Transactions of the Materials Research Society of Japan 28 [3] 785-788 (2003)

Effect of pH on Rheological Properties of Mono-dispersed Spherical Silica Suspension

Song KyongHwan, Hirotaka Fujimori, Koji Ioku and Seishi Goto
Graduate School of Science and Engineering and
Graduate School of Medicine, Yamaguchi University,
2-16-1 Tokiwadai, Ube 755-8611, Japan
FAX: 81-836-85-9601, e-mail: sgoto@po.cc.yamaguchi-u.ac.jp

Rheological behavior such as viscosity and yield stress are influenced by the flocculated structure of the suspension. Here, we prepared suspensions of mono-dispersed spherical silica powder and controlled the structure of suspension by changing solid contents in the range of 42 to 55.5% and pH of suspension in the range of 2 to 10, which was controlled with HCl and NaOH solutions. In regardless of solid contents, the suspensions of pH6 and pH10 behaved as almost Newtonian fluid and those of pH2 and 3.5 indicated non-Newtonian. The suspensions of pH2 and pH3.5 showed structural viscosity and partially dilatancy due to the changes in the flocculated structure of suspension by changes in balance of flocculating and deflocculating speeds of particles under shear rates. The silica particles in higher pH suspension were well dispersed and those in lower pH one were significantly flocculated. Consequently, the influences of pH and solid contents on the rheological behaviors of mono-dispersed spherical silica suspension were observed.
Key words: Rheological flow curves, Mono-dispersed spherical silica, Solid content, Apparent viscosity, Yield stress.

1. INTRODUCTION

The rheological properties of concentrated suspension are of great interest to various industries, such as ceramics, paints, biomaterials, transportation of materials, slip casting and so on. Rheological behaviors of suspension are affected by many factors such as particle (volume content, surface area, particle size distribution, shape and density) and liquid medium (viscosity, surface tension and wettability). Since the complex interaction occurs between solids and also between solid and liquid during the flow of slurry, the slurry behaves rheologically in the complex way. The apparent viscosity depends on the shear rate and time of shear flow. Sometimes the structure of slurry may be partially broken down, sometimes made up by shear force [1-3].

Viscosity is one of the most useful factors for controlling a process in industry [4, 5]. Mixedness, flowability, strength and density are influenced by the rheological properties of viscosity and state of flocculation. Rheological properties such as viscosity, yield stress and flow curve are generally influenced by the solid content and the flocculated structure of particles [6, 7].

Here, we investigated the effects of the degree of flocculation on the rheological properties of concentrated suspension of mono-dispersed spherical silica powder. The structure and degree of flocculation of suspension were controlled by the solid content and pH. Changes in the structure of suspension during shear flow were also discussed.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of suspension

Mono-dispersed spherical silica powder (Adamatechs Co.Ltd, 2 μm) was used as the starting material. This powder was high purity in SiO_2 (>99.99%), and had a density of 2.3 $g \cdot cm^{-3}$ and a specific surface area of $2.5 m^2 \cdot g^{-1}$. The solid contents of suspensions were prepared with 42, 46.5, 51 and 55.5 volume %. Deionized and distilled water was used as liquid medium. To break up agglomerates, suspensions were treated with ultrasonic for 10minutes. The pH was adjusted to 2, 3.5, 6 and 10 using HCl ($0.5 mol \cdot dm^{-3}$)

and NaOH (0.01mol•dm^{-3}) solutions.

Because silica has an iso-electric point nearly at pH2, the zeta-potential (-mV) increase with increase of pH. The change of surface charge with pH may be expressed as following equations; M is oxide [5].

