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Effect of aqueous graphite dispersion on alumina-zircon suspension

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The effect of two dispersants (Glydol N1055 and kx9009) on high solids content graphite suspensions were characterized by rheological behavior, sedimentation test and zeta potential. Only the Glydol N1055 dispersant was effective for the wettability of graphite, and kx9009 dispersant being superior to Glydol for graphite suspension as a result of a greater zeta potential and lower viscosity or sedimentation behavior. Alumina-zircon-graphite suspensions were prepared using alumina and zircon powders and graphite dispersion. These suspensions had shear-thinning behavior and could be dispersed using the Dolapix CE-64 dispersant (0.5 wt.%) as well as Glydol (4 wt.%) and kx9009 (0.3 wt.%). Graphite dispersions displayed no sedimentation when alumina-zircon powders and Dolapix were added.

Key words: Graphite, Alumina-zircon suspension, Rheological behavior, Zeta potential, Sedimentation test.

Introduction

Using submicrometer particles is one method to obtain a relatively low sinter temperature, fully dense and fine-grain microstructures [1]. Control of the properties of final products in the processing of ceramic parts can be achieved by preparing concentrated ceramic aqueous suspensions. Consolidated compacts with high wet and green strength are the result of stable suspensions with high solids loadings [2]. To obtain a ceramic suspension with high solids content that can be successfully processed, low viscosity must be achieved and stability must be maintained. These goals can be accomplished by preparing a dispersed colloidal suspension of high solids volume and relatively low viscosities [3].

In order to achieve a uniformly dispersed colloidal suspension electrostatic, steric, or electrosteric stabilization mechanisms should be used in ceramic processing [4]. This requires the presence of efficient additive or dispersant such as polyelectrolytes and a significant electrical double-layer repulsion [5].

Effect of some additives (SDS, Tiron, CMC, PVA, polyethylene Glycol, ...) on aqueous dispersion of graphite powder has been already reported by many researchers [6-10].

Some experimental investigations have been carried out on alumina-zircon-SiC aqueous suspensions which are generally used for preparing alumina-mullite-zirconia-SiC composites [11, 12]. Rheological measurements of alumina-zircon-SiC suspensions have been reported previously [13]. Results showed that even though the use of SiC particles can improve the stability of alumina-zircon suspensions, but the density of final composites decreased because of the lower sinterability of SiC rather than alumina. Thus, in order to achieve more dense composite, graphite powder was used as a SiC precursor. The fabrication of Al_2O_3/SiC nanocomposites by a new technique involving the in situ synthesis of nano-sized SiC particles has been reported by Gustafsson [14]. Homogeneous green bodies containing SiC precursors can be obtained by this method. The carbothermal reduction of clay was also used to production of Al_2O_3-SiC mixtures [15]. Therefore, the stability of concentrated graphite suspensions should be taken into consideration. In this study, the stability of alumina-zircon-graphite suspension has been characterized by rheological behavior, sedimentation test and zeta potential measurements using two kinds of additives (Glydol and kx9009). To our knowledge, the use of these polyelectrolytes for aqueous processing of graphite powder has not yet been explored, but a few studies have been carried out using other additives (CMC, Tiron, SDS, etc).

Experimental Processing

Materials

The α-alumina (MR70, Martinswerk, Germany), zircon (Zircosil, Johnson-Matthey, Italy) and Graphite (GMP Co, China) powders with mean particle size of 0.6 and 1.4 and 23 μm, respectively, were used as the starting materials. Dispersants such as Dolapix CE64, Glydol N1055 and kx9009, were prepared from Zschimmer and Schwarz (Germany).

Suspension preparation

Graphite suspensions

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The graphite suspensions were prepared by mixing the graphite powder with dissolved additives in water using a planetary mill (150 rpm) for 45 min. Each suspension named by a code (G*x*-kx*y*); *x* indicates the amount of Glydol and *y* indicates the amount of kx9009 by weight percent for graphite suspension. Any other dispersant was identified by proportional code (D for Dolapix in alumina-zircon-graphite suspensions). According to Moraru *et al*. [16], the stability of the graphite particles is favored when the pH level of the dispersed phase assumes values between 6 and 8. Therefore the pH level of graphite suspensions was measured (6.8) and kept constant.

