

Shear-induced Gelation of  
Aqueous Colloidal Silica Suspensions  
in the Presence of Poly(ethylene oxide)

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# Shear-induced Gelation of Aqueous Colloidal Silica Suspensions in the Presence of Poly(ethylene oxide)

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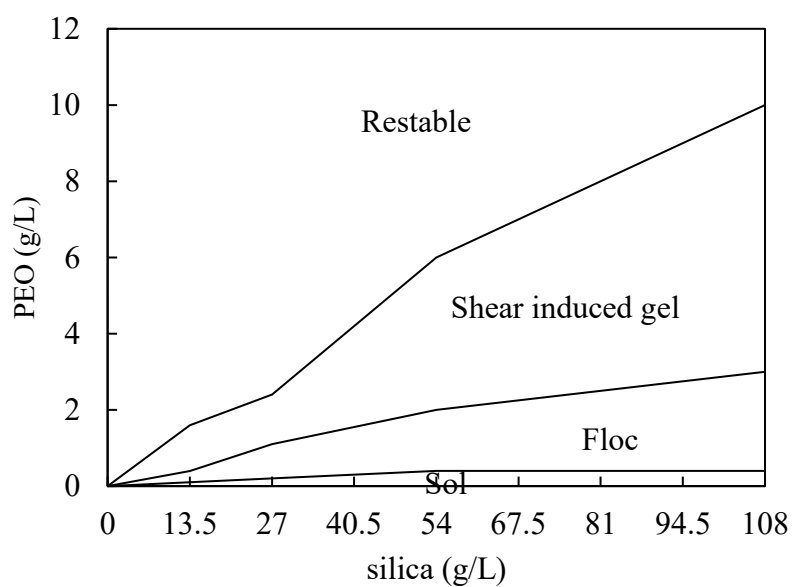
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# 1. Introduction

## 1.1 Background and previous studies

Aqueous colloidal suspensions are encountered in many fields. Especially, aqueous silica colloidal suspensions are widely used in environmental restoration [1], oil drilling and food [2], medical industries [3]. In these areas, controlling the state and the rheological properties of silica suspensions is important. As a usual method, adding polymers to silica suspension is often used. When polymers are added, they adsorb to the surface of silica particles, and the characteristic of the silica surfaces changes. Due to this adsorption behavior, polymers alter the interaction between silica particles, and this also induces the various state of the suspensions [4,5]. Therefore, revealing the effect of polymers to the state of suspensions is necessary for us to deepen our understanding of colloidal suspensions.

Colloidal suspensions with/without polymers show a change in their viscosity with shear rate [6–9]. The phenomenon of increase of viscosity with shear rate is called shear-thickening [8,9]. Along with the viscosity, some of the suspensions gel by shear flow. These gels are called shake-gel [9–11]. Shake-gels can even show the phenomenon of relaxation, which means that shake-gel turns back to a sol state after leaving stand. Cabane et al. [9] conducted experiments with silica particles and poly(ethylene oxide) (PEO) and reported the mixed suspension can be shake-gel. They observed the state, gelled or not, of silica-PEO suspension under several silica and PEO concentrations. They confirmed that the suspensions gel at appropriate silica and PEO concentrations (Fig. 1). By using small-angle neutron scattering, they found the interference pattern of suspension changes before and after shaking. This result indicates that the microscopic structure of suspension changes in the gelation process.

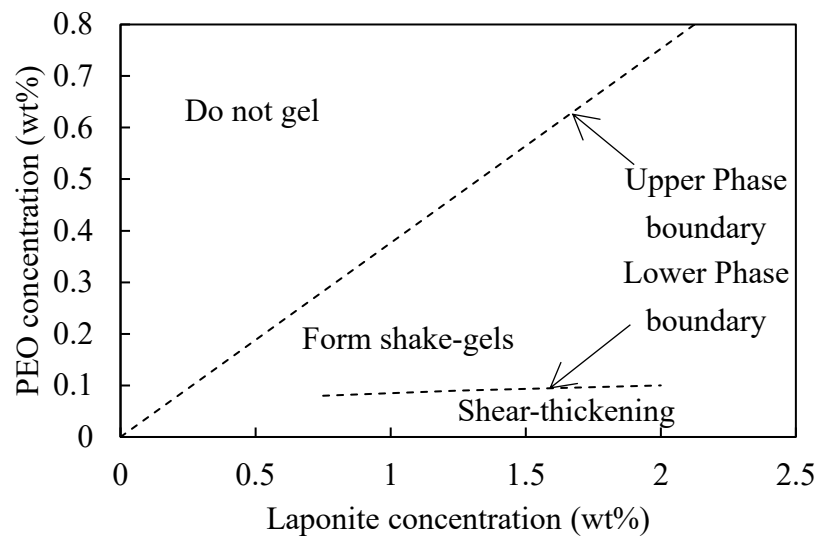


**Fig. 1** State diagram of suspensions consisted of silica (diameter 26 nm) and PEO (molecular weight 2000 kDa) in water at pH 8 and ionic strength of 0.5 mM. Data are taken from Cabane et al. (1997) [9].

Zebrowski et al. [10] reported that the mixed suspension of synthetic clay particles laponite and PEO showed the shake-gel phenomenon. Their study showed that shake-gel phenomenon occurs in a limited range of laponite and PEO concentrations (Fig. 2), which is similar with the results of Cabane et al. [9]. They measured the time for shake-gels returning to the sol state by direct observation and defined the time as a relaxation time of shake-gel. The relaxation time was found to decrease with increasing PEO concentration and changed up to  $10^4$  times with slight change in the PEO concentration.

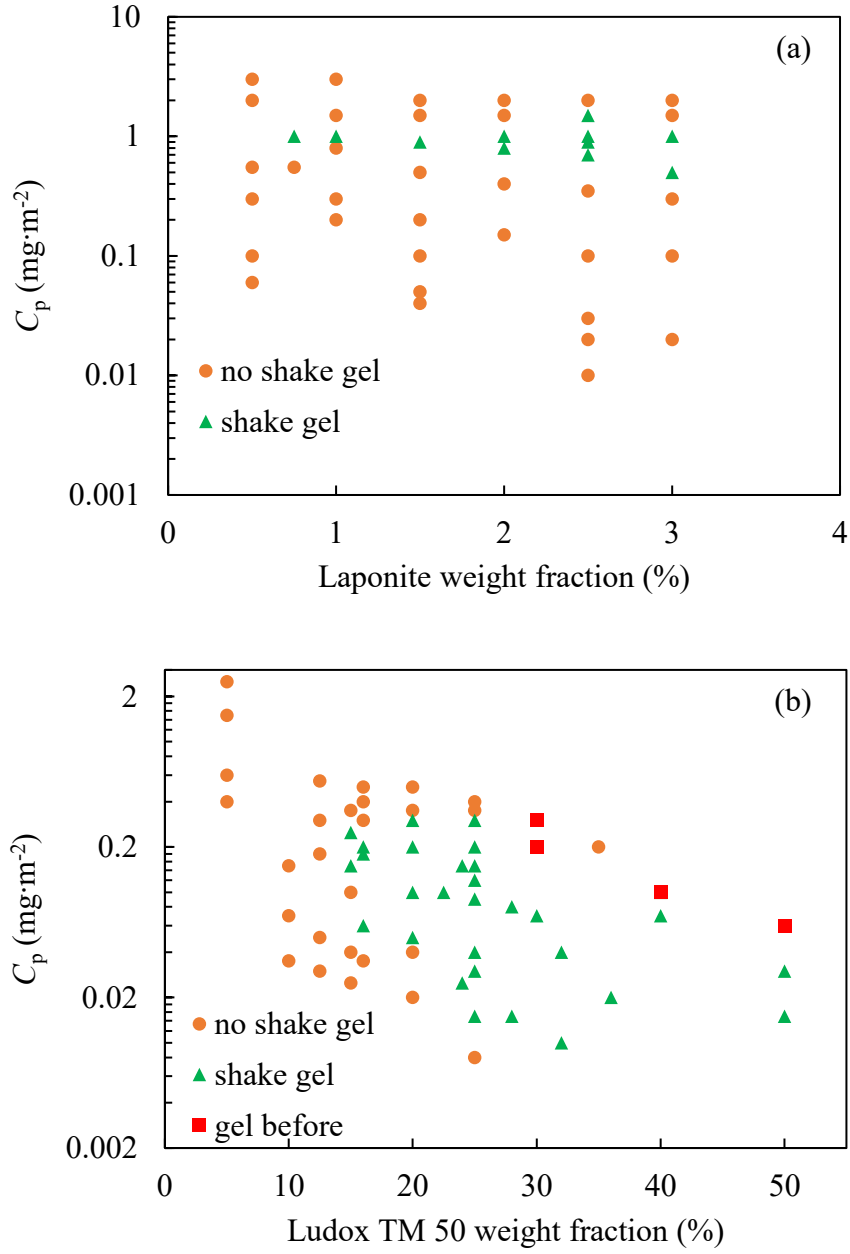
Mar Ramos-Tejada et al. [11] also prepared shake-gels with silica, laponite, bentonite particles and PEO polymers. They examined the state of the suspensions that depends on the weight fraction of nanoparticles and PEO and then plotted these results into a state diagram. Instead of PEO concentration, they used the PEO dose per particle surface area (called  $C_p$  in this thesis) to evaluate the PEO coverage (Fig. 3). They found that even though the particle concentration was different, if the  $C_p$  was in an appropriate range, the suspension can be shake-gel. This conclusion is important and indicates that PEO coverage on particles is the definitive factor rather than concentration. As well as the observation of state, they identified and discussed the increase of complex modulus of shake-gel in the gelation process.

Previous studies above used different materials and methods to observe the state and rheological properties of shake-gels. Based on their results, they hypothesized that the bridging effect of PEOs is a prerequisite of shake-gel (Fig. 4). In this hypothesis, added PEO chains can adsorb to several particles and form small aggregates. Before shaking, PEOs keep a random-coil-like state, and thus the suspension acts as sol. When the suspension is shaken, shear flow stretches PEOs to an elongated state. Elongated PEOs build more bridges between the small aggregates, inducing the formation of reversible gel network. However, the gel network is unstable because PEOs tend to return to the random-coil-like state due to the low free energy once shear is stopped. Therefore, after stopping the shake,

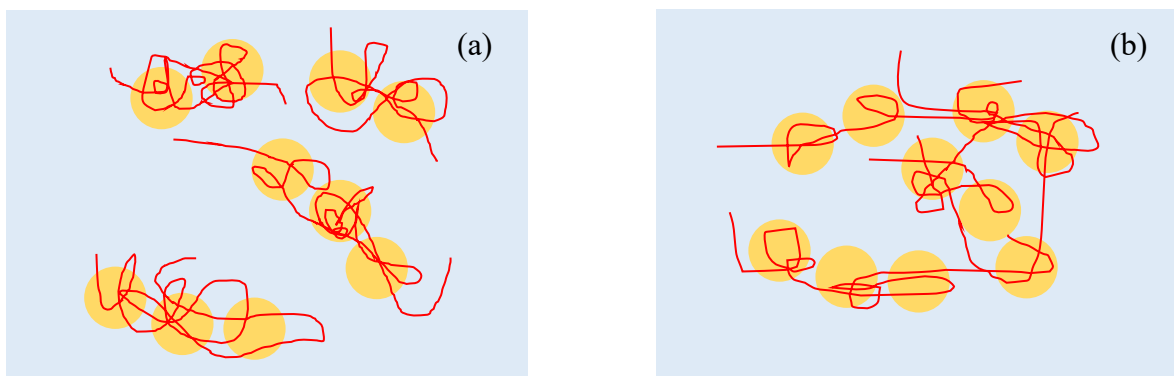


**Fig. 2** State diagram of suspensions consisted of laponite and PEO (molecular weight 300 kDa) in water. Data are taken from Zebrowski et al. (1997) [9].





**Fig. 3** State diagram of suspensions consisted of (a) laponite and PEO, and (b) silica and PEO in water. The molecular weight was 400 kDa. Data are taken from Mar Ramos-Tejada et al. (2015) [9].