Low pH: $M \cdot OH + H^+ + OH^- \leftrightarrow M \cdot OH_2^+ + OH^-$
High pH: $M \cdot OH + H^+ + OH^- \leftrightarrow M \cdot O^- + H_2O + H^+$

2.2 Viscosity measurement

A unique device (Chichibu Cement Co. Ltd, Japan, CJR120) was used for measuring the viscosity of the suspension, where the tuning-folk type of resonance vibration was applied as shown in Fig.1. This viscometer has a pair of plate springs with a circular sensitive plate on the end. When the sensitive plate is operated in a suspension by a driving electric current (I), the values of amplitude of resonance vibration (R) are obtained. The shear rate is obtained from equation (3), and the apparent viscosity (η) is calculated from the relation between shear stress (τ) and shear rate (D_s) as shown in following equations [8].

$$\tau(Pa) = 1588 \cdot I(A) \quad (1)$$
$$R = I(A) / E(mV) \quad (2)$$
$$\eta(Pa \cdot s) = \tau(Pa) / D_s(1/S) \quad (3)$$

A driving electric current was continuously increased until 300 mA or up to 1000 s^{-1} of shear rate. The yield stress was obtained by Bingham equation ($\tau - \tau_y = \eta D_s$).

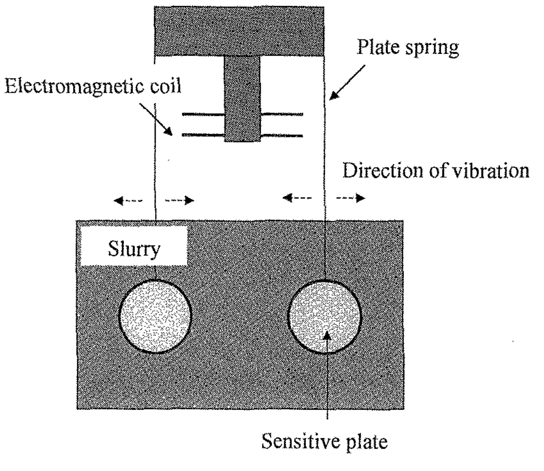

Fig. 1 System of viscosity mearsurement

3. RESULTS AND DISCUSSION

3.1 Properties of rheological flow curves

Figure 2 showed the relation between shear stress (τ) and shear rate (D_s) for suspensions with solid contents of 42, 46.5, 51 and 55.5 volume %, which were adjusted to pH2, pH3.5, pH6 and pH10 by HCl and NaOH solutions. In regardless of each solid content, flow curves were changed from Newtonian fluid to non-Newtonian fluid with the decrease of pH. The suspensions of pH6 and pH10 closely followed an empirical power law equation, $\tau = k(D_s)^n$ [1], where k is the consistency index and n is the shear thinning constant which indicates the departure from Newtonian behavior (n=1).

On the other hand, systems of pH2 and pH3.5 behaved as non-Newtonian fluids, which showed Bingham and pseudoplasticity (n>1) with some yield stress (τ_y) described by the equation ($\tau - \tau_y = \eta D_s$) [1].

From a view of hysteresis areas between increase and decrease of shear rate, a hysteresis did not indicate directly the dispersion state of suspension, but it could be thought that suspensions of pH2 and pH3.5 showed more thixotropic than those of pH6 and pH10 [4,7].

3.2 Properties of apparent viscosity

Figure 3 shows the dependence of apparent viscosity on shear rate, in the range from 50 s^{-1} to maximum point of shear rate in this experiment. According to the increase of solid contents as 42, 46.5, 51 and 55.5 volume %, values of apparent viscosity for suspensions of pH6 or pH10 were approximately 35, 40, 90 and 120 mPa•s or 55, 100, 140 and 200 mPa•s at the shear rate of 50 s^{-1}. Moreover, those values were almost constant in the range of shear rate more than 50 s^{-1}. It indicated that suspensions of pH6 and pH10 behaved as Newtonian fluid. On the other hand, as increasing solid contents, values of apparent viscosity for suspensions of pH3.5 or pH2 indicated about 180, 200, 300 and 560 mPa•s or 220, 280, 600 and 720 mPa•s at the shear rate of 50 s^{-1}, but those values were sharply changed about 120, 140, 200 and 300 mPa•s or 150, 210, 310 and 450 mPa•s at the shear rate of 300 s^{-1}. Suspensions of pH2 and 3.5 showed structural viscosity, that is, an apparent viscosity gradually decreased with an increase of shear rate [2,5].

