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Original Research Paper

Development of preparation method to control silica sol–gel synthesis with rheological and morphological measurements

Aya Kaide, Takashi Saeki *

Graduate School of Science and Engineering, Yamaguchi University, 2-16-1, Tokiwadai, Ube, Yamaguchi 755-8611, Japan

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ABSTRACT

In this paper, we report the effects of pH and salt on the gelling properties of silica (SiO_2) sols and gels which were measured both by dynamic viscoelasticity measurement and by creep test equipment. The network structures built by SiO_2 particles formed under different conditions were observed by a scanning probe microscope (SPM). N_2 adsorption measurements were also conducted in order to analyze the characteristics of dried gel powders including specific surface area, pore volume, and pore size distribution. The objective of this study is to characterize the SiO_2 sol, gels, and powders obtained by a Y-shaped reactor under different pH and salt conditions.

1. Introduction

Amorphous silica (SiO_2) is a safe material for both humans and ecosystems. Promising applications of amorphous SiO_2 include its use in flocculants, absorbents, soil hardeners, and retention aids. Also, functionalized SiO_2 products with a thixotropic property, matting, and hardness are used in sealant, paint, synthetic rubber, and tires. Normally, SiO_2 sols are produced by the neutralization of sodium silicate ($Na_2O{\cdot}nSiO_2$, called alias water glass) and sulfuric acid (H_2SO_4) as shown in Eq. (1), which is an easy and convenient progression for industrial mass production:

$$H_2SO_4 + Na_2O \cdot nSiO_2 \rightarrow nSiO_2 + Na_2SO_4 + H_2O \quad (1)$$

Generally, SiO_2 sols are produced by adding $Na_2O{\cdot}nSiO_2$ solution to a batch vessel with the appropriate amount of H_2SO_4. During production, especially at higher SiO_2 concentrations, rapid and localized gelling frequently occurs, which is an obstacle to producing homogenous sols. Recently, a Y-shaped reactor has been developed for use in an alternative production method in which diluted $Na_2O{\cdot}nSiO_2$ and H_2SO_4 collide with each other at the intersection of the reactor [1]. The produced SiO_2 sols gradually increase in viscosity and finally form gels under a limited condition in which the percolation of SiO_2 nanoparticles may occur and a network structure is built [2]. It is also known that sol pH strongly affects the gelling time. In spite of the fact that the isoelectric point of SiO_2 particles is pH = 2, the particles tend to disperse around this pH. The gelling time decreases with increased pH up to pH = 6, at which it reaches the minimum value. Then, the gelling time increases again with the increase of pH. This trend means that the electrostatic interaction does not affect the particle bonding. The decrease of the gelling time from pH = 2 to 6 can be explained as a result of the condensation reaction that is catalyzed by OH-groups [3]. The increase of gelling time for pH values larger than 6 can be explained by the increase of the surface charge and the corresponding increase of Coulomb repulsion. Iler described how particles aggregate into three-dimensional networks and form gels in acid solutions or in the presence of flocculating salts. Particles in sol grow in size and decrease in number in basic solutions [2]. The properties of industrial absorbent SiO_2 gels can be controlled by limiting the preparation pH to below 4, and it has been clarified that the pH of a SiO_2 sol mainly affects the size to which the particles grow before they form a gel [4,5]. Since it is difficult to obtain homogeneous basic sols due to their rapid localized aggregation, most experiments were conducted under acidic conditions.

For some years, our group has been interested in the factors which can control the properties of SiO_2 gels during their production. It is convenient to use a Y-shaped reactor which ensures complete gelling and prevents localized gelling. We produced various sols under different conditions and evaluated their rheological properties [6–8]. We found that the heating of gels played a role in the decrease of gelling time, while increasing pH affected not only the gelling time but also the elastic properties of the gels obtained [9]. We also evaluated the gelling property of alkaline sol (pH = 11) compared with that of acid sol (pH = 2) in more detail

* Corresponding author. Tel./fax: +81 (836) 85 9242.
E-mail address: saeki@yamaguchi-u.ac.jp (T. Saeki).

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and found that the alkaline gel was more plastic than that obtained under acid conditions [10].

Therefore, in this paper, we continue our research by focusing on the effect of salts, which have some influence on SiO_2 gelling [2]. We selected sodium chloride as a salt and compared the gelling structures for the addition of a salt with that for the changing of the pH. The properties of powders obtained from dried SiO_2 gels under different production conditions is also of interest in terms of their applicability to industrial products. The objective of this study was to evaluate the effect of the preparation condition on the gelling time, gel structure, and adsorption property of dried gel powder using the Y-shaped reactor and to summarize the control methods for SiO_2 gels and powders.