Alumina-zircon-graphite suspensions

The mass ratio of alumina to zircon in all mixtures was 85/15. Alumina, zircon and graphite powders were added to the solution of the dispersant in water (including 0.5 or 0.6 wt.% Dolapix here). The resultant slurry was stirred for 20 minutes in a planetary mill at 200 rpm. The order of mixing could significantly affect the rheological behavior of the suspension; therefore graphite powder was first added to the Glydol solution and then mixed with the alumina-zircon suspension prepared by Dolapix dispersant.

Characterization

Rheological behavior of graphite suspensions were evaluated at a temperature of 25 ± 0.1 ºC using a controlled stress rheometer (MCR 301, Anton Paar Physica, Germany). Zeta potential measurement was carried out by zetasizer (Zetasizer3000 H_{AS}, Malvern). Zeta-Potentials experiments were done using 2 vol% suspensions. For sedimentation test the aqueous suspension was kept aside for 24 hours and the height of the sedimentation (floated graphite or clarity part of suspension) was measured every 1 hour. The sedimentation test was calculated according to Yu [17], when the graphite particles had floated to the top of the suspension, the graphite particles were collected and dried to a constant weight and then the weights of the floating graphite particles were determined.

When a suspension has more than one solid phase, it is necessary to find a pH range in which all of the particles have a substantial surface charge of the same sign so that irreversible agglomeration is prevented [18]. Therefore, the pH level of alumina-zircon-graphite suspensions which found to be near 9 was kept constant.

Results and Discussion

Rheology

The viscosity and shear stress of graphite suspensions exhibited a strong dependence on the dispersant concentration. However, the rheological properties of these graphite suspensions show nearly Newtonian behavior. For these suspensions, the shear stress is in direct proportion to the shear rate applied and the apparent viscosity is constant with changing shear rates. In fact the viscosities of suspensions were independent of the shear rate.

The reported viscosity measurements were taken at shear rate of 10 s^{-1}. Using graphite at concentrations higher than 50 wt. %, suspension had shear thinning behavior and reached a gel-like consistency (high viscosity). As a result, 50 wt. % was chosen for the following experiments. Glydol was used at 4 concentrations (2, 3, 4 and 5 wt. %), and kx9009 was used at 3 concentrations (0.1, 0.3 and 0.5 wt. %). Some experimental tests showed that dispersant concentration less than above mentioned values are not suitable for preparing graphite suspension. The relationships between viscosities of 50 wt. % graphite suspensions and two dispersants concentrations are shown in Fig. 1 and 2. Figure 1 shows that the viscosity of graphite suspensions varies from 0.21 to 0.11 Pa.s when the Glydol concentration changes from 2 to 4 wt. %. However, when 5 wt. % Glydol is used, the viscosity increases up to 0.12 Pa.s. The optimum viscosity of 0.11 Pa.s is obtained when 4 wt. % Glydol was used (G4 graphite suspension).

While continually introducing kx9009 to the G4 graphite suspension, the viscosity of graphite suspensions decreases correspondingly and Newtonian behavior is observed again. Figure 2 shows that the viscosity varies from 0.11 to 0.05 Pa.s when the kx9009 content changes

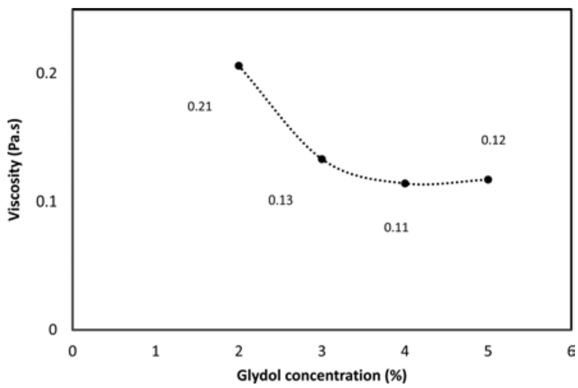

Fig. 1. Viscosity dependence of graphite suspension versus Glydol concentrations.

