Effect of pH on rheology of aqueous Al_2O_3/SiC colloidal system

Xiaoqing ZHANG, Yanli ZHANG, Han CHEN, Lucun GUO*

College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, China

Abstract: The rheological behavior of aqueous Al_2O_3/SiC suspensions at different pH values was investigated by rheological measurement. Experimental results showed that at pH = 3–6, Al_2O_3 and SiC particles have opposite surface charges, and the binary suspensions have lower viscosity than the unary suspensions at shear rates of 0–300 s^{-1}. Furthermore, at pH = 3–12, the stability of the Al_2O_3 component seemed to dominate the overall rheological behavior of the Al_2O_3/SiC binary suspensions. The tendency mentioned above showed little variations in various ionic strengths, particle diameters and component fractions.

Keywords: alumina; silicon carbide; mixed colloidal dispersion; rheology

1 Introduction

The dispersion and stability of a colloidal system are the main issues in colloidal processing. These properties influence not only the green compacts and sintering performance, but also the quality of the final products. Understanding and predicting the stability of a ceramic colloidal suspension is of particular interest [1–5]. Numerous related studies have been reported in the literature [6–10]. Unary suspension, which is composed of one kind of particles, has been extensively studied, but the behavior of multiple suspension (i.e., suspension with several types of particles) is much less understood although dispersion of such system is commonly found in nature and in various applications [11–14]. One of the major reasons is the complexity of the phenomena involved. The stability of multiple system depends not only on many basic parameters, such as nature of solvent and particles, ionic strength, and size and charge of particles, but also on the

interactions among the particles, including electrostatic force and van der Waals force. For a two-component system containing different particles A and B, the forces of A–A, B–B and A–B are involved. The two kinds of particles differ in various factors, such as Hamaker constant and surface charge. The factors such as volume fraction and number ratio affect the total energy of a colloidal system simultaneously. Internal structures are difficult to observe experimentally at a microscopic level [15–19]. Probing the experimental system in such detail is not an easy task, specifically the system with more components and dispersants.

Some interesting experimental results on multicomponent system have been found in previous studies. Wang *et al*. [20,21] revealed that the addition of salt improves the colloidal stability in systems that contain different particles in a certain pH range between the isoelectric points (IEPs) of the two types of particles. Uricanu *et al*. [22] studied the stability in colloidal mixtures containing particles with a large disparity in size. The results supported that the composite heteroparticles behave in many ways like a silica sol, as the small silica particles are adsorbed onto the latex ones and the surface characteristics of latex

---

* Corresponding author.
E-mail: lc-guo@163.com

cores are modified simultaneously. In recent years, alumina matrix composite ceramic materials attracted widespread attention due to their excellent mechanical properties, especially alumina/silicon carbide ceramics [23]. The study of dispersion properties about Al_2O_3/SiC colloidal system is of great significance to the subsequent process.

The present study aims to investigate the effects of pH, ionic strength, particle size and component fraction on the rheological behavior of aqueous Al_2O_3/SiC binary suspension, focusing on the comparison with the unary suspensions of Al_2O_3 and SiC and the surprising stability of initially oppositely charged particle mixtures.

2　Experimental

2.1　Material

All of the experiments were conducted with Al_2O_3 (Zhengzhou Aluminum Co., Henan, China, purity > 99% (in mass)) and SiC (Jiangsu Leyuan Factory, Jiangsu, China, purity > 99% (in mass)). The average particle sizes (D_{50}) of the powders were 31.63 μm and 0.92 μm, respectively, which were characterized by laser diffraction (NSKC-IA, Nanjing University of Technology, China). The Al_2O_3 powder was ground into different particle diameters (1.44 μm and 0.55 μm) for further use. Scanning electron microscopy (SEM) photographs of 1.44 μm Al_2O_3, 0.55 μm Al_2O_3 and 0.92 μm SiC are shown in Fig. 1, observed with a scanning electron microscope (JSM-6360LV, JEOL Led., Tokyo, Japan). The IEP values of the powders were obtained from Zetasizer (3000HSA, Malvern Instruments Ltd., Malvern, UK).

