Relaxation time assessment in nanoparticle containing bimodal and mono-disperse shear thickening fluids

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Abstract. When an applied shear to a fluid results in steep rise in its viscosity, it is referred to as Shear Thickening Fluid (STF). In this study, we investigate rheological response of bimodal against mono-dispersed nano sized silica particles in an STF system. Two sizes of nano-silica particles (50 nm fumed silica and 12 nm colloidal silica) were dispersed in polyethylene glycol in various compositions and were compared with mono-dispersed STF. Results showed lower critical shear rate for shear thickening in bimodal nanoparticle containing STF than mono-dispersed STF. Higher viscosities were also observed in different compositions of bimodal system. Examination of both STF systems under oscillatory stress condition revealed faster response by the bimodal system. Results also indicated that the storage and loss modulus for the bimodal STF system had low critical angular frequency compared to mono-dispersed STF. Study of relaxation time spectrum diagram for the two STFs showed that relaxation time for mono-dispersed STF was faster than that for bimodal STF system.

1. Introduction

Shear-Thickening Fluids (STFs) are concentrated colloidal suspensions composed of non-aggregating solid particles suspended in fluids. These suspensions have the property of increasing fluid viscosity with increasing shear rate [1].

STFs have been the focus of attention for the scientists involved in processing technology, and not many consider that they offer positive advantages in industrial situations.

Initially, interest in shear thickening derived mainly from its association with damage to processing equipment, e.g. particle aggregation, which is known to compromise a range of properties. However, due to its highly nonlinear behaviour, the potential for damping application and machine mounts was explored [2,3]. In the past two decades, extensive research effort has been directed towards understanding the rheological behaviour of STF, including study of different particles' size, geometry, concentration, and continuous phase viscosity. Keller and Keller [4] investigated a bimodal mixture of coal particles at 0.77 and 7.9 μm and observed an increase in volumetric particle concentration compared to mono-disperse suspension, but no shear thickening tendencies were reported for the bimodal suspension. Wagstaff and Chaffey [5] showed that the suspensions of larger particles thickened at lower shear rates and polydispersity increased the critical shear rate and reversible thickening only in systems that had predominately repulsive interactions. Experimental evidence by small angle neutron scattering and light scattering by Bender and Wagner [6] showed that shear thickening occurred without the shear induced order-disorder transition. They also found out that measurements on bimodal mixtures verified the scaling laws derived from the force balance and provided a strategy for controlling the shear thickening transition. Raghavan and Khan [7] investigated shear thicken-

Table 1. Physical properties of nano-particles used in this study.

Nano-particle	Particle size (nm)	Bulk density (g/l)	BET (m^2/g)	Chemical name
Silica OX50	40	70	50 ± 15	Hydrophilic fumed silica SiO$_2$
Silica 406	12	50	200 ± 25	Colloidal silica SiO$_2$

ing as well as strain thickening behaviour of non-flocculated fumed silica suspensions in polypropylene glycol under oscillatory shear. They reported two distinct regimes of strain thickening with first occurring at high critical strains and low frequencies and the second occurring at high critical frequencies and a constant lower strain. Maranzano and Wagner [8] predicted scattering SANS spectra for polydispersed hard sphere, which conformed to the hard sphere interactions in experimental results. Maranzano and Wagner [9] affirmed that the hydrocluster formation resulted in the shear thickening transition. Brown et al. [10] demonstrated that shear thickening could be masked by a yield stress and could be recovered when the yield stress decreased below a threshold. During the period 2002-2010, most research on shear thickening fluids has been on the usage of STFs in some applications, in particular damping and impact application. Waitukaitis and Heinrich [11] in their study published in the journal of Nature demonstrated that these stresses originated from an impact-generated solidification front that transformed an initially compressible particle matrix into a rapidly growing jammed region, ultimately leading to extraordinary amounts of momentum absorption. They assert that "prior interpretations of the impact resistance as dominated by shear thickening need to be revisited". Crawford et al. [12] exhibited irreversible thickening behaviour by investigating fumed silica slurries; it appears to be a complex interplay between cation hydration, silica surface hydration, and hydrodynamic shear forces. Fahool and sabet [13] observed the shear induced transient hydrocluster formation in shear thickening fluids using UV-visible spectrum. Their study showed that the amount of aggregations in bimodal STF was higher than that in the mono-disperse mode. They attributed this to the interaction of more particles, i.e. the presence of smaller particles among the larger particles. Lee et al. [14] showed rheology and microstructure of concentrated hard sphere suspensions in the liquid and crystal coexistence region by the lattice Boltzmann method coupled with the smoothed profile method. Their result clearly showed how strong the ordered structure was in relation to the shear stress distortion.