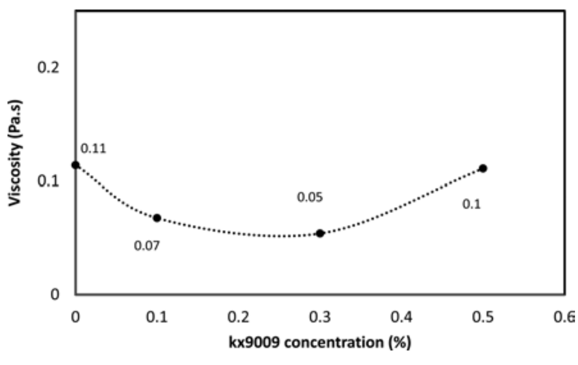

Fig. 2. Viscosity dependence of graphite suspension versus kx9009 concentrations.

from 0.1 to 0.3 wt. %. Like as Glydol, the same trend was observed for kx9009. The viscosity of suspension increases to 0.1 Pa.s for 0.5 wt. % kx9009.

Higher amount of viscosity for lower amount of dispersant than the optimum value (in the range from 2% to 4% Glydol or 0.1% to 0.3% kx9009) is due to a combination of two effects: probably the zeta potential is low in magnitude and incomplete adsorption results in polymer bridging where two or more particles can mutually adsorb polymer chains [3]. The increase of viscosity at 5% Glydol or 0.5% kx9009 (higher amount of dispersant than the optimum value) is also because of immersing the excessive dispersant into the medium. Free electrolytes in a suspension disturb the electrostatic forces within the particles and decrease the amount of available solvent and subsequently increase the viscosity of the suspension [19]. As reported [20], the existence of free polyacrylate has a detrimental effect on the stability of a suspension with the promotion of the flocculation. The minimum viscosity of 0.05 Pa.s is obtained when 4 wt.% Glydol and 0.3 wt.% kx9009 were used (G4-kx0.3 graphite suspension).

Figure 3 shows the rheology behavior of the graphite and alumina-zircon-graphite suspensions using Dolapix CE-64 as a dispersant. All alumina-zircon-graphite suspensions demonstrated shear-thinning behavior. Without Dolapix, the suspension is viscous comparatively (shear stress is 123 Pa and viscosity is 56 Pa.s) and also shows

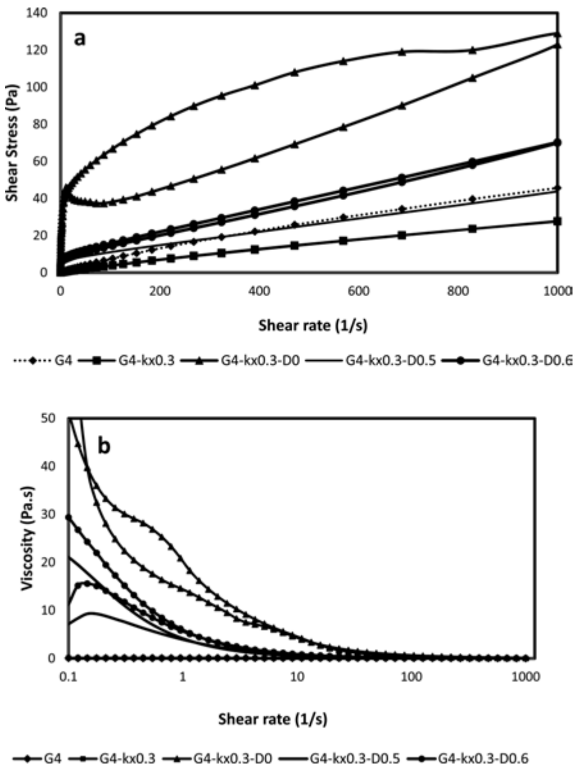

Fig. 3. Rheology behavior of suspensions (a) shear stress and (b) viscosity (note that G4 and G4-kx0.3 are graphite suspensions, G4-kx0.3-D0, G4-kx0.3-D0.5, and G4-kx0.3-D0.6) are alumina-zircon-graphite suspensions).