2.2　Sample preparation

The ceramic powders were dispersed in deionized water. The pH was then adjusted to the desired value using standardized analytical-grade HCl or NaOH solution. NaCl was used to adjust ionic strength. Finally, the mixture was ball-milled using an agate grinding ball as media at a specific rotational speed for about 24 h at room temperature to ensure equal interaction between the particle surfaces. The unary suspensions were prepared in volume fraction, as 25 vol% for Al_2O_3 and 35 vol% for SiC. The binary suspensions were the mixture of unit ones according to powder mass ratio (1:1 in weight percentage).
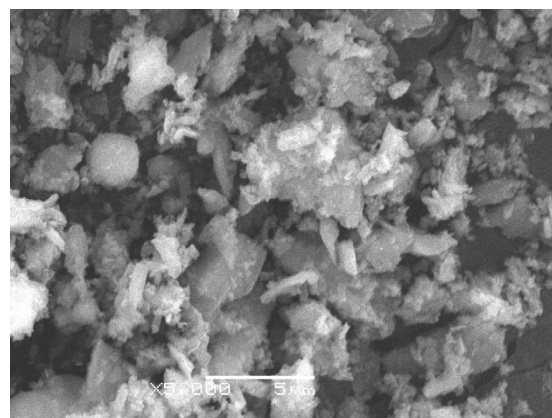
(a)
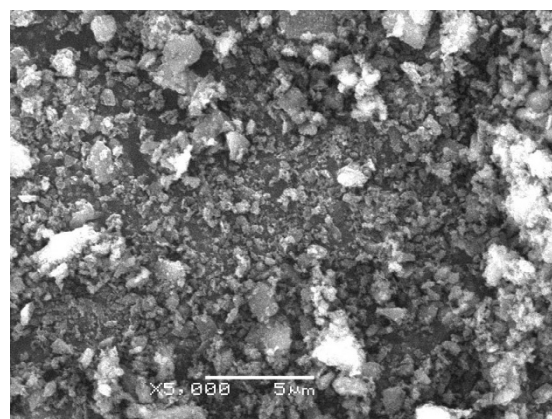
(b)
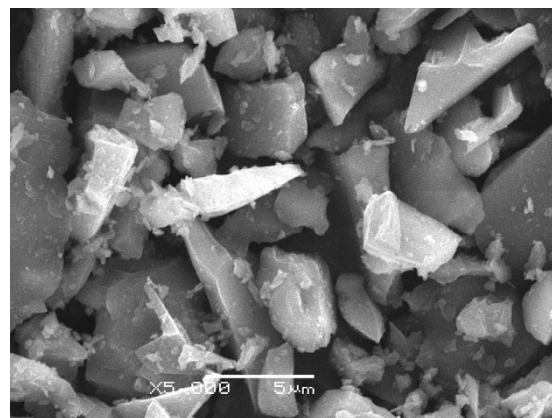
(c)

Fig. 1　SEM photographs of (a) 1.44 μm Al_2O_3, (b) 0.55 μm Al_2O_3 and (c) 0.92 μm SiC.

2.3　Rheological measurement

An R/S rheometer (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) was used to assess the rheological properties of the colloidal suspensions. The central part of the measuring

instrument was a concentric cylinder. By determining the shear stress and viscosity under various shear rates, the shear rate–shear stress and shear rate–viscosity curves were drawn to reflect the rheological properties of the suspensions.

The test program was divided into the following phases: the fresh suspensions were sheared at an identical rate of $100 \, s^{-1}$ for 2 min to homogenize; to avoid the undesirable effect of uneven slurry loading and different mechanical histories, the samples were left standing for an additional 2 min before the measurement; and with a linear increase of the shear rate ramps from 0 to $300 \, s^{-1}$ in 200 s and a linear decrease from $300 \, s^{-1}$ to 0 in 200 s, 50 data points were determined.

In most cases, viscosity is assumed to rely on shear rate in reflecting the dispersion state, whereas yield stress is commonly used as an effective single indicator/descriptor of the stability of the system.

