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Time and frequency dependent rheology of reactive silica gels

Miao Wang [a,b], H. Henning Winter [b], Günter K. Auernhammer [a,*]

[a] *Max-Planck Institute for Polymer Research, Ackermannweg 10, Mainz, Germany*
[b] *Chemical Engineering, University of Massachusetts, Amherst, MA, USA*

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ABSTRACT

In a mixture of sodium silicate and low concentrated sulfuric acid, nano-sized silica particles grow and may aggregate to a system spanning gel network. We studied the influence of the finite solubility of silica at high pH on the mechanical properties of the gel with classical and piezo-rheometers. Direct preparation of the gel sample in the rheometer cell avoided any pre-shear of the gel structure during the filling of the rheometer. The storage modulus of the gel grew logarithmically with time with two distinct growth laws. The system passes the gel point very quickly but still shows relaxation at low frequency, typically below 6 rad/s. We attribute this as a sign of structural rearrangements due to the finite solubility of silica at high pH. The reaction equilibrium between bond formation and dissolution maintains a relatively large bond dissolution rate, which leads to a finite life time of the bonds and behavior similar to physical gels. This interpretation is also compatible with the logarithmic time dependence of the storage modulus. The frequency dependence was more pronounced for lower water concentrations, higher temperatures and shorter reaction times. With two relaxation models (the modified Cole–Cole model and the empirical Baumgaertel–Schausberger–Winter model) we deduced characteristic times from the experimental data. Both models approximately described the data and resulted in similar relaxation times.

1. Introduction

Aggregated colloids (colloidal gels) are important in everyday life and for fundamental research. The tunability of the system and the analogy to atomic systems have motivated a strong scientific interest in the dynamic behavior of colloidal gels [1–5]. In colloidal and molecular systems gelation is introduced by attractive interactions between the constituents (molecules, colloids or even more complex hierarchical structures like crystallites). The detailed mechanism may differ significantly from system to system. According to the durability of the bond between the constituents, gels are often classified as either chemical [6,7] or physical gels [8–11], where chemical gels are assumed to have bonds of an infinite life time and physical gels have bonds of a finite life time. For both, the constituents aggregate and the growth of clusters eventually leads to the formation of a system spanning network. Often the state of a gel depends on its history, i.e., the system is non-ergodic. Whereas chemical gels typically approach a final state, physical gels get trapped in non-equilibrium states and tend to age even after long periods of time.

Similarities between physical and chemical gels have been demonstrated by many studies. In the percolation model, the gel point is defined as the time, when the ratio between the real and imaginary part of the shear modulus, i.e., the loss tangent, is independent of the frequency. This behavior has been found in polymer (chemical) gels [12,13] and physical gels [14,15]. The physical gel of PVC plastisols exhibits the same power law relaxation as a chemically cross-linking system [15]. Furthermore, physical gels and glassy systems were often compared in the literature. It was reported that the dynamics of gelatin gels (physical gel) share characteristics with glassy systems on ergodic-to-non-ergodic transition kinetics [16], memory [17] and aging [18] effects. The relaxation to a non-ergodic background in gelatin gel was also found to be very similar to the relaxation pattern in glasses [19].

Besides the scientific interest, further understanding of gel systems has considerable impact for industry. Inorganic particles are widely used as filler particles in many applications. Examples include plastic parts, paints, coatings, pharmaceuticals, cosmetics, and food products. A cheap and efficient way of making such filler particles is to synthesize particle aggregates and mill them afterwards to the desired size. A prominent example is precipitated silica gel, also called silicic acid gel. Almost spherical silica particles are formed by fragmentation of the gel [20,21].

The characterization of precipitated silica gel began already in the 1920s [22]. In a series of the studies, Hurd discussed the influence of reactant variations [23,24] and temperature [25] on the gelation time. The chemical process and gelation phenomenon were detailed by Iler and Brinker [20,26]. By acidifying a soluble silicate, the silicic acid is firstly formed, which then reacts to form

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* Corresponding author. Fax: +49 6131 379 100.
E-mail address: auhammer@mpip-mainz.mpg.de (G.K. Auernhammer).

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primary particles by condensation. The suspended particles grow further and aggregate with each other. That leads to a particle network, which extends throughout the system and forms a gel [20,27].

The time-dependence of the viscosity was investigated for the precipitated silica gel before its gel point by rheological measurement. Two stages were noted: a slow increase of viscosity during the preliminary stage, which was attributed to the formation of colloidal particles, followed by a rapid viscosity growth, for which the particle size determines the rate [28].

The relaxation processes in silica gels were studied theoretically [29] and experimentally by the 3-point bending method [30,31]. Wet gel bar samples were immersed in the bath of their medium liquid and the modulus was measured as the load required to produce a constant deflection [32]. The relaxation is understood as the sum of hydrodynamic and viscoelastic relaxation, which is caused by flow of the liquid medium in the system and irreversible deformation of the network under load. The chemical attack, i.e., hydrolysis, of the medium liquid on the gel was believed to be the reason for the relaxation in silica gel. When there is water in the medium, the silica bonds dissociate in the water (bond breakage) [30].

