

Effect of bimodal size distribution of dense colloidal silica suspensions in PEG on reversible shear thickening

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ABSTRACT

We investigated the reversible shear thickening transition of highly concentrated bimodal suspensions of silica in polyethylene glycol (PEG) with a molecular weight of 400 g/mol as a function of the volume fraction ratio of the large particles (R). It was found that the zero-shear viscosity and shear thickening behavior are non-monotonic functions of R . Sample with $R=0.6$ showed the lowest zero-shear viscosity and the weakest shear thickening behavior. Additionally, the empirical model for hydrocluster formation was used to discuss hydrodynamic and thermodynamic contributions to the viscosity and to determine the shear rate characterizing the onset of hydrocluster formation, Pe_{HC} . The lowest Pe_{HC} was obtained for sample with $R=0.6$.

INTRODUCTION

Concentrated hard sphere colloidal suspensions subjected to increasing shear stress display a reversible, rise in viscosity with increasing shear rate known as shear thickening. Shear thickening in colloidal suspensions often limits formulations for coating and spraying operations, as well as flow rates for pumping concentrated dispersions.¹ Therefore, shear thickening at high shear rates and its relationship with the structure of colloidal suspensions have been the subject in numerous investigations.²⁻⁶

The mechanism for reversible shear thickening in colloidal suspension is driven by the dominance of short-range lubrication hydrodynamic, denoted as “hydroclusters,” first predicted by Stokesian dynamic simulations, and then confirmed experimentally by rheo-optical methods.⁷ Kalman et al.⁸ investigated the colloidal microstructure under steady flow conditions by ultra-small angle neutron scattering (USANS) measurements to characterize the formation of hydroclusters. They demonstrated that the hydrocluster formation has a characteristic length scale of a few particle diameters. For concentrated suspensions, they showed that the cluster formation takes place only at high shear rates, where a substantial shear thickening is observed. In this work, we studied the reversible shear thickening of the highly concentrated bimodal suspension of silica/polyethylene glycol (PEG) with a molecular weight of 400 gr/mol at a constant volume fraction $\phi=0.61$ and different relative volume fraction of large particles, $R= \phi_l/\phi$ with particle size ratio $\delta=d_l/d_s$ equal to 3.27. Additionally, we used empirical model by Gopalakrishnan et al.⁹ for hydrocluster formation to determine hydrodynamic and thermodynamic contributions to the viscosity, and determined the shear rate characterizing the onset of hydrocluster formation.

EXPERIMENTAL SECTION

Monodisperse silica particles are synthesized by a method that is developed by Stöber et al.¹⁰ Two different sizes are prepared with $D_l = 270 \pm 10$ nm (referred to as large particles) and $D_s = 80 \pm 11$ nm (referred to as small particles). The concentrated silica particle suspensions are mixed with PEG and the mixture was then thoroughly mixed using an ultrasonic bath for 120 min in room temperature. The final mixtures are placed into a vacuum oven with temperature kept above 50 °C to remove ethanol solvent. All the rheological measurements were performed using a stress/strain controlled rheometer, UDS 200, Paar Physica. The experiments were carried out using cone-plate geometry at temperature of 27 °C. Continuous shear rate was applied to study the viscosity as a function of applied shear rate.

RESULTS AND DISCUSSION

In order to study the flow properties of suspension exposed to a continuous shear rate, the steady-state relative viscosity, η_r , and dimensionless shear stress, τ^* , were plotted versus Peclet number as presented in Fig. 1. η_r , τ^* and Peclet number are defined as follows, respectively:

$$\eta_r = \frac{\eta}{\eta_m} \quad (1a)$$

$$\tau^* = \frac{\tau(D)^3}{4k_B T} \quad (1b)$$

$$Pe = \frac{3\pi\eta_m \dot{\gamma}(D)^3}{4k_B T} \quad (1c)$$

where η and η_m are the viscosity of suspension and PEG matrix, respectively. For a fixed Peclet number, the relative viscosity is a non-monotonic function of R and the lowest η_r is obtained for $R=0.6$. As can be seen for all samples, the zero shear

viscosity is no longer probed at low Pe and shear-thinning behavior is evident at low Pe regime. All suspensions exhibit a shear-thinning behavior for $10^{-4} < Pe < 1$ which can be fitted by the Herschel–Bulkley model:

$$\tau = \tau_y + K\dot{\gamma}^n \quad (2)$$

where τ , τ_y , K and n are the shear stress, the yield stress, the consistency index and the flow index, respectively. The dimensionless fitting parameters are summarized in Table 1. As seen, all bimodal suspensions can be adequately fitted with $n=0.5$. The transition from shear-thinning to a narrow window of constant viscosity takes place in $1 < Pe < 2$ range. At Pe higher than ~ 2 , the behavior changes to shear thickening. In ascending and descending sweep experiments, the shear thickening transition behavior is reversible for all samples with little or no observable hysteresis as shown in Fig. 2. For the suspension with $R=0.25$ (the strongest glassy behavior among studied binary systems), the viscosity curve at the shear thickening transition becomes discontinuous.

