Influence of bound water layer on the viscosity of oxide nanopowder suspensions

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Abstract

Nanopowder suspensions exhibit much higher viscosities compared to micron size powders. The current viscosity models greatly underestimate the viscosity of nanopowder suspensions and hence are inaccurate. Recently, it was shown that a bound water layer around the particles is partially responsible for the high viscosities of alumina nanopowder suspensions. In the present study, the existence and effect of the bound water layer on suspension viscosity has been validated for other oxide systems such as zirconia, yttria stabilized zirconia and titania. The water melting events were studied by low-temperature differential scanning calorimetry (LT-DSC) to investigate the nature of the bound water and how it varied by different oxide systems. Onset of the bound water for these oxides varied from -1 to $-7\,^{\circ}C$. The variation in melting behavior of bound water was related to the presence of charged species in solution and gel-like hydroxide formation. The bound water content was estimated and incorporated into a modified Krieger–Dougherty (K–D) equation. The modified equation was employed to interpret the experimental data. Intrinsic viscosity values were estimated as 11.6, 6.6, 5.1 and 3.1 at a shear rate of $50\,s^{-1}$ for alumina, titania, zirconia and YSZ, respectively. Increasing shear rate predicted lower intrinsic viscosity values. Modified K–D equation could predict the suspension viscosity much better than the other available models in literature while distinguishing the differences between oxide systems.

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1. Introduction

Alumina,[1–8] zirconia,[9–16] yttrium stabilized zirconia (YSZ),[17–19] and titania[20–22] are some of the most widely studied ceramic nanopowder systems. An understanding of the surface properties and the rheological behavior of oxide nanopowder suspensions is essential for many applications, including nanofluids,[23–27] advanced ceramics,[10,28,29] nanocomposites,[25,30] and others. Lower suspension viscosities facilitate improved end-product quality as they indicate better dispersed systems, and lower production costs.

Typically, the suspension viscosity increases with decreasing particle size.[16,31] However, nanopowder suspensions exhibit unexpectedly high viscosities. A possible explanation is the fact that the separation distances between particles are much shorter in nanopowder systems resulting in excessive agglomeration. Existing models do not fully explain this phenomenon. The current models underestimate the viscosity of nanopowder suspensions and it is a topic of current debate.[5,23–26,32–35]

We suggested the "bound water" mechanism to explain the relatively higher viscosities of nanopowder suspensions.[36–38] Since the bound water, which exists around the nanoparticles, does not serve as a solvent in the system, but behaves as a part of the powder, the effective solids content increases and is partially responsible for the high viscosities of alumina nanopowder suspensions. It was shown that while the bound water fraction is negligible for sub-micron size powders, it becomes substantial for nanopowders, leading to much higher viscosities than predicted by existing models.[36] Therefore, understanding and control of the bound water is crucial for colloidal processing in order to predict the properties of suspensions, increase the solids content to the desired level, and/or obtain high quality end-products.

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The bound water manifests itself by the appearance of lower temperature melting events in the presence of alumina powders as indicated in low temperature differential scanning calorimetry (LT-DSC). The fraction of bound water is unaffected in the presence of indifferent electrolytes (i.e., NaCl or KNO_3), whereas the presence of potential determining ions (like H^+ and OH^-) leads to changes in the fraction of bound water.[37] Thus, bound water is directly associated with the particle surface and its role is different than the well-known electrical double layer phenomenon.[37] It was reported that the bound water layer can be modified by low molecular weight saccharides.[36,38,39] Presence of fructose does not show steric or electrostatic effects, but releases or changes the nature of bound water, which decreases the bound water fraction and reduces the suspension viscosity. Very recently, we have demonstrated that modification of these two distinct layers, electrical double layer and bound water layer, could be used to control the green body structure.[40] While shrinkage of electrical double layer leads to smaller pores, shrinkage of bound water layer increases the structural integrity of the green body samples obtained by slip casting of alumina nanopowder suspensions.

