Ultrasonics Sonochemistry 17 (2010) 947–952

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Sonochemical synthesis and rheological properties of shear thickening silica dispersions

Tarig A. Hassan, Vijaya K. Rangari *, Shaik Jeelani

Materials Science and Engineering, Tuskegee University, Tuskegee, AL 36088, USA

ARTICLE INFO

Article history:
Received 20 August 2009
Received in revised form 3 February 2010
Accepted 3 February 2010
Available online 8 February 2010

Keywords:
Shear thickening fluid
Silica nanoparticles
Sonochemical technique

ABSTRACT

A sonochemical method has been developed to synthesize shear thickening fluid. This shear thickening fluid (STF) is composed of hard silicon dioxide nanoparticles and polyethylene glycol (PEG) liquid polymer. The combination of flow-able and hard components at a particular composition, results a material with remarkable rheological properties that is suitable for liquid body armor applications. In the present study nine types of STF's have been synthesized with two different types of silica nanoparticles (15 nm and 200 nm) and polyethylene glycol at various weight fractions using a high intensity ultrasonic irradiation. The resultant STF samples were tested for their rheological and thermal properties. The advantages and disadvantages of this process have been discussed.

1. Introduction

Shear thickening is a non-Newtonian flow behavior and defined in the British Standard Rheological Nomenclature as the increase of viscosity with increase in shear rate. This is distinguished from rheopexy which is defined as the increase of viscosity with time while the shear rate in constant [1]. Dilatancy is another term used to describe shear thickening, however, it has been avoided since it usually implies an increase in the volume on deformation, which is not considered in this case [2]. The shear thickening trend can take place in concentrated colloidal suspensions that have been shown to exhibit reversible shear thickening resulting in large, sometimes discontinuous, increases in viscosity above a critical shear rate. In order to explain this behavior, two theories of shear thickening phenomenon were reported: the order–disorder transition [3–7] and the "hydrocluster" mechanism [8–13]. This transition from a flowing liquid to a solid-like material occurs due to the formation and percolation of shear induced transient aggregates, or "hydroclusters", that dramatically increase the viscosity of the fluid. Rheological, rheo-optics and flow-SANS experiments have been demonstrated in support of the hydrocluster mechanism of shear thickening phenomenon [14,15] in addition to computer simulations [16]. It was reported in the literature that shear thickening has been observed for a wide variety of suspensions such as clay–water [17], calcium carbonate–water [18], polystyrene spheres in silicon oil [19], iron particles in carbon tetrachloride [20], titanium dioxide-resin [21], silica-poly propylene glycol [22] and silica-ethylene glycol [23].

Many researchers have reported the synthesis of materials that show shear thickening behavior. Raghavan and Khan stated that suspensions of fumed silica in polypropylene glycol exhibit shear thickening under steady shear and "strain-thickening" under oscillatory shear. He also explained the combination of shear and strain thickening behavior through a clustering mechanism which attributes the thickening phenomena to the presence of temporary, flow-induced clusters. These clusters are being generated by the action of hydrodynamic forces on silica aggregates [22]. Each suspension was made in 60 ml batch by adding the liquid polymer to ~14 nm spherical silica particles and mixed in a blender for approximately 1 min and placed under vacuum for 12 h to get rid of air bubbles. The samples concentrations were varied from 3% to 10% weight basis.

Lately Lee et al. [23] reported the applications of STF in liquid body armor fabrication. They also studied the ballistic impact characteristics of Kevlar woven fabrics impregnated with a colloidal shear thickening fluid. The STF was prepared from 466 nm spherical colloidal silica particles and ethylene glycol. The synthesis procedure started with 3 h of centrifugation for the colloidal solution at 3900 rpm to separate the silica particles from the aqueous-based supernatant. The silica sediment was then crushed using a spatula and re-suspended in ethylene glycol using a vortex mixer. This process was repeated four times in order to minimize the amount of residual aqueous supernatant present within the samples. Ballistic impact results of Kevlar fabrics impregnated with this STF sample showed significant enhancements in ballistic penetration resistance of the STF impregnated fabrics compared to neat Kevlar due to the addition of STF without any loss in material

* Corresponding author. Tel.: +1 334 724 4875; fax: +1 334 724 4224.
E-mail address: rangariv@tuskegee.edu (V.K. Rangari).

1350-4177/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2010.02.001

flexibility. They have also prepared the STF from solvent exchange method. In this method colloidal silica was heated to evaporate water from colloidal solution and the evaporated amount of water was replaced with an equivalent amount of ethylene glycol. This process continued until all the water was replaced with 57% or 62% of ethylene glycol by volume. The rheological measurements of these samples also showed a shear thickening behavior [24,25].

Recently high-power ultrasound irradiation has been extensively used in the dispersion of nanoparticles in liquids [26,27] and it is also considered as one of the efficient techniques to disperse nanoparticles into materials [28,29]. Intense ultrasound waves traveling in liquids generate growing cavities. When the cavity attains a critical size it implodes, generating extreme conditions of intense heat and tremendous pressure that provide an unusual chemical environment for chemical reactions. The formation, growth, and implosive collapse of bubbles in a liquid irradiated with ultrasound are the physical phenomenon responsible for most of the sonochemistry. Ultrasound is produced in liquids by means of piezoelectric or magnetostrictive materials: materials that expand or contract when they are placed in electromagnetic fields. Exposing such materials to a field alternating at an ultrasonic frequency produces ultrasound [30–34].

