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Short Communication

Combined effect of fructose and NaCl on the viscosity of alumina nanopowder suspensions

Simge Çınar *, Daniel D. Anderson, Mufit Akinc

Department of Materials Science and Engineering, Iowa State University, 2220 Hoover Hall, Ames, IA 50011, United States

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Abstract

Many ceramic processing operations involving powder suspensions aim to optimize the solids loading while maintaining low viscosity. Use of nanopowder suspensions are challenging as they exhibit unexpectedly high viscosities. Low molecular weight saccharides were added to decrease the viscosities of alumina nanopowder suspensions as they modify effective solids content. It was also recently reported that suspensions with very low ionic strengths exhibit lower viscosities as they create high repulsive barrier between the particles. In the present study, the effect of the combination of these two additives on the viscosity is reported. Low temperature differential scanning calorimetry (LT-DSC) and *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) results showed that two additives act independently. Suspensions containing NaCl and fructose yield green compacts with lower porosity and higher strength.

Keywords: Rheology; Alumina nanopowder; Colloidal suspensions; Bound water; Stabilization

1. Introduction

Rheological properties of colloidal oxide powder suspensions greatly affect the quality of the final product.[1–6] Stable suspensions of homogeneously dispersed powders yield lower viscosities than agglomerated ones. However, it is rather difficult to obtain lower viscosities when nanopowders were used. Nanopowders tend to agglomerate due to their high surface area and the small separation distances between particles in concentrated systems.[1,3,7] Thus, understanding the interaction between particles in concentrated suspensions is even more critical for controlling the suspension viscosity.

Use of low molecular weight saccharides for viscosity reduction of alumina nanopowder suspensions was suggested by Schilling et al. [8] a decade ago. Since then, there has been several studies reported revealing their mechanism of viscosity reduction[8–16] and applications in various fields.[13,17,18] Schilling et al. [8] reported that additions of oligo- or polysaccharides decrease the viscosity of micron or sub-micron alumina suspensions; however, when nanopowders are used, the viscosity of suspensions increase. Bridging caused by large saccharide molecules was suggested as a reason for increase in viscosity. Instead, they used mono- or di-saccharides or sugar alcohols. Yar et al. [16] studied the addition of polyalcohols which have similar chemical structure to low molecular weight saccharides. Polyalcohols have multiple hydroxyl groups on their linear or branched backbones, while saccharides have hydroxylated ring structure. They concluded that polyalcohols adsorb on the alumina surface and reduce the viscosity. Li and Akinc [14,15] related the effect of fructose to availability of water in suspensions. They reported that a fraction of water associated with powder, called "bound water", which has lower mobility than the bulk water. Falkowski et al. [13] used 1-*O*-methyl-D-fructose, glucose, 3-*O*-acrylic-D-glucose, and showed that substitution of $-OCH_3$ for OH group decreases the viscosity of suspensions even further. They supported the mechanism of "bound water" to explain their

* Corresponding author. Tel.: +90 545 780 3875.
E-mail addresses: simgecnr@gmail.com, scinar@iastate.edu (S. Çınar), ddander2@illinois.edu (D.D. Anderson), makinc@iastate.edu (M. Akinc).

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observation by the fact that substituted molecules are relatively less compatible with water, so they will release more bound water or associate weakly with bound water leading to lower viscosities. We recently reported that bound water is directly related with the powder surface area, so although it can be negligible in micron size powder suspensions, its influence on nanopowder suspensions is significant.[9,11,12] The effect of fructose in viscosity reduction of alumina nanopowder suspensions cannot be explained with steric or electrostatic mechanisms alone, but its presence modifies the bound water layer, decreases the effective solids content, thus the viscosity of suspensions.[12]

While fructose molecules are able to modify the bound water, addition of NaCl does not lead to any changes in bound water, yet it decreases the viscosity of the suspension.[9] Effect of NaCl on the viscosity of alumina nanopowder suspensions has been recently studied by our group.[9] We showed that addition of small amounts of NaCl leads to a substantial decrease in viscosity which cannot be explained with bound water phenomena, but modification of the electrostatic double layer. It was concluded that bound layer and electrostatic double layer are two distinct layers around oxide particles.