Despite extensive research report about STF behaviour, little attention has been given to bimodality effect on STF behaviour in a particular relaxation time after shear stress removal. No report in open literature was found on the assessment of relaxation time and reversibility rate for the STF systems. This study examine bimodal combination of nano sized silica particles in a polyethylene glycol as a shear thickening fluid. The particular focus of the work is on relaxation time associated with the fluid containing bimodal silica particles and their comparison with monodispersed system.

2. Materials and method

In order to study the response of shear thickening fluid containing bimodal particles, two types of nano-particle sized hydrophilic silica were used for the preparation of the Shear Thickening Fluid (STF). Fumed silica OX50 from Evonic-Degussa (Germany) and colloidal silica 406 from West system (UK) were used as suspending agents. Table 1 provides details for the nano-particles used. Polyethylene glycol (PEG) with molecular weight of 400 g/mol from Sanaye Shimiyaee Kimiyagaran Emrooz (Iran) was used as the continuous phase for preparing the STF. Neat polyethylene glycol has a viscosity of 120 mPa.s and density of 1.126 g/ml at 20°C. The reason for selecting PEG is that it is a non-toxic, easy to handle, and thermally stable material and its flow behavior is of Newtonian nature.

2.1. STF preparation
As all the received nano-silica particles are in agglomerated state, careful steps must be taken to ensure uniform dispersion of the particles in the continuous phase; this task becomes even more complicated when two particles of different sizes are to be added together. Predetermined amounts of nano-size silica OX50 and colloidal silica 406 were consecutively mixed with 50 ml of PEG using a mechanical mixer at 1000-100 rpm (depending on nanoparticle concentration) for a period of 2 hrs; the compound was then irradiated with high-intensity ultrasonic horn (Ti-horn, 20 kHz, 90 W, 30 mm) for 10 min. The samples were then placed in a vacuum oven for 24 hrs to eliminate the air bubbles generated during mixing operation. Mono-disperse STF compounds containing 35, 40, and 45 wt%. OX50 silica were also prepared in the same manner for comparison. Weight ratios for bimodal system 35 wt% are 20 wt% fumed silica OX50 (20FS) and 15 wt% Colloidal silica 406 (15CS).
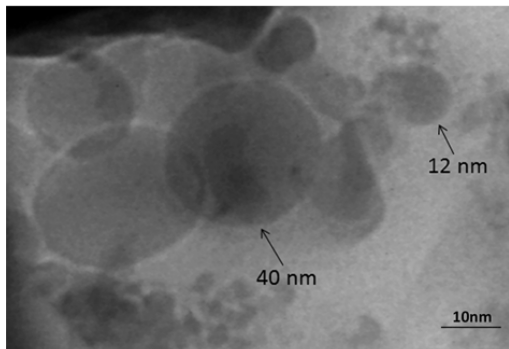
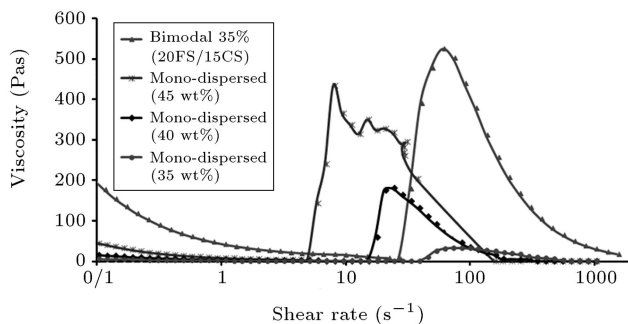**Figure 1.** TEM micrograph of nano-particle in 40 and 12 nm.

