

Rheological Behavior of Nanosilica Suspensions in Poly(Ethylene Oxide) Solutions with Sodium Chloride

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Abstract

Suspensions of silica nanoparticles showed shear-thickening profiles under steady shear conditions up on addition of a small amount of poly(ethylene oxide) (PEO). The suspensions turned into gels upon shaking and their fluidity was recovered several minutes after resting. We studied the rheological properties of these shake gels with small amounts of sodium chloride (NaCl). Gelation occurred at lower shear rates upon addition of small amounts of NaCl. In addition, the time taken by the gelated samples to recover their original viscosity increased with the increasing NaCl content. The weakened repulsive interactions between the silica particles upon NaCl addition lead to particles in closer proximity, and three-dimensional networks of PEO chains are easily formed as the electric double layer of the particles becomes thinner.

Keywords

Suspension, Nanoparticles, Shake Gel, Sol-Gel Transition, Electric Double Layer

1. Introduction

When considering suspensions of fine particles in polymer solutions, the polymer chains can adsorb to different particles, binding them together and creating polymer bridges [1] [2] [3] [4]. In order to bridge large particles, several polymer chains must attach to the surface of the particles. In this scenario, each polymer molecule binds the particles at multiple positions of the chain and it is hard to break all those points of attachments imultaneously. Therefore, polymer bridging is considered irreversible. On the other hand, for small particles of diameter <30 nm, only a few points are required to bind the particles [5] [6] [7], and the polymer bridges can be broken by thermal motion, leading to reversible bridging

[8] [9]. Such colloidal particle/polymer mixtures are commonly applied in industrial and environmental fields [10] [11] [12] [13].

Poly(ethylene oxide) (PEO) is a well-known water-soluble polymer. PEO has many ether oxygen atoms in the main chain and, upon contact with silica, hydrogen-bonds with the silanol groups are formed [9]. When a small amount of PEO is dissolved in a silica particle suspension, adsorption of the polymer on the particles influences its rheological properties. For example, such a suspension would show shear-thickening behavior under steady shear flow. Specifically, discontinuous viscosity jumps are observed at certain shear rates, and the suspensions turn into gels after shaking [14]. It is believed that gelation occurs due to elasticity of the polymer chains between each two points of attachment on the surface of the particles [15]. Furthermore, such gelled suspensions recover their original fluidity under quiescent conditions [9] [14]. The temporary networks created under shear flow collapse after thermal motion treatments under these conditions. Therefore, nanoparticle suspensions with polymers show sol-gel transitions controlled by shaking or flow-speed conditions [14]. It is considered that the number of silica particles attached to each polymer chain increases and temporary 3D network structures are created by shaking the suspensions [9]. This phenomenon has been observed for clay nanoparticles (laponite) suspended in PEO aqueous solutions [16].

In this study, we added small amounts of sodium chloride to nanosilica suspensions containing PEO and measured the rheological properties of the resulting mixtures. From the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [17] [18] [19] which explains the dispersion stability of aqueous suspensions, the electric double layer interactions between particles are weakened upon salt addition and the dispersion stability of suspensions is also weakened. It is expected that small amounts of salts influence the polymer chain network structures and the rheological properties of nanosilica suspensions with PEO. We compared the rheological properties of samples with PEO of different molecular weight and studied the influence of the polymer chain length. In addition, we evaluated the time dependence of the viscosity of gelled samples at low shear rates and determined the time taken by the fluidity to return to its original value.

2. Materials and Methods

2.1. Materials

We used colloidal silica suspensions (Cataloid SI-30, Catalyst & Chemicals Ind. Co., Ltd. (Japan), silica 30wt%). The diameter of the spherical particles was 11 nm. Sodium chloride (NaCl) and poly(ethylene oxide) (PEO) samples of molecular weight 500,000 and 2,000,000 were obtained from Wako Pure Chemical industries, Ltd. (Japan). APEO sample of molecular weight $M = 200,000$ was provided by Polysciences Inc. (U.S.). When we added NaCl crystals to the colloidal silica suspensions directly, the silica particles aggregated drastically and NaCl could not be dissolved in the suspensions. Therefore, we first dissolved NaCl and PEO in water (about 10 g) and then, colloidal silica and rest of water

were added gradually. The weight fraction of silica nanoparticles in all the samples used in this study was 15wt%. Before rheological analysis, the samples were mixed at 40 rpm for at least 24 h on a rolling device (mix rotor VMR-5R, AS ONE Co., Japan).