In the present investigation, we have used a high intensity ultrasonic irradiation technique for synthesis of STF. PEG is used as suspending liquid phase because of its non-toxicity, thermal stability, easy to handle and easily available in bulk quantities which make it useful for bulk production. In this technique we have also used ethanol as a solvent because its sonochemical effects have been well studied [35,36] and also it is used as a solvent in the impregnation process of STF on Kevlar and nylon fabric for body armor applications.

2. Experimental work

2.1. Materials

Colloidal silica and dry powder silica nanoparticles have been used for this study. The dry powder silica nanoparticles are spherical in shape and ~15 nm in size. These nanoparticles were purchased from Nanostructured and Amorphous Materials, Inc., Los Alamos, NM. The 200 nm spherical colloidal silica solution (MP-1040 40% concentration of silica nanoparticles) was purchased from Nissan Chemicals, Japan. PEG-200 and ethyl alcohol were purchased from Sigma–Aldrich Chemicals, St. Louis, MO.

2.2. Synthesis of shear thickening fluid

Different STF samples were prepared using different weight fraction of silica nanoparticles in PEG/ethanol by sonochemical technique. Known weight percentages of PEG and silica nanoparticles (dry powder or colloidal silica solution) were mixed in an excess amount of ethanol (40:60 STF:ethanol ratio was used) (one and half times more than STF) for colloidal silica solution no ethanol was used. The reaction mixture was irradiated with high intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W/cm^2 at 50% amplitude) for 5 h and the reaction temperature was maintained using a chiller at 10 °C. The solvent (water or ethanol) was later removed from the reaction mixture via an evaporation process by heating at about 100 °C. The concentrations of as-prepared STF samples (sample (A)–sample(I)) are presented in Table 1.

For comparison purposes STF sample (I) was synthesized using mechanical mixing method.

In this method a known weight percentage of silica powder and PEG were mixed for 10 min at room temperature using a THINKY hybrid mixer ARE-250.

2.3. Characterization

2.3.1. Rheological measurements

Rheological studies were performed for all as-prepared STF samples to investigate the effect of shear rate increase on the viscosity. These tests were carried out using a TA Instrument Rheometer-AR2000 at room temperature, 0 °C and 40 °C. All the test were carried out using a peltier plate and a cone plate of size 40 mm and 2° angles in a steady state flow mode and shear ramp rate of 0–125 s^{-1}.

2.3.2. Thermal analysis

Thermogravimetric analyses (TGA) experiments were conducted to estimate the weight ratios of silica and polyethylene glycol in as-prepared STF samples. TGA samples were prepared by adding a few drops of as-prepared STF samples (10–20 mg) to a known weight of alumina crucible. TGA experiments were carried out using a Mettler Toledo TGA/SDTA 851 from room temperature to 800 °C at heating rate of 5 °C/min under nitrogen atmosphere.

2.3.3. Scanning electron microscopy (SEM)

SEM studies were carried out using a JEOL JSM 5800 scanning electron microscope. The SEM samples were prepared by uniformly spreading the as-prepared STF samples on a double-sided carbon tape and coated with gold/palladium to prevent charge buildup by the electron absorption.

2.3.4. Transmission electron microscopy (TEM)

TEM investigation of as-received silica nanopowder and colloidal silica nanoparticles were carried out using a JOEL-2010 microscope. TEM samples were prepared by dispersion of nanoparticles in ethanol and a drop of solution was placed on a copper grid (carbon coated copper grid-200 mesh) then dried in air and used for TEM analysis.

3. Results and discussion

The rheological properties of as-prepared STF samples were studied to understand shear thickening or shear thinning behavior rate at room temperature. Fig. 1A shows the viscosity of STF sample (A) as a function of the shear rate. STF sample (A) demonstrates shear thickening behavior in the range of 10–30/s shear rate and the sample viscosity increases from ~2 Pa s to ~17 Pa s. Fig. 1B (sample B), with a lower concentration of silica nanoparticles (52 wt%), shows a shear thickening effect in the range of ~2–40/s shear rate and with increase in the viscosity from 2.5 Pa s to 8 Pa s before a reversible trend is seen. The rheological properties of STF samples (sample (A) and sample(B)) indicate that the increase of the weight fraction of the suspending phase (PEG) in the sample gives better shear thickening fluid as the samples become more viscous. Fig. 2C shows the rheological graph of sample (C) where the silica weight fraction was decreased to 42 wt % and the weight fraction of PEG was increased to 58 wt%. This Fig. 2C shows a significant shear thickening behavior with an increase in the viscosity from ~10 Pa s to ~270 Pa s between 7 and 20/s shear rates. The increased value of viscosity indicates that the sample exhibits an incredibly high shear thickening effect. Sample (D) contains a relatively larger amount of PEG (60 wt%) and shows a shear thickening behavior. These results are presented in Fig. 2D and the viscosity changes from ~20 Pa s at 5/s shear rate to 410 Pa s at 12/s shear rate before a reversal trend is seen. Shear rate values for shear thickening transitions are lower than the results reported in similar studies [23]. These results clearly show that the sonochemical mixing before evaporation significantly improves the shear thickening effect. The rheological graph of STF sample (E)