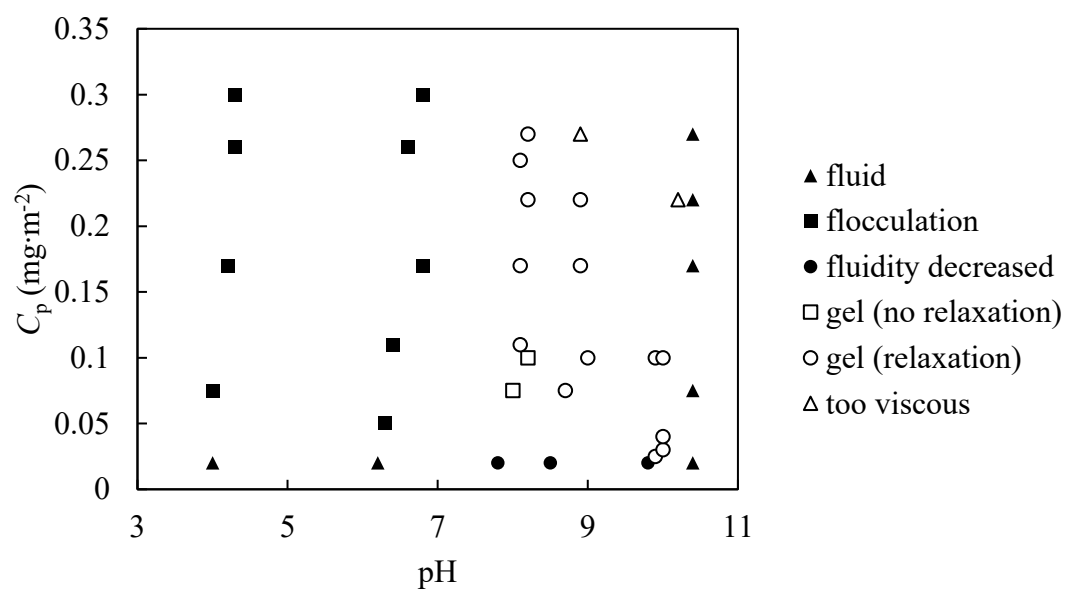


**Fig. 4** The image of silica-PEO suspension (a) before shaking and (b) after shaking. This image is taken from Cabane et al. [9] and Saito et al. [12], and almost of the previous studies assumed similar images. PEOs absorb to the surface of silica and bind several particles by bridging effect. Thus, small aggregates appear in the suspension. Before shaking, because the PEO network is not formed yet, suspensions show a sol state. After shaking, PEOs are stretched to elongated state to build more bridges to connect the small aggregates. Due to the complete of gel network, suspensions transfer to the gel state.

PEO bridges break up with time, and shake-gels relax to sol state. Saito et al. [12] and Shibayama et al. [13] also showed similar images about the gelation and relaxation.

Focusing on this hypothesis, we notice that parameters influencing the adsorption and bridging of PEO may also influence the formation of shake-gel. For example, silica and PEO concentrations, pH, molecular weight of PEO, and suspension temperature can be possible factors affecting shake-gel. The studies mentioned above reported the results about the effect of PEO concentration and particle concentration on shake-gel. These two parameters are inferred to be related to the bridging of PEOs. The bridging effect is considered to determine the attraction between particles. Nevertheless, they did not consider the adsorbed amount of PEO, even though the added PEO may not adsorb completely. Moreover, repulsion between particles should also be discussed. In colloidal suspensions, pH can be a parameter influencing both the adsorbed amount and repulsion. It is widely known that pH alters the adsorbed amount and conformation of PEO on silica [14] and the electric double layer (EDL) repulsive force between silica particles [15]. The adsorbed PEO amount is related to the bridging effect and EDL repulsion determine the microscopic structure of suspensions and thus the state of them [9]. Furthermore, almost no studies showed the photos of different state of silica-PEO suspension. This makes us unable to recognize the state of suspension. It is also an unsolved issue that continuous observation of relaxation process is lacking, even though relaxation is the most unique phenomenon of shake-gel rather than normal gels.

To solve the remaining issues mentioned above, Kawasaki et al. [16] conducted a series of experiments to study the effect of pH and the relaxation process by time. They showed that shake-gels only occurred in a pH range of 8-9.4. At lower and higher pH, the silica-PEO suspension showed cloudy state and high viscosity sol state, respectively (Fig. 5). They mentioned that pH influences the adsorbed amount and EDL repulsion of silica, and thus pH affects the formation of gel. It is known



**Fig. 5** State diagram of suspensions consisted of silica (diameter 30 nm) and PEO (molecular weight 1000 kDa). Data are taken from Kawasaki et al. (2018) [16].

that lowering pH induces low magnitude of zeta potential of silica [15] and thus weakens the EDL repulsion. Moreover, the adsorbed amount of PEO is reported to decrease with increasing pH [14]. At low pH, too weak EDL repulsion promotes the aggregation of silica [17,18], and the suspension became cloudy. Meanwhile, if pH increases, a strong EDL repulsion is expected. At the same time, PEO adsorbed amount decreases. Therefore, increasing pH above 10 reduces the bridging of PEO along with increasing the EDL repulsion, and the gel does not appear. They also took photos of shake-gels at different time and confirmed the difference of relaxation under various pH. However, the time scale of their study was too short, for only 100 s, and the suspensions chosen to take photos were few. This results in the difficulty in comprehending the overall trend of relaxation time against pH and  $C_p$ .

Besides the direct observation introduced so far, rheological behaviors of shake-gels were also examined [12,19–21]. Viscosity and complex modulus were found to increase during the gelation process. However, the discussion on the fundamental mechanism of gelation was not sufficient and the experimental conditions were limited. In addition, we also notice that no study provided a detailed and reproducible method to shake the suspensions, even though the type of flow is highly possible to influence the formation of gel. Because of the lack of experimental information, we cannot make the shake-gel phenomenon reproducible to everyone. These problems prohibit us to develop more detailed understanding of shake-gels.

## 1.2 Objective

This research has aimed to reveal the mechanism of shake-gel phenomenon. Based on the previous studies, we have focused on the parameters which are highly possibly influencing the state of silica-PEO suspension but have not been fully

studied in detail. The parameters chosen are pH, PEO dose, silica particles concentration, PEO molecular weight and suspension temperature. We have examined the state of silica-PEO suspensions under various conditions and observed the relaxation process for longer time. We concentrated on three topics of shake-gel in this thesis: the state, the relaxation time, and the viscosity of suspension against the shear rate.

The contents of this thesis are as follows:

1. The state of silica-PEO suspension is an obvious phenomenon that is observable by eyes. We changed the parameters mentioned above and observed the state of silica-PEO suspensions. Based on these results, we tried to explain why and how the factors affect the gelation of suspensions.
2. Relaxation is the most unique phenomenon of shake-gels, and the relaxation time can be an intuitive index to evaluate the speed of relaxation of shake-gels. This information cannot be shown in state diagram and is useful to judge the stability of shake-gels. Therefore, besides the state diagram of silica-PEO suspension, we planned to gain insight into the relaxation time of suspensions. We took photos of silica-PEO suspensions after shaking continuously for up to 24 h and obtained the relaxation time at each condition from the photos. We used these results to discuss the stability of shake-gels.
3. It is known that the elasticity and viscosity increase when a suspension starts to be transformed to gel state. Therefore, shear-thickening phenomenon can be used to detect the gelation. We applied shear flow to the suspensions by a viscometer and acquired the viscosity as a function of shear rate. Through this experiment, we tried to classify the conditions into promoting or preventing the formation of gel.

In this study, we figured out the condition to prepare shake-gels and the parameters influencing the relaxation process of shake-gels. This information is valuable for us to prepare gel products which can satisfy our needs of rheology and relaxation time and to perform detailed rheological measurements in the future. We consider that the state diagrams and relaxation time under different conditions can be a novel fingerprint of colloidal silica-PEO suspensions.

### **1.3 The outline of this thesis**

In this thesis, we introduce the background, the previous studies, and the objective in Chapter 1.

From Chapter 2 to Chapter 5, we state our experiments of this study. First, to understand the properties of the materials used, we characterize the silica suspension and the PEO polymer used in this study in Chapter 2. In Chapter 3 to 5, we show the results of shake-gel of silica-PEO suspensions by using state diagrams, recording the relaxation time, and measuring the viscosity against the shear rate, respectively. Based on the results above, we discuss how the parameters mentioned influence the shake-gel phenomenon.

In Chapter 6, we make a summary of the whole thesis.

## **2. The characterization of the silica suspension and PEO polymers**

### **2.1 Introduction**

In this thesis, we chose silica particles and PEO polymers as the materials to prepare shake-gels. To understand the rheological change of silica-PEO suspensions against the pure silica suspensions and pure PEO solutions, we need to know the properties of silica suspension and PEO solutions before mixing. Furthermore, as introduced in Chapter 1, EDL repulsion between silica particles and adsorption of PEO are important parameters influencing the state of silica-PEO suspension. Therefore, data of zeta potential of silica particles and adsorption of PEO are necessary.

In this chapter, we measured the hydrodynamic radius of silica particles to confirm the size of silica by dynamic light scattering (DLS). Furthermore, we measured the viscosity of pure silica suspension and pure PEO solutions. We also state the information of zeta potential of silica and the adsorbed amount of PEO through existing models and previous studies. By comparing the results in this chapter and that of silica-PEO suspensions, we can reveal the influence of mixing of silica and PEO. Then, the data of zeta potential and adsorption of PEO can help us to understand the effect of them to the state of silica-PEO suspension.

## **2.2 Experiments**

### **2.2.1 Materials**

We used silica nanoparticle suspension (LUDOX TM-50, Sigma-Aldrich) as received without any further purification in this study. The mass fraction of stock



silica suspension is 49.9%.

Poly(ethylene oxide) is a non-ionic linear polymer. PEO powders are purchased from Sigma-Aldrich and used without any purification. In this chapter, the average PEO molecular weight we used are 400, 600, 1000, 2000 and 4000 kDa (product ID is 372773-250G, 182028-250G, 372781-250G, 372803-250G, and 189464-250G, respectively). Szekely et al. [22] reported that polymers synthesized by the classical polymerization are polydisperse polymers. We considered the polymers we used are polydisperse without more details about the synthesis methods from the manufacturer.

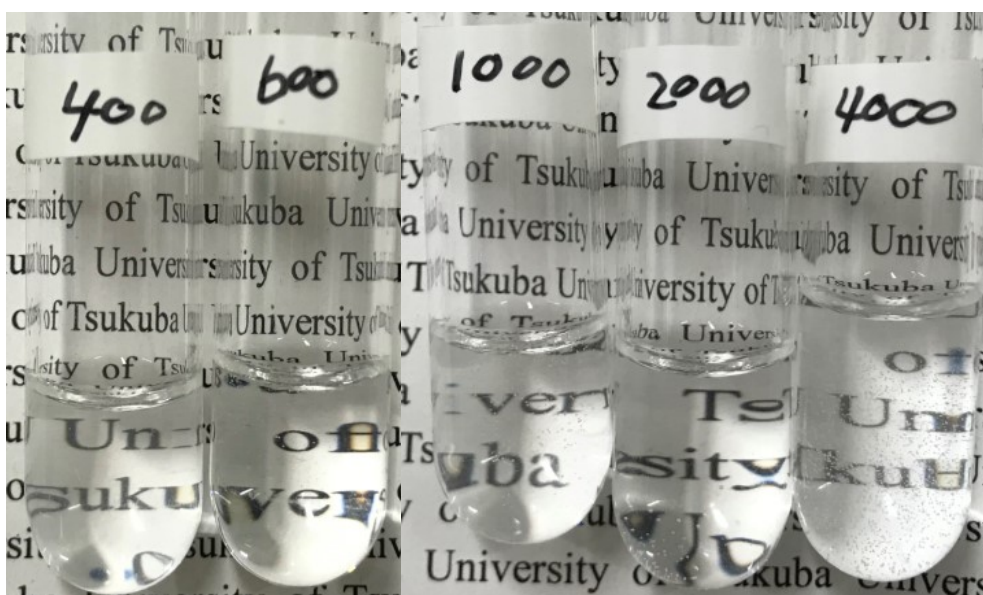
Deionized water (Elix Advantage 5, Millipore) was used to prepare solutions and suspensions in this study. The electric conductivity of freshly prepared deionized water was about 0.07  $\mu\text{S}/\text{cm}$ .

## **2.2.2 Methods**

### **2.2.2.1 The preparation of silica suspensions and PEO solutions for measurements**

For DLS measurements, we diluted the stock silica suspension into 2 wt% by using deionized water. The total mass of the diluted silica suspension was set to 5 g. After the dilution, the diluted silica suspension was mixed by test tube mixer (PresentMixer, TAITEC) for several minutes.

