Shear Thickening Fluids Comparative Analysis Composed of Silica Nanoparticles in Polyethylene Glycol and Starch in Water

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Abstract

Shear thickening fluid (STF) occurs in dispersions of highly condensed colloid particles and is categorized as a non-Newtonian fluid whose viscosity increases under shear loading which makes them beneficial in protective and impact resistance applications. The aim of this study is to synthesis two different STFs and characterize their microstructural properties to provide a data base for comparing the final macrobehavior of the two fluids under mechanical testing. Therefore, fumed silica and polyethylene glycol STF and starch with water STF-based dispersions were prepared. The particle size, zeta potential, SEM micrographs, and rheological analysis were performed for each type of STF. The effect of filler concentration was observed by using 10–30 weight% filling material. The rheological properties of STFs show higher viscosity measurements at same shear rates for starch/water STF than silica/PEG with maximum viscosity reaching 523.6 Pa s and 178.9 Pa s, respectively. Larger starch particle size over silica recorded as 303.7 nm and 16.49 nm, respectively, and zeta potential analysis recorded particle electrostatic charges as 22.6 mV and 12.8 mV, respectively, leading to more dispersion stability and obvious thickening effect at higher particle concentration leading to greater jump in viscosity at sudden shear rate. The results indicate the capability of trying more protective applications with more flexibility and less thickness when STF is implemented and a good database for the fluids to choose from according to their behavior.

1. Introduction

Shear thickening fluids (STFs) represent a subset of certain fluids that exhibit non-Newtonian fluid behavior with abrupt changes in viscosity at a particular shear intensity. Shear thickening takes place in tightly dense colloids and suspensions. Such suspensions behave like thin liquids if they are agitated at a low shear rate, but they are very dense if they are agitated at a high shear pace. Increased viscosity, though, presents other disadvantages for STF industries. Yet, this function renders them suitable for damping and shock absorption applications. With this versatility in mind, STFs are used to boost impact-resistant fabrics such as athletic equipment or liquid armor [1].

Rheology is a discipline established by the American Rheological Society in 1929 as the study of the deformation and flow of matter. Rheology is a Greek word derived from rheos (work) and logos (science) [2]. The various behaviors of all materials rely upon their underlying micro- and chemical structures. For commercial systems, thus, behavior regulation plays a significant role. Conservation laws and constitutive relations are the principal theoretical concepts that control the rheology kinematics. Kinematics discusses geometrical aspects of deformation and movement, while conservation law includes forces, sharing of energy, stresses, and the different relationships between body groups. Rheology is the product of the application of these scientific principles and tests to solve problems relevant to engineering in polymer process, food production, printing, lubrication, and many other technologies [2, 3].

By definition, fluid materials are systems that move when stress is applied. It is the core of rheological research and a complicated question how they react to a stress. Several kinds of fluids are available: pure, mixtures, dispersions, and
solutions fitting into either simple or structured fluid. If exposed to stress, every system has its own unique actions. Typically, it is referred to as a simple fluid when the content has a uniform phase, for example, a solution or a pure substance. Materials with multiphase, such as dispersions, emulsions of immiscible liquids are structured fluids since the rheological behavior is governed by the constituents’ interactions. Structured fluids behavior is affected by many factors. The viscosity of the fluid phase of dispersions typically plays a significant role in the material’s flux properties. Dispersions provide large variations in output in the continued phase in which the particles are suspended based on particle size, shape, concentration, and any attraction. If the electrostatic forces between the particles are repulsive, they appear not to settle easily rather than create a network. The flowing behavior of fluids due to these factors is normally identified either as a Newtonian or a non-Newtonian fluid [4, 5].

The shear stress generated by the shear flux in certain suspensions does not match the shear intensity linearly. In the case where the shear stress is not directly proportional to the shear rate, the magnitude of the viscosity is no longer a fixed value and is a function of the shear rate, called the apparent viscosity and the fluid is non-Newtonian fluid. Non-Newtonian fluid behavior can depend on time. Non-Newtonian fluid time-dependence is defined as (thixotrophy). Time-independent fluxes may on the other hand be categorized as thinning fluids (pseudoplasticity) and thickening fluids (dilatant fluids). [5, 6].