3 Results and discussion

The zeta potentials of Al_2O_3 and SiC particle suspensions in water are shown in Fig. 2 as a function of pH. The IEP of SiC aqueous suspensions is found to be at pH ≈ 3.0. The particles are negatively charged over a wide pH range. The zeta potential value of SiC increases marginally with the increase of pH. For the pure alumina particles, the IEP is at pH ≈ 8.5. The highest positive potential is 40 mV (pH = 3.0). The sign of zeta potential is reversed from positive to negative at IEP [24,25]. In the pH range of 3–6 where the experiments were done, alumina and silicon carbide particles are oppositely charged.
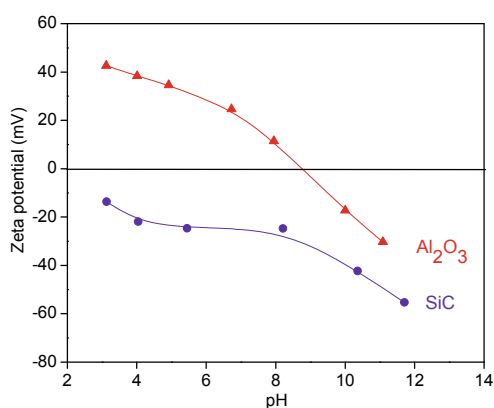

Fig. 2   Zeta potentials of Al_2O_3 and SiC as a function of pH.

pH value is a major controlling factor in determining the stability of ceramic suspensions [26]. Figure 3 shows the influence of pH on the rheological behavior of Al_2O_3, SiC and Al_2O_3/SiC suspensions. At pH = 3.0, Al_2O_3 particles have a zeta potential of about 40 mV, which leads to a well-dispersed suspension with weak or no inter-particle network [11]. Given that the pH is near the IEP of the SiC, the particles have low zeta potential value. SiC suspension is difficult to be dispersed by the weak electrostatic repulsion between particles eventually leading to the flocculation. The viscosity of SiC suspension is much larger than that of Al_2O_3. At the same component mass ratio, the binary suspension has lower viscosity than the unary suspensions, and the linear behavior points to its near Newtonian behavior (Fig. 3(a)). Analogous result can be clearly seen at pH = 4.0 (Fig. 3(b)).

As pH is increased to 5.0, the zeta potential of Al_2O_3 particle is slightly reduced. The suspension shows shear thinning behavior because of the existence of inter-particle network. However, the binary suspension still exhibits lower viscosity than the Al_2O_3 and SiC systems (Fig. 3(c)).

When pH is shifted to 6.0, the Al_2O_3 particles become strongly flocculated. The stability of the Al_2O_3 suspension is further reduced, whereas the stability of the SiC suspension is increased with the increase in the absolute value of the zeta potential. At this point, the binary suspension becomes slightly flocculated, but still completely follows the trend of decrease in viscosity by mixing unit suspensions together (Fig. 3(d)).

