

## The effects of particle concentration, ionic strength and shearing on the microstructure of alumina nanorod suspensions

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### Abstract

In the present study we investigated the microstructure of suspensions of alumina nanorods while varying particle loading and pH. The diameter and length of rod particles were 10 and 50 nm, respectively and particle loading was varied from 1 to 5 vol%. Using the optical microscopy, dynamic light scattering, Turbiscan and rheological measurement, we showed that the suspensions existed as weakly flocculated gels at pH = 4 while they became strongly flocculated gels when pH was 7 or 11. The cryo-SEM images confirmed that the rod suspensions had gel structures. Strong shearing by milling or sonication changed the microstructure to a certain degree but the basic honeycomb structure was maintained.

**Keywords** : microscopy, dynamic light scattering, Turbiscan, cryo-SEM, gel, honeycomb

### 1. Introduction

Suspensions are ubiquitous. Inks, blood, some foods and nanofluid are typical examples among many different types of suspensions. Since a suspension consists of at least two phases it should have microstructures within the base fluid and the control of the structure is of significant importance when using it. The microstructure can be changed by flow reversibly or irreversibly and usually it can be probed by several methods including rheological measurements. When the particle loading in a suspension is sufficiently small, the suspension has the random microstructure. As particle loading increases various microstructures can be developed depending on conditions such as pH, temperature, additives and flow. The microstructure changes by shear flow are sometimes reversible but not always.

Low particle loading suspensions are now widely used in the field of printed electronics, pharmaceuticals, nanofluids and biosystems. There have been significant progresses in understanding the microstructure of low particle loading systems including gelation and their properties. In the present study we have focused on the alumina suspensions of low particle loading noting that alumina suspensions are used in many different areas. Alumina has been used as fillers for plastics due to its chemical inertness and high refractive index, in other words, whiteness. Alumina suspensions are used as precursors of catalysts and absorbents. The transparent alumina is also used in coating suspensions

in compact fluorescent lamps. Especially alumina suspensions can be used for 3D printing (Melcher *et al.*, 2011) using the inkjet technology.

pH at which the zeta potential is zero is known as the isoelectric point. In general it is different from the point of zero charge which is the pH required to neutralize the surface of the particle (Larson, 1999). The IEP of an alumina aqueous suspension is between 8 and 10 (Singh *et al.*, 2005). If pH of an alumina suspension is much different from the IEP, the electrostatic repulsion among particles is strong enough to separate particles from each other and hence the colloidal suspension is stable. For an initially stable sol composed of colloidal particles, the gelling agent which is usually a pH modifier, an electrolyte, or a polymer produces gelation by reducing repulsive particle-particle interactions, so that van der Waals attractions or a depletion force can draw particles into near contact. If the particle concentration is high enough (around a few vol% or higher) a space-spanning network of such contacts forms producing a solid-like gel phase (Larson, 1999). Colloidal glasses can form at a high particle concentration and low attractive interaction between particles. However, fractal gels form at the low particle concentration and high attractive interaction between them that have space-spanning systems described by the diffusion limited cluster aggregation (DLCA) theory (Trappe *et al.*, 2001; Trappe and Sandkuhler, 2004).

Suspensions with glass or gel structures can show almost constant shear stresses at low-shear rate regime. This phenomenon is called shear-banding (Fielding, 2005). The two different states have some similarities in that both of the states show the shear-banding and a plateau in the fre-

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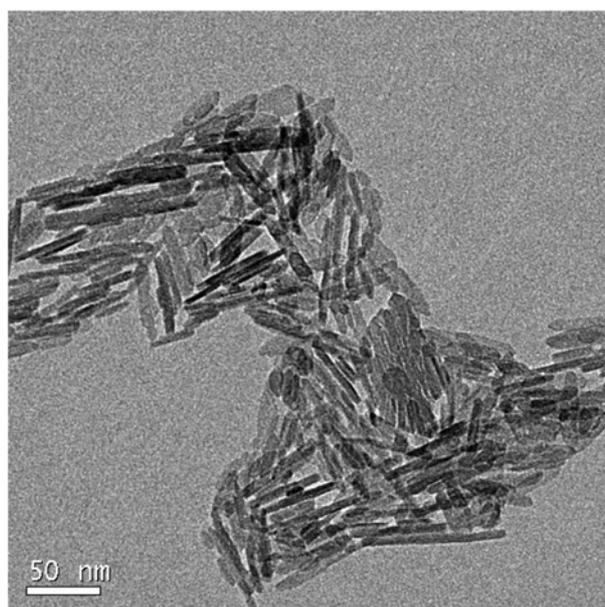
quency dependent elastic modulus (Chaplain *et al.*, 1994; Trappe and Weitz, 2000).