For viscosity measurements of silica suspension, we diluted the stock silica suspension into 20 wt% by using deionized water. The total mass and the method of mixing were the same as that of DLS measurements.



**Fig. 6** The photo of PEO stock solutions with molecular weight of 400, 600, 1000, 2000 and 4000 kDa, respectively. All the stock solutions were clear, indicating that the PEO polymers dissolved completely. In high molecular weight solutions, many bubbles existed in the solution, because of the high viscosity of the solution.

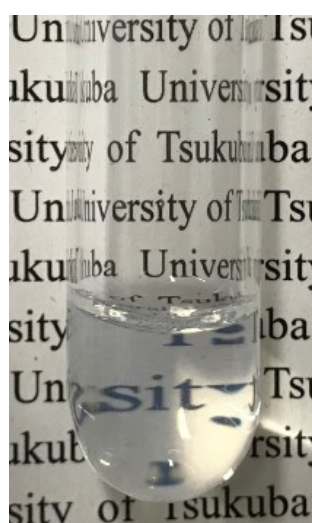
For PEO polymers, because we purchased the powder from the manufacturer, we needed to prepare stock solutions by using the powder and deionized water first. Stock solutions of PEO were prepared by dissolving PEO powder in deionized water, and the solutions were then stirred for 72 h to ensure the complete dissolution. We confirmed the PEO solutions were clear (Fig. 6), and it means all the polymers dissolved. The PEO mass fraction of stock solutions was set to 2%. After the preparation of stock PEO solutions, we diluted them into 0.112 wt% to make solutions for measurement.

#### **2.2.2.2 The method of dynamic light scattering measurement**

The dynamic light scattering (DLS) measurement was conducted with Zeta Sizer Nano (Malvern). 1 mL of diluted silica suspension was injected into plastic disposal cell, and the measurement was started. The temperature was controlled to 20°C.

#### **2.2.2.3 The method of viscosity measurement**

The viscosity measurement was conducted by a capillary type viscometer (MicroVISC, RheoSense). We changed the shear rate to 1000, 2000, 4000 and 8000 s<sup>-1</sup> to measure the viscosity of silica suspension and PEO solutions. The temperature of the viscometer was fixed to 20°C.



**Fig. 7** The photo of diluted silica suspension for DLS measurement. The mass fraction was 2%. The diluted suspension was clear, and we cannot find obvious flocs.

## **2.3 Results and discussion**

### **2.3.1 The results and discussion of DLS measurements**

By the DLS measurements, we got the average hydrodynamic diameter of silica particles is about  $38.31 \pm 0.07$  nm. It is a bit larger than the results of 30-34 nm by the electron microscopy [23] and the results of  $32.35 \pm 0.22$  nm by DLS measurement in previous study [16]. Even though the result of hydrodynamic diameter is a bit large, the suspension was clear, and we could not find obvious flocs in the suspension (Fig. 7). Therefore, this can be an error of the measurement.

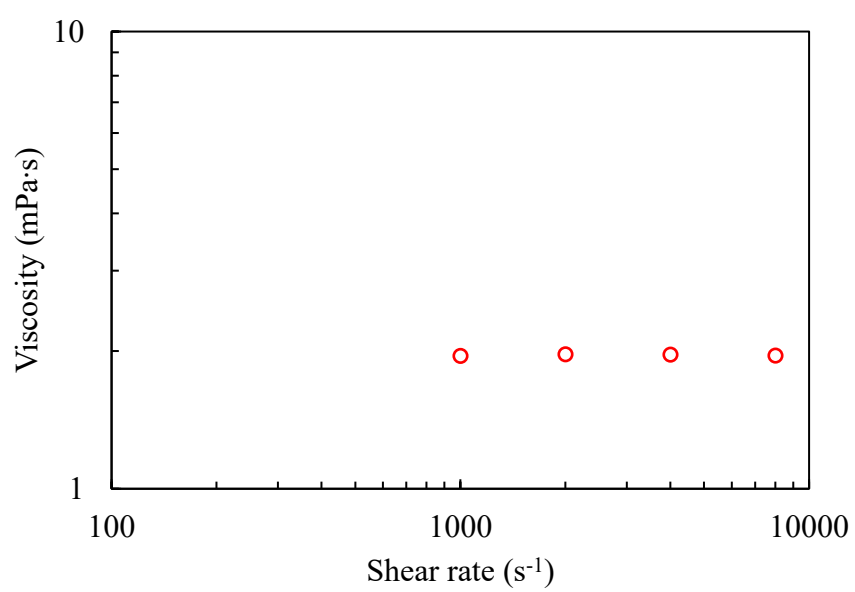
### **2.3.2 The results and discussion of viscosity measurements**

The results of viscosity of silica suspension are shown in Fig. 8.

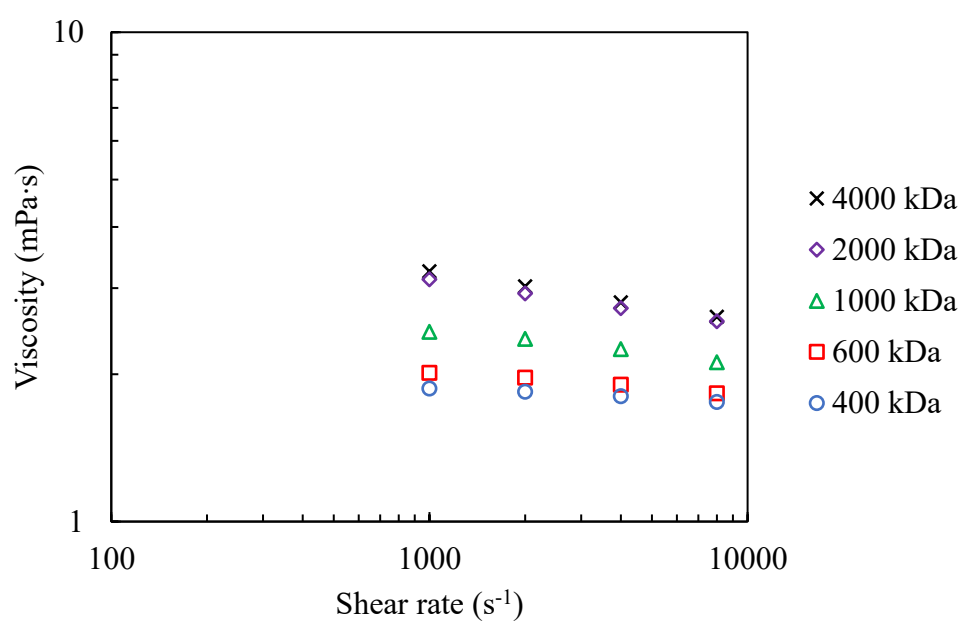
We can see that the viscosity of 20 wt% silica suspension is about 1.9 mPa·s at low shear rate. Even though the shear rate increases, the viscosity almost did not change. It means that the pure silica suspension can be regarded as a Newtonian fluid at this condition.

For the results of viscosity of PEO solutions with different molecular weight, we show the results in Fig. 9. We find the viscosity of PEO solutions decreases with the increasing shear rate. This phenomenon is called shear-thinning [24]. Because the mass fraction of PEO is so low, the difference in viscosity between different molecular weight of PEO polymers is very small, and all the solutions used in this chapter have low viscosities which are near that of water. These results agrees with that of Ebagninin et al [25].

Both the pure silica suspension and pure PEO solutions did not show the shear-thickening.



**Fig. 8** The viscosity of pure silica suspensions against shear rate. The silica concentration was 20 wt%. The temperature was 20°C.



**Fig. 9** The viscosity of pure PEO solutions against shear rate. The PEO concentration was 0.112 wt%. The temperature was 20°C.

### 2.3.3 The zeta potential of silica nanoparticles

#### 2.3.3.1 The theory of 1pK basic Stern model

The charge of silica particles was reported that can be described by a model called 1pK basic Stern model [15]. In this model, an acid dissociation constant and the theory of EDL are used to describe the charging behavior of silica.

The charge of silica is due to the dissociation of the silanol groups on the silica surface



The concentration of dissociated silanol groups  $[\text{SiO}^-]$ , protonated silanol groups  $[\text{SiOH}]$  and total silanol groups  $\Gamma_r$  can be related by

$$\Gamma_r = [\text{SiOH}] + [\text{SiO}^-] \quad (2)$$

The surface charge density  $\sigma$  is due to the dissociation of silanol group, so  $\sigma$  can be written as

$$\sigma = -e[\text{SiO}^-] \quad (3)$$

where  $e$  is the elementary charge. The amount of dissociated silanol groups is influenced by the pH and electrolyte concentration, the equations can be written as

$$\frac{a_{H^+}^s [-\text{SiO}^-]}{[-\text{SiOH}]} = K \quad (4)$$

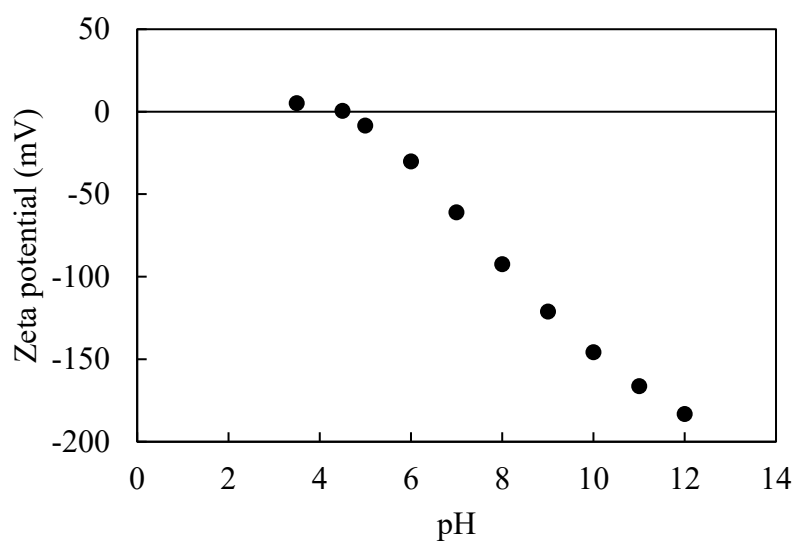
$$a_{H^+}^s = a_{H^+} \exp\left(\frac{-e\psi_0}{k_B T}\right) \quad (5)$$

where  $a_{H^+}^s$  is the activity of proton on the surface of particles,  $a_{H^+}$  is the activity of proton in the bulk,  $\psi_0$  is the surface potential of particles, and  $K$  is the acid dissociation constant of silanol groups.

According to the Stern model, a Stern layer is assumed to be near the surface of silica. The Stern layer is modeled as a condenser with capacitance  $C_s$ , and diffuse layer develops outside the Stern layer. In an 1:1 electrolyte solution, the Stern model can be written as

$$\sigma = C_s(\psi_0 - \psi_d) \quad (6)$$





**Fig. 10** The zeta potential of silica nanoparticles against the pH calculated by 1pK basic Stern model with a condition of 20 mM 1:1 electrolyte. Silica particles were negatively charged at most pH. The magnitude of zeta potential decreased with decreasing pH. At pH about 4, silica particles showed charge neutralization and almost no EDL repulsion existed.

$$\sigma = -\sigma_d = \left( \frac{2\varepsilon_r \varepsilon_0 \kappa k_B T}{e} \right) \sinh \left( \frac{e\psi_d}{2k_B T} \right) \quad (7)$$

With these equations, we can calculate the surface charge density  $\sigma$ , the charge density in diffuse layer  $\sigma_d$ , the surface potential  $\psi_0$ , and the diffuse layer potential  $\psi_d$  at any pH and electrolyte concentration.

