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Research paper

Effect of acid and temperature on the discontinuous shear thickening phenomenon of silica nanoparticle suspensions

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A B S T R A C T

The discontinuous shear thickening (DST) phenomenon of silica nanoparticle suspensions was investigated in this article. First, the non-aggregated silica nanoparticles were synthesized and characterized. The results indicate that the silica nanoparticles are spherical particles with a narrow size distribution with a diameter of approximately 90 nm. Next, the influence of nitric acid concentration and temperature on the DST phenomenon of shear thickening fluids (STFs) was investigated. The results indicate that the concentrated fluids with nitric acid concentration below 8.50 mmol/L and at a temperature below 40 °C exhibit a readily noticeable DST phenomenon.

1. Introduction

Shear thickening is a rheological property of non-Newtonian fluids [1,2], which means that the viscosity of fluids increases with increasing shear rate when the shear rate is above a critical value [3]. If the viscosity of a concentrated suspension increases sharply and steeply, it is called as discontinuous shear thickening (DST) [4]. The shear thickening phenomenon of colloidal particle suspensions, associative polymers (sulfonated polystyrene in toluene), worm-like micelles (cetyltrimethyl ammonium bromide (CTAB) and sodium salicylate (NaSal) in water) and polymer solutions (polyethylene or its copolymer in xylene) have been studied extensively [5]. In particular, the rheological properties of colloidal particle suspension have been explored. According to the published studies, the dispersed phase of colloid suspensions can include silica particles [6], calcium carbonate particles [7], metal oxide particles [8], polystyrene particles [9] and others. Among these candidates, the silica particles, which have low density, low refractive index and high hardness, are the most promising materials for the preparation of high performance shear thickening fluids (STFs) [9,10].

The investigation of factors that impact the rheological properties of STFs is important to improve the performance of liquid body armor and damper [11–15]. Over the last several decades, the factors that impact the rheological properties of STFs have been discovered gradually. Hoffman and his co-workers proposed that the particles in colloid suspensions will undergo a process of transition from an ordered to a disordered state (ODT theory) during shear thickening [16]. They found that the concentration of particles can affect the rheological properties of STFs. Later, Wagner and his co-workers found that the ODT theory could not adequately explain the shear thickening phenomenon [3,17]. Therefore, the hydrodynamic lubrication theory was proposed [3,10]. The hydrodynamic lubrication theory indicates that when the shear rate is larger than a critical value, the hydroclusters will form in the suspension during shear thickening. Additionally, it shows that the strength of hydroclusters and intensity of shear thickening depend on the hydrodynamic lubrication force, which is a type of short range force, between the particles [17,18]. According to the hydrodynamic lubrication theory, the factors that impact the shear thickening phenomenon include particle size, polydispersity, interactions between particles and the properties of the continuous phase [10]. Recently, Romain Mari and his co-workers proposed that the shear thickening, especially the DST, occurs due to the formation of frictional contact networks (jamming transition theory) [4,19]. In this case, the geometry of particles, especially the surface

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roughness of particles and the steric hindrance for contacting, are the key parameters for the rheological properties of STFs.

The factors that impact the DST phenomenon have been investigated by many scientists [20–24], as well. These researchers found that the concentration and the shear rate can greatly influence the DST behavior of STFs. However, the influence of the impacting factors, the acid concentration and temperature, on the DST behavior has not been investigated until now. Therefore, in this work, studies have been conducted to investigate the influence of the concentration of nitric acid and temperature on the DST behavior of STFs.

In this paper, the silica nanoparticles were synthesized by the modified Stöber method on a large scale [25,26]. Afterward, STFs comprising 54 vol% of silica nanoparticles and 0.00 mmol L^{-1}, 4.50 mmol L^{-1}, 8.50 mmol L^{-1}, 12.50 mmol L^{-1} and 16.50 mmol L^{-1} nitric acid were prepared and characterized, respectively. Finally, the STF with 54 vol% of silica nanoparticles and 4.50 mmol L^{-1} of HNO_3 was measured under 20 °C, 40 °C, 60 °C, 80 °C and 100 °C, respectively. Moreover, the relationship of the concentration of nitric acid and temperature with the DST behavior of STFs was thoroughly analyzed by the hydrodynamic lubrication theory and jamming transition theory.

2. Materials and methods

2.1. Materials

Tetraethoxysilane [TEOS, 98%, Aladdin], absolute ethanol [99.9%, Aladdin], ammonium hydroxide [25%, Aladdin], polyethylene glycol with molecular weight 200 g mol^{-1} [PEG200, 98%, Aladdin], nitric acid [HNO_3, 68%, Aladdin], and 3-(trimethoxysilyl) propyl methacrylate [TPM, 97%, Aladdin] were directly used without any purification.