thixotropic behavior. G4-kx0.3-D0 suspension has a great yield stress (40 Pa) which shows the resistance of suspension particles at the beginning of shear rate. When 0.5 wt. % Dolapix is used, the shear stress and viscosity of the suspensions decrease to 43 Pa and 9 Pa.s , respectively. Also the amount of yield stress reduced to 6 Pa and showed trace amount of thixotropy. More Dolapix content (0.6 wt. %) increases both values of shear stress and viscosity and is not preferred. The optimum amount of Dolapix CE-64 was reported [13] to be 0.5 wt. % for alumina-zircon suspensions; therefore it seems that it should be kept constant here as well. Higher viscosities of alumina-zircon-graphite suspensions are due to the more solid volume concentration of powders in suspensions. This is due to the fact that graphite suspension which was first prepared had 50 wt. % solid, this value reached to 80 wt. % when alumina and zircon added to graphite suspension.

Sedimentation

The effect of adsorbed dispersants on stability and wettability of the powders was determined by sedimentation experiments. Figure 4 shows the results of sedimentation test for the suspensions with different concentration of additives. Pure graphite/water mixture (0% additive) shows a large amount of floating particles (100%) because of the high hydrophobicity of graphite powder. Lower amounts of Glydol (< 2 wt. %) were also showed the same behavior. This results because the binding energy between the graphite particles is high and this amount of Glydol cannot improve the wettability of the graphite particles. In contrast, figure 4 shows that at higher concentrations of Glydol (> 3%), the binding energy between particles is low and the graphite particles display a relatively more wettability (the floating height reaches nearly 0% for G4 suspension). When Glydol is added to the graphite/water mixture, the dispersant present in the suspension medium adsorbs on the graphite particle surfaces and increase their wettability in water.

When Glydol concentration is lower than 3 wt. %, a

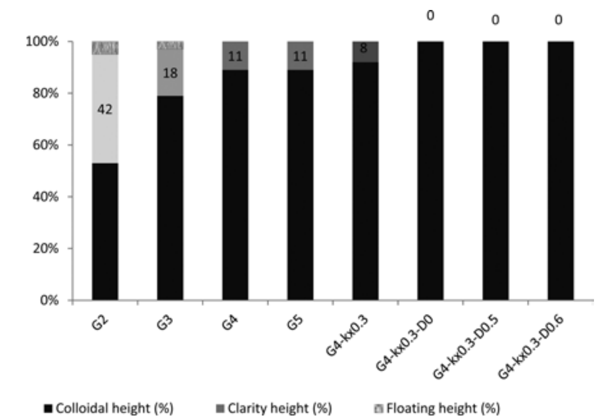

Fig. 4. Colloidal, clarity and Floating height of suspensions.

high amount of clarity part for the suspensions can be observed (42%), and after that a decline is reached with increasing the concentration of Glydol (18%). At 4 wt. % Glydol concentration, a further gradual decrease in height of clarity is observed (11%). Further increase of Glydol did not improve the stability of suspensions anymore. Therefore, the dispersion concentration at 4 wt. % is confirmed as an optimal one, providing a stable suspension.

The graphite suspension prepared using kx9009 as well as Glydol dispersants showed a gradual decrease in floating height (8%) by the addition of 0.3 wt. % kx9009. However, clarity or floating heights were not observed in the case of alumina-zircon-graphite suspensions prepared using Glydol, kx9009 and Dolapix CE-64 as dispersants. Figure 4 shows that trace amounts of floating graphite (< 0.1%) and large amount of colloidal height can be observed for G4-kx0.3, G4-kx0.3-D0.5 and G4-kx0.3-D0.6 suspensions. These data also correlate with the other experimental determinations.

Zeta potential

Zeta potential of graphite suspensions has been reported in many literatures, but some differences exist among their results. Therefore, the isoelectric point (IEP) of graphite is reported in the pH range of 2.5-5 [21]. Hence, the surface charge of graphite should be negative at basic pH. Zeta potential of suspensions as a function of different dispersants is shown in figure 5. This figure shows that with incorporation of Glydol to graphite aqueous suspension (G4), the zeta potential is −32.9 mV. The zeta potential approaches a value of −35.7 mV when 0.3% kx9009 was used. The increase of zeta potential value shows that the dispersant was adsorbed on graphite surfaces and enhanced its negative surface charge. The zeta potential of graphite suspension (G4-kx0.3-D0) did not change significantly by adding alumina and zircon particles, while the deviation of test results was increased and graphite suspension became unstable. The stability of graphite suspension was improved by adding 0.5 wt. % Dolapix and the zeta potential value reached −38.9 mV. The higher amount of zeta potential was measured for G4-kx0.3-D0.5 suspension.