Figure 2. Rheological behavior of STFs with total particle compositions of 35, 40, and 45 wt% for mono-dispersed and 35 wt% for bimodal systems.

2.2. Characterization

The prepared STF samples were investigated for rheological properties using rheometer MCR-501. Tests were conducted at room temperature in a steady state flow mode and shear rate ramp of 0.01-1000 s^{-1} using a cone plate of size 50 mm and angle of 1°. Minimum of three tests has been run on each specimen and the average value has been reported, here. The silica particles distribution was investigated using transition electron microscopy. Figure 1 shows TEM micrograph of the nano-particle used in this study.

3. Results and discussion

Figure 2 shows rheological behavior of polyethylene glycol fluid containing nano-size bimodal and mono-dispersed silica particle comprising 406 colloidal silica and OX50 fumed silica with total particle compositions of 35, 40, and 45 wt% for mono-dispersed and 35 wt% for bimodal system. This shear thickening characteristic occurs when dispersed solid particles in the continuous medium are in contact and hydrocluster phenomenon forms this result in transient fluctuations of particles. This transient fluctuation of particles results in frictions between particles and leads to abrupt increase in fluid viscosity.

The figure presents three distinct regions; a relative shear thinning happens at low shear rate for all systems containing silica compositions and at high shear rates, the fluid experiences a sudden transition with an increase in viscosity, which signifies shear thickening behavior and finally a shear-thinning-like behavior. The critical shear rate at which shear thickening occurs in both compositions is 1 to 100 s^{-1}. A similar line of research on shear thickening fluid for other materials has also been reported. Franks et al. [15] demonstrated that critical shear rate of silica and alumina suspensions containing 60 wt% were 72 and 600 s^{-1}, respectively. Also, Brown and Jaeger [16] reported that the critical shear rate of cornstarch in 60 wt% was almost 0.1 s^{-1}. Therefore, comparing the effective shear rate domains and critical shear rates in different mixtures included in the current research reveals considerable variability. This difference in behavior between the shear thickening fluids may be attributed to the differences in surface energy and surface groups on the particles.

Generally, STF materials have good reversibility characteristic after shear stress removal, but controlling the rate of reversibility allows wider application of the STF. This reversibility is directly related to the speed of steady state transition after shear stress removal, i.e. returning from hydrocluster condition; this is vital when energy absorption applications are envisaged for these types of materials. This reversibility can be investigated by considering relaxation time spectrum diagram, where relaxation time (τ) versus $H(\tau)\tau$ is considered. Here, $H(\tau)$ is the relaxation time spectrum that is associated with the dynamic parameters such as the storage and loss modulus. The relaxation time spectrum is a quantity characteristic describing the viscoelastic properties of polymer melts and polymer solutions [17]. For determination of this function, i.e. ($H(\tau)$), various empirical formulations have been proposed [18,19], e.g. Alfrey approximation [20]. He presented an approximation for estimation of $H(\tau)$; see Eq. (1):

$$G(t) = \int_0^\infty \frac{H(\tau)}{\tau} e^{-t/\tau} d\tau = \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d\ln \tau, \tag{1}$$

where $G(t)$ is stress relaxation modulus at the time t (modulus obtained from a stress-relaxation experiment, where the sample is held at constant strain and the decaying stress is recorded). This parameter is related to the storage and loss moduli that are calculated by Eqs. (2) and (3):

$$G'(\omega) = \int_0^\infty H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \frac{d\tau}{\tau}, \tag{2}$$