Shear thickening fluids (STFs) are a non-Newtonian fluid defined as elevation in viscosity by increasing the shear rate by the UK Standard Rheological Nomenclature [7]. STF is a colloidal fluid suspension with a rise in viscosity where the shear rate is greater than a critical point. Colloid generally suggests the dispersed phase of a two-component structure that is too small a portion of its dispersed phase for the optical microscope to be readily detected and that has other forces affecting its movement. Shear thickening fluids typically have the effect of shear thinning at low shear or shear stresses. For elevated shear stress, the viscosity of STFs increases and shifts from the shear thickening to the shear thickening region in either a gradual or direct way. The sudden rise of viscosity of STFs is known as discontinuous thickening of STFs. The viscosity changes are reversible, which means that, if the shear stress is reduced from the material, the viscosity will automatically continue to decrease [8, 9].

For scientists who deal primarily with its chemical and structural base, the causes for shear-thickening phenomena are of significant research areas. In 1885, Osborne Reynolds first discussed the dilatant nature of containing suspensions of solids. He said that when at rest, the voids in condensed suspensions are of small size and the solution is only sufficient to fill the voids. The liquid lubricates the passage of one molecule over the other when the lower shear levels are applied. Shear thickening is identified in early studies as a rise in viscosity with increasing shear before Hoffman reports that dense concentrated suspensions of colloidal particles actually display a discontinuous jump in viscosity at a critical rate of shear [10].

“order-disorder transition” (ODT) is the changeover from ordered to broken particles [11]. The hydrodynamic clustering theory suggests the other theory for shear densification, which results in shear densification resulting from creation of particle clusters. In case of a sudden critical shear rate because of energy of a sudden impact that exceeds the repulsive forces between the particles, particles in the STF bind together to form hydroclusters [12].

In recent research, a new hypothesis, namely, the contact rheology hypothesis, is proposed as well as the hydroclustering theory. For the thickening stage where the colloidal particles contact each other at elevated shear frequencies, contact forces grow stronger. Contact networks have the ability to resist the applied shear forces, and by means of this, suspension introduces viscosity growth and development of yield stress. At this point, it should be noted that the key contribution to the rise in viscosity stems from interparticle contacts rather than hydrodynamic interactions and the process functions in a manner where particle attraction only induces contact network formation; these expanded branch-like structures are immune to shear. [13].

The STF consists of a liquid carrier and rigid colloidal particles. The normal observation that the corn starch (a hydrophilic particle) shear develops in water is a common example. Nevertheless, work has concentrated on other viable particles for the industry such as colloidal silica, and polyethylene glycol is the most common carrier material utilized. For the thickening purpose, the particles remain in the liquid at a high concentration (max. 55–65% volume). The true character of the shear thickening depends on the physical parameters of the suspended phase: the fraction of the particle, particle size and distribution, particle structure, and suspended phase. Most carrier fluids such as water, ethylene glycol (EG), and polyethylene glycol (PEG) are commonly utilized. Nevertheless, because of high stability, low boiling point, and flammable properties, PEG is the most commonly used fluid carrier in STF. [14, 15].

Scientists have been focusing on colloidal dispersions and they have been studied for decades for unusual flux activities in diverse industries, ceramics, foods, sculptures, pulp and paper mineral slurs, insulation, hardened plastics, and packaging elastomers, for example. In fact, the need to develop new applications for the use of colloidal suspensions stems from the growth in nanotechnological developments and nanocomposites.

The general objective of this study is to investigate the effect of colloidal particle concentration of two prepared STFs on rheology to understand the thickening phenomena based on the differences on the microscale. The research will develop different STF multisystems: one composed of silica and polyethylene glycol and the other one is starch and water. The research will provide a primary comparison between the properties of the prepared STFs while comparing their rheology, particle size, zeta potential, and SEM images of the particles. The attained results will acquire the designer of the STF applications to choose among the
suitable fluid system based on the final properties of the fluid.