### 2.3.3.2 results of zeta potential of silica particles

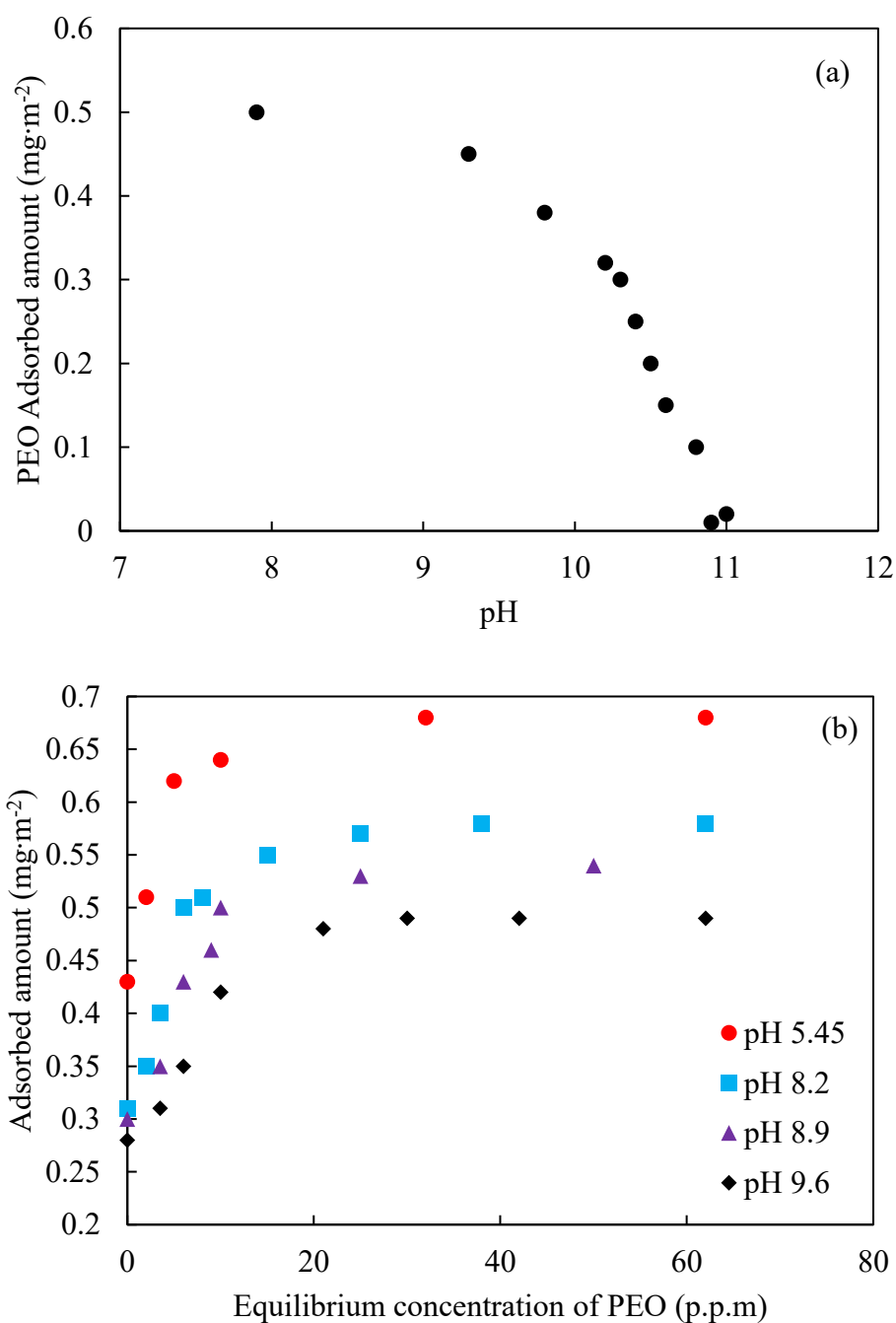
LUDOX TM-50 silica nanoparticles were used in this thesis. The salt concentration of stock suspension was measured to be about 80 mM [16]. We diluted the stock suspension in this study, and the salt concentration of diluted suspension was in a range of 16-48 mM. As a representative, we calculated and showed the zeta potential of silica particles at a salt concentration of 20 mM in this thesis. The results of zeta potential were summarized as a function of pH in Fig. 10.

Silica particles were negatively charged at most pH. The magnitude of zeta potential decreased with decreasing pH. At about pH 4, silica particles showed charge neutralization. The EDL repulsion is determined by zeta potential, therefore, EDL repulsion is low at low pH and increases with pH.

### 2.3.4 Adsorption of PEO to silica surface

The adsorption behavior of PEO to silica surface was studied by previous studies [14,26]. Therefore, we summarized the results of adsorbed amount of PEO which were done by previous studies instead of measuring them in our research.

The results of PEO adsorbed amount are shown in Fig. 11.



**Fig. 11** (a) PEO adsorbed amount to the silica surface against the pH of suspension and (b) Isotherm of PEO. The adsorbed amount of PEO slightly decreased at first, and suddenly decreased rapidly around pH 10. At pH above 11, almost no PEO can absorb to silica. PEO saturation concentration is about 0.5 mg·m<sup>-2</sup>. Data are taken from van der Beek et al. [14] and Rubio et al [26].

In Fig. 11(a), we can find that the PEO adsorbed amount slightly decreased in the pH range of 8-9, and suddenly decreased rapidly in pH 9-11. When pH was above 11, the adsorbed amount of PEO was almost zero. PEO polymers adsorb to silica surface through hydrogen bonds with silanol groups and it is known that silanol group dissociate more at higher pH. Therefore, high pH decreases the hydrogen bonds between PEO and silica, inducing the reduction of PEO adsorbed amount.

In Fig. 11(b), we confirmed that at pH 9.6, silica surface was saturated by PEO with an adsorbed amount of  $0.5 \text{ mg}\cdot\text{m}^{-2}$ .

## 2.4 Summary of this chapter

In this chapter, we measured the size of silica particles, and the viscosity of pure silica suspensions and pure PEO solutions. We also calculated the zeta potential of silica particles by 1pK basic Stern model, and summarized the PEO adsorbed amount against the pH by using the data of previous studies.

The conclusions of this chapter are summarized below:

1. The hydrodynamic diameter of the silica particles is about 38 nm, a bit larger than the measurement by electron microscopy.
2. Pure silica suspension can be regarded as a Newtonian fluid at the measured condition. Pure PEO solutions showed shear thinning phenomenon. Both the pure silica suspension and the pure PEO solutions do not show shear-thickening, and no shake-gel occurs in the measurement process.
3. Zeta potential of silica particles can be calculated by 1pK basic Stern model. At high pH, the magnitude of zeta potential is large, and it decreases with decreasing pH. When pH is around 3, charge neutralization of silica happens.

4. PEO adsorbed amount was reported to decrease with increasing pH. More silanol groups of silica dissociate at high pH, thus hydrogen bonds between PEO and silanol groups decrease. This induces the decreasing in adsorbed amount.

In next chapter, we mixed the silica suspension and PEO solution to observe the state of the mixing suspensions.

### 3. The state diagram of silica-PEO suspensions

In this chapter, we prepared silica-PEO suspensions at various pH, PEO dose, PEO molecular weight and silica concentration. We observed and plotted the states of silica-PEO suspensions into state diagrams. Based on the diagrams, we tried to explain the mechanism of shake-gel, and how the parameters above influence the state of silica-PEO suspension.

The conclusions of this chapter are summarized below.

1. Silica-PEO suspensions show a state change of cloudy, permanent gel, shake-gel, and high viscosity sol in different conditions. Bridging effect of PEO polymers among silica particles seems to be the most possible reason of the state change.
2. pH influences the state by changing the zeta potential of silica and the adsorbed amount of PEO polymers. Too low pH leads to too strong bridging effect and weak electric repulsion of silica, thus the suspensions turn to cloudy. Too high pH decreases the adsorbed amount of PEO and increases the electric repulsion. This inhibits the formation of gel, and the suspensions show a high viscosity sol state. Shake-gel only occurs at appropriate pH range.
3. PEO dose also affects the state of silica-PEO suspension. If the PEO dose is small, the amount of PEO polymers is not enough to make gel network. In this case, suspensions show a cloudy state. If the PEO dose is too high, the surface of silica may be saturated by the polymers, and this prevents the formation of bridges between particles.
4. Longer PEO polymers promote the formation of gel. PEO polymers with high

molecular weight has more monomers in one polymer chain. It is easier for longer polymers to bind more particles to make gel.

5. Higher silica concentration also promotes the gelation of silica-PEO suspensions. The silica particles act as connecting points between PEO polymers. Therefore, more particles are helpful to build get network.
6. Whether the suspension gels or not can be determined by the average distance of silica particles and length of PEO polymers. We plan to do more experiments about this.

In next chapter, we discuss the shake-gel phenomenon by observing the relaxation time of the silica-PEO suspensions.

## **4. The relaxation time of silica-PEO suspensions**

### **4.1 Introduction**

Relaxation is a specific phenomenon for shake-gel suspensions. We can divide the gelled suspensions into permanent gel and shake-gel by the gel will relax or not. Long relaxation time represents that the gel state is stable, while for unstable gels, the relaxation time can be short or even difficult to observe. For shake-gel, the relaxation time is determined by the composition of suspension. Furthermore, the information about relaxation time cannot be obtained from state diagrams in Chapter 3. Therefore, measuring and showing the relaxation time as a function of composition are important methods to evaluate the stability of a shake-gel suspension affected by composition.

In this chapter, we define the relaxation time, and calculated the relaxation time from the photos we took in Chapter 3. Based on the results of relation between the relaxation time and the composition, we discuss how the composition influences the stability of shake-gels.

### **4.2 Experiments**

#### **4.2.1 Materials**

The materials used in this chapter were the same with that in Chapter 3.

#### **4.2.2 Methods**

The methods in this chapter were the same with that in Chapter 3.

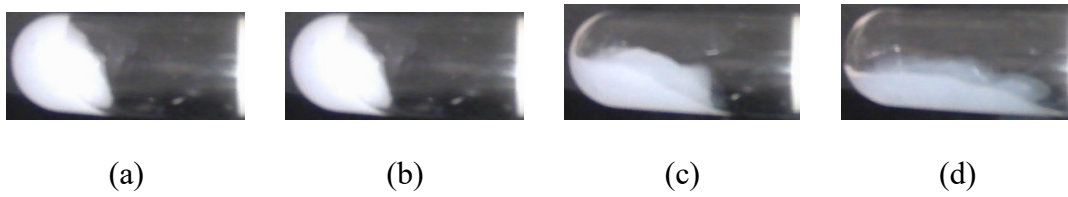


## 4.3 Results and discussion

### 4.3.1 The relaxation process of shake-gels and the definition of relaxation time

When we stopped shaking silica-PEO suspensions, the relaxation process started. In the relaxation process, we were able to find some obvious changes in the state of suspensions by time. Immediately after the shaking, the suspensions showed a gel state. The elasticity of gelled suspensions can support their weight themselves, so the interface between gel and air can make a large angle or even be vertical to the ground (Fig. 19(a)). Along with the time, the gels started to relax, and the angle between interface and ground decreased. In this regime, the gels kept sticking to the upper wall of the test tube (Fig. 19(b)). Then, the relaxation process proceeded continuously, the elasticity of the suspension decreased again. The suspension became no longer able to support their weight, and the gels slid or flowed down from the upper wall of the test tubes (Fig. 19(c)). After this regime, the angle between interface and ground decreased continuously. Finally, the interface became horizontal (Fig. 19(d)).

Measuring the relaxation time of the suspensions can help us understand the effect of component to the stability of shake-gel. However, it is difficult to measure the time of interface becoming horizontal exactly. Thus, in this thesis, we defined the condition that the gel sticks to the half of the bottom of the test tube as a relaxed state (like Fig. 19(c)). The time from finishing the shaking to the relaxed state is defined as the relaxation time of this suspension. The photos used to confirm the states and calculate the relaxation time are summarized in the Appendix A (Fig. A1-A7).

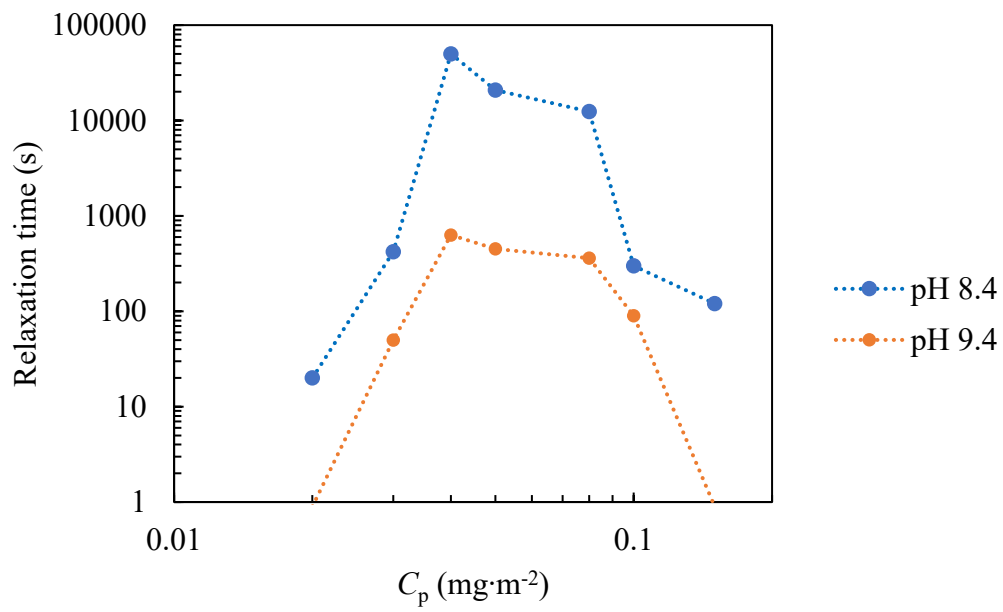


**Fig. 19** The relaxation of silica-PEO suspension after shaking. (a) Immediately after shaking, making a large angle or even be vertical to the ground, (b) In the relaxation process, even keeping sticking to the upper wall of test tubes, (c) Due to decrease of elasticity by relaxation, gel slid or flowed down from the upper wall, (d) The angle between interface and ground decreases continuously. The inner diameter of the test tubes was 15 mm.