2.2. Methods

For the rheological measurements, we used a rheometer (Haake, RheoStress RS75) with double cylinder geometry with 20 and 22 mm diameter cylinders. The temperature was set to 298 K and the shear rate was varied from 1.0 to 631 s^{-1} . Once the viscosity of the sample had increased at a low shear rate, the sample was injected in the rheometer, the cup was covered with aluminum foil, and the sample was left until the viscosity decreased (about 1 h).

In order to measure the time taken by the viscosity of the shaken sample to return to its original value, the shear rate of the rheometer was set to 631 s^{-1} and kept at that rate for 1 min. The shear stress was then set to 1.0 Pa and the shear rate was measured.

3. Results and Discussion

3.1. Effect of Sodium Chloride

Figure 1 shows the viscosity dependence on the shear rate for nanosilica suspensions in 0.5wt% PEO (average molecular weight: $M = 500,000$) solutions at different NaCl concentrations. Viscosity jumps and gelation were not observed at NaCl concentrations of 0 and 0.10wt%. The samples with 0.15wt% - 0.30wt% NaCl showed shear-thickening behavior and the shear rate at the viscosity jump points decreased with the increasing NaCl concentration. When the NaCl concentration was 0.40 wt%, the sample showed shear-thinning. In conclusion, as the ionic strength increases, the electric double layers become thinner and the repulsive interactions between the particles become weaker. When the suspensions are shaken, the particles are able to get closer, easily forming network structures.

On the other hand, the values after the viscosity jumps (at high shear rates) were found not to depend on the NaCl content (0.15wt% - 0.30wt%). The shear stress (about 100 Pa) was also independent of the shear rate and NaCl content. This phenomenon indicates that no big differences exist among the network structures of PEO and silica after gelation of samples containing varying amounts of NaCl, which suggests that similar distributions of silica particles are obtained under fast shear flow conditions regardless of the percentage of NaCl and the strength of the repulsive interactions between particles.

3.2. Effect of Molecular Weight of PEO

The viscosity curves for suspensions with PEO ($M = 200,000$) and varying amounts of NaCl are shown in **Figure 2**. The samples with $\leq 0.30\text{wt}\%$ NaCl exhibited Newtonian profiles. In the case of the 0.50wt% NaCl sample, shear-thinning be-

havior was observed at as hear rate of 10 s^{-1} , but the maximum viscosity value was $\sim 0.50\text{ Pa s}$. This value is much smaller than that of the suspension with heavier PEO ($M = 500,000$) and 0.30 wt\% NaCl (5.4 Pas at 20 s^{-1}). The strength of the gel decreased and gelation did not occur until more NaCl was added.

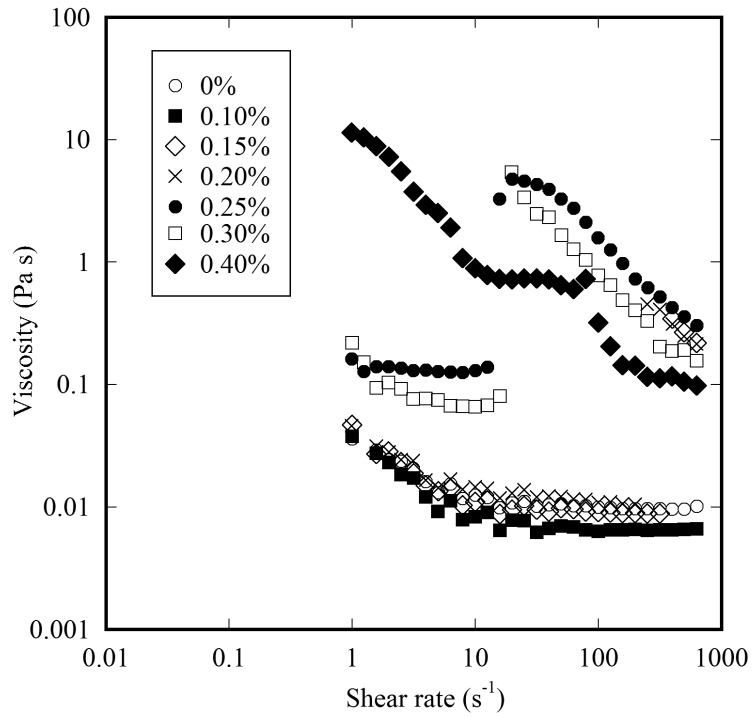


Figure 1. Viscosity dependence on the shear rate for silica nanoparticle (11 nm, 15wt%) suspensions with PEO of average molecular weight 500,000 (0.50wt%) and varying amounts of sodium chloride.

