities obtained for the washed gels were almost identical, *e.g.* ~0.28 g/cm³ regardless of initial density and washing conditions. By studying the details in Fig. 2 it can be seen that the highest G modulus is measured for the gels with the lowest permeability and vice versa. Hence, by applying the model for predicting shrinkage,[1] the xerogel density should be similar. The broad particle size distribution of the present water glass gels enhances Ostwald ripening weakening the gel instead of neck growth. Hence, the
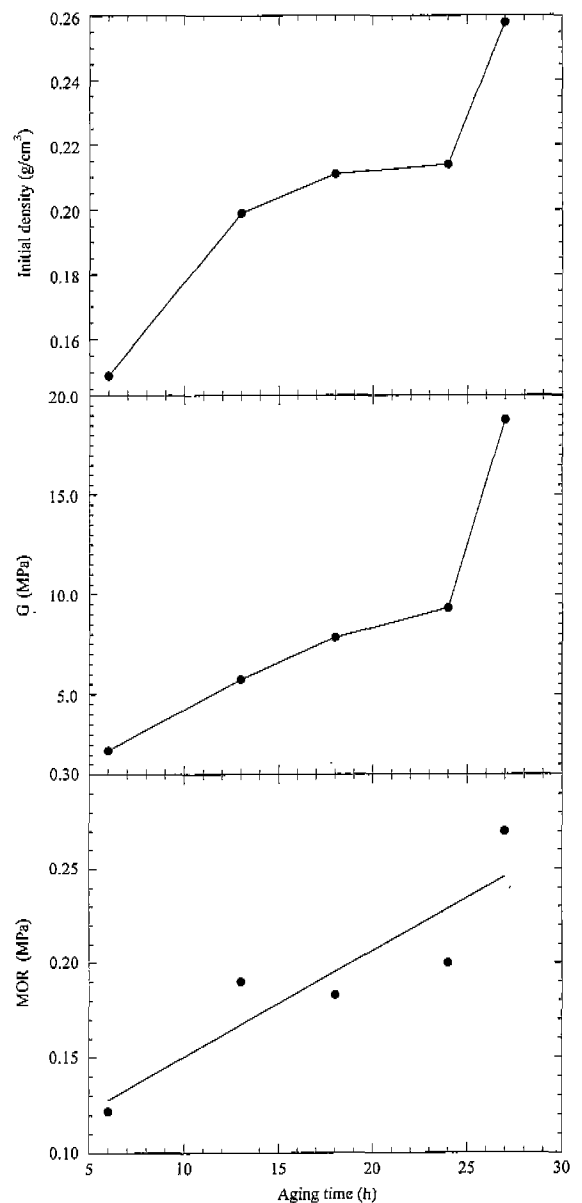
that pH=9.0 is a too high value for increasing the strength of water glass based gels by washing at 70°C.

The water glass based gels were dried from n-hepthane and the resulting linear shrinkage and xerogel density are presented in Fig. 3. The shrinkage of a gel during drying is driven by the capillary pressure, p_c, which is given by Eq. (1)[2,23] assuming that the contact angle is zero.[24]

$$P_c = -2\gamma_{LV}/(r_p - t) \qquad (1)$$

γ_{LV} is the surface tension of the pore liquid, r_p is the pore radius, and t is the thickness of a surface adsorbed layer. In a model developed by Smith *et al.*[1] shrinkage occurs until the capillary pressure is resisted by the bulk modulus of the gel (*i.e.* modulus of the drained gel network which is proportional to G),[23] hence the parameters of importance for predicting shrinkage are initial density, pore size (here represented by permeability) and G modulus under identical conditions in gel structure and solvent. The gels prepared with the highest initial density shows the lowest amount of shrinkage, however the shrinkage is ~20%. Before washing in the water solution,

Fig. 4. Initial density, G modulus and MOR of water glass based gels aged in 70 vol% TEOS/ethanol solution at 70°C as a function of aging time. Uncertainty is ±0.005 g/cm³ for initial density, ±1.8 MPa for G modulus and ±0.05 MPa for MOR. Lines are drawn as a guide to better distinction.

task to increase the strength and stiffness of these gels by washing in water solutions is more demanding compared to alkoxide based gels.

Since the washing conditions used for the present gels were not suitable to reduce the density of the xerogels below 0.28 g/cm^3, the initial density of the gels with the lowest silica content was increased by aging in a TEOS solution providing fresh monomers to react with the wet gel network. Fig. 4 includes important properties of the water glass based gels aged in a 70 vol% TEOS/ethanol solution as a function of aging time.