It is noticed that systems of solid contents 55.5 volume % at pH2 and pH3.5, and 51 volume % at pH2

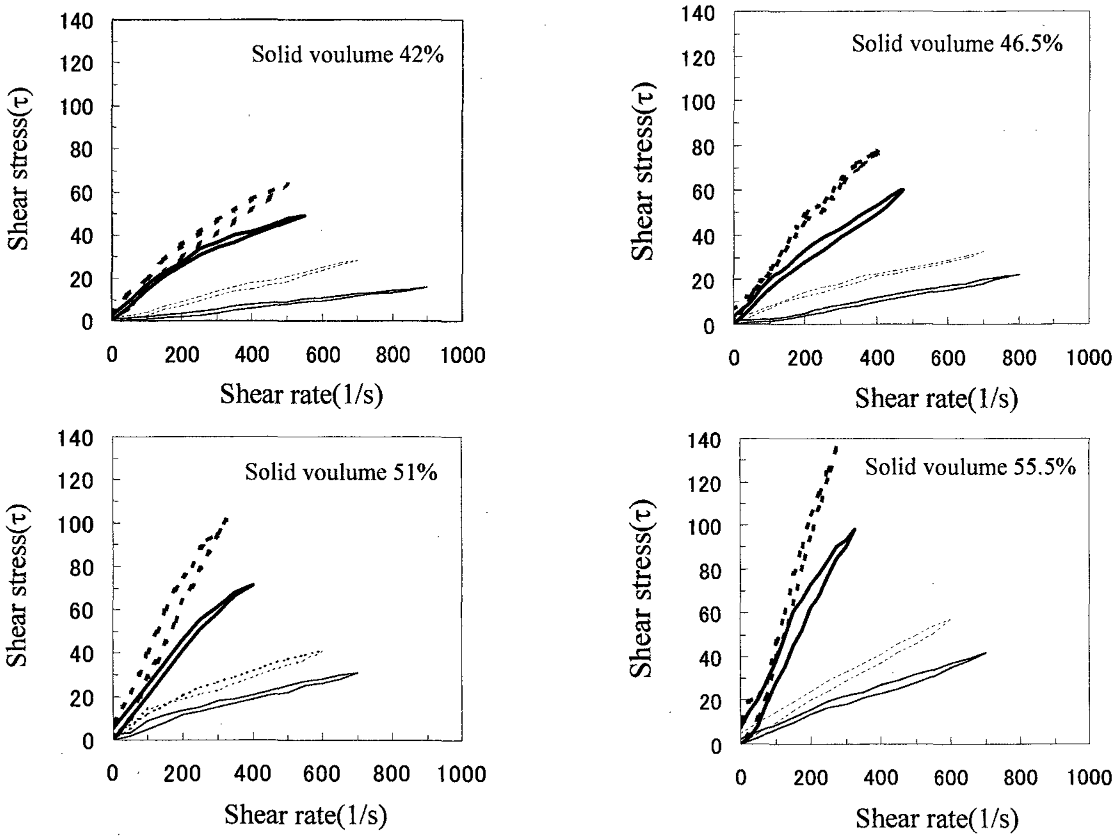

Fig. 2 Flow curves of shear stress versus shear rate for different solid volume under different pH
(—: pH10, ---: pH6, ▬: pH3.5, ---: pH2)