The knowledge of rheological behavior is necessary because the effect of rheological properties of suspensions on the casting behavior and the properties of final products is significant. As the Glydol concentration increases, the stability and viscosity of suspension increase. Ceramic suspensions can be generally stabilized electrostatically, but incorporating polymeric additives can improve the dispersion of suspensions. Using polyelectrolytes such as kx9009 or Dolapix can be drastically reduced the viscosity of graphite suspension. The increased stability and dispersion of the 4% Glydol-0.3% kx9009 suspension may be due to an electrosteric stabilization of two additive combinations.

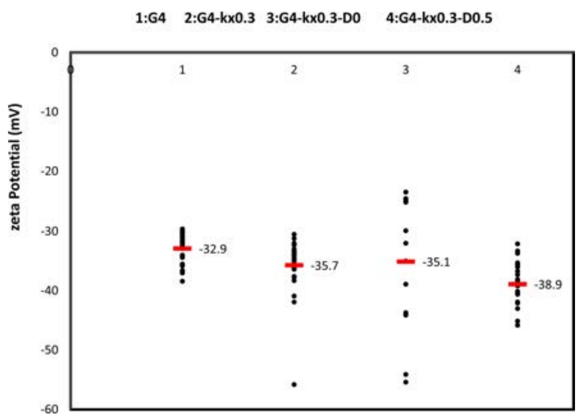

Fig. 5. Zeta potential of 1, 2: graphite suspensions and 3, 4: alumina-zircon-graphite suspensions.

The mechanism of these two dispersants is electrosteric as mentioned by manufacturer. Steric repulsion is believed to play an important role in the stabilization of systems with high solids loading. In sterically stabilized systems flocculation is prevented since the total energy interaction is repulsive also at very short distances provided that the surfaces are completely covered with polymer [22]. Adsorption of dispersant provides negative surface charge to the particles. This results in a well dispersion of powders in aqueous medium.

However, the formulation and mechanism by which the Glydol enhances graphite powder dispersion is not disclosed. It is only known that Glydol N1055 is a Wetting agent for carbon and has Polyarylsulfonate Chemical basis as stated by manufacturer (Zschimmer and Schwarz). It means that Glydol contains the functional group SO_3^-. Kx9009 is also a stabilizer polyalcohol (alcohol containing more than one hydroxyl groups). It appears that more than one functional group associate through complex formation results in more stabilization. On the other hand, Dolapix CE-64 is a synthetic polyelectrolyte and its chemical base is carboxylic acid ester which contains COO− group. As the fraction of functional groups (COO−) increases, the polymer charge varies to highly negative. The absolute value of zeta potential has a tendency to increase with incorporating two dispersants. When using Dolapix, the surface charge increases with pH and it would be expected that the high density of carboxylate groups obtain by polymeric dispersants [22]. Low viscosity of alumina-zircon-graphite suspension in presence of these additives is attributed to the combination of electrostatic and steric contributions which provide sufficient stability.

Conclusions

Stability properties of graphite particles dispersed with two dispersants were evaluated with rheometry, zeta potential and sedimentation measurements. The graphite suspension prepared by Glydol N1055 and kx9009 complex solution showed lower viscosity and higher zeta potential compared to that prepared by only Glydol. The wettability of graphite powder was improved by adding 4 wt. % Glydol as depicted by lower floated graphite in suspensions.

A well dispersed alumina-zircon-graphite suspension was obtained at a concentration of 4 wt. % Glydol, 0.3 wt. % kx9009 and 0.5 wt. % Dolapix CE-64 at which the viscosity and thixotropy behavior of the suspension decreased to a minimum value and the zeta potential of the suspension increased to a maximum value.

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