To gain further insight into the above observation, Fig. 4 is constructed. The viscosity values are derived from the flow curves of the suspensions at a fixed shear rate of $50 \, s^{-1}$ (vertical axis) and pH (lateral axis). As zeta potential of Al_2O_3 is higher than 30 mV for pH below 5.0, the three Al_2O_3 unary suspensions get optimal dispersion based on strong electrostatic stabilization. As can be seen from the figure, the viscosity values for Al_2O_3 suspensions at pH = 3.0–5.0 have little change. At pH = 3–6, the binary suspensions have lower viscosity than the unary suspensions. At shear rate of $0–300 \, s^{-1}$, the situation is the same as that in the viscosity values at $50 \, s^{-1}$. By comparing the zeta potential curves of Al_2O_3 and SiC suspensions (Fig. 2), the Al_2O_3 and SiC particles have opposite charges at this pH range (pH = 3.0–6.0). The Al_2O_3/SiC binary suspensions are expected to be strongly flocculated at the strong electrostatic forces. The reason behind this phenomenon is not yet known clearly. This observation
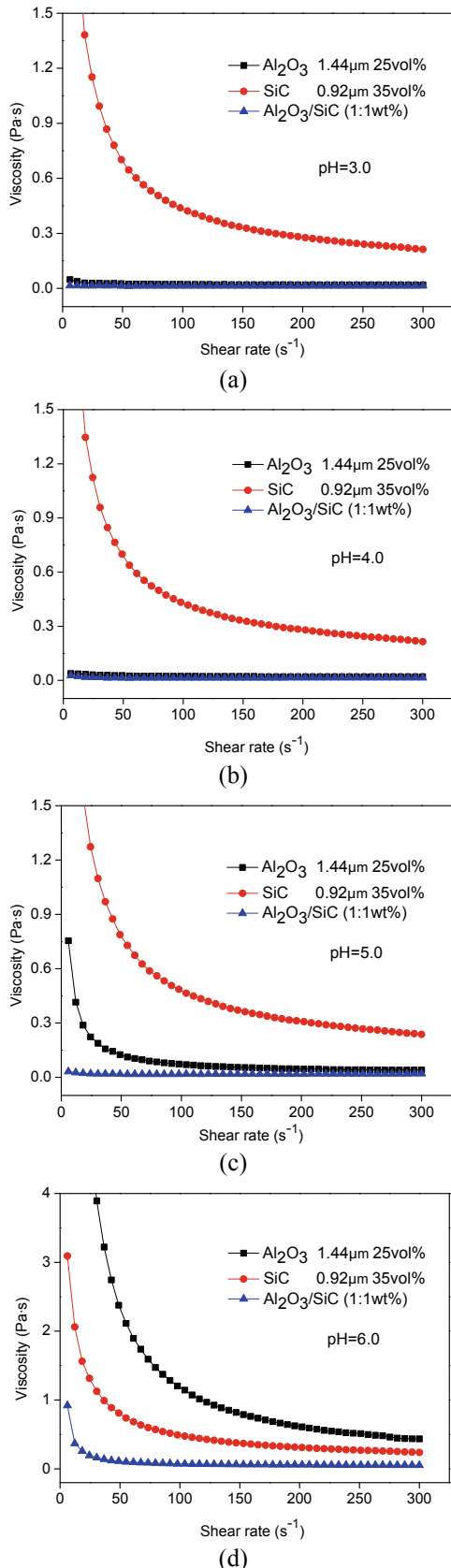
(a)

(b)

(c)

(d)

Fig. 3   Flow curves of 25 vol% Al_2O_3 suspension, 35 vol% SiC suspension and the binary suspension at pH equal to (a) 3.0, (b) 4.0, (c) 5.0 and (d) 6.0.
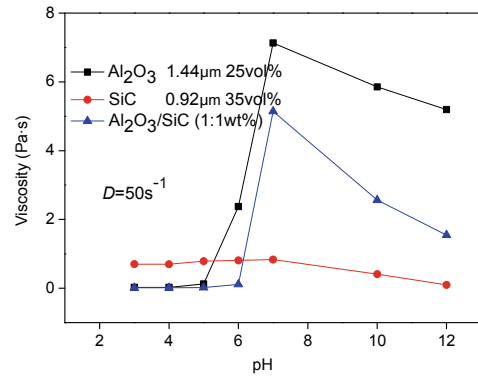

Fig. 4   Viscosity of the suspensions as a function of pH.

may be partly related to the change in Hamaker constant (A) between different particles, i.e., $A_{Al_2O_3–SiC}$ may be significantly lower than $A_{Al_2O_3–Al_2O_3}$ or $A_{SiC–SiC}$, resulting in a reduction of van der Waals force in system. No relevant data on this phenomenon is available. However, in some special cases, the Hamaker constant can be negative when the dielectric properties of the intervening medium are intermediate between those of the two interacting media, thereby resulting in a repulsive van der Waals force. Hence, the Hamaker constant may not necessarily cause the flocculation in systems and sometimes be able to offset the effect of electrostatic attraction [1].

Electrostatic heterocoagulation phenomenon is also found in multiple systems where the small particles are adsorbed onto large ones by the efficient driving force of electrostatic interaction [27–30]. However, this may be not true for the present situation. In the case of electrostatic heterocoagulation, the large disparity in particle size is extremely important. Due to the very limited difference in size of unlike particles, the state that one kind of particles is surrounded with the other cannot be reached in our experiment.

As pH increases to 7.0, the viscosity of Al_2O_3 suspension increases rapidly due to approaching to the IEP of Al_2O_3 particles (pH = 8.5). The rheology behavior of SiC almost has no change. Figure 4 shows that Al_2O_3/SiC binary suspension has an intermediate viscosity value between the unary ones. As pH is higher than 8.5, the absolute zeta potential of Al_2O_3 increases and the viscosity decreases accordingly. The similar result that the stability of binary suspension is at a midway between unary ones is obtained. It should be noted that the particles are both negatively charged at pH range of 10–12, which is a different situation from that at pH = 3–6.