#### **4.3.2 The results and discussion of the relaxation time of suspensions consist of 1000 kDa PEO polymers**

In Fig. 20, we show the results of relaxation time with changing pH. The relaxation time varies from several minutes to several hours. Generally, the relaxation time at pH 8.4 is longer than that at pH 9.4. In both conditions of pH 8.4 and 9.4, we can see the relaxation time increases to a maximum and then decreases again with the increasing  $C_p$ . The longest relaxation time occurred at about  $C_p = 0.04 \text{ mg}\cdot\text{m}^{-2}$ .

As a reason of the effect of pH on the relaxation time of shake-gel, we consider that the change in the adsorbed amount of PEO and electric repulsion between silica particles by pH induced the variation in relaxation time. If pH is low, a lot of PEO polymers can adsorb to the surface of silica [14] and the bridging attraction becomes strong. Simultaneously, the electric repulsion between silica particles is weak due to the low zeta potential [30]. Therefore, the hydrogen bonds between silica and PEO particles are difficult to break up. Silica nanoparticles are hard to be dispersed, thus the relaxation time at pH 8.4 is longer than that at pH 9.4.

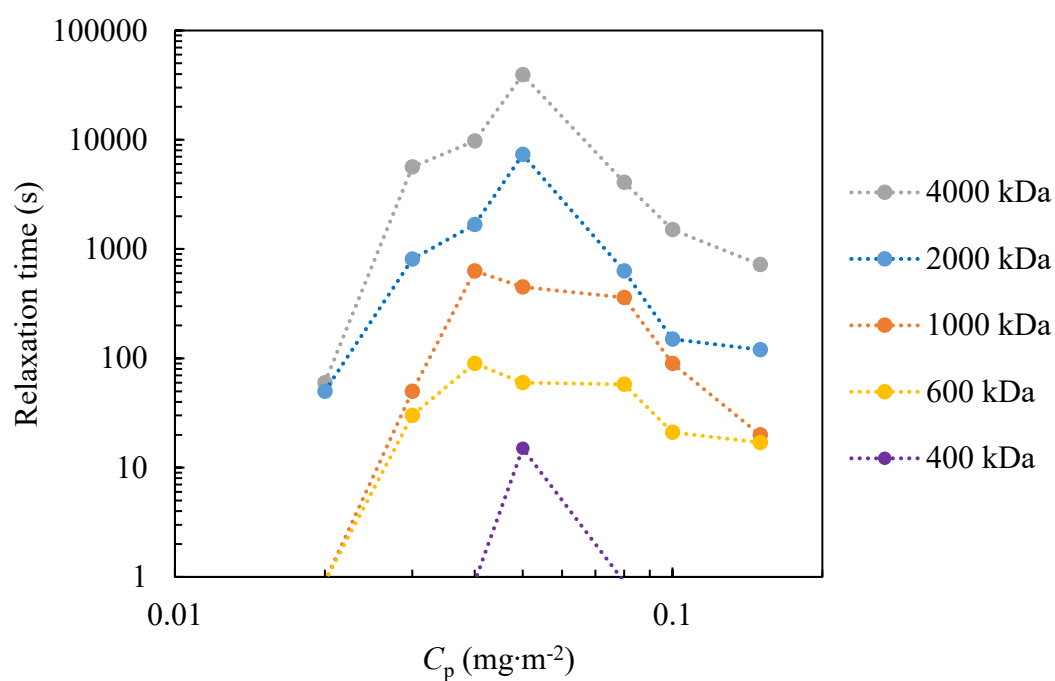


**Fig. 20** The relaxation time of silica-PEO suspensions consisted of 1000 kDa PEO under the pH of 8.4 and 9.4. The temperature was 20°C. The dotted line is eye guide. For suspensions at pH 10, almost of the silica-PEO suspensions did not show a gel state. We cannot measure the relaxation time of them.

### 4.3.3 The results and discussion of the relaxation time of suspensions at pH 9.4 with different polymer molecular weight

The results of relaxation time of suspension at pH 9.4 is summarized in Fig. 21. For 400 kDa silica-PEO suspensions, we found all the relaxation times were several seconds. The relaxation time was too short that we could not measure the time of suspensions consisted of 400 kDa PEO correctly. When the molecular weight increased, we observed the increase in relaxation time for all  $C_p$  suspensions. For 4000 kDa suspensions, the relaxation time was very long, even reached several hours. We also found that longest relaxation time occurred at about  $C_p = 0.04-0.05 \text{ mg}\cdot\text{m}^{-2}$ , regardless of the molecular weight. Furthermore, the  $C_p$  of longest relaxation time is also the same with different pH.

Higher molecular weight PEOs induce longer relaxation time due to long polymer chains. If  $C_p$  is the same, even though the molecular weight of PEO changes, the number of monomers of PEO is almost the same. Therefore, the differences of relaxation time between different molecular weight are mainly caused by the size of PEO. PEO with larger molecular weight has long loop and tail. Long loop and tails of polymer chain means that a polymer chain can attach one silica particle at more points and can also trap more particles. This induces a stronger gel network. Because of the increasing of adsorption points, the gel network becomes more stable. Additionally, stretched chains are calculated to tend to relax slowly to the random-coil-like state if the shear flow disappears [36]. Especially, large molecular weight polymers are reported to have longer rheological relaxation time by experiments [37]. These mean that large polymers need more time to relax to the random-coil-like state. Due to the reasons above, the suspensions consisted of higher molecular weight PEO polymers have longer relaxation time. On the contrary, PEOs of molecular weight of 400 and 600 kDa have a shorter loop. Thus, the suspensions are difficult to form gels, and the relaxation time is shorter for the shake-gels.

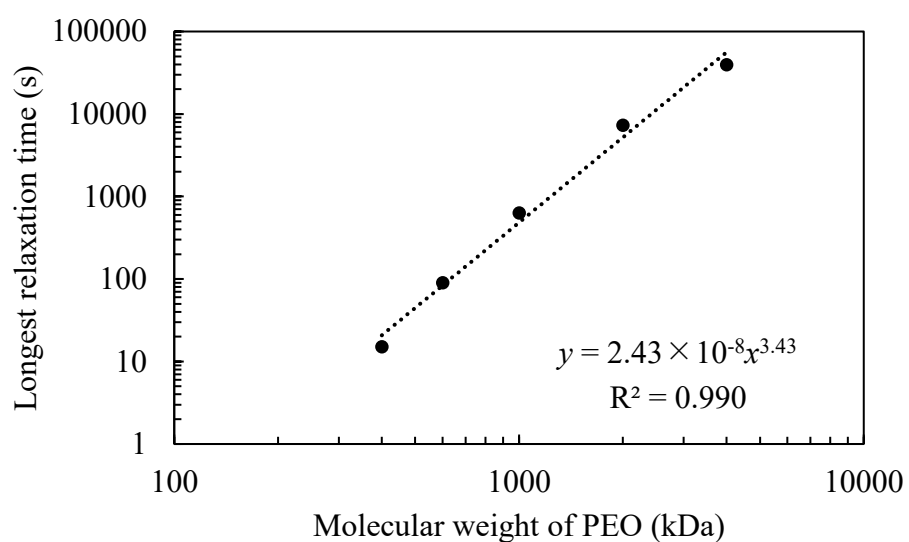


**Fig. 21** The relaxation time of silica-PEO suspensions consisted of 400, 600, 1000, 2000 and 4000 kDa PEO. The pH was 9.4. The dotted line is eye guide. The temperature was 20°C. The suspensions consisted of 400 kDa PEO slid or flowed down so quickly that it was difficult to measure the relaxation time of them.

#### 4.3.4 The effect of $C_p$ to the relaxation time of shake-gels

Through both the experiments on the effect of pH and PEO molecular weight, we noticed that, when  $C_p$  increased, the relaxation time of silica-PEO suspension increased to the maximum and decreased again. Moreover, at about  $C_p = 0.04-0.05 \text{ mg}\cdot\text{m}^{-2}$ , silica- PEO suspension always showed their longest relaxation time.

$C_p$  influences the relaxation time of silica-PEO suspensions by affecting the adsorbed amount of PEO. If  $C_p$  is low, increasing PEO dose promotes the bridges between particles. The bridges among silica particles increase, and thus the gel structure gets more stable. This makes the relaxation time of shake-gel increase to the maximum. If  $C_p$  increases further, more PEOs adsorb to the surface of silica and the available adsorption sites on the silica surface decrease. Silica surface is saturated by PEO polymers, and it becomes difficult for polymers to connect several particles. In this condition, PEO polymers are easier to desorb from particle surfaces, because of fewer hydrogen bonds per polymer chain. Therefore, the relaxation time decreases. Furthermore, the result that longest relaxation time always occurs at about  $C_p = 0.04-0.05 \text{ mg}\cdot\text{m}^{-2}$ , irrespective of pH and the molecular weight of PEO, is such interesting. This indicates that PEO dose per surface area seems to be the most definitive factor which influences the relaxation of shake-gel. This also supports the hypothesis that enough available adsorption site on the silica surface is necessary to build and keep the bridges between silica particles.



**Fig. 22** The longest relaxation time of suspensions consisted of each molecular weight PEO under the pH of 9.4. The temperature was 20°C. The longest relaxation time increased with the increasing molecular weight of PEO. The relaxation time showed a power-law relationship with molecular weight.



#### 4.3.5 Discussion about the longest relaxation time and PEO molecular weight

As discussed in Chapter 4.3.3, relaxation time of silica-PEO suspensions is related to the molecular weight of PEOs. If we try to exclude the effect of  $C_p$  to relaxation time, we may find some essential relationship between relaxation time and PEO molecular weight. We found the longest relaxation time always occurred at the same  $C_p$ , so maybe it is interesting to discuss the relationship between longest relaxation time and molecular weight. We show the longest relaxation time as a function of PEO molecular weight at pH 9.4 in Fig. 22.

We can confirm that the longest relaxation time increases with the increasing molecular weight of PEO, and they follow the power-law relationship. The power is 3.4.

To explain this phenomenon, we notice that de Gennes et al. [38,39] promoted the reptation model. This model predicts a power-law relationship between relaxation time of polymer melt and polymer molecular weight due to the restriction in movement of polymers. By this model, polymers are confined in tubes [40] and can only move in their own tube by snake-like motion. Furthermore, Doi [24] showed that entangled polymers also showed similar conclusions in polymer melts. Even though the definition of relaxation time of previous studies and our research is different, the similar power-law relationship and the same index are worth to be discussed. Relaxation process is inferred to relate to the deformation that linear-like PEOs turn back to random-coil-like and this deformation occurs with the cancelation of entanglement and the movement of PEOs. Therefore, the similar power-law relationship and index indicate that not only the adsorption but also the entanglement may occur in the gelation of silica-PEO suspension. Furthermore, limitation of movement of PEOs may also contribute to the relaxation process.

## 4.4 Summary of this chapter

In this chapter, we define the relaxation time of shake-gels, and measured the relaxation time with the photos of shake-gels in relaxation process. Based on these results, we discussed the stability of shake-gel along with the changing pH,  $C_p$ , and molecular weight of PEO.