As samples show yield stress at high volume fractions, the method proposed by Russel and Grant¹¹ for colloidal dispersions is used to obtain “zero shear” viscosities. Note that in this method, the apparent zero shear viscosity is obtained by subtracting the calculated yield stress of Herschel–Bulkley model from the measured stress in low shear rate regime, and then, averaging the resultant low shear viscosities. Sample with $R=0.6$ have the lowest yield stress and zero-shear rate viscosity (Table 1).

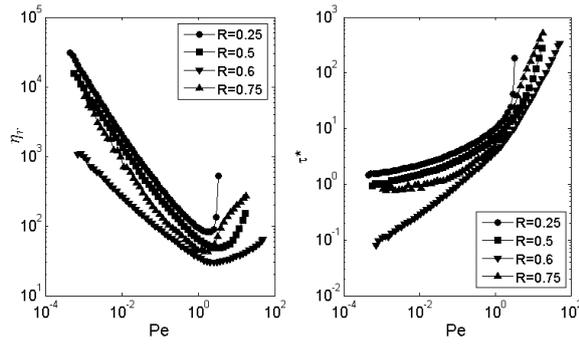


Figure 1. Flow curves of (a) dimensionless stress versus Peclet number, and (b) relative viscosity versus Pe for suspensions with different fractions of large particles R .

We used the empirical model proposed by Gopalakrishnan et al.⁹ to discuss hydrodynamic and thermodynamic contributions to the viscosity and determine the shear rate characterizing the onset of hydrocluster formation, Pe_{HC} . The viscosity is described in terms of the thermodynamic and hydrodynamic contributions as follows:

$$\eta_{total} = \eta_H + \eta_T \quad (3)$$

where η_{total} is the measured viscosity, η_T is the thermodynamic contribution associated with the interparticle and Brownian forces, and η_H is the hydrodynamic contribution to the viscosity associated with the viscous interactions. The η_T is estimated by Cross equation¹³ as follows:

$$\eta_T = \frac{\eta_0 - \eta_\infty}{1 + \left(\frac{Pe}{Pe_{1/2}}\right)^m} + \frac{\tau_y^* \times \left(\frac{3\pi\eta_m \langle D \rangle^3}{4k_B T}\right)}{Pe \times \left(\frac{\langle D \rangle^3}{4k_B T}\right)} \quad (4)$$

where η_0 is the limiting low shear viscosity and η_∞ is the high shear viscosity. $Pe_{1/2}$ is the characteristic Pe at which $\eta_{Total} = \eta_\infty + \frac{1}{2}(\eta_0 - \eta_\infty)$.

The hydrodynamic contribution is defined by the following equations:¹⁴

$$\begin{cases} \eta_H = \eta_\infty, & Pe < Pe_{HC} \\ \eta_H = \eta_\infty + B \log \left[\frac{Pe}{Pe_{HC}} \right], & Pe > Pe_{HC} \end{cases} \quad (5)$$

The logarithmic term in the above equation accounts for the contribution of the lubrication stresses arising from hydroclusters. For studied samples, the coefficient B and Pe_{HC} are determined from the best fit of the model to the total viscosity at Pe higher than ~ 2 , where the behavior changes to shear thickening.

Fig. 2 shows the fitting of the model to the suspension viscosities (parameters shown in Table 1). As can be seen, hydrocluster formation in all samples occurs at Pe_{HC} higher than the Pe of the minimum in total viscosity, Pe_c , except the sample with $R=0.6$ in which the value of Pe_{HC} is close to value of Pe_c . At intermediate Pe , the viscosity reaches an apparent high shear plateau predominantly due to hydrodynamic contributions to the stress. This hydrodynamic component is nearly constant up to high Pe (Pe_{HC}), where a significant rise in hydrodynamic stresses leads to an overall shear thickening behavior, which is in agreement with Kalman et al.⁷

The sample with $R=0.6$ has the lowest Pe_{HC} and weakest shear thickening (the smallest value of B). This result can be explained as hydrocluster formation at systematically lower shear rates, while the smaller and fewer clusters form compared to other samples.

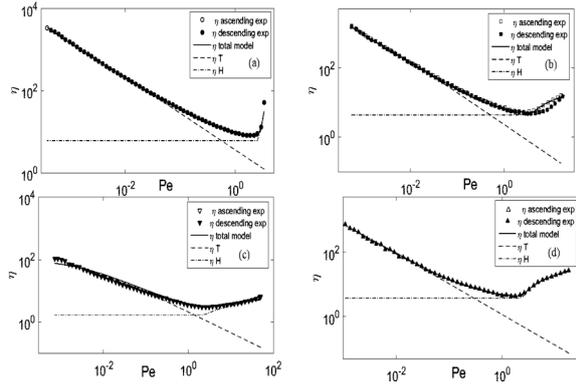


Figure 2. The ascending (filled symbols) and descending (open symbols) flow curves for: (a) $R=0.25$, (b) $R=0.5$, (c) $R=0.6$, and (d) $R=0.75$ samples. The fitting of Gopalakrishnan et al.⁹ empirical model on the ascending flow curves are also shown. The symbols represent the experimental data, whereas the lines are the prediction of the empirical model.