2.2. Synthesis and characterization of silica nanoparticles

The silica nanoparticles were prepared by the modified Stöber method [25,26], and the details were as follows. First, 1000 ml absolute ethanol, a defined volume of deionized water and ammonium hydroxide were mixed in a 3000 ml three-necked flask which was placed in a 30 °C thermostatic water-bath and stirred for 30 min. Next, 5.20 g tetraethoxysilane (TEOS) was added to the flask and the reaction was conducted for 3 h. Next, 216.00 g deionized water was added into the flask, and 10 min later, 104.00 g TEOS was added to the flask and the reaction was allowed to proceed for another 12 h. Finally, a defined amount of 3-(trimethoxysilyl) propyl methacrylate (TPM) was used to modify the surface of the silica nanoparticles for 12 h at 30 °C. The silica nanoparticles were obtained by centrifugation. The density of the silica nanoparticles is 1.42 g cm^{-3}, as measured by pycnometer. The size, shape and size distribution of the silica nanoparticles was characterized by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM), and zetasizer (Malvern, Nano ZS) as well.

2.3. Preparation and characterization of shear thickening fluids

First, STF samples comprising different concentrations of nitric acid (0.00 mmol L^{-1}, 4.50 mmol L^{-1}, 8.5 mmol L^{-1}, 12.50 mmol L^{-1}, 16.50 mmol L^{-1}) were prepared, and the samples were named STF 0.0, STF 4.5, STF 8.5, STF 12.5 and STF 16.5, respectively. In detail, a defined amount of silica nanoparticles and a specific volume of HNO_3 were added into PEG200 and mixed by grinding and ultrasonic dispersion alternatively several times. The concentration of silica nanoparticles was approximately 54 vol%. The rheological characterization of the STF samples was conducted at 25 °C by rheometer (Anton-Paar MCR302) with parallel plates having a diameter of 25 mm, and the distance between the two plates was 0.50 mm. Finally, the rheological properties of sample STF 4.5 were measured at 20 °C, 40 °C, 60 °C, 80 °C, and 100 °C, respectively. The pretreatment details of the suspension samples before measurement have been reported elsewhere [10].

3. Results and discussion

3.1. Characterization of silica nanoparticles

The rheological properties of STFs are largely dependent on the particle shape, size and size distribution [10,19,27]. STFs comprising particles with diameter smaller than 1 μm and narrow size distribution often exhibit a shear thickening response [10,28,29]. The SEM and TEM images of particles shown in Fig. 1(a) and (b) indicate that all silica nanoparticles are spherical with a narrow size distribution.

The average diameter of silica nanoparticles is approximately 90 nm. The DLS curve shown in Fig. 1(c) also demonstrates that the nanoparticles are not aggregated in a narrow size distribution.

3.2. Effect of the concentration of HNO_3 on DST phenomenon

The relationship of the rheological properties of STFs with the concentration of HNO_3 is shown in Fig. 2. Fig. 2(a) shows that each sample with a different concentration of HNO_3 shows shear thickening behavior after shear thinning. The samples with 0.00 mmol L^{-1}, 4.50 mmol L^{-1}, 8.50 mmol L^{-1} and 12.50 mmol L^{-1} nitric acid exhibit a readily noticeable DST phenomenon. However, the intensity of DST changes largely with the variation of the concentration of nitric acid. It can also be observed from Fig. 2(a) that the viscosity in the shear thinning regime decreases with increasing concentration of HNO_3 up to 8.50 mmol L^{-1}, and then it increases with the increasing concentration of HNO_3. Fig. 2(a) also shows that the maximum viscosity during shear thickening increases with the increase of added HNO_3 until the concentration of HNO_3 increases to 8.50 mmol L^{-1}, whereas when the concentration of HNO_3 is above 8.50 mmol L^{-1}, it decreases with the increasing concentration of HNO_3. Fig. 2(b) indicates that first the critical shear rate for the occurrence of shear thickening decreases with increasing concentration of HNO_3. Then, the critical shear rate increases with increasing HNO_3 concentration when the concentration of HNO_3 is greater than 8.50 mmol L^{-1}. The viscosity of each sample decreases with increasing shear rate after shear thickening, which could be due to the changing microstructure (hydroclusters or contact networks breakdown, slip plane formation, shear melting, etc.) under the outside shear [30,31].

According to the jamming transition theory, the DST behavior is mainly attributable to the formation of frictional contact networks when the shear force is larger than a critical value [4,19]. Generally, the silica nanoparticles surface is negatively charged [32,33]. Therefore, when the concentration of HNO_3 of suspension increases, the negative charges on the surface of the particles will be neutralized [32,33]. As a result, the repulsive force between particles will decrease. Consequently, a much smaller shear force is required for particles to form frictional contact networks [19]. Essentially, the critical shear rate for the occurrence of shear thickening decreases with increasing HNO_3 concentration. Because a suspension prepared by particles with a smooth surface cannot exhibit a shear thickening phenomenon, the surface of the silica particles used in this article should be rough [19]. The surface of silica particles should have many asperities. Additionally, the distance between particles and the thickness of the medium layer