Colloids and Surfaces A: Physicochem. Eng. Aspects 348 (2009) 39–44

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Synthesis and characterization of cubic cobalt oxide nanocomposite fluids

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ARTICLE INFO

Article history:
Received 24 November 2008
Received in revised form 10 June 2009
Accepted 18 June 2009
Available online 26 June 2009

Keywords:
Rheology
Shear thickening
Relative viscosity
Cobalt oxide and cubic particles

ABSTRACT

Narrow size distribution cubic Co_3O_4 nanoparticles were synthesized and rheological properties of suspensions of the cubes in oligomeric polyethylene glycol (PEG) were explored over a range of particle volume fractions and rotational shear flow conditions. At low and high particle volume fractions, the relative viscosity of the suspensions is described by a Krieger–Dougherty formula with an intrinsic viscosity consistent with expectations for suspensions of ideal cuboids. At intermediate to high particle loadings, the suspensions manifest complex rheological behavior, including shear thinning and shear-thickening features. These observations are discussed in terms of the charge carried by the cubes and the shear rate/volume fraction dependency of the transition from shear thinning to shear thickening.

1. Introduction

The ability of particles to modulate the viscosity of liquids in which they are suspended is of tremendous practical and scientific importance. The economic impact of even an abbreviated list of such examples, blood, inks, paints, lotions and cosmetics, milk and associated foods, is sufficient to justify this importance. At low volume fractions ϕ, suspended particles simply fill space and the viscosity of a suspension in a Newtonian host fluid is proportional to the product of the particle volume fraction and the intrinsic viscosity determined by the particle shape, but is independent of the particle size, $\eta = \eta_s(1+[\eta]\phi)$ [1–3]. Here η_s is the suspending medium viscosity and $[\eta]$ is the intrinsic viscosity of the particles. At higher particle loadings, hydrodynamic and many-body forces between suspended particles significantly change this simple law and more complex equations proposed by Batchelor [4,5], Thomas [6], and by Krieger and Dougherty [7] are required to predict the suspension viscosity. The ability of the latter two equations to predict/organize shear viscosity data for a wide range of concentrated suspensions of spheres has been extensively investigated for decades [6–9]. The viscosity models of Thomas and of Krieger and Dougherty have also been employed to fit viscosity data for suspensions of non-spherical and of charged particles [10].

Advances in particle synthesis techniques are rapidly increasing the library of shapes and surface chemistries available for detailed investigations of suspension mechanics and rheology. For example, cube-shaped particles are now available in a range of sizes, densities, and chemistries, including cobalt oxide [11], lead sulfide [12], and sodium magnesium fluoride [13]. Because of their planar faces, we hypothesize that cube-shaped colloids can more readily form layered structures in a shear flow than spherical ones. Subsequent break-up of these structures at high shear rates should therefore lead to more dramatic increases in viscosity (shear thickening) in suspensions of cubes than possible in a suspension of spheres of comparable size. Recently, materials displaying some form of reversible shear thickening have been receiving increasing attention for applications as so-called liquid body armor, wherein shear-induced particle clusters are thought to dramatically retard motion of high-speed projectiles [14]. To the authors' knowledge, this work is the first to report on the shear rheology of suspensions of well-defined, nano-sized cubes. If our hypothesis regarding the ability of cubes to more readily form layered structures is correct, suspensions of cubes will prove interesting targets for this and similar applications.

For particles in the nanometer size range, thermal forces are large enough to prevent settling even when the density of the particles is substantially larger than that of the suspending fluid. This feature is important because it means that suspension behavior of nano-sized cubes can be investigated over a range of flow conditions without concerns about changes in fluid structure produced by particle settling. Furthermore, if the particles are charged and the concentration of salt in the suspension is low, long range electrostatic forces can be exploited to stabilize the particles against aggregation. Consequently, although the bulk density (6070 kg/m^3) of cobalt oxide is high relative to typical suspending fluids, it is suitable for this study.

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doi:10.1016/j.colsurfa.2009.06.025

Cobalt oxide is an important functional material used for applications in pigments [15], sensors [16], catalysis [17], electrochemistry [18], magnetism [19], energy storage [20] and glasses [21]. Under appropriate synthetic conditions it is also known to form crystals, rods, cubes and spherical structures [11,20,22,23]. When selecting a material to disperse in the form of nanocubes, cobalt oxide was chosen over other materials that form nanocubes because the synthesis is straightforward and cobalt oxide is magnetic which may facilitate additional advantages with respect to liquid body armor applications and soldier safety.

2. Experimental

2.1. Materials

Polyethylene glycol MW 400, ethanol, cobalt nitrate and sodium nitrate were supplied by Aldrich (Milwaukee, USA). Sodium hydroxide was purchased from Fisher Scientific (Pittsburgh, USA). Water was purified by a Milli-Q water filtration system from Millipore (Billerica, USA).