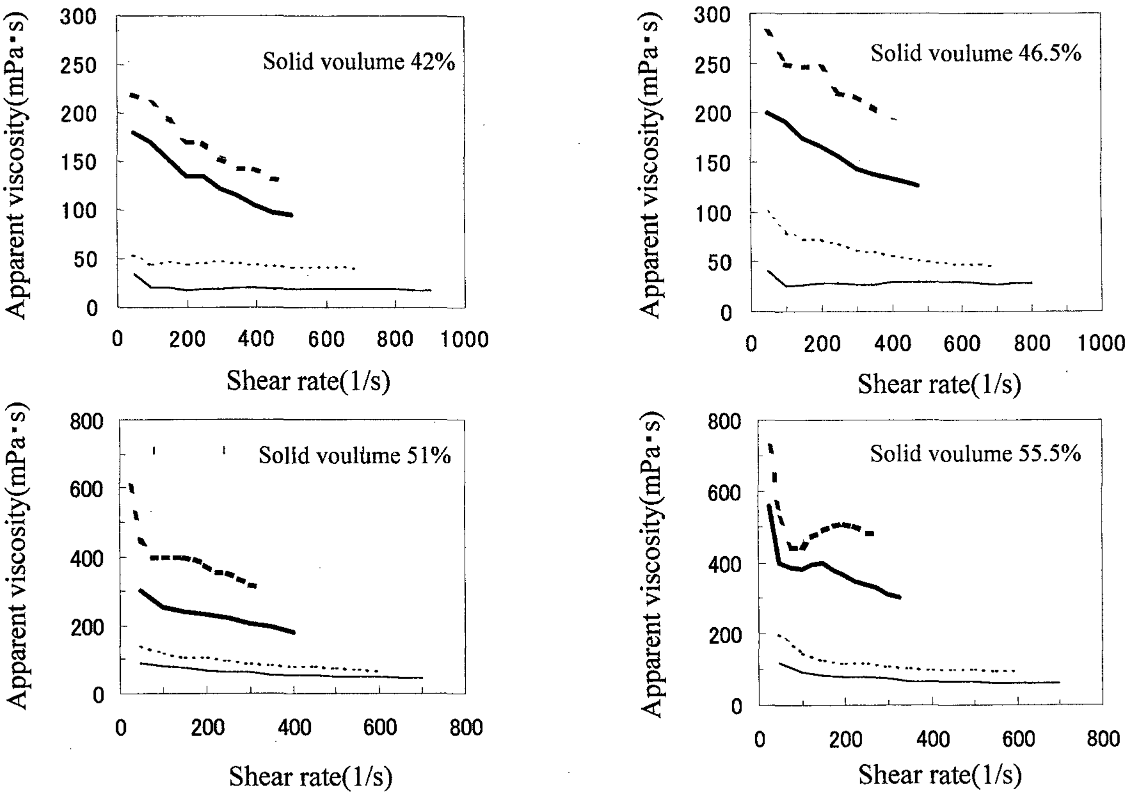

Fig. 3 Changes in the apparent viscosity on the shear rate for a suspension with different solid volume under different pH
(—: pH10, ---: pH6, ▬: pH3.5, ---: pH2)

showed increases in apparent viscosity in a range from 100 s^{-1} to 200 s^{-1}. These systems changed from pseudoplasticity to dilatancy in this range of shear rate [7]. From this data, the flocculated structure of particles seems to break easily under the shear rate lower than 100 s^{-1} and to re-flocculate under the shear rate in the range between 100 to 200 s^{-1} due to increasing the chance of collision between particles.

3.3 Properties of yield stress

Figure 4 showed the changes in Bingham yield stress with pH and solid content. The values of the yield stress for suspensions of pH10, as increasing solid contents of 42, 46.5, 51 and 55.5 volume %, indicated approximately 1.5, 2.0, 2.6 and 3.0 Pa. But those values largely changed about 3.0, 4.5, 8.0 and 11.0 Pa at pH 2. By the reason that silica has isoelectric point approximately at pH2, particles lose their surface charges with a decrease of pH and consequently accelerate in the flocculation between particles.