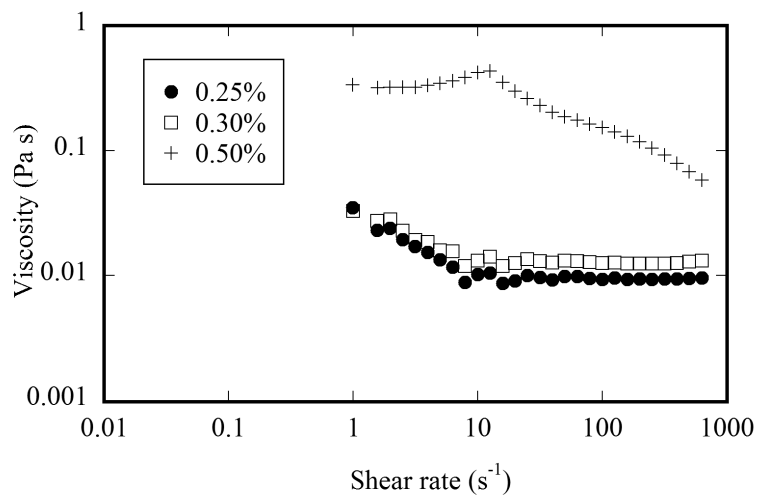


Figure 2. Viscosity dependence on the shear rate for silica nanoparticle (11 nm, 15wt%) suspensions with PEO of average molecular weight 200,000 (0.50wt%) and varying amounts of sodium chloride.

Figure 3 shows the viscosity curves of suspensions with high molecular weight PEO ($M = 2,000,000$). A viscosity jump was observed for the suspension with no NaCl and also for the sample with 0.10wt% NaCl at low shear rates. The sample with 0.25wt% NaCl exhibited a shear-thinning profile. As in the case with PEO of $M = 500,000$ (**Figure 1**), the viscosity after gelation did not depend on the NaCl content.

The viscosity curves of samples showing a viscosity jump at $\sim 10 \text{ s}^{-1}$ are compared in **Figure 4**. The viscosity of the gelled sample with the heaviest PEO was higher than that of the sample with the lightest PEO. In this study, the size and number of silica particles and the total amount of PEO were constant. It can be concluded that the density of adsorption points is also independent of the molecular weight of PEO, since the oxygen atoms of the PEO main chains are adsorbed on the surface of the silica particles.

The different conformations of polymer chains on solid surfaces are classified as trains (segments directly attached to the surface), loops (segments between trains not attached to the surface), and tails (segments not attached including one polymer chain end) [9] [20] [21]. The number of end groups of each polymer chain and of segments floating in water (tails) increased with the decreasing molecular weight of PEO. Thus, it was concluded that the bridging density, strength of the gel, and its viscosity decreased.

3.3. Time for the Recovery of The Viscosity in the Gelled Samples

Figure 5 shows the time dependence of the shear rate of gelled samples with PEO ($M = 500,000$, 0.50wt%) and varying amounts of NaCl up on reducing the shear stress to 1.0 Pa. The normalized data for the shear rate once the viscosity returned to its original value for the 0.15 and 0.20 wt% NaCl samples are also plotted in **Figure 6**. Immediately after the measurements started, the shear rate