$$G''(\omega) = \int_0^\infty H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} \frac{d\tau}{\tau}. \tag{3}$$
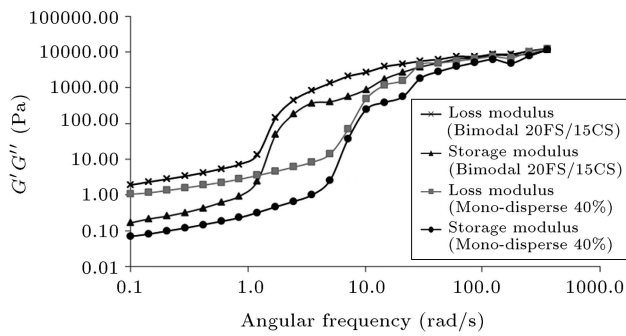
And so $G(t)$ is computed in the following way:

Figure 3. Storage (G') and loss (G'') moduli versus angular frequencies for the two STF systems.

$$G(t) \simeq G'(\omega) - \sum a_k G''(2^k \omega) - \sum b_k \left\{ G'(2^{k+1}\omega) \right.$$

$$\left. - G'(2^k \omega) \right\}, \tag{4}$$

where ω is angular frequency, a_k and b_k are numerical constants that are to be chosen in such a way that the formulae become as accurate as possible [21].

Figure 3 depicts storage (G') and loss (G'') moduli behavior for the two STF systems in different angular frequencies.

Figure 3 shows that exactly at the point where complex viscosity experiences sudden increase, the storage and loss modulus also increases. Further study of the figure indicates that the storage and loss modulus for the bimodal STF system has a lower critical angular frequency than that of mono-dispersed system.

Estimation of the relaxation time spectrum $H(\tau)$ from Eq. (1) is only possible by the Laplace transform or the Fourier transforms formulation. In this work, the rheometer's software directly calculates $H(\tau)$ while performing frequency sweep test. The peak point in the diagram indicates relaxation time for the concerned material. The sharpness in the curve's peak indicates close relaxation times for the particles, i.e. the whole STF material relaxes at the same time. On the other hand, not very sharp peak shows non-uniform relaxation times by the material. Relaxation times for both STF materials are presented in Figures 4 and 5. Comparison of relaxation times for both STF materials reveals that the relaxation time of mono-dispersed STF ($\tau = 0.089$ s) is faster than that of bimodal STF ($\tau = 0.33$ s). This may be directly attributed to closer packing of particles in bimodal system, i.e. small diameter particles being located between larger particles. This closer packing in bimodal STF results in higher friction between particles, which in turn leads to longer time for relaxation and return to the original state condition.

To give better physical meaning to our argument, an epoxy resin was also used to compare relaxation time spectrum between them; see Figure 6.
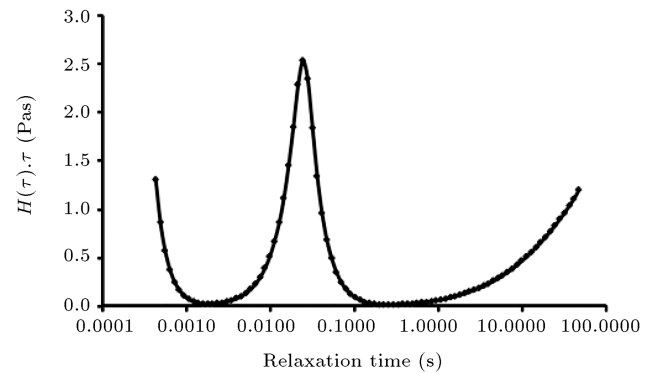

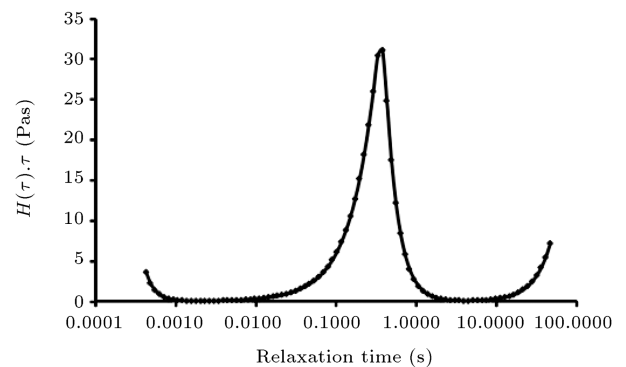**Figure 4.** Relaxation time for mono-disperse system at 40 wt%.