2.2. Synthesis of Co_3O_4 nanocubes and suspension characterization

Co_3O_4 nanocubes were synthesized using a simple one-step approach reported by Feng and Zeng [11]. Briefly, 60 g of $NaNO_3$ is added to a three neck flask with a condenser attached. Thirty milliliters of 1 M NaOH and 70 mL of de-ionized water are subsequently added to the flask. The flask is placed in a silicon oil bath set to a temperature of 120 °C. A continuous supply of air at 50 mL/min is bubbled into the system. Twenty milliliters of 1 M $Co(NO_3)_2$ is added drop wise to the flask after the temperature in the flask has equilibrated. The reaction is allowed to proceed for 22 h and yields a black suspension. A well-known disadvantage of this chemistry is that the yield of particles is low. This shortcoming is compensated for by the method's simplicity and by the narrow particle size distributions that can be achieved without the need for surfactants.

After synthesis, the reaction mixture is cooled for 5 min and 100 mL of 0.1 M of HCl is added to the contents of the flask. Next, the mixture is maintained at room temperature for 24 h to allow solid side products produced in the synthesis to be dissolved and separated from the target product, Co_3O_4 nanocubes. The supernatant is discarded, and the bottom phase centrifuged at 6000 rpm for 30 min to further separate the by-products. This procedure is repeated three times to enhance the purity of the Co_3O_4 product. Next, ethanol is added to the bottom phase and thoroughly mixed into the particles. The ethanol and water mixture is gradually displaced with predetermined amounts of low molecular weight, liquid polyethylene glycol (PEG) to produce nanocomposite

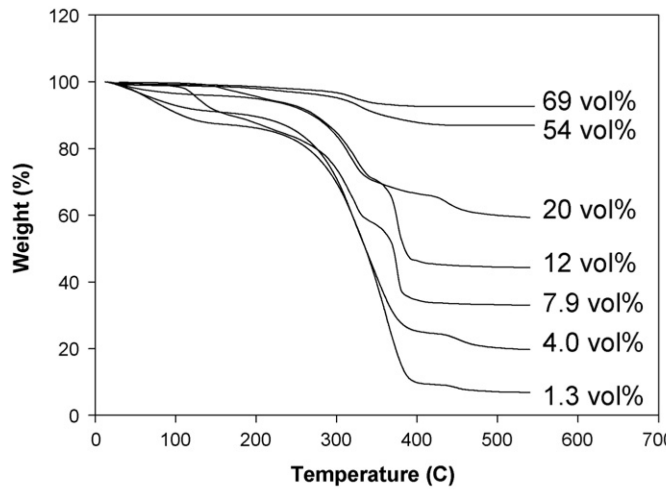

Fig. 1. Sample TGA data for Co_3O_4 suspension characterization.

Co_3O_4/PEG suspensions covering a range of particle concentrations. Residual ethanol and water in the suspensions are driven off by freeze drying at −150 °C for 48 h (low particle content) or by direct vacuum suction (for high particle content).

Thermal Gravimetric Analysis (TGA) revealed the final compositions of Co_3O_4 in PEG. Representative TGA plots are given in Fig. 1 where the *y*-axis represents the weight percentage of material remaining. Additionally, each plot is labeled with the corresponding particle volume fraction for the suspension. At 550 °C, the endpoint of the TGA analysis, all that remains is cobalt oxide. Initially, several suspensions were analyzed up to much higher temperatures, but it was concluded that 550 °C is sufficient to accurately characterize the suspensions.

2.3. Particle size characterization

The synthesized Co_3O_4 nanocubes were characterized by Transmission Electron Microscopy (TEM) at a magnification of 165k. Fig. 2 is a typical TEM micrograph of the materials, which shows the cubic shape and excellent shape control of the cobalt oxide particles. Analysis of multiple TEM micrographs using Igor Pro Image Analysis Software yields an ensemble averaged edge length of 56 ± 8.4 nm.

2.4. Zeta potential

Surface chemistry is an important factor in determining the rheological properties of colloidal suspensions. Interactions present between the particles brought on by colloidal forces influence both the structure and mechanical properties of the suspension. Char-

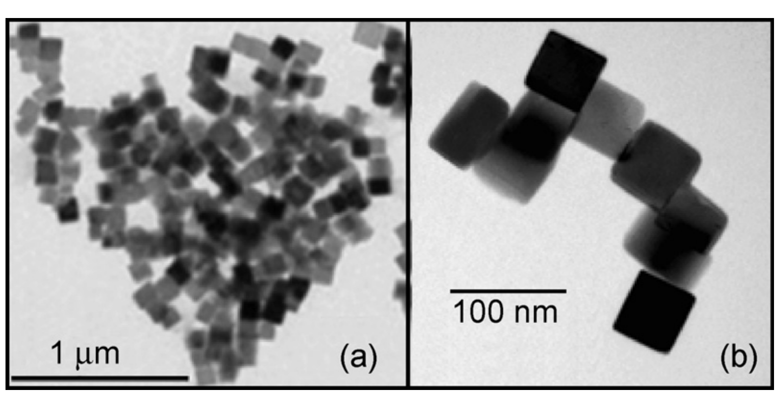

Fig. 2. TEM micrographs of Co_3O_4 nanocubes: (a) 1 μm length scale (b) 100 nm length scale.