Attractive systems like a gel structure are very sensitive to shear history, in other words, shearing rate and time (Mewis and Wagner, 2009). During the preparation of colloidal suspensions strong shearing is usually imposed such as sonication, beads milling, homogenization and so on. If sheared strongly enough, the equilibrium microstructures can be destroyed and the sheared suspension behaves as a sol. After sufficient aging, however, the microstructure is restored from a sol to a gel spontaneously or from a very weak network to a relatively strong network that can be confirmed by the increase in viscosity and an almost constant shear-stress in the low shear-rate regime (Fielding *et al.*, 2009). The aging is also a kind of the non-equilibrium characteristic for a weakly flocculated gel. A time effect which is not related to reversibility is called aging while it is separately called rejuvenation when it is related to reversibility. The rheology of gels or glasses shows bifurcation by the competition of spontaneous restructuration, in other words, aging, and the destruction of the internal structure, in other words, shear rejuvenation (Bonn *et al.*, 2004). These characteristics manifest themselves as poor reproducibility and sensitivity to shear history in sample preparation (Larson, 1999).

In the present research we have investigated the equilibrium microstructure and microstructural changes of the alumina suspension rheologically and morphologically while changing particle loading, pH and shear. The result shows that, the alumina suspension has a network structure at the equilibrium and this network structure is not easily destroyed by a strong shear like sonication.

## 2. Experimental Methods

Rod-type alumina nanoparticles (Dispax X0, Sasol) were supplied from the Sasol North America Inc. The TEM image in Fig. 1 shows that the average length and diameter of an individual nanoparticle are 50nm and 10nm, respectively. Alumina nanofluids were prepared by dispersing nanoparticles in deionized water (Reverse osmosis water purification system, Biolab Tech.) in a beaker while stirring for 3 hrs with a magnetic bar following the manufacturer's suggestion. The pH of the nanofluid was 4. From the manufacturer's specification Dispax X0 contains less than 2% of acetic, nitric or formic acid. A part of the nanofluid was further treated by a beads-mill (The Laboratory Batch Mill, Netzsch Co.) for 1 or 5 hrs at 1,700 rpm. The bead size was 300  $\mu\text{m}$ . Another part of the sample was sonicated for 2hrs using an ultrasonicator (VCX-750 Sonic Materials Inc., 750 W, 20 KHz, 20% amplitude). To make the nanofluid a strongly flocculated gel pH was varied noting that the van der Waals attraction between particles changes with pH. To increase pH a



**Fig. 1.** TEM image of the alumina rods.

proper amount of 3.0 M NaOH aqueous solution was added. A concentrated NaOH solution was used not to dilute the alumina dispersion significantly by the addition of the solution. The alumina suspensions were observed under an inverted optical microscope (Olympus IX-51, 60X objective lens) to check the dispersion status.

The size of dispersed particles (or aggregates) was investigated since thermal and rheological properties can vary with size and shape of the primary particles. The dynamic light scattering (DLS) technique (Brookhaven Goniometer, BI-200SM) was used to measure particle size and its distribution in the diluted state. The fitting function was the CONTIN provided by the manufacturer. To check whether sedimentation and/or change in size should occur during the measurement or storage, Turbiscan<sup>TM</sup> was used. The Turbiscan<sup>TM</sup> measures the transmission and back scattering of the incident laser light from a sample along the gravity direction with time, from which one can determine the change in particle concentration and particle size along the gravity direction with time.