CONCLUSION

The shear-thickening behavior has been studied in concentrated binary suspension with size ratio $\delta=d_l/d_s=3.4$ and a constant volume fraction $\phi = 0.61$. The Herschel–Bulkley model with $n=0.5$ was found to correlate well with the behavior of these

suspensions in the shear thinning regime. The zero-shear viscosity and shear thickening behavior were found to be non-monotonic functions of R . Sample with $R=0.6$ showed a minimum in zero-shear viscosity and the weakest shear thickening behavior. Sample with $R=0.6$ has the lowest Pe_{HC} and weakest shear thickening due to the formation of smaller and fewer hydroclusters at systematically lower shear rates compared to other bimodal samples.

Table 1. The dimensionless rheological parameters of Herschel–Bulkley (H-B) model, relative zero-shear viscosity calculated according to Russel et al.¹¹,

R	n	K^*	τ_y^*	H-B fitting R-squared	$\eta_{r,0}$
0.25	0.5	8.87	1.30	0.99	3127.3
0.5	0.5	6.41	0.79	0.99	2426.8
0.6	0.5	3.24	0.00	0.99	1058.8
0.75	0.5	3.22	0.67	0.97	1424.2

Table 2. The apparent high shear viscosity, the critical shear stress for transition to shear-thickening behavior, and fitting parameters from the empirical model proposed by

Gopalakrishnan et al.⁹: $Pe_{1/2}$, m , B , and, Pe_{HC} .

R	η_{∞}	$Pe_{1/2}$	m	B	Pe_{HC}
0.25	6.2	3.3×10^{-3}	0.85	155	2.85
0.5	4.45	3.7×10^{-3}	0.90	7.1	2.90
0.6	1.67	2.9×10^{-3}	0.67	1.2	2.35
0.75	3.75	2.0×10^{-3}	0.90	11	2.45

REFERENCES

- Lootens, D, Hébraud, E, Lecolier E, and Van Damme, H. (2004), "Gelation, shear thinning and shear-thickening in cement slurries", *Oil Gas Sci Technol Rev Inst Fr pet.*, **59**, 31-40.
- Maranzano, B.J. and Wagner, N.J.,(2001), "The effect of particle size on reversible shearthickening of concentrated colloidal dispersions", *J Chmical Phys.*, **114**, 10514-10527.
- Franks, G.B., Zhou, Z, Duin, N.J. and Boger, D.V. (2000), "Effect of interparticle forces on shear thickening of oxide suspensions" *J. Rheol.*, **44**, 759-779.
- Bender, J.W. and Wagner, N.J. (1996), "Reversible shear thickening in monodisperse and bidisperse colloidal dispersions", *J. Rheol.*, **40**, 899-916.
- Zukoski, C.F. and Jiang, T. (2013), "Rheology of high density glass of binary colloidal mixtures in unentangled polymer melts", *Soft Matter.*, **9**, 3117-3130.
- de Kruif, C. G., van Iersel, E.M.F., Vrij, A. and Russel, W.B. (1985), "Hard spheres colloidal dispersions: Viscosity as a function of shear rate and volume fraction", *J. Chem. Phys.*, **83**, 4717-4725.
- Bender, J.W and Wagner, N.J. (1995), " Optical measurement of the contributions of colloidal forces to the rheology of concentrated suspensions", *J. Colloid Interface Sci.*, **172**, 171-184.
- Kalman, D. P. and Wagner, N.J. (2009), "Microstructure of shear-thickening concentrated suspensions determined by flow-USANS", *Rheol. Acta.*, **48**, 897-908.
- Gopalakrishnan, V, and Zukoski, C. F. (2004), "Effect of attractions on shear thickening in dense suspensions", *J. Rheol.*, **48**, 1321-1344.
- Stober, W, Fink, A, Bohn, E. (1968), "Controlled growth of monodisperse silica spheres in the micron size range", *J. Colloid Interface Sci.*, **26**, 62-9.
- Russel, W.B. and Grant, M.C. (2000), "Distinguishing between dynamic yielding and wall slip in a weakly flocculated colloidal dispersion", *Colloids Surf A.*, **161**, 271.-282
- Jiang, T. and Zukoski, C.F. (2012), "Role of Particle Size and Polymer Length in Rheology of Colloid-Polymer Composites" , *Macromolecules.*, **45**, 9791-9803.
- Cross, M. M. (1965), "Rheology of non-Newtonian fluids: a new flow equation for pseudoplastic systems", *J. Colloid Sci.*, **20**, 417-437.
- Foss, D.R. and Brady, J.F. (2000), "Structure, diffusion and rheology of Brownian suspensions by Stokesian dynamics simulation", *Journal of Fluid Mechanics.*, **407**, 167-200.