2. Materials and Experimental Approach

2.1. Materials. Nano-sized hydrophilic (Aerosil 200) fumed silica particles purchased from EVONIK Industries Corporation are the solid particles used in preparing STF number one. The used silica has specific surface area of 200 m²/g and silica content > 99.8% [16]. Polyethylene glycol (BioUltra 400) is purchased from SIGMA-ALDRICH Company. It is the carrier liquid used in preparing the first STF with silica. Due to its low volatility, thermal stability, nontoxicity, and H-bond efficiency, PEG was chosen as the solvent. The used polyethylene glycol (PEG) has an average molecular weight of 380–420 g/mole and viscosity of 120 mPa·s at 20°C [17]. Corn starch of commercial food grade is used in preparing the second STF composed of distilled water and starch. Generally, starch is a large macromolecule, with the formula of C_{27}H_{48}O_{20} and a molecular weight of 692.65802 grams/mole [18].

2.2. Experimental Work. The tests involve preparation of multisystem STF composed of silica with polyethylene glycol and starch with water, each with 10, 20, and 30% filler concentration. The prepared STF samples will be prepared with similar conditions in order to prepare them for fair comparison. Characterization of the prepared STFs is conducted using SEM, particle size detection, and zeta potential tests using Zetasizer Nano ZS device from Malvern Panalytical Company to investigate the average particle size of the used silica nanoparticles and starch and the stability of the dispersed particles in their carrier mediums, respectively. Because of the repulsive forces between particles, colloids with high zeta potential are electrically stabilized, and colloids with low zeta potentials appear to coagulate. Rheological characterization is performed using concentric cylinder viscometer Model 35A purchased from Fann Instrument Company in order to understand the overall performance of the samples under shear rate. The mixing of fumed silica in PEG and starch in water was performed with Lab Homogenizer (KRH-II) from Konmixchina Company adjusted at high rpm for 3 hours to disperse the particles homogeneously into their carrier fluids. Prepared samples with various weight fractions of fillers were fixed for both systems at concentrations 10, 20, and 30% weight to weight for the rheological tests. The final results of the rheological test illustrate in logarithmic plots the viscosity range against the change in shear rate applied.

3. Results and Discussion

Results cover the output of the microstructural and rheological characterization of prepared STF as comprehensive as possible.

3.1. Particle Size Determination. The average particle size of the used fumed silica nanoparticles and starch is determined using Zetasizer Nano ZS operating using the dynamic light scattering (DLS) technique. The concentration of particles used in the DLS experiments is sufficiently low to exclude any possible effect of the concentration on the measurement. Size distribution of the fumed silica nanoparticles and starch powder is given in Figures 1 and 2, respectively. The ultrasonically scattered particles of each form using (Hielscher UP400S Ultrasound Technology, 24 kHz) at a maximum of 70 percent were dispersed in the water medium for 3 hours before analytical research to increase particle dispersion and homogeneity.

The output data for the nanosize fumed silica sample are obtained in terms of intensity or percentage of particles within a specific size. As it is seen in Figure 1, the size of 84.5% of the fumed silica particles has average size of 16.49 nm. The average size of 89% starch particles is determined as 303.7 nm as shown in Figure 2. Both filling materials used (fumed silica and starch) show different particle sizes which is a major factor in the overall performance of the STF. Starch particles are bigger than silica which causes easier collision between particles as larger particles hinder the movement of particles and form larger agglomerations quickly at high shear rates which rise the viscosity easier than smaller particles which takes more time to gather and form large clusters.

3.2. Zeta Potential Analysis. Zeta potential is a significant value to determine the stability of colloidal dispersions. Therefore, silica and starch were both subjected to zeta potential analysis using Zetasizer Nano ZS. The results show that starch has higher zeta potential value (22.6 mV) than silica (−12.8 mV) as shown in Figures 3 and 4, respectively. This indicates that starch colloid systems are electrostatically more stabilized, while silica colloids with low zeta potentials showing less stable colloid system. This is due to the repulsive electrostatic forces between particles which allow colloids to remain stable for a long time.