The rheological properties of nanofluids were measured with a stress-controlled rotational rheometer (AR2000, TA Instruments). The Couette geometry (Inner diameter of 14mm, outer diameter of 15 mm) was used for most of the measurements. However the cone-and-plate geometry was used for the measurements of pH varied samples which had large viscosities and hence it was almost impossible to load the sample in the Couette geometry. Steady flow measurements were performed by varying shear rate. The linear viscoelastic measurements were performed after confirming the linear viscoelastic regime by strain sweep tests. To minimize the effect of different aging times for

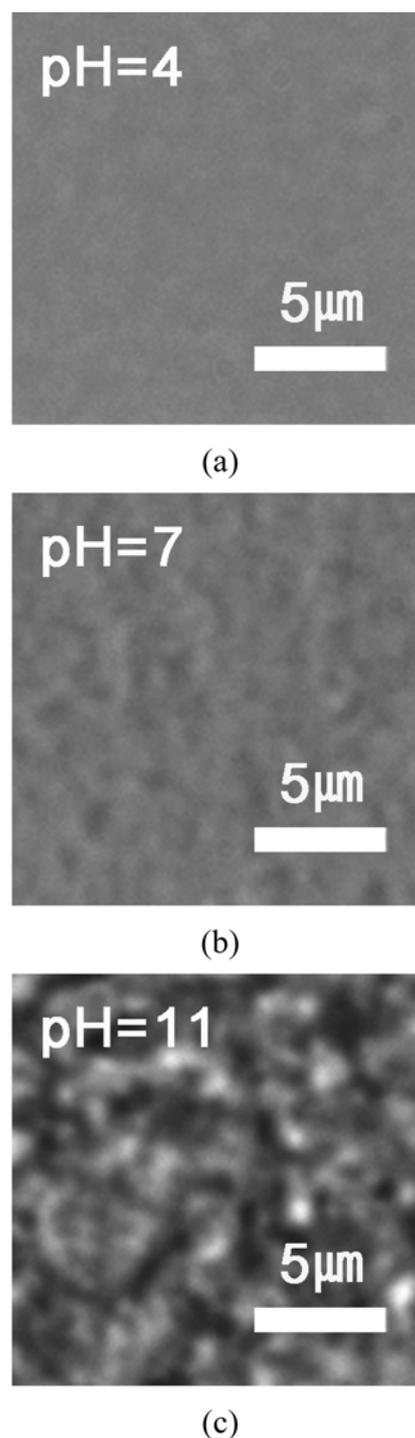
different samples, the measurement was started by waiting for an hour without stirring after sonication for 120 mins (750 W, 20% amplitude and 20 kHz). The sampling time was maintained for 3 mins to reach the equilibrium to avoid fluctuations which appeared when the equilibrium was not reached especially in the case of attractive system. When the sampling time was longer than 3 mins the results were almost independent of sampling time, while fluctuations appeared if sampling time was shorter than 3 mins.

To investigate the microstructure by direct observation Cryogenic Field Emission Scanning Electron Microscopy (Cryo-FESEM) was used. To obtain a vitrified sample, a gel sample mounted on a copper specimen holder ( $2.5 \times 3.0 \text{ mm}^2$ ) was placed in the jet freeze device (JFD 030, BAL-TEC, cooling rate of 40,000 K/s) which was full of liquid nitrogen at  $-180^\circ\text{C}$  for 24 hrs. The vitrified sample was transferred into preparation device (MED 020 GBE, BAL-TEC). The sample preparation process included fracturing, etching and coating. The vitrified specimen was fractured with a cutting knife at  $-120^\circ\text{C}$  under vacuum condition, and then etched to remove water from the sample by sublimation while rising temperature from  $-120$  to  $-60^\circ\text{C}$  for 20 mins under  $7 \times 10^{-7}$  mbar. The etched sample was coated by platinum under an argon gas condition for 70 secs. After the preparation, the specimen was transferred to FESEM (S-4700, Hitachi) using a high vacuum cryo-transfer system (VCT 100, BAL-TEC) and examined at 5 kV low acceleration voltage condition keeping the temperature at  $-140^\circ\text{C}$ .

### 3. Result and Discussion

Fig. 2 shows the microscopic images for 3% suspensions at three different levels of pH. Since the diameter and length of particles are 10 and 50 nm, respectively, individual particles cannot be seen. To the resolution of the microscope the original suspension at pH of 4 (without added NaOH solution) is homogeneous while the suspensions at pH of 7 and 11 show aggregated structures of different length scales. It is known that the formation of such a flocculated structure is caused by the changed van der Waals attraction among particles with the change in pH. The fact that a strongly flocculated gel can be formed from a dilute suspension as low as only 3% may raise a question on the microstructure of the same suspension before the strong network is formed. In the following we have described the dispersion stability and microstructure studies on the alumina suspension before and after strong flocculation.