The conclusions of this chapter are summarized below:

1. Low pH increases the adsorbed amount of PEO and decreases the electric repulsion between silica particles. This leads to a long relaxation time in shake-gels.
2. High molecular weight PEO polymers promote the formation of bridges between particles because of the long loop and tails. Large polymers can also bind multiple particles to make the gel network more stable. Thus, the relaxation time becomes longer.
3.  $C_p$  also influences the relaxation time of shake-gels. When  $C_p$  increases, the relaxation time increases to the maximum, and then decreases. The reason seems to be that increasing PEO dose promotes the formation of gel network at low  $C_p$ , but saturates the surface of silica and prohibits the bridging at high  $C_p$ .
4. The longest relaxation time shows a power-law relationship with the molecular weight of polymer. The index is the same with the relaxation time of polymer melts, even though the definition is different. This result indicates that the entanglement of PEO polymers occurs as well as the adsorption of PEO, and the limitation of movement of PEOs also contributes to the relaxation process.

In next chapter, we discussed the viscosity of silica-PEO suspensions with different shear rates.

## 5. The viscosity of silica-PEO suspensions under different shear rates

In this chapter, we obtained the relationship between viscosity of silica-PEO suspensions and the shear rate with different components and different temperature.

The conclusions of this chapter are summarized below:

1. The shear-thickening occurs at the same time with the gelation of silica-PEO suspensions. We used the shear-thickening phenomenon to recognize the start of gelation in this experiment.
2. Lower molecular weight of PEO polymers and higher pH prevent the gelation of silica-PEO suspension. Suspensions with  $C_p = 0.04-0.05 \text{ mg}\cdot\text{m}^{-2}$  show the highest viscosity regardless of the molecular weight of PEO. These results agree with the results of relaxation time in Chapter 4.
3. Increasing temperature prohibits the formation of gel. The possible cause may be the decreasing solubility of PEO and the activation of thermal motion of silica particles.

In next chapter, we look back to all the experiments, and summarize the conclusions of the whole research.

## 6. Summary of this thesis and perspectives

### 6.1 Summary of this thesis

To gain further understanding of shear-induced gelation of silica-PEO suspensions, we conducted a series of experiments in this research.

In Chapter 2, we characterized the materials that used in this thesis. We measured the size of silica particles, and the viscosity of the pure silica suspensions and the pure PEO solutions. Furthermore, we calculated the zeta potential of silica under different pH by using 1pK basic Stern model and showed the adsorbed amount of PEO to silica surface with the data of previous study. We found that the pure silica suspensions can be regarded as a Newtonian fluid, and the PEO solutions showed the shear-thinning. No shake-gel occurred in the measurement process. Silica particles had almost no charge at about pH 3 and showed negative charge when pH was above 3. The magnitude of zeta potential of silica increased with increasing pH above 3, and the adsorbed amount of PEO decreased with increasing pH.

In Chapter 3, we mainly observed the state at various compositions by using state diagrams. We prepared the silica-PEO suspension with different pH, PEO dose, PEO molecular weight and silica concentration. After the preparation we pre-mixed the suspensions, left them stand for 24 h to relax, and shake them with a constant rotation for 60 s to observe the state change of suspensions. We found the shake-gel almost occurred in a pH range of 8 to 9.4 because pH influenced the adsorbed amount of PEO and the electric repulsion between silica particles.  $C_p$  also influenced the gelation by affecting the adsorbed amount and the number of polymer bridges. High molecular weight polymers promoted the formation of gel because of their long loop and tail. High silica concentration also promoted the gelation process because more silica particles can act as crosslinkers of PEO polymers. Furthermore, we found that  $R_g$  of PEO being larger than the average distance between nearest

silica surfaces was necessary to form gels.

In Chapter 4, we measured the relaxation time of suspensions to evaluate the stability of shake-gel. We started to take photos of suspensions immediately after the shaking, and the photos were taken continuously to complete relaxation or up to 24 h. Then, we defined the time after shaking to relaxed state as the relaxation time. We found that at low pH suspensions had longer relaxation time, means the low pH suspensions were more stable. It may be due to the increase of adsorbed amount of PEO, and the decrease of the electric repulsion of silica particles. Molecular weight of PEO also influenced the relaxation time. Suspensions consisted of higher molecular weight PEO polymers showed longer relaxation time. We inferred it was because of the long loop and tail of the larger polymers, which can trap and bind more particles to make gel network stable. We also found that the longest relaxation time always occurs at  $C_p=0.04-0.05 \text{ mg}\cdot\text{m}^{-2}$  regardless of the pH and molecular weight. Furthermore, the longest relaxation time with different molecular weight had a power-law relationship with the molecular weight. The relationship is similar with the relaxation time of polymer melt, even though the definition of relaxation time is different. This result indicates that not only the adsorption, but also the entanglement may occur in the gelation process. Furthermore, reptation model might also explain the relation between relaxation time of shake-gels and PEO molecular weight.

In Chapter 5, we measured the viscosity of silica-PEO suspensions. A part of suspensions showed the shear-thickening at the critical shear rate, and at the same time the gelation of suspensions occurred. Compared to the suspensions consisted of 400 kDa PEO, the suspensions consisted of 1000 kDa PEO polymers had lower critical shear rate, indicating that higher molecular weight PEO promoted the formation of gel. When pH increased to about 10, we cannot confirm the shear-thickening phenomenon. This means that increasing pH prevented the bridging effect due to the decrease of adsorbed amount and the increase of electric repulsive

force. Then the gelation was prohibited. The results above agree with that in Chapter 3 and 4. We also verified the viscosity of suspensions with different temperature. We found that the critical shear rate increased with the temperature, and finally we could not observe the shear-thickening at 40°C. Therefore, we consider that the high temperature prevented the gelation. This may be due to the decreasing solubility of PEO and higher activation of thermal motion of silica particles at high temperature.

## **6.2 Perspectives and recommended future studies**

In this thesis, we verified the hypothesis by previous studies that the main cause of the shake-gel phenomenon is the bridging effect of PEO polymers, and obtained the results supporting this hypothesis. As parameters influencing the bridging effect of PEO, pH,  $C_p$ , molecular weight, silica concentration, and suspension temperature were chosen to discuss their effect to the state, relaxation time and viscosity of silica-PEO suspensions.

Through this research, we showed that appropriate pH and  $C_p$  were needed to form shake-gels. We also found that high silica concentration, high molecular weight and low temperature promoted the formation of gels.

Moreover, we promoted two new hypotheses. One is that it is necessary for PEO polymers to be larger than the distance between silica particles to form gels. The other one is that the relaxation phenomenon of shake-gel relates to the entanglement and reptation of PEO polymers.

However, almost all the results in this research were obtained by direct observation. Therefore, we may not be able to recognize the border between sol and gel state correctly. Furthermore, the definition of relaxation time may be ambiguous. To solve the problems above, we recommend doing viscoelasticity measurements to recognize the gelation and relaxation process. As another advice, a method of

observing the gelation by scattering was reported by Prof. Shibayama. We think this can also be used into the research of shake-gels.



## **Appendix A: The photos to calculate the relaxation time at various types of condition**

In Appendix A, we showed the photos we used to calculate the relaxation time of suspensions.

The figures are from Fig. A1 to A7.

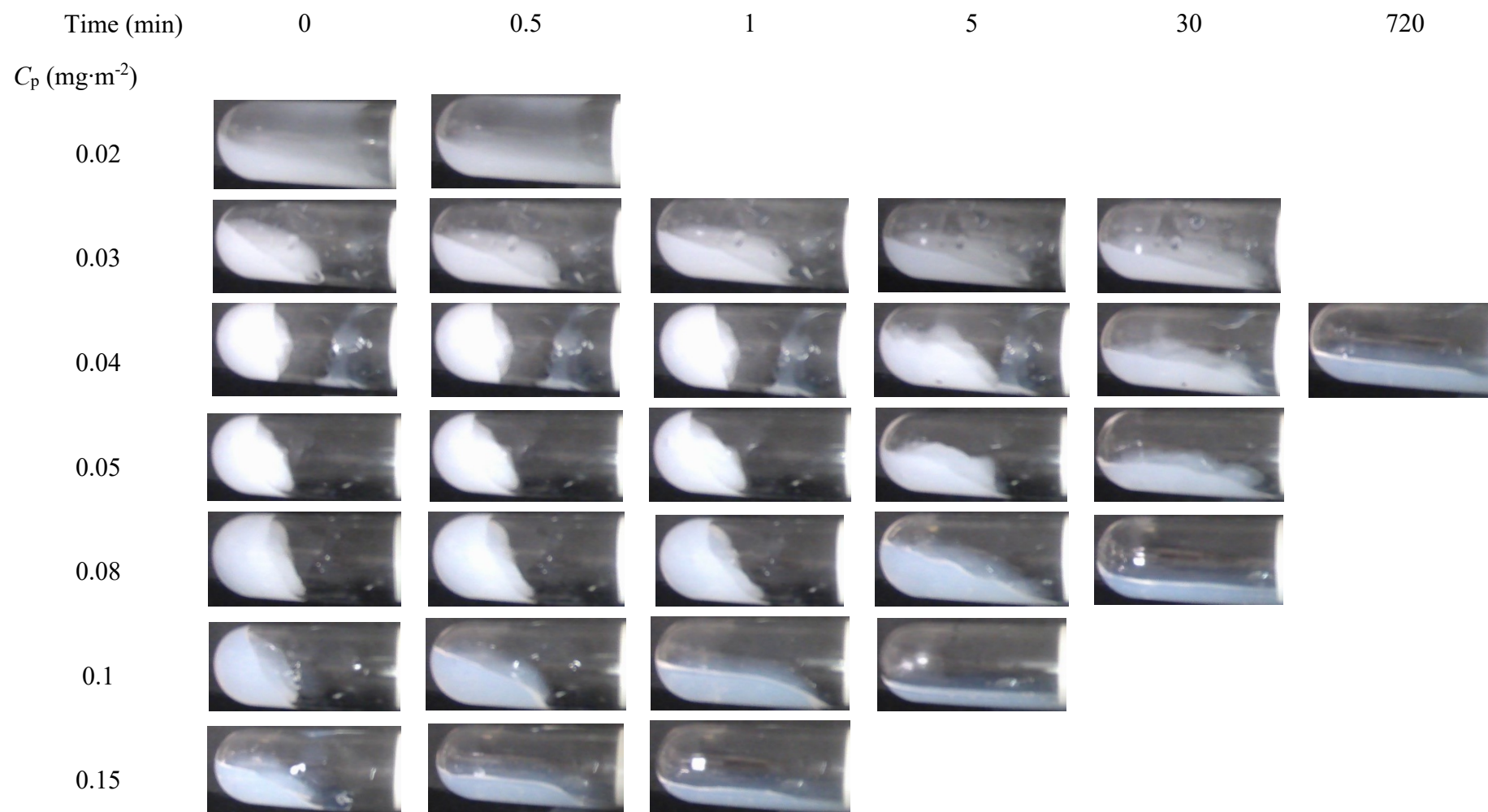


Fig. A1 Temporal change of the 20% silica suspensions with different  $C_p$  of PEO with 1000 kDa at pH 9.4. Almost all the suspensions were shake-gels. At about  $C_p=0.04$  mg·m<sup>-2</sup>, the relaxation time was longest. The inner diameter of the test tubes was 15 mm.