Even though the presence of the bound water layer and its influence on colloidal processing were thoroughly studied, these studies were all focused on alumina systems. The goal of the present work is to extrapolate our findings to other oxide nanopowder systems, specifically zirconia, 3 mol% yttria-stabilized zirconia (YSZ), and titania, and to develop a model of suspension viscosity, which can explain the higher viscosities of different oxide nanopowder systems. The suspension viscosity was studied by rheometry and the bound water layer by LT-DSC. The effective solids content of the nanopowder suspensions was estimated using bound water fractions by LT-DSC, which were subsequently employed in the modified K–D equation to predict and compare the viscosities of different oxide systems. The intrinsic viscosity values predicted by the model were discussed.

2. Experimental

2.1. Materials

While alumina (Lot number: AAGL 1201) and titania (Lot number: T90121–01) nanopowders were purchased from Nanophase Technology Corporation (Burr Ridge, IL, USA), zirconia (Lot number: IAM6280NZ0) and yttria stabilized zirconia (Lot number: IAM3180NYZ3) nanopowders were purchased from Inframat Advanced Materials (Manchester, CT, USA). All powders had a purity of at least 99.0%. Fig. 1 shows the transmission electron microscopy (TEM) images of the nanopowders used in this study. The alumina and titania nanopowders were almost perfectly spherical, while the morphology of zirconia and YSZ were less well-defined. Zirconia powders were agglomerated to a degree that the boundaries between individual particles
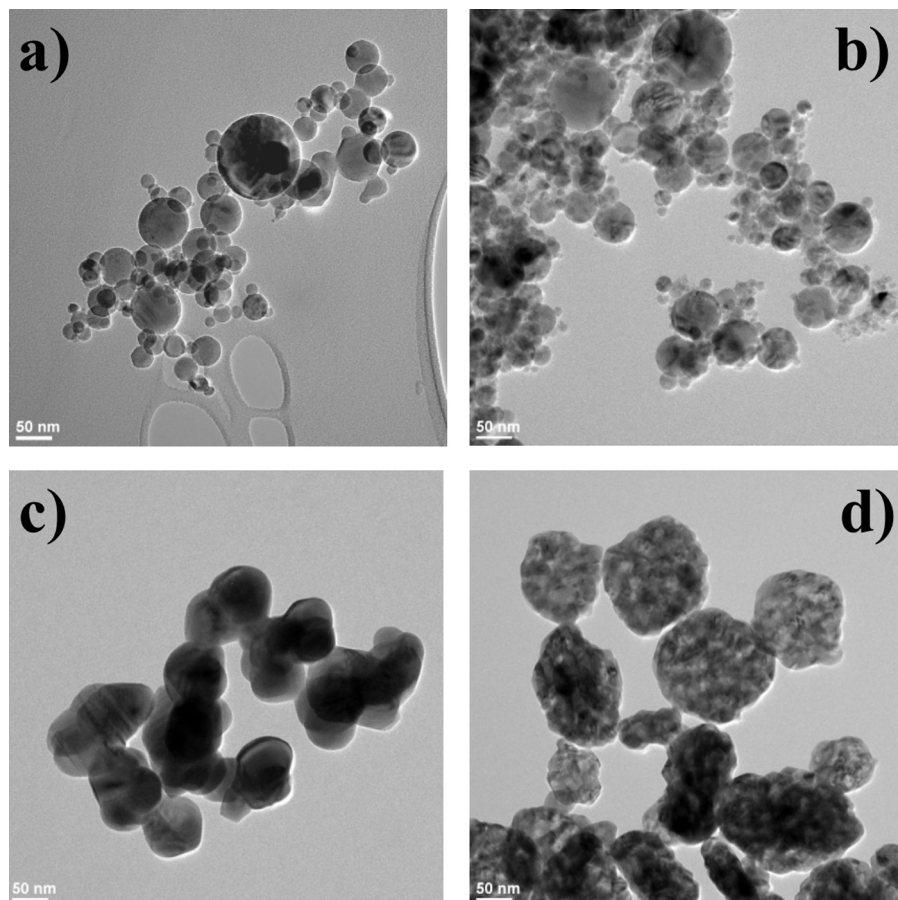

Fig. 1. TEM micrographs of alumina (a), titania (b), zirconia (c), and YSZ (d) nanopowders.