Fig. 3 shows the sedimentation characteristics of the suspensions. If particles are not aggregated and exist as individual particles, the Brownian effect of the nanoparticles will be much larger than the gravitational force and hence there will be no sedimentation. Hence sedimentation can be a criterion for the existence of aggregation in a large



**Fig. 2.** Microscopic images of 3% suspensions at three different levels of pH: (a) pH = 4, (b) pH = 7, and (c) pH = 11.

scale without network. If there is sedimentation of particles a gradient in transmission intensity will develop with time along the gravity direction. Since particles are heavier than the liquid in this case, intensity will decrease from top to bottom. The samples when pH = 7 and 11 show, as

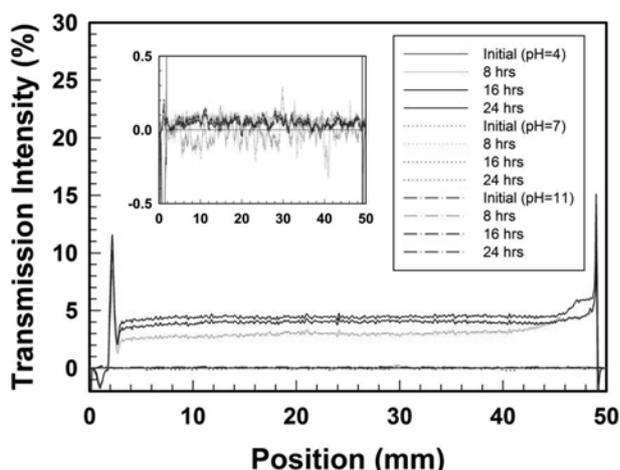


Fig. 3. Sedimentation characteristics of the suspensions by Turbiscan.

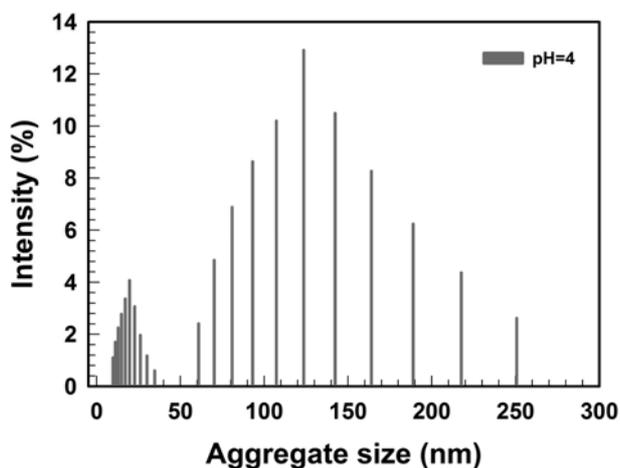


Fig. 4. Average cluster or particle size and particle size distribution of a diluted sample measured by the dynamic light scattering technique.

expected, uniform and constant intensity profiles with distance and time, respectively. The sample when pH = 4 shows that uniform intensity profiles along the gravity direction except at the meniscus region (Kim *et al.*, 2011). This means that sedimentation is virtually negligible during the 24 hr period. However, the transmission intensity of the sample increases with time. This is because the average aggregate size increases with time.

Fig. 4 shows the average cluster or particle size and particle size distribution measured by a dynamic light scattering technique. In the present study, to avoid multiple scattering, samples had to be diluted. Therefore the average particle size at particle loading of 3% should not be exactly the same as shown in Fig. 4. Since, as particle loading increases the attractive interaction among particles can vary, which results in the change in aggregate size. Since