Figure 4 shows that in the observed range of pH = 3–12, the curve for Al_2O_3/SiC binary suspension is similar to that of the unary Al_2O_3 suspension. In other words, the stability of the Al_2O_3 component dominates the overall rheological behavior of the Al_2O_3/SiC binary suspension. The mechanism behind this result is still not clear. However, for binary or other multicomponent systems, a component whose stability dominates the system should be considered.

Figure 5 shows the effect of ionic strength on the rheological behavior of unary and binary suspensions at pH = 3.0. High ionic strengths are often observed in aqueous ceramic suspensions due to ion dissolution of materials. In the presence of electrolyte, the increase in concentration of the counter ions results in the compression of the diffuse electric double layer and the attenuation of the electrostatic interaction. An electrostatically stabilized system may become unstable at high ionic strengths [12]. In the present study, it is seen that the presence of electrolyte in Al_2O_3 and Al_2O_3/SiC suspensions results in a consistent increase in the apparent viscosity respectively, indicating the strengthening of inter-particle network. However, the stability of binary system still precedes that of the unary ones. It can be well corresponded to the results above.

Figure 6 illustrates the viscosity curves of the Al_2O_3 particles with different sizes (0.55 μm and 1.44 μm) with and without SiC at pH = 3.0. For the unary system, a dramatic decrease in viscosity from 0.55 μm Al_2O_3 to 1.44 μm Al_2O_3 is observed. This result is directly determined by particle size. Although the net solid content of the slurries is the same, the smaller powder needs more water to be wet and it holds more space than the coarser powder. The smaller powder has higher viscosity in a certain size range [31]. Similarly, the curves of the Al_2O_3/SiC suspensions are lower than the corresponding Al_2O_3 suspensions. The distinction in particle size does not affect the trend.

In order to confirm whether the trend mentioned above is retained in systems with smaller Al_2O_3 particles and extra electrolyte, measurements are carried out. Extra electrolyte (0.05 M NaCl) is added to the suspensions containing 0.55 μm Al_2O_3 particles. A similar trend is observed in Fig. 7.

The solid loading of suspensions significantly affects the rheological behavior. In Fig. 8, the solid loading of the two unary suspensions is adjusted to an equivalent level (30 vol%) and the ratio of components is 1:1 in volume percentage in the binary suspension.

In this case, the flow curves for the Al_2O_3 and SiC suspensions intersect each other at a shear rate of ~120 s^{-1} because of their different rheological properties [32]. The apparent shear viscosity of the Al_2O_3/SiC system is still the lowest. The binary suspension maintains its stability. Hence, the change in solid loading and ratio of powder has no influence on the experimental result.
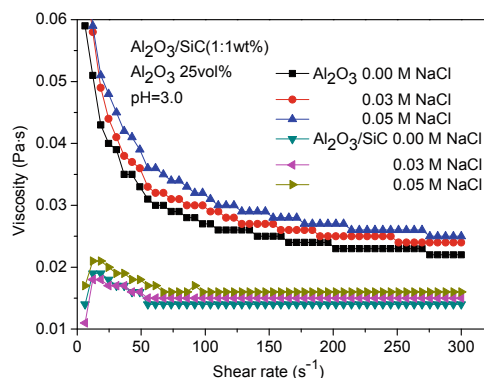

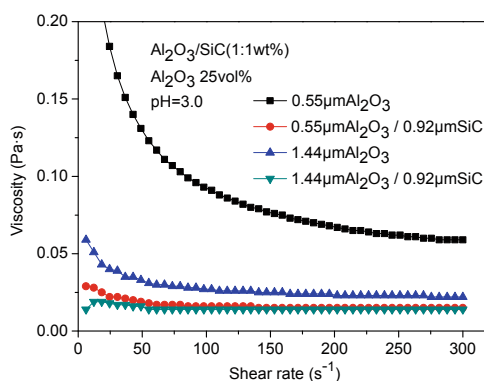Fig. 5 Flow curves of the Al_2O_3 and Al_2O_3/SiC suspensions as a function of ionic strength.