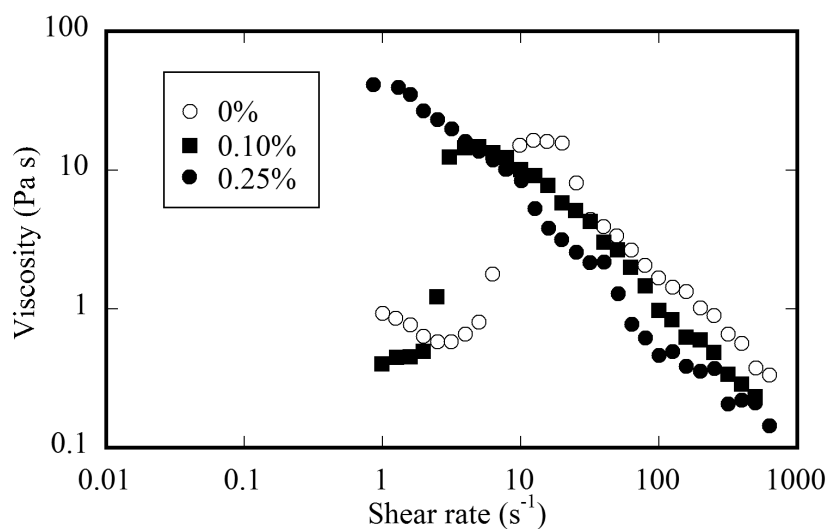


Figure 3. Viscosity dependence on the shear rate for silica nanoparticle (11 nm, 15wt%) suspensions with PEO of average molecular weight 2,000,000 (0.50wt%) and varying amounts of sodium chloride.

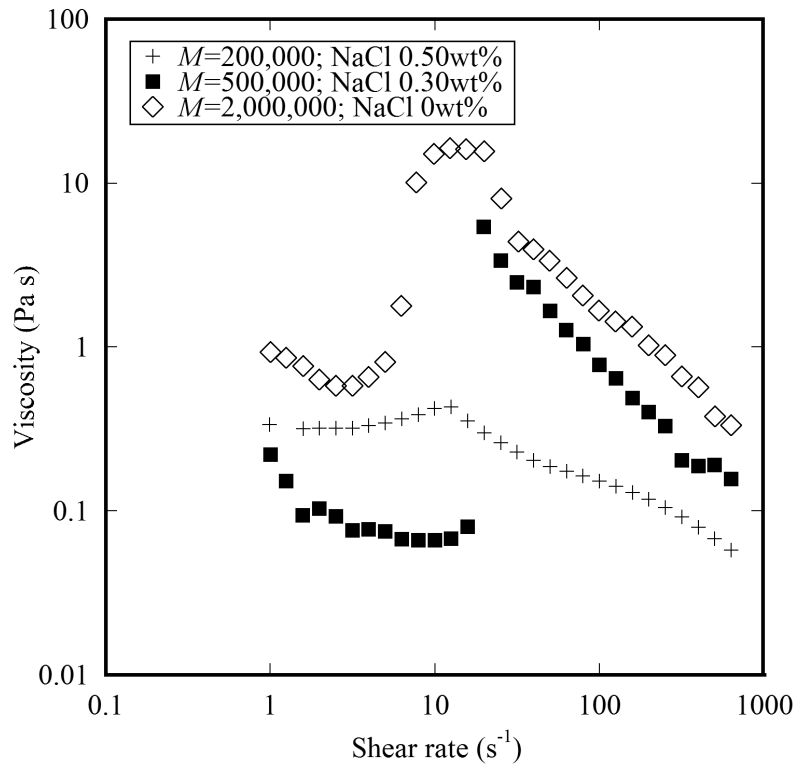


Figure 4. Viscosity dependence on the shear rate for silica nanoparticle (11 nm, 15 wt%) suspensions with PEO (0.50wt%) and sodium chloride.