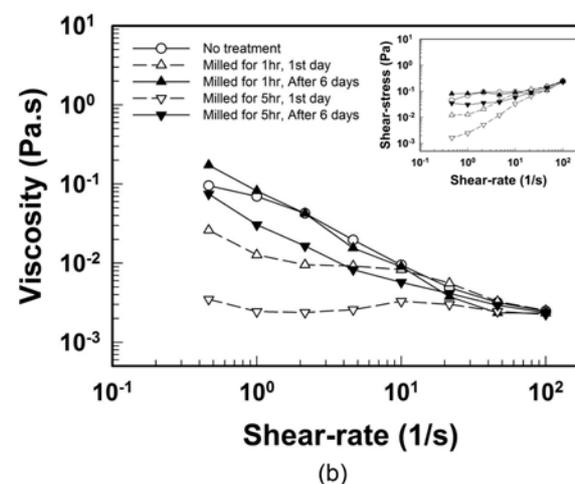
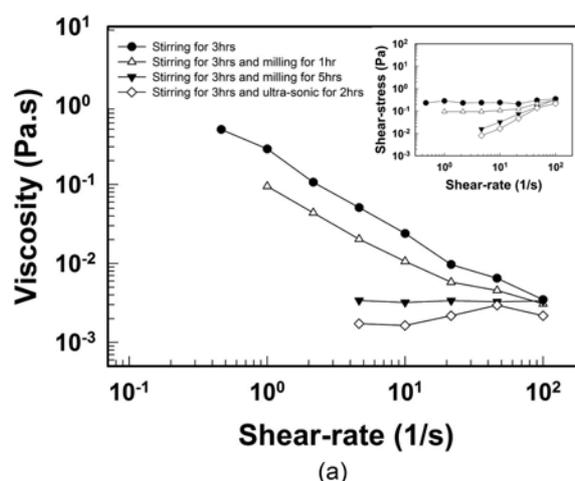


Fig. 5. Viscosity of nanofluids before and after extra shearing: (a) Viscosities of the 3% suspension with or without additional shearing by sonication or milling; (b) Viscosities of a 4% suspension.

no strong shear was imposed, however, no significant change in the microstructure should occur during dilution for DLS measurement. The DLS study shows that individual particles and aggregates coexist. Even though the measurement was done only for very dilute suspension, the result suggests that aggregates should exist in more concentrated suspensions and the average aggregate size should be at least the same as or larger than the average size in the dilute suspension.

Fig. 5(a) shows the rheological properties of the 3% suspension with or without additional shearing by sonication or milling with a beads-mill. The rheological properties were measured after waiting one hour for stabilization. By the stabilization the effect of differences in handling time and mixing characteristics could be excluded. The Figure shows that the additional shearing strongly affects the rheological properties hence the microstructure. The untreated sample shows a strong shear thinning and the

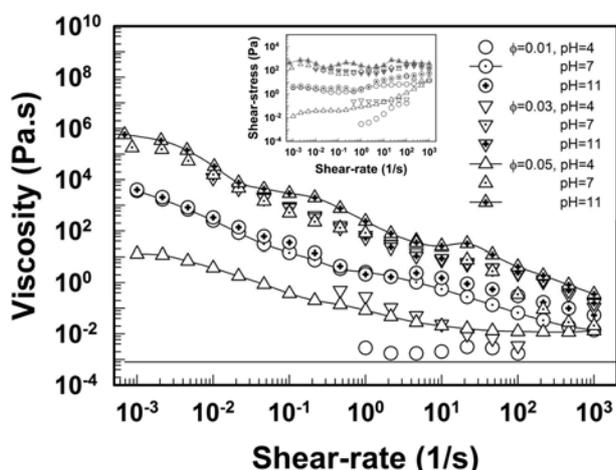


Fig. 6. Viscosities of suspensions before and after adding NaOH solution.

zero shear viscosity is not reached even at shear rate of  $0.5 \text{ s}^{-1}$ . In other words the equilibrium is not reached at this shear rate. This also means that the microstructure is fragile and hence easily breakable under a low shear stress. After milling the low shear viscosity of a 4% suspension of the same alumina particles was lowered by one or two orders of magnitude and then viscosity was recovered after 6 days in Fig. 5(b) (Kim *et al.*, 2011). This implies that the equilibrium microstructure should be broken at least partly due to shearing and the structure should be restored when no shear was imposed for a prolonged time. We note that the shear stress level of the stirred sample without additional shearing is almost constant regardless of shear rate except at the high shear rates (The power law index vanishes for this case). The constant shear stress for a range of shear rate is called shear banding and is known to be a typical characteristic of a gel. The constant shear stress in the low shear region and the changes in stress with time indicate that the suspension has a network structure and this network structure breaks down by milling or sonication. As milling time increases viscosity decreases and after 5 hrs of milling it appears that the large scale structure is almost completely destroyed. Sonication has a similar or even stronger effect on the microstructure. However, shear stresses at high shear rates remain virtually the same regardless of shearing, which also indicates that the equilibrium microstructure is broken at this high shear stress level. At the present time it is not certain whether the microstructure under the high shear stress is the same as the microstructure of the additionally sheared sample at low shear rates.