Fig. 6 Flow curves of the Al_2O_3 and Al_2O_3/SiC suspensions with different particle diameters.

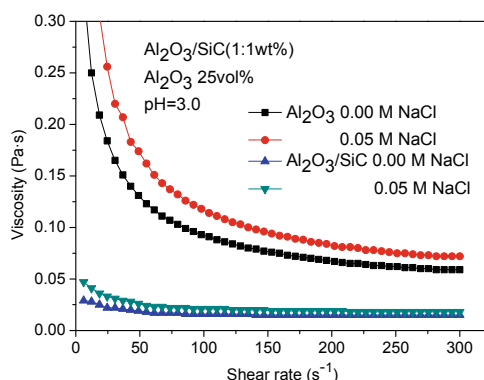Fig. 7 Flow curves of the Al_2O_3 and Al_2O_3/SiC suspensions as a function of ionic strength, with 0.55 μm Al_2O_3.
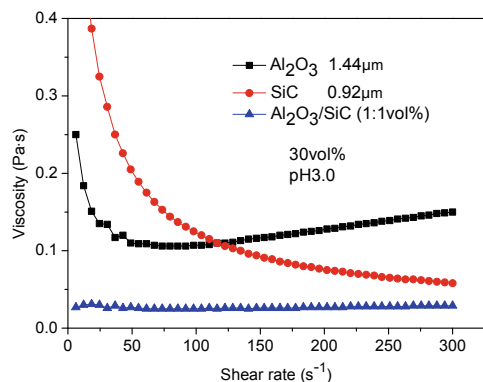
Fig. 8   Flow curves of 30 vol% Al_2O_3 suspension, 30 vol% SiC suspension, and the 1:1 (in volume percentage) binary suspension at pH = 3.0.

4   Conclusions

Based on this study, the following conclusions are drawn. For aqueous Al_2O_3/SiC binary suspensions at pH = 3–6, Al_2O_3 and SiC particles have opposite charges, and the binary suspensions are more stable than the unary suspensions. Furthermore, at pH = 3–12, the stability of the Al_2O_3 component dominates the overall rheological behavior of the Al_2O_3/SiC binary suspensions. Additionally, the stability of binary suspension is not always the least among the systems at every pH value. The tendency shown above has little variations in various ionic strengths, particle diameters and component fractions.

References

[1] Israelachvili JN. *Intermolecular and Surface Forces*. London: Academic Press, 1992.
[2] Lange FF. Powder processing science and technology for increased reliability. *J Am Ceram Soc* 1989, **72**: 3–15.
[3] Kong D, Yang H, Yang Y, *et al*. Dispersion behavior and stabilization mechanism of alumina powders in silica sol. *Mater Lett* 2004, **58**: 3503–3508.
[4] Cesarano J, Aksay IA. Processing of highly concentrated aqueous α-alumina suspensions stabilized with polyelectrolytes. *J Am Ceram Soc* 1988, **71**: 1062–1067.
[5] Wnek WJ. An analysis of the dependence of the zeta potential and surface charge on surfactant concentration, ionic strength, and pH. *J Colloid Interface Sci* 1977, **60**: 361–375.
[6] Lu K, Kessler C. Colloidal dispersion and rheology study of nanoparticles. *J Mater Sci* 2006, **41**: 5613–5618.
[7] Wang J, Stevens R. Zirconia-toughened alumina (ZTA) ceramics. *J Mater Sci* 1989, **24**: 3421–3440.
[8] Bijsterbosch HD, Cohen Stuart MA, Fleer GJ. Adsorption of graft copolymers onto silica and titania. *Macromolecules* 1998, **31**: 8981–8987.
[9] Vamvakaki M, Billingham NC, Armes SP, *et al*. Controlled structure copolymers for the dispersion of high-performance ceramics in aqueous media. *J Mater Chem* 2001, **11**: 2437–2444.
[10] Moreno R. The role of slip additives in tape-casting technology: Part I—solvents and dispersants. *Am Ceram Soc Bull* 1992, **71**: 1521–1531.
[11] Cerbelaud M, Videcoq A, Abélard P, *et al*. Self-assembly of oppositely charged particles in dilute ceramic suspensions: Predictive role of simulations. *Soft Matter* 2010, **6**: 370–382.
[12] Xiao C, Chen H, Yu X, *et al*. Dispersion of aqueous alumina suspensions with biodegradable polymers. *J Am Ceram Soc* 2011, **94**: 3276–3281.
[13] Cerbelaud M, Videcoq A, Abélard P, *et al*. Heteroaggregation between Al_2O_3 submicrometer particles and SiO_2 nanoparticles: Experiment and simulation. *Langmuir* 2008, **24**: 3001–3008.
[14] Raşa M, Philipse AP, Meeldijk JD. Heteroaggregation, repeptization and stability in mixtures of oppositely charged colloids. *J Colloid Interface Sci* 2004, **278**: 115–125.
[15] Hütter M. Local structure evolution in particle network formation studied by Brownian dynamics simulation. *J Colloid Interface Sci* 2000, **231**: 337–350.
[16] López-López JM, Schmitt A, Moncho-Jordá A, *et al*. Electrostatic heteroaggregation regimes in colloidal suspensions. *Adv Colloid Interfac* 2009, **147–148**: 186–204.
[17] Hartley PA, Parfitt GD. Dispersion of powders in