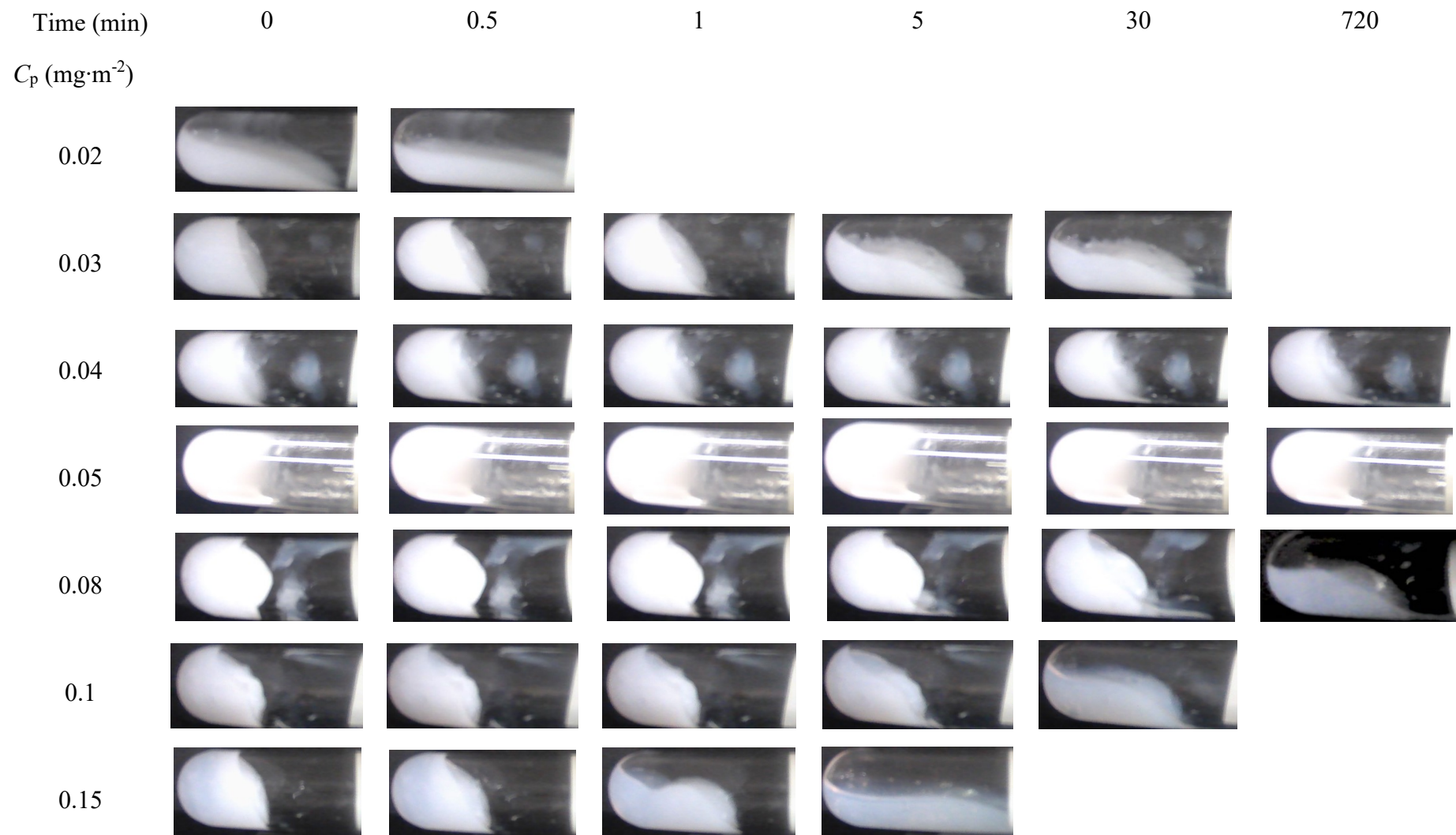


Fig. A2 Temporal change of the 20% silica suspensions with different  $C_p$  of 1000 kDa at pH 8.4. Almost the suspensions were shake-gels. However, the relaxation time was longer than that of pH 9.4. At about  $C_p=0.04$  mg·m<sup>-2</sup>, the suspensions showed longest relaxation time. The inner diameter of the test tubes was 15 mm.

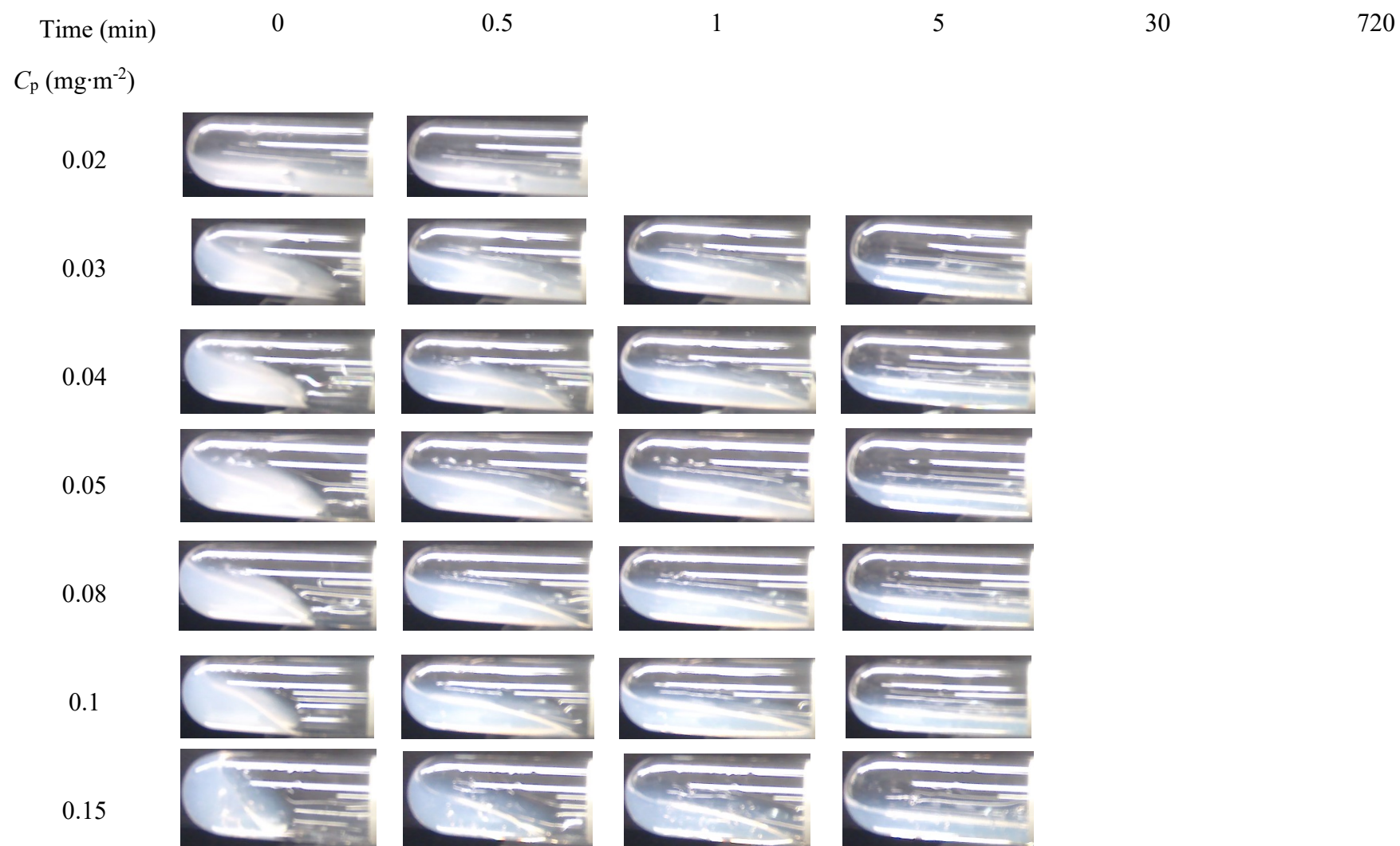


Fig. A3 Temporal change of the 20% silica suspensions with different  $C_p$  of PEO with 1000 kDa at pH 10. Almost all the suspensions were high viscosity sols. The inner diameter of the test tubes was 15 mm.

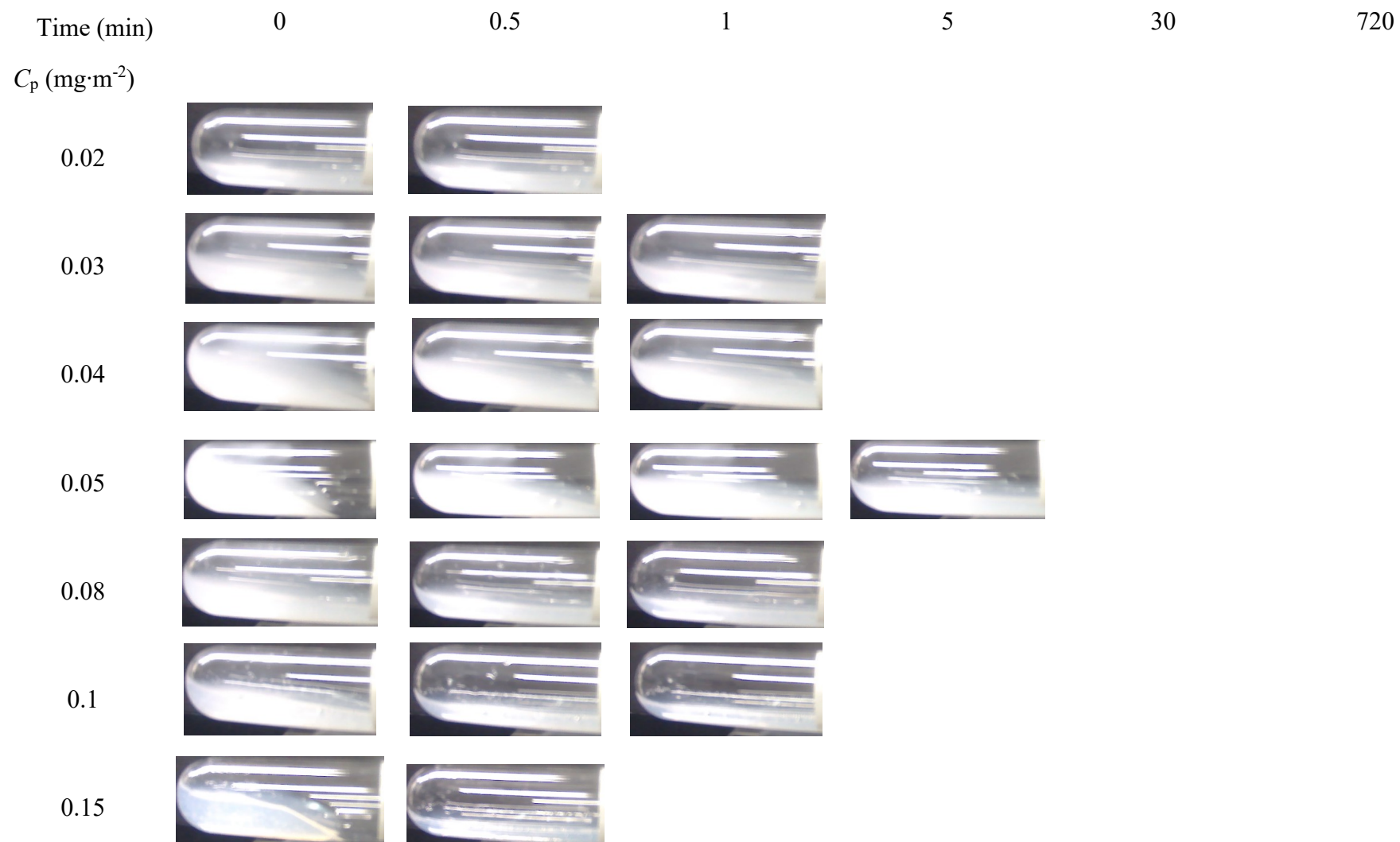


Fig. A4 Temporal change of the 20% silica suspensions with different  $C_p$  of PEO with 400 kDa at pH 9.4. The existence of shake-gel was confirmed. However, the relaxation time was too short, and they relaxed before the capture equipment was set. We were not able to measure the relaxation time correctly. The inner diameter of the test tubes was 15 mm.