Fig. 6 shows the viscosities of suspensions before and after adding NaOH solution (Kim *et al.*, 2011). In this case the pH is increased beyond the isoelectric point of aqueous solutions. When pH is increased, the viscosity of the sus-

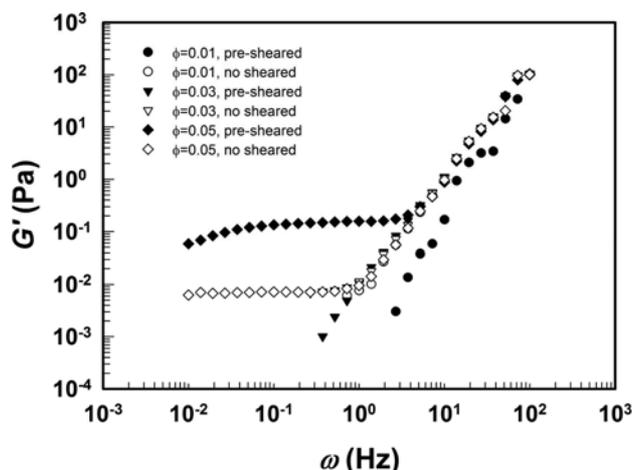
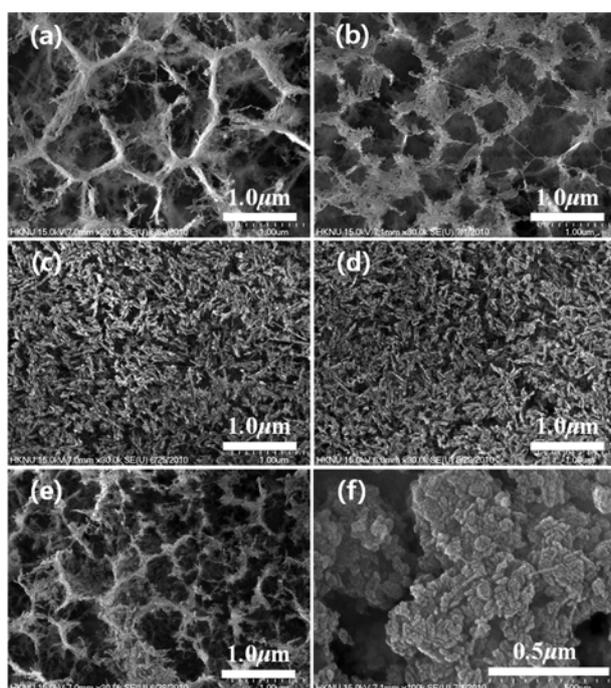


Fig. 7. Linear viscoelastic properties of the samples with and without preshear.

pension increases by 3 orders of magnitude and the shear stresses below shear rate of  $10 \text{ s}^{-1}$  are virtually the same regardless of shear rate. Also the high shear viscosities are still higher than the viscosity of water. This means that the microstructure is not easily breakable as in the case of the sample without NaOH and the suspensions become strongly flocculated gels from weakly flocculated gels by the pH increase. The optical microscopic images and Turbiscan data also support the change as described before.

Fig. 7 shows the linear viscoelastic properties of the samples with and without preshear. The preshear was imposed for 10 mins at angular frequency of 1 Hz followed by 20 mins rest. The 3% and 5% samples without preshear show plateaus in  $G'$  at frequencies below  $1 \text{ s}^{-1}$ , meaning that they have sufficiently large elastic properties and they would not flow easily. This is one of the typical characteristics of flocculated gels. Also the 1% sample without preshear also shows non-negligible  $G'$ . When the preshear is imposed,  $G'$  of the 1% sample is reduced by 1 order of magnitude near 1 Hz while  $G'$  at high frequency is virtually the same. The 3% sample shows almost the same  $G'$  after preshear except near 1 Hz. The 5% sample shows larger  $G'$  values after preshearing at the low frequency regime ( $<4 \text{ Hz}$ ). This means that the shear can induce even stronger microstructure when particle loading is high. This is possible since a densely packed sample can be rearranged to have a stronger structure as shown in shear thickening suspensions while the structure developed in a loosely arranged sample at the equilibrium can be broken.