3.3. Scanning Electron Microscope (SEM). Silica and starch microstructure and surface morphology as powder were investigated with scanning electron microscope (SEM). The particle size and shape in the powder form may differ from the size and shape in the liquid suspension, since they tend to appear larger in the powder form due to static agglomerations, while in liquid suspensions, the particles are well sonicated to break up any aggregates and hence show accurate size measurements. Figure 5 shows the SEM micrographs of the silica and starch as powder particles at 500 and 1000x magnifications, respectively. Although the particle size analyzer states that the starch particles are bigger than silica, it might seem falsely from Figure 5 that silica particles are bigger, which is false. This is only due to some agglomerations of the silica particles before the test. The images show that both silica and starch have no significant difference in the shape factor as both almost show a spherical shape. Therefore, the final behavior of both systems would not rely on the shape effect in this case since both particles are almost similar in shape.
3.4. Rheological Characterization. The rheological properties of STFs synthesized with varying concentrations of silica in PEG 400 g/mole and commercial starch in water are investigated. Silica and starch concentrations are ranged between 10–30% weight to weight of the carrier fluid. Measurements are carried out using a rotational rheometer operated by Model 35A–R1B2. The fan reading was recorded with every change in the rpm scale and then the viscosity is plotted against shear rate.

Rheological measurement tests help to determine the influence of silica and starch concentrations in their carrier fluids. Viscosities of STFs indicate a rising pattern with raising concentrations of fillers. Viscosity changes of all STFs prepared having filler concentration of 10 up to 30 weight percent are plotted according to the filler concentration used in the prepared STFs. The shear rate applied to pure PEG and liquid water does not change in its viscosity, since they are Newtonian fluids in pure form. On the other hand, the viscosity curves of STFs demonstrate the characteristic shear thickened behavior by incorporating nanoparticles of fumed silica and starch as fillers. Critical shear rate (CRS) characterizes the start of this shear thickening region. This value is determined by analyzing the viscosity curves and identifying the shear rate at which the viscosity begins to increase sharply with increasing shear rate.
is essential in impact resistance applications to determine the operating range.

Figures 6 and 7 show in logarithmic plots the viscosity change against the variation in shear rate and show that shear thickening happens for all STFs as particle weight fractions increase from 10 to 30 wt% silica particles in PEG 400 g/mole or starch in water, respectively. STFs show a shear thinning behavior at first, at low rates of shear, which is followed by a shear thickening region after reaching the critical shear rate value. This shear rate value is known as the critical shear rate. Remarkable thickening effects begin to increase with increasing particle concentration which makes the shear thickening phenomenon easier to observe. This can be obviously seen from the curves indicating sharp viscosity increase. Critical shear rates, viscosities at critical shear rates, and maximum viscosities of all STFs prepared with silica in PEG 400 are listed in Table 1, while those for starch in water in Table 2. The highest value of viscosity reached was obtained for silica 30% as 178.9 Pa s and the critical shear rate value of 10.5 s$^{-1}$. The rise in viscosity of this STF through the shear thickening region is from 17.87 to 178.9 Pa s.

Table 2 shows that all the STFs prepared with starch and water have shear thickening behavior. The highest value of viscosity reached is for starch 30% reaching 523.6 Pa s while the critical shear rate value is 10.5 s$^{-1}$. The jump in viscosity of this STF is from 23.5 to 523.6 Pa s within the shear thickening region. While the critical viscosity is not affected by the particle weight fraction as much, the maximum viscosity rises with the increase of the starch particle weight fraction, most notably at fractions of 30%.