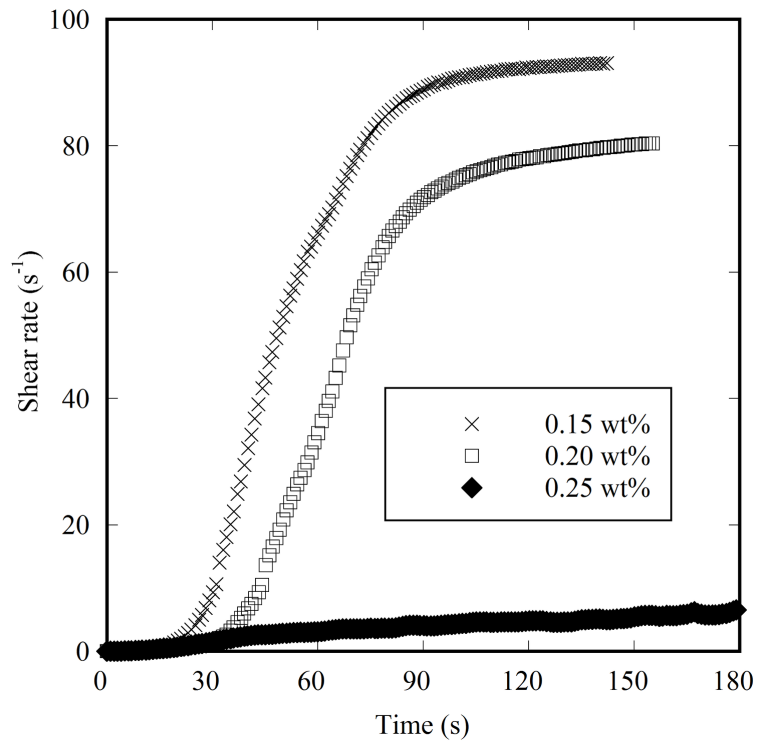


Figure 5. Time dependence of the shear rate for gelled silica nanoparticle (11 nm, 15wt%) suspensions with PEO of average molecular weight 500,000 (0.50 wt%) and varying amounts of NaCl under shear stress of 1.0 Pa.

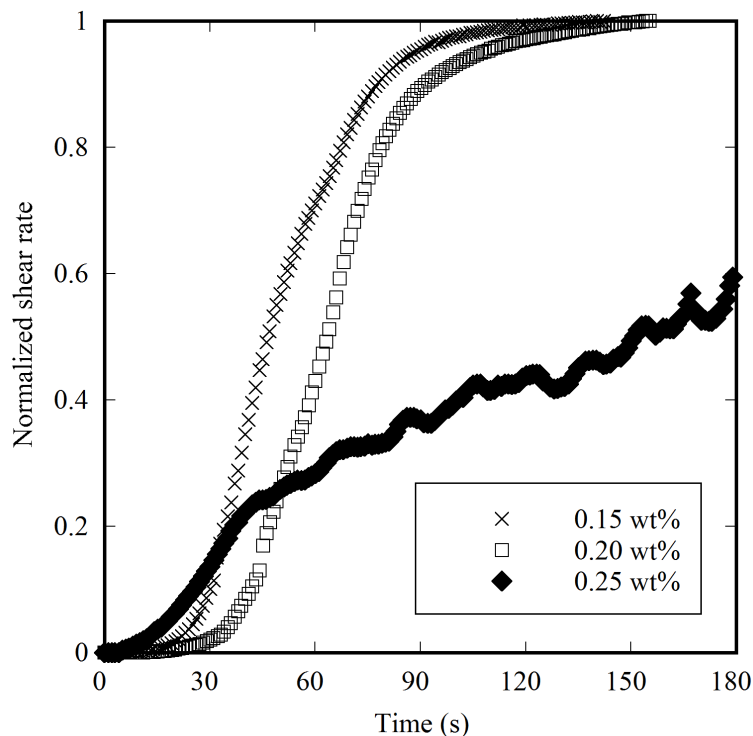


Figure 6. Normalized shear rate curves for gelled silica nanoparticle (11 nm, 15wt%) suspensions with PEO of average molecular weight 500,000 (0.50 wt%) and varying amounts of NaCl under shear stress of 1.0 Pa.

was almost zero as the samples gelled sufficiently. The shear rate took longer to increase for suspensions with larger amounts of NaCl. The decreased viscosity after reducing the share stress was caused by the thermal motion of the particles and polymer chains [7] [9]. From these results, it can be concluded that, when the presence of NaCl weakens the repulsive interactions between particles, the PEO chains cannot detach easily from the silica surface by thermal motion and longer times are required to regain the original fluidity of the gelled samples.

4. Conclusion

Addition of NaCl to silica nanoparticle/PEO aqueous shake gels results in the easy formation of networks between the silica and PEO molecules. The shear rate is reduced upon gelation due to weakening of the repulsive interactions between silica particles. The shear rate dependence of the viscosity in the gelled samples was found to be independent of the salt content, and the shear stress was about 100 Pa for some of the samples with silica (11 nm, 15wt%) and PEO ($M = 500,000$, 0.50wt%). It is suggested that the structure of the molecular networks in the gelled samples was not changed upon salt addition. On the other hand, increasing the molecular weight of PEO also decreased the shear rate at the viscosity jumps, although the viscosity of the gelled samples also increased. From these results, the elasticity of shake gels of nanosilica with PEO can be controlled by increasing the molecular weight of PEO or adding NaCl. In addi-

tion, NaCl addition resulted in the gelled state lasting longer. The viscoelastic behavior of gels composed of temporary networks with nanoparticles depends on the salt content and strength of the repulsive interactions between particles. It is thus concluded that, we can control the flow behavior of nanosilica suspensions with PEO and salts by controlling the salt content, polymer content, and molecular weight of polymer.

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