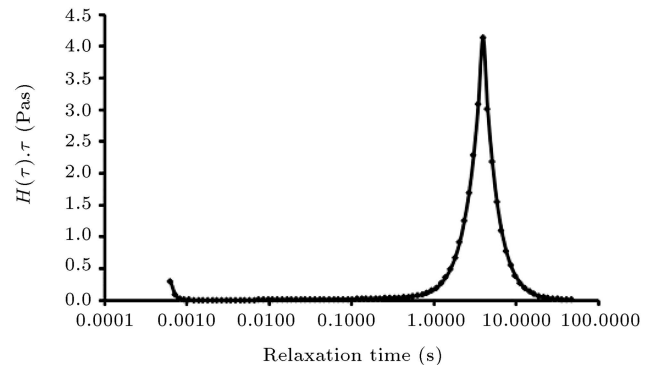**Figure 5.** Relaxation time for bimodal system at 35 wt%.

Figure 6. Relaxation time curve for epoxy resin.

In Table 2, the data related to relaxation times of the shear thickening fluid in different modes are given for comparison. The table shows reversibility time of epoxy resin at $\tau = 3.93$ s compared to that of $\tau = 0.089$ s for the mono-dispersed STF and that of $\tau = 0.33$ s for the bimodal particle containing STF. Comparison of the three τ values indicates that relaxation time speed of shear thickening fluids is more than that of epoxy resin, while the initial viscosities of STF and epoxy resin are approximately equal. Therefore, relaxation time of STFs is much less than that of conventional fluids. These results are consistent with the observed shear thickening behaviour.

Table 2 shows that based on the trend of change

Table 2. Relaxation time for different fluids.

Epoxy 828 (pure)	Bimodal STF 35 wt%	Mono-dispersed STF 45 wt%	Mono-dispersed STF 40 wt%	Mono-dispersed STF 35 wt%	Sample type
3.93	0.33	0.0164	0.089	0.22	Relaxation time(s)

in relaxation time for a mono-disperse fluid, reduction in the relaxation time associated with an increased concentration of the dispersed phase is probably due to the increase in shear thickening property caused by increasing dispersed particle concentration. Also, comparison of the relaxation time (τ) values indicates that the relaxation time speed of shear thickening fluids is more than that of epoxy resin, while the initial viscosities of STF and epoxy resin are approximately equal.

Therefore, relaxation time of STFs is much less than that of conventional fluids. These results are consistent with the observed shear thickening behavior.

4. Conclusions

Rheological behavior of bimodal shear thickening fluid made of two sizes of nanoparticles and mono-dispersed system was successfully investigated. Hydrocluster formation, onset of shear thickening, critical shear stress, elastic and damping response, reversibility, and relaxation time spectrum are among the considered parameters. The result shows better interaction between particles in the bimodal system, thus, demonstrating the strong shear thickening transfer at a shear rate lower than that of mono-dispersed system and also at lower concentration. Comparison of bimodal combinations with mono-disperse systems shows superior properties of the bimodal STFs in terms of increase in viscosity for all the corresponding composition ratios tested.

Oscillatory stress condition revealed faster response by the bimodal system. The storage and loss modulus of the bimodal STF system has a lower critical angular frequency than that of mono-dispersed STF. Comparison between relaxation times of both STF materials reveals that mono-dispersed STF has less relaxation time than bimodal STF. Relaxation time is one of the main factors in damping applications. With this study, we are able to design STF damping system with specific relaxation time for use in sensitive applications.

Nomenclature

τ	Relaxation time
$H(\tau)$	Relaxation time spectrum
t	Time
$G(t)$	Stress relaxation modulus
ω	Angular frequency
G'	Storage modulus
G''	Loss modulus

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