In the current study, we aimed to investigate these two effects concurrently, bound layer modification and control of interparticle forces, to obtain suspensions with very low viscosities while testing our ability to design better systems with our current knowledge. We first reported the rheological behavior of suspensions and compare the individual and combined effect of additives on viscosity, then carried out experiments using low temperature differential scanning calorimetry (LT-DSC) and *in situ* attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to reveal the mechanism of combined effect. Lastly, we compared the green body microstructure and mechanical strength of slip cast alumina suspensions with and without additives.

2. Experimental

Alumina nanopowder (Lot number: AAGL 1201) was purchased from Nanophase Technology Corporation (Burr Ridge, IL). Average particle size of powders were 42 nm and 30 ± 21 nm as determined by specific (BET) surface area and TEM micrographs, respectively. More than 99% of the powders were in the range between 10 nm and 100 nm in diameter. TEM micrograph and properties of alumina nanopowders were reported before.[9–11]

D-Fructose (99%) and NaCl (ACS certified) were purchased from Alfa Aesar (Lancashire, UK) and Fisher Scientific (Fair Lawn, NJ), respectively.

Ultrapure water with the resistivity of 18.2 MΩ cm and total organic content (TOC) <3 ppm (Milli-*Q* Gradient A-10 model, Millipore Company, Billerica, MA) was used for sample preparation.

For the preparation of suspensions, the alumina content was calculated as the volume percentage of the suspension. The fructose addition was calculated as weight percent of the dried alumina powder. The volume of fructose was taken into account in calculating the required volume of water to maintain volume percent of solids in suspension accurate. NaCl amount was expressed as mole per liter, M, of solution.

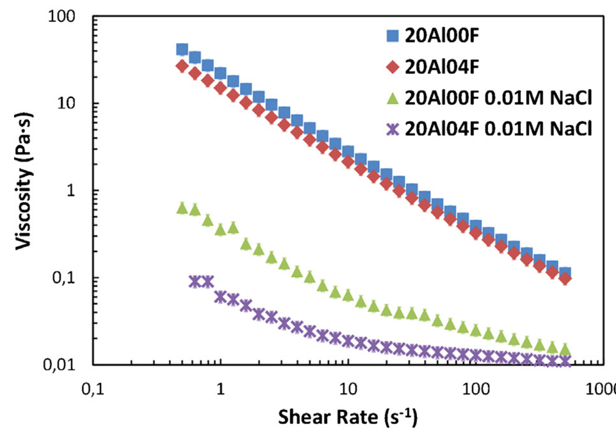

Fig. 1. Viscosity of suspensions (20 vol%) with no addition (20Al00F), 4 wt% fructose (20Al04F), 0.01 M NaCl (20Al00F 0.01 NaCl) and the combination of 4 wt% and 0.01 M NaCl (20Al04F 0.01 M NaCl).

Alumina nanopowder was dried at 110 °C for 2 h prior to preparation of suspension to minimize the level of moisture content. Required amount of fructose was mixed with water, then alumina powder was added slowly. The suspension was shaken for 24 h to establish equilibrium condition. NaCl was added 2 h prior to analysis.

Details of viscosity, LT-DSC and ATR-FTIR measurements were explained elsewhere.[9–12]

Pellets were cast using gypsum plate as base with an acrylic cylindrical cavity (around 2.5 cm in diameter, 1 cm in height). Alumina nanopowder suspensions with 20 vol% solids were used for casting. The pellets were dried for 48 h at room temperature and kept in desiccator for analysis. Pellets were fractured for visual and microscopic observation.

Microhardness measurements were made on cast samples embedded in epoxy resin at room temperature using the LECO microhardness tester (LM-247AT model, MI, USA). At least six indents under a load of 100 gf for a dwell time of 13 s were made on each sample.

3. Results and discussion

3.1. Viscosity

Individual effects of fructose and NaCl on the viscosity of alumina nanopowder suspensions were reported before.[9,12–15] It was shown that while fructose reduces the viscosity by replacing the bound water on the surface, NaCl additions modify the electrical double layer.[9,11] Fig. 1 and Table 1 show the effect of fructose, NaCl and their combination on the suspension viscosity. 4 wt% of fructose addition was chosen as a benchmark fructose concentration since it is a high enough concentration to show the reduction in viscosity. Previous work showed that 0.01 M NaCl gives the lowest viscosity for similar alumina nanopowder suspensions. The data in Table 1 shows that the