Aging the wet gels in a solution of TEOS causes silica to precipitate from the aging solution onto the silica network.[15-17] The precipitation of silica gives an increase in the initial density of the wet gel as can be seen from Fig. 4 and a weight increase of ~70% has occurred after 27 h. This increase in initial density gives a significant increase in G modulus and MOR. An increase in G modulus up to 20 MPa has been obtained for an aging time of 27 h compared to about 100 h for a corresponding 2-step TEOS based alkogel[15] showing the high reactivity of this system, i.e. possible condensation sites for TEOS. This increased reactivity is promising for the preparation of ambient pressure dried aerogels from cheap precursors. The highest value of the G modulus obtained for the water glass based gels washed in water solution was ~4 MPa (Fig. 2) and for the corresponding alkoxide based gels ~3 MPa (Fig. 1).

Drying the aged water glass based gels from n-heptane as the last solvent, the resulting linear shrinkage and xerogel density are given in Fig. 5. The gels show a decrease in linear shrinkage up to 24 h of aging followed by an elimination of the shrinkage. At this initial density the gel is stiff enough to withstand the capillary pressure and no shrinkage will occur during drying. However, one should be aware of the possibility of some elastic recovery of the gels if they are not pushed beyond the yield point during drying giving a lower density than expected from the capillary pressure.[23] This elastic recovery is most likely to occur for the gels with the highest initial densities. There is a corresponding decrease in density up to about 24 h of aging followed by a linear increase because silica is still precipitating from the aging solution after the point where shrinkage stops. The minimum density that can be obtained by aging the present water glass based gels in TEOS is hence ~0.22 g/cm^3. However, changing the parameters during the sol-gel processing, a gel with a different structure and even lower density might be possible. In previous work on alkoxide based gels a comparable density down to ~0.2 g/cm^3 has been obtained by increasing the strength and stiffness by aging in TEOS solution.[8,15-17] Generally, the gels were dried without fracture.

IV. Conclusions

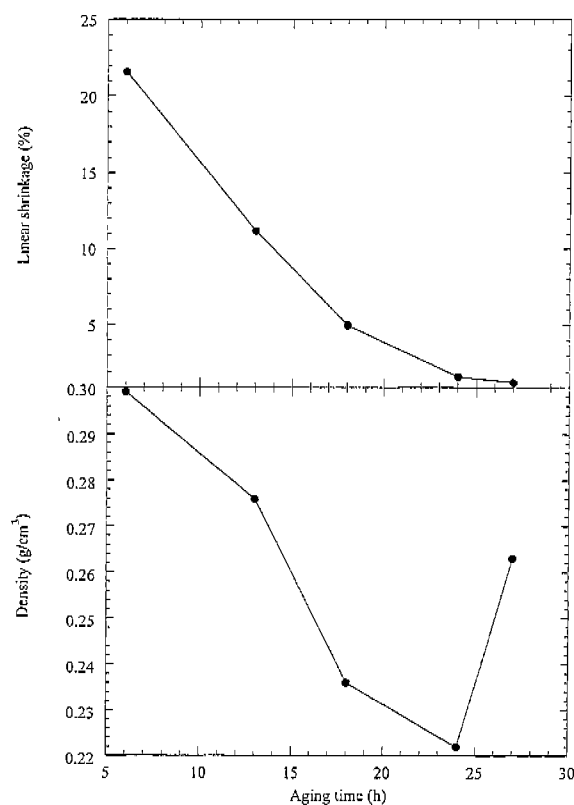During washing of wet gels in water solutions at ele-

Fig. 5. Linear shrinkage and G modulus of water glass based gels aged in 70 vol% TEOS/ethanol solution at 70°C as a function of aging time. Uncertainty is ±1.4% for initial density and ±0.02 g/cm^3 for initial density. Lines are drawn as a guide to better distinction.

vated pH, dissolution and precipitation of silica occurred either leading to neck growth between the primary particles or Ostwald ripening if the particle size distribution is broad. A maximum in G modulus of ~3 MPa for alkoxide based gels and ~4 MPa for water glass based gels is thus obtained during washing in water at elevated pH. For the present water glass based gels this gives a density of 0.28 g/cm^3 regardless of initial density and washing conditions.

Aging in monomer solutions is a simple and easy way to enhance stiffness and strength of wet gels. Stiffening the wet gel eliminates shrinkage during drying when drying from a low surface tension liquid. Aging water glass based gels in a solution of TEOS permits xerogels with density down to ~0.2 g/cm^3 to be prepared.

Acknowledgement

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