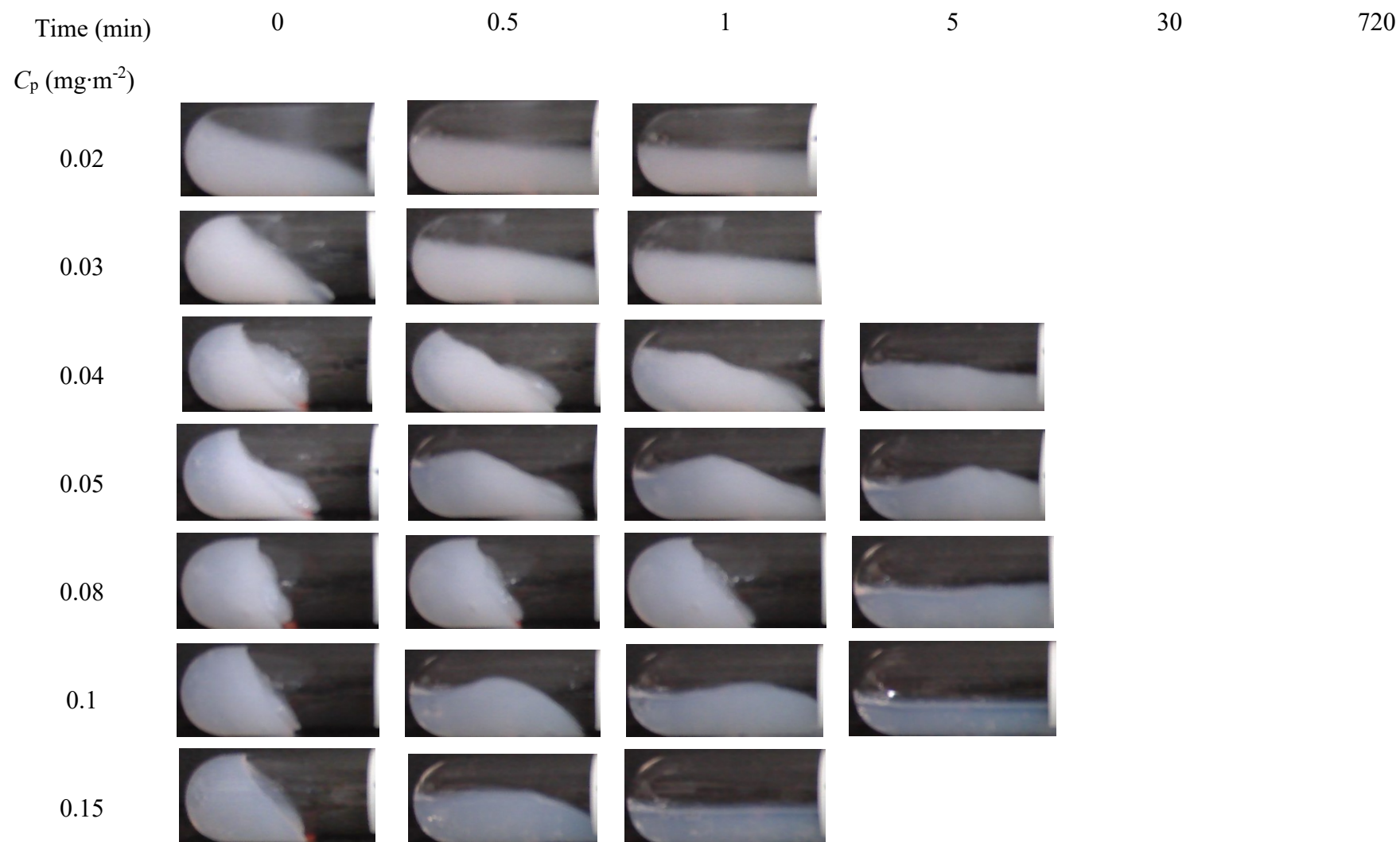


Fig. A5 Temporal change of the 20% silica suspensions with different  $C_p$  of PEO with 600 kDa at pH 9.4. Gelled suspensions were more than the ones consisted of 400 kDa PEO polymers. The inner diameter of the test tubes was 15 mm.

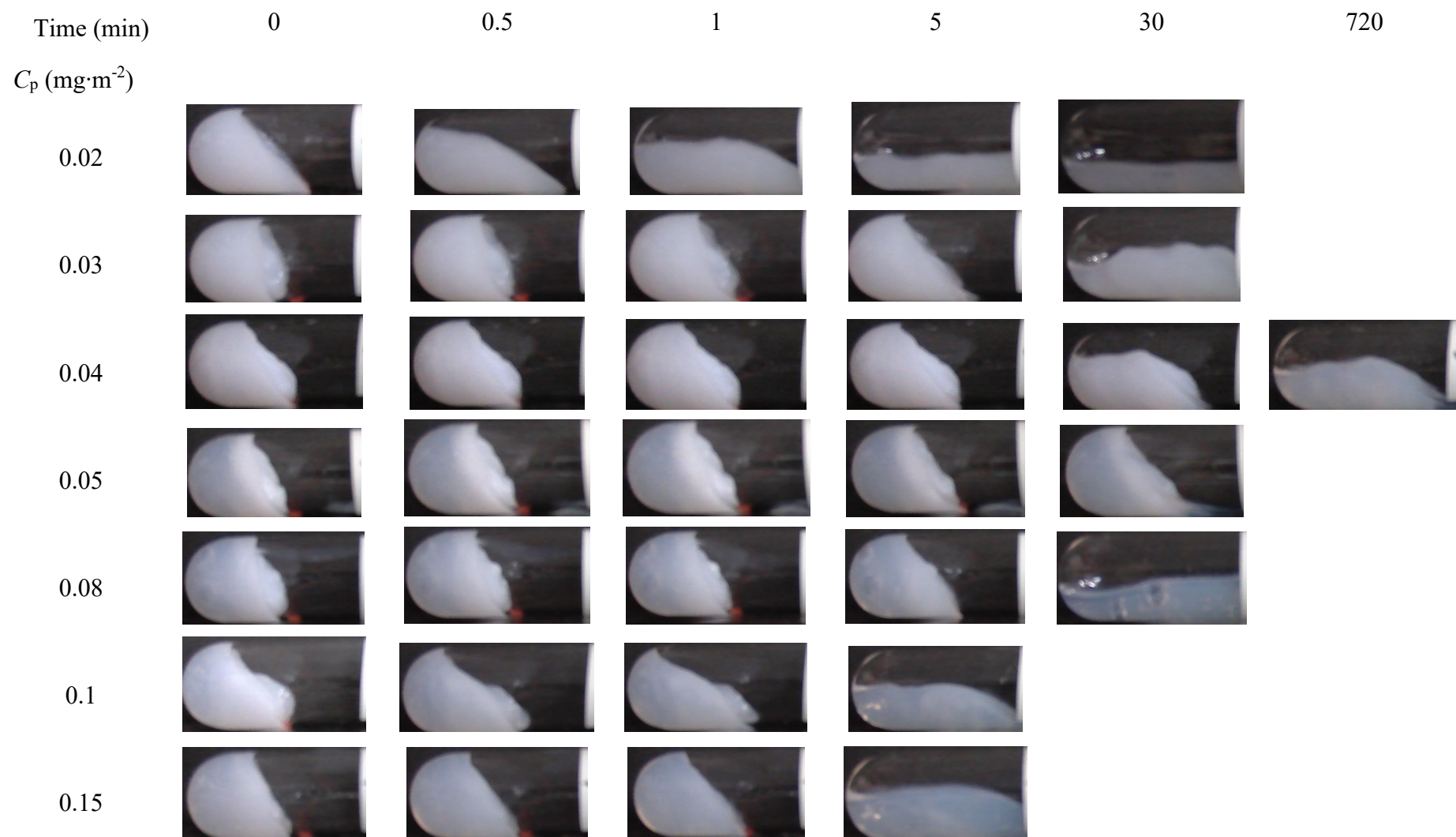


Fig. A6 Temporal change of the 20% silica suspensions with different  $C_p$  of PEO with 2000 kDa at pH 9.4. Almost of the suspensions were shake-gels. The inner diameter of the test tubes was 15 mm.

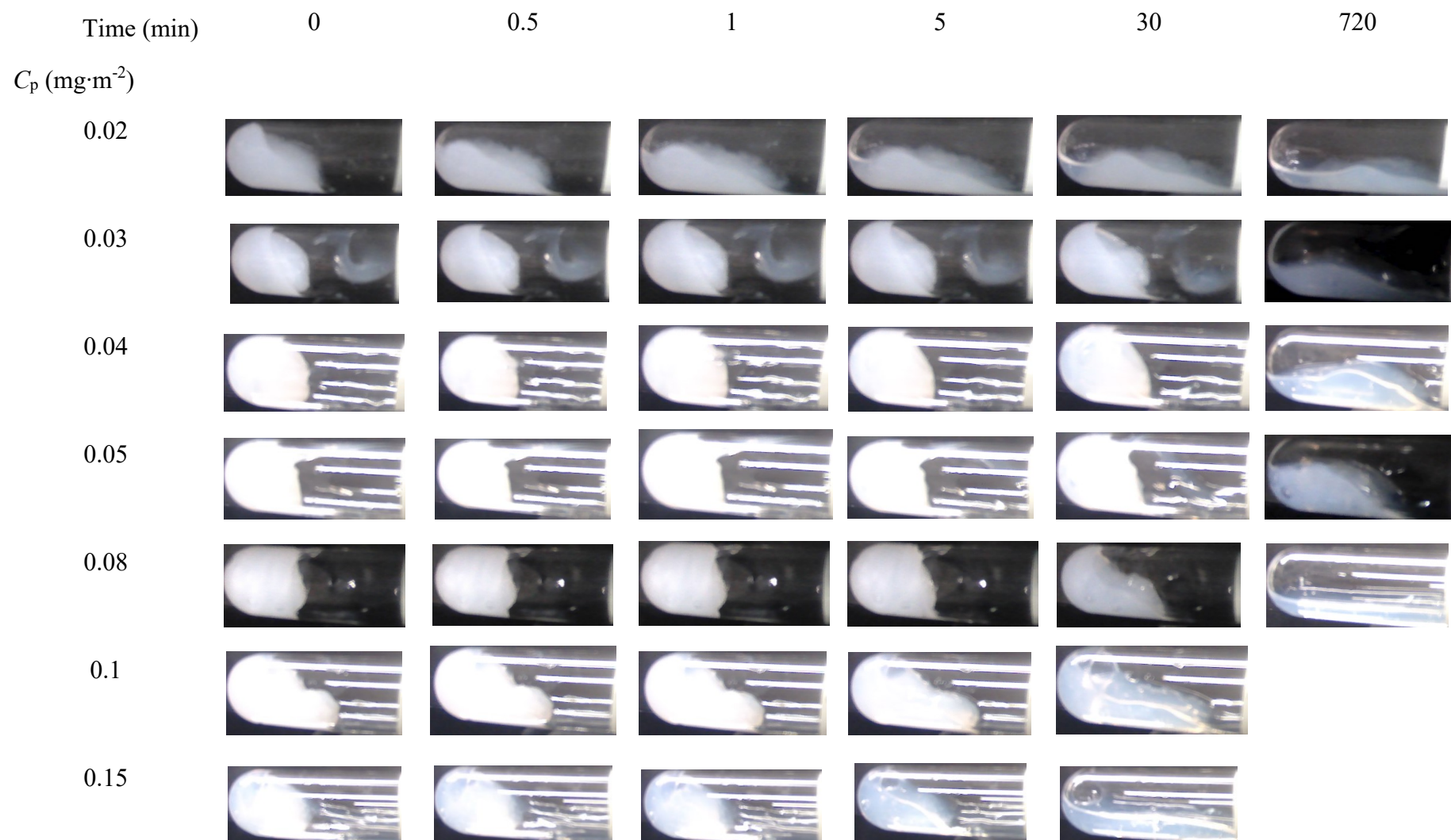


Fig. A7 Temporal change of the 20% silica suspensions with different  $C_p$  of PEO with 4000 kDa at pH 9.4. All the suspensions were shake-gels. The relaxation time were the longest. The inner diameter of the test tubes was 15 mm.



## Appendix B: The small angle X-ray scattering (SAXS) experiments

In this chapter, we did the SAXS measurement of silica-PEO suspensions. We used Generalized Indirect Fourier Transformation (GIFT) to determine the structure factor  $S(q)$  and pair distance distribution function  $p(r)$ . Based on these two functions, we discussed about the shape and the average distance between silica particles during the gelation and relaxation process.

The conclusions of this chapter are summarized below:

1. No obvious change was observed in the size of silica particles, indicating no aggregation occurred in the gelation process.
2. The peak of  $S(q)$  changed with  $C_p$ , and the highest peak appeared at  $C_p=0.05$  mg/m<sup>2</sup>. This means that the dose determined the interaction between silica particles. Furthermore, this also showed that  $C_p=0.05$  mg/m<sup>2</sup> may be the optimum for the formation of shake-gel.
3. The peak of  $S(q)$  showed obvious difference before and after shaking. In the relaxation process, the interaction between silica particles return to the state before shaking gradually.

## **Appendix C: The shake-gel of silica-PEO suspension in the presence of lysozyme**

In this chapter, we measured the viscosity of silica-PEO suspensions in the presence of lysozyme. We compared the viscosity against shear rate with and without lysozyme. We also measured the viscosity of PEO-lysozyme mixture. We discussed the effect of lysozyme with results above.

The conclusions of this chapter are summarized below:

1. Critical shear rate of silica-PEO suspension in the presence of lysozyme is smaller than that without lysozyme, indicating that lysozyme promotes the formation of shake-gel.
2. We cannot confirm shear-thickening phenomenon in PEO-lysozyme mixture, and we did not observe any change in viscosity even though the mass fraction of lysozymes changed either. Therefore, the cause of promoting gelation by lysozyme may be the adsorption of lysozyme onto the surface of silica.

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