2. Experimental details

2.1. Sol–gel synthesis of SiO_2

Sodium silicate, $Na_2O{\cdot}nSiO_2$, was produced by reacting sodium carbonate and quartz sand (both supplied by Tokuyama Co., Japan) as shown in Eq. (2).

$$Na_2CO_3 + nSiO_2 \rightarrow Na_2O \cdot nSiO_2\ (\text{solid}) + CO_2 \quad (2)$$

The thus-obtained solid $Na_2O{\cdot}nSiO_2$ (called "cullet") was dissolved in water in an autoclave as follows:

$$Na_2O \cdot nSiO_2\ (\text{cullet}) + H_2O \rightarrow Na_2O \cdot nSiO_2\ (\text{solution}) \quad (3)$$

It is known that the value n for these reactions is 3 and the obtained product is called sodium silicate solution no. 3. SiO_2 sols are produced from the reaction of $Na_2O{\cdot}nSiO_2$ with H_2SO_4 (90% Tokuyama Co., Japan) in a Y-shaped reactor. The experimental apparatus for the production of SiO_2 sols consisted of a H_2SO_4 line and a $Na_2O{\cdot}nSiO_2$ line. Each line is composed of a tank, a pump, and a flow meter. The two lines are connected to the respective inlets of the Y-shaped reactor. The two jets collide with each other at the intersection of the reactor at velocities greater than 10 m/s. The produced SiO_2 sols exit from the outlet of the reactor and go into a beaker. Details of the system have been reported previously [7]. We prepared H_2SO_4 by adding an amount of sodium chloride (NaCl) (99.5% Wako) equivalent to 2–4 times the amount of Na_2SO_4 and produced acid SiO_2 sols. Also, acid SiO_2 sols of around pH = 2 were first produced with the excess rate of H_2SO_4 set at 1.1. Immediately thereafter, 5% aqueous ammonia (NH_3) (28% Wako) was added to the sols to obtain a pH of 3–6.45. The alkaline sols with a pH of around 11 were obtained directly from the outlet of the Y-shaped reactor with the excess rate of H_2SO_4 set at 0.4. The concentration of SiO_2 sol was 8 wt% for all the expreiments in this study.

2.2. Rheological measurements

Viscoelastic measurements were conducted to monitor the SiO_2 sol–gel transition over time. The method of forced oscillation is useful technique for quantifying dynamic behavior [11]. The viscoelasticity at each frequency is analyzed according to the Maxwell model, which consists of a spring and a dash pot in a series. When a sinusoidal strain is imposed upon a sample, a sinusoidal stress will result at the same frequency at a phase-shifted defined by the angle δ. The complex viscoelastic modulus G^* is then defined as the ratio of the stress and strain amplitude. The stress–strain relation may be represented as having a component in phase with the strain and a component which is 90° out of phase with the strain. The former represents the elasticity, which is defined as the storage modulus G' (Pa), while the latter is the loss modulus G'' (Pa). These relations can be represented by the following equations:

$$G' = G^* \cos\ \delta \quad (4)$$

$$G'' = G^* \sin\ \delta \quad (5)$$

We used a coaxial-cylinder rotating rheometer (Rheologia A-300, Elquest Co., Japan) having the inner diameter of the outer cup, the diameter of the inner cylinder, and the length of the cylinder were 21.0 mm, 19.4 mm, and 37.4 mm, respectively. Beginning immediately after the sols emerged from the Y-shaped reactor, a sine wave oscillation was continuously applied to the sol under an angular frequency of 1 Hz and a strain of 0.1. We had previously confirmed that a strain of 0.1 did not affect the aging time of the sols.

Creep characteristics provide useful information relating to the network structure of gels [12]. The physical properties of the gels were measured using creep test equipment (Rheoner RE2-33005S, Yamaden Co., Japan) [13–15]. A cubic gel sample 30 mm on each side was pressed by a round plunger with a speed of 0.1 mm/s. The plunger diameter was 55 mm. The loaded stress of the plunger due to deformation of the sample gel was monitored, and the maximum stress was defined as the breaking stress where the gel broke. Fig. 1 shows a typical creep and recovery curve obtained in this measurement. The applied load was set at two-thirds of the breaking stress for each sample for 60 s. The load was then released, and the stress continued to be monitored during sample recovery. We adopted a four-component model (Burger's material), as also shown in Fig. 1, which consisted of the Maxwell model and the Voigt model, to express the relation between the stress and the time. Here, E_0 and E_1 are the elastic moduli, while η_N and η_1 represent viscosity. The elastic modulus, especially the instantaneous modulus E_0, is related to the rigidity of the gel, whereas the Newtonian viscosity η_N, represents its resistance to flow over a long period [16]. Therefore, we focused on E_0 and η_N, which might be related to the structure of the SiO_2 particle network and the progress of the gel vitrification, respectively. All measurements were carried out at 25 °C.

2.3. Morphological images analyses

The surface observation of the gels was conducted by using scanning electron microscope (SEM; VE-8800, Keyence Co., Japan) at an accelerating voltage of 2 or 5 kV. Gel block samples were not coated with anything. Here, we were concerned about damage to the minute particle network during measurements because the SEM observations were conducted under vacuum conditions. In addition, since the resolution of our SEM equipment was not so high (30 nm), we used a scanning probe microscope (SPM,

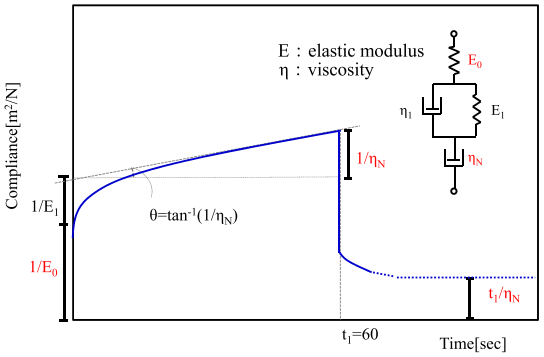

Fig. 1. Typical creep and recovery curve and four-component model.