Our study focuses on the time and frequency dependent dynamic moduli of precipitated silica gel. The rheological properties of our silica gel exhibited a number of similarities to physical gels and weak colloidal gels. We observed a logarithmic growth of the storage modulus with time as previously found with physical gels [15,18]. This logarithmic time dependence is usually attributed to bond reversibility which can lead to a structural change, different from a chemical gel. The dynamic similarity between precipitated silica gels and physical gels was also found in the frequency sweep test. In comparison, a gel of chemically bound hard particles is expected to show a constant, frequency independent storage modulus at low frequencies, since the relaxation time exceeds the experimental time window [33,34]. The experiments we performed were at concentrations close to the percolation threshold, i.e., close to the minimal concentration of reactants, which is necessary to form a system spanning network. The behavior of the system was sensitive to external parameters. The influence of water concentration, temperature and time on the frequency dependence was studied. To understand the frequency dependence further, we applied two relaxation models: the modified Cole–Cole and Baumgaertel–Schausberger–Winter (BSW) models to analyse the experimental data.

In the discussion, we concentrate on the following points: 1. Is the precipitated silica gel at high pH-value a “real” chemical gel? 2. Can the relaxation models developed for polymer systems describe the relaxation behavior of silica gel? 3. Are there any unifying relaxation features for the silica gel in comparison to physical gel behavior?

2. Material and methods

2.1. Material

The reactants are sodium silicate solution (Natronwasserglas 37/40°, 40 wt.%, kindly provided by KRUSE-GROUP, Hanau, Germany) and sulfuric acid (96.4 wt.%, Fisher Scientific GmbH, Schwerte, Germany), which was diluted with milli-Q water to 3.2 wt.%. All reactants were used as provided without further purification. The sodium silicate has a molar SiO_2:Na_2O ratio of 3.3, which is typical for the production of precipitated silica and gels. The volume ratio between the sodium silicate solution and the diluted sulfuric acid solution was fixed as 1:2. As detailed below, if desired, the solution was further diluted with milli-Q water. The concentrations were chosen to adjust the gelation time in an experimentally accessible time window. Depending on the water content, the time to form a gel varied from about 20 min to 5 h, long enough to prevent gelation during experiment preparation, and short enough to efficiently avoid evaporation (see below). All samples originated from the same batch of sodium silicate to avoid batch-to-batch variations.

Silica gel without additional water was alkaline with a pH-value of 11.0 ± 0.1 at room temperature $T = 23$ °C, as measured with a pH-meter (Lab 850, Schott Instruments, Mainz, Germany). The pH-value remained constant during the reaction. The pH-value decreased to 10.9 ± 0.1 when the temperature was increased to 50 °C.

The solubility of silica in water increases strongly with pH [28]. Silica bonds can dissolve at pH-values above 9. The silica gel becomes reactive and quickly assumes a reaction equilibrium. The chemical reactions involved have been described in detail previously [20,21,35] and can be written as [35]:

$$Na_2O \cdot xSiO_2 + H_2SO_4 \rightleftharpoons xSiO_2 + Na_2SO_4 + H_2O$$

with $x = 3.3$ in this study. The appearance of the sample changed from a transparent and colorless solution immediately after preparation to a slightly turbid solid at the gel point to a white gel after several hours. The gel consisted of aggregates of primary particles, which were visible in scanning electron microscopy (SEM) images (Fig. 1A). The image illustrates the typical size of aggregates with diameters of 60–130 nm. The sample for SEM was prepared 1 h after mixing the reactants and was then kept at $T = 100$ °C for 3 days in a vacuum oven to remove the water from the sample.

In order to investigate the influence of the reactant concentration, extra water was added to the reaction mixture. We denoted the amount of extra water by the ratio R, defined as the additional water volume divided by the total solution volume (including the additional water).

$$R = \frac{V_{additional\ H_2O}}{V_{solution}} \tag{1}$$

We varied R from 0% to 20%. The silica volume fraction in the samples with $R = 0\%$, 10% and 20% were 8.6%, 7.3% and 6.3%, respectively. The pH-value at $T = 23$ °C decreased from 11.0 ± 0.1 for $R = 0$ to 10.9 ± 0.1 for $R = 20\%$. By slightly decreasing the pH value, additional water shifts the reaction equilibrium in the direction of undissolved silica bonding since silica solubility decreases. Furthermore, the temperature controls the rate at which bonds form and open. So the life time of the silica bonds can be adjusted by these parameters.

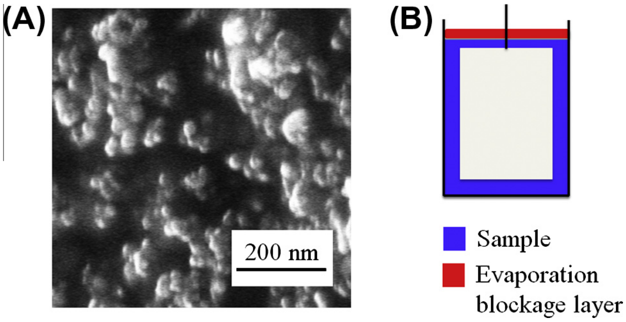

Fig. 1. (A): SEM image of the silica gel. The sample was prepared 1 h after mixing of the reactants and kept at $T = 100$ °C for 3 days in a vacuum oven for complete drying. (B): Setup of rheometer Couette cell with sample (blue) and evaporation blockage layer (red). The inner cylinder rotated oscillatorilly. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)