Until now the microstructure of the suspensions has been probed by indirect methods. To have a correlation between such indirect methods and real microstructure the microstructure has been observed directly by vitrifying the sample. Fig. 8 shows that the suspension has a network structure of decreasing cell size with increasing concen-



**Fig. 8.** Cryo-SEM images of alumina (a – e) and titania (f) suspensions: (a)  $\phi = 0.01$ ; (b)  $\phi = 0.03$ ; (c)  $\phi = 0.05$ ; (d)  $\phi = 0.03$  at pH = 7; (e)  $\phi = 0.03$ , sonicated; (f) titania suspension,  $\phi = 0.03$ .

tration up to  $\phi = 0.03$ , as predicted by the rheological measurement. Even the sample of  $\phi = 0.01$  shows a network structure. This is consistent with the rheological data showing a weak elasticity. However the structure is very fragile and hence it flows easily. This manifests itself as a small viscosity. As particle loading increases from 1% to 3%, the cell size of honeycomb structure decreases. This appears to be the reason for the change in rheological properties. When  $\phi = 0.05$  (c), the network structure no longer exists and particles get aggregated to develop a stacked structure. It is an established theory that aqueous dispersions of metal oxides become gels when pH is adjusted to have the isoelectric point (Larson, 1999). The order of magnitude change in viscosity of the sample near the isoelectric point indicates that the pH adjusted sample became a strongly flocculated gel. The strongly flocculated gel of the suspension of  $\phi = 0.03$  at pH = 7 and the fresh suspension of  $\phi = 0.05$  show almost the same morphology of a stacked structure, from which we can be sure that the 5% sample is also a gel. In the case of the sonicated sample (e) particles are arranged with fuzzy networks compared with the fresh one (b). The microstructure is destroyed only partly by the strong shear from sonication. Therefore it will be restored when no shear is applied for a prolonged time as described above.

Regarding the microstructure observed by cryo-SEM,

Piau argued that the honeycomb structure shown in the Carbopol images should be an artifact occurred during vitrification (Piau, 2007). If his argument is true the cryo-SEM technique cannot be used for any material. However we note that Piau's suggestion may not applicable to this case. In Piau's case the liquid sample had a finite size (It was a drop) and therefore the cooling rate was not fast enough. It is known that when the cooling rate should have an order of  $10^5$  K/s, the liquid sample becomes vitrified without being crystallized. In our case it was 40,000 K/s (The jet freeze device), similar to  $10^5$  K/s. So the honeycomb structure shown in our samples should not be an artifact caused by slow cooling. Also we have a doubt whether Piau was right regarding this matter because of the following reason: In Fig. 7 of Piau's paper, the honeycomb size is about 300  $\mu\text{m}$ . This means that Carbopol chains had to diffuse 150  $\mu\text{m}$  and get aligned by rotation before it is frozen. If we consider the usual size of a polymer molecule of 0.01  $\mu\text{m}$ , the Brownian diffusivity in water at the room temperature is 4.4  $\text{m}^2/\text{s}$ . Then the diffusion length in one dimension for 1sec is  $\sqrt{2Dt} \approx 9.4$   $\mu\text{m}$  ( $\ll 150$   $\mu\text{m}$ ). In real case the freezing time is less than 0.01 sec and the viscosity should be much larger than 1 mPa·s because the temperature drops with time. Therefore the diffusion length scale should be much shorter than this value. Also this is for the translational diffusion only. It will take much longer time to rotate and to have such a regular structure. Therefore Piau's suggestion does not seem to be right. Actually Piau just suggested and gave no reason. The artifacts in cryo-SEM are well documented in Ma, *et al.* (2005). From Ma *et al.*'s paper one can see that the techniques we used would not raise any experimental artifacts that could alter the microstructure during freezing. To confirm this we also took an image using titania suspension and found no such structure as shown in Fig. 8(f). This confirms that the honeycomb structure is not an experimental artifact occurred during the sample preparation process.

#### 4. Conclusion

In the present study we have investigated the microstructure of suspensions of alumina rod particles while varying particle loading and pH. Using the optical microscopy, dynamic light scattering, Turbiscan and rheological measurement, we have shown that the suspensions exist as weakly flocculated gels at pH = 4 while they become strongly flocculated gels from the isoelectric point. The cryo-SEM images clearly show that the rod suspensions have a gel structure. Strong shearing by milling or sonication changes the microstructure to a certain degree but the basic honeycomb structure is maintained. Even though the microstructures changes are not significantly changed by strong shearing, the rheological properties are changed by an order of magnitude at low frequency or low shear

rate. This means that even though the apparent morphology looks similar there should be a large difference in the true, detailed microstructure.

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