The yield stress is also an important parameter that defines whether a system is well dispersed or not [5,9]. The increase of solid contents causes much interaction among particles due to decrease interparticle spacing. Subsequently, it could be thought that systems of pH10 and pH6 showed well dispersed, which predicts low viscosity, but system of pH3.5 had smaller unit of the flocculates than that of pH2. The network structure causes high yield stress to prevent the suspension from flowing until a yield stress. A high yield stress could predict the stronger or larger flocculation between particles and subsequently high viscosity as suspension of pH2 [5,10,11].

4. SUMMARY

The suspensions of mono-dispersed spherical silica powders were studied with solid contents in the range of 42 to 55.5 volume % and in the range of pH2 to pH10, which was controlled by using HCl and NaOH solutions. In regardless of solid contents, the suspensions of pH10 and pH6 behaved as almost Newtonian fluid and those of pH2 and pH3.5 did as non-Newtonian. The suspensions of pH2 and pH3.5 showed structural viscosity and partially dilatancy due to the changes in the flocculated structure of suspension by balance of flocculating and deflocculating speeds of particles under the shear rates. Reflocculation behavior was observed in

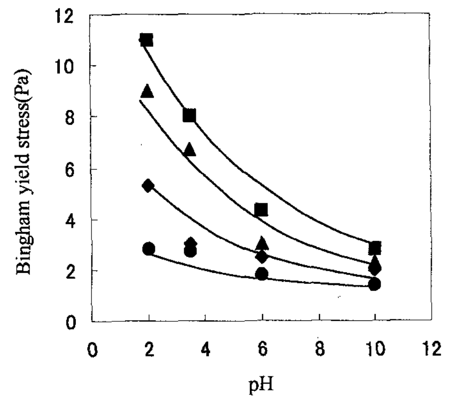

Fig. 4 Changes in Bingham yield stress with pH and solid contents.
(●: 42%, ◆: 46.5%, ▲: 51%, ■: 55.5%)

the shear range of 100 to 200 s^{-1} for suspensions of pH2 and pH3.5, especially in high solid content. The silica particles in suspension with higher pH suspension were well dispersed and those with the lower pH were significantly flocculated. Consequently, the influences of pH and solid contents on the rheological behaviors of mono-dispersed spherical silica suspension were obtained.

REFERENCES

[1] James S. Reed, "Introduction to the Principles of Ceramic Processing", John Wiley & Sons (1988).
[2] Robert J. Hunter, "Foundations of Colloid Science", Oxford University Press (1994).
[3] H. Nakamura and K. Tachi, *J. Soc. Rheol. Jpn*, **24** [10], 133-138 (1996).
[4] R.G. Pileggi, A.R. Studart and V.C Pandolfelli, J. Soc. *J. Am. Ceram. Soc. Bull.*, **80**, 38-42 (2001).
[5] I.R. Oliverira, P. Sepulveda and V.C Pandolfelli, *J. Am. Ceram. Soc. Bull.*, **80**, 47-53 (2001).
[6] T. Kanno and K. Umeya, *J. Mater. Sci. Jpn.*, **30**, 83-88 (1981).
[7] H. Kambe, *J. Mater. Sci. Jpn.*, **17**, 459-466 (1968).
[8] S. Ishiwata, M. Harashi, H. Ohshima and O. Suzuki, *J. Soc. Rheol. Jpn*, **24** [10], 133-138 (1996).
[9] M. Benna, N. Kbir-Ariguib, A. Magnin, *J. Colloid, Interface Sci.*, **218**, 442-455 (1999).
[10] T. Kimura and M. Nakamura, *J. Soc. Powder Tchnol., Jpn*, **27** [2], 597-602
[11] Y. Nagase and K. Okada, *J. Soc. Powder Technol., Jpn*, 17 [7], 392-399 (1980).

(Received December 21, 2002; Accepted February 17, 2003)