liquids. 1. The contribution of the van der Waals force to the cohesiveness of carbon black powders. *Langmuir* 1985, **1**: 651–657.

[18] Bergström L. Hamaker constants of inorganic materials. *Adv Colloid Interfac* 1997, **70**: 125–169.

[19] López-López JM, Schmitt A, Moncho-Jordá A, *et al.* Stability of binary colloids: Kinetic and structural aspects of heteroaggregation processes. *Soft Matter* 2006, **2**: 1025–1042.

[20] Wang X, Zhang H, Guo L. Effect of ionic strength on the stability of binary ceramic suspensions. *J Am Ceram Soc* 2007, **90**: 3435–3440.

[21] Wang X, Guo L. Effect of ionic strength on rheological properties of binary Al_2O_3/ZrO_2 suspensions. *Colloids Surf A* 2007, **297**: 7–13.

[22] Uricanu V, Eastman JR, Vincent B. Stability in colloidal mixtures containing particles with a large disparity in size. *J Colloid Interface Sci* 2001, **233**: 1–11.

[23] Kordani N, Vanini AS, Asadi A, *et al.* Optimization of fracture behavior of alumina/silicon carbide nano ceramic. *Neural Comput Appl* 2013, **23**: 2379–2385.

[24] Yang Q, Troczynski T. Dispersion of alumina and silicon carbide powders in alumina sol. *J Am Ceram Soc* 1999, **82**: 1928–1930.

[25] Majidian H, Ebadzadeh T, Salahi E. Stability evaluation of aqueous alumina–zircon–silicon carbide suspensions by application of DLVO theory.

[26] Xiao C, Ni Q, Chen H, *et al.* Effect of polyvinylpyrrolidone on rheology of aqueous SiC suspensions dispersed with poly (aspartic acid). *Colloids Surf A* 2012, **399**: 108–111.

[27] Matijević E, Kitazawa Y. Heterocoagulation. *Colloid & Polymer Sci* 1983, **261**: 527–534.

[28] Matsumoto H, Nagao D, Konno M. Repetitive heterocoagulation of oppositely charged particles for enhancement of magnetic nanoparticle loading into monodisperse silica particles. *Langmuir* 2010, **26**: 4207–4211.

[29] Li G, Yang X, Wang J. Raspberry-like polymer composite particles via electrostatic heterocoagulation. *Colloids Surf A* 2008, **322**: 192–198.

[30] Minami H, Mizuta Y, Suzuki T. Preparation of raspberry-like polymer particles by a heterocoagulation technique utilizing hydrogen bonding interactions between steric stabilizers. *Langmuir* 2013, **29**: 554–560.

[31] Das S, Murthy VSR, Murty GS. Particulate size effect on the rheology of SiC–glass composites. *J Mater Sci* 1999, **34**: 1347–1352.

[32] Guo L-C, Zhang Y, Uchida N, *et al.* Adsorption effects on the rheological properties of aqueous alumina suspensions with polyelectrolyte. *J Am Ceram Soc* 1998, **81**: 549–556.