With an increased concentration of filler particles, the distance between particles decreased and particle friction
increased, creating growing hydroclusters leading to elevated shear thickening effect. Thus, at such high shear rates, small and compact aggregates are formed directly and their break-up or restructuring does not occur at all. The possible explanation is that at very high shear rates, the distribution of flow rate is more uniform (there are smaller differences in shear rates at different parts of the mixed volume) than at low shear rates, and aggregates are not allowed to grow large enough to be subject to break up [19]. The sudden rise in viscosity is accompanied by a second shear thinning that shows the STF’s reversible behavior. The system comes to a viscosity plateau until the wall slip happens and lower viscosity values are noticed. This wall slip is clarified due to some break-ups that result in the clusters due to elevated shear and induced creep where the separation of the broken aggregates return the viscosity levels to lower values and thinning behavior dominates the fluid performance again. As mentioned in the introduction, in case of low shear rates, particles organize itself in an organized lattice, which translates the thinning behavior of STF at first. The sudden increase of shear rate overcomes the electrostatic charges stabilizing the dispersed particles and leads to stacking of the particles in very confined areas which form clusters that raise the fluid viscosity to higher values in a sharp increase.

### 4. Conclusion

This research strives to exploit the shear thickening fluid (STF) behavior in enhancing performance of energy absorption applications. The superior performance of STF goes back to its definition which is a non-Newtonian fluid made up of colloid dispersed particles in a carrier fluid that has an ultimate increase in viscosity in the case of high unexpected shear levels acting briefly as a solid matrix, when full load is achieved and returning to liquid form upon elimination of the load. Fumed silica nanoparticles were dispersed in polyethylene glycol of 400 g/mol and commercial starch in water in order to recognize improvements in STF behavior with increasing filler content concentrations of 10% to 30% by weight in this study.

The characterization experimental results showed that starch particles used in this study have particle size equal to 303.7 nm larger than silica with 16.49 nm which causes easier collision between particles and hinder the movement of particles by forming larger agglomerations quickly at high shear rates. Zeta potential analysis performed for silica and starch particles revealed that starch particles have higher zeta potential value (22.6 mV) than silica (−12.8 mV) on its surface leading to more stability of the dispersed particles in the carrier medium. Therefore, more homogeneous distribution of the particles in the fluid and better performance throughout the fluid have been achieved. SEM images showed more clarifying view of the microstructure of the particles showing similar spherical shape without a huge significance that might affect the final behavior of the fluid system. In order to note the final rise in its viscosity when subjected to high shear rate and the effect of the filling content concentration of 10–30 percent on this change, the rheological properties of STFs have already been investigated by stress regulated rotational rheometer. All STFs have

| STF prepared          | Critical shear rate (1/sec) | Viscosity at critical shear rate (Pa.s) | Maximum viscosity (Pa.s) |
|-----------------------|----------------------------|----------------------------------------|--------------------------|
| PEG 400, silica 10%   | 10.2                       | 10.12                                  | 81.31                    |
| PEG 400, silica 20%   | 10.5                       | 12.34                                  | 179.8                    |
| PEG 400, silica 30%   | 10.5                       | 12.34                                  | 179.8                    |

| STF prepared          | Critical shear rate (1/sec) | Viscosity at critical shear rate (Pa.s) | Maximum viscosity (Pa.s) |
|-----------------------|----------------------------|----------------------------------------|--------------------------|
| Distilled water, starch 10% | 10.2                   | 13.87                                  | 249.5                    |
| Distilled water, starch 20% | 10.4                   | 18.9                                   | 378.5                    |
| Distilled water, starch 30% | 10.5                   | 23.5                                   | 523.6                    |
a shear thickening function that is increasing viscosity with increased shear stress and shear rate. The scale of shear thickening increases as the weight of filling particles increases. It was found that in STFs with higher starch concentrations, the viscosity rise in the shear thickening zone was greater. Rheological tests showed the larger maximum viscosity achieved in case of starch/water system which was recorded as almost 2.5 times bigger than that of silica/PEG when subjected to similar shear rate values. The maximum available viscosity for starch and water STF was obtained for starch 30% as 523.6 Pa s, while for 30% silica and PEG was 178.9 Pa s. The results showed the superior performance for STFs, especially starch/water STF, in showing a viscosity rise when sudden shear rate is applied opening the door for wide range of applications concerned with energy absorption, damping, and flexible personal protection.

**Data Availability**

The data used to support the findings of this study are included within the article.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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