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RHEOLOGICAL PROPERTIES OF MAGNETIC PARTICLE SUSPENSIONS

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Abstract - The viscometric technique is used to study the effects of microstructure on the viscosity (viscosity vs. concentration or shear rate) of magnetic particle suspensions. In this characterization, measurement of suspension viscosity is used to obtain the dependence of viscous energy dissipation on microstructural state of dispersions. Microstructural shape effects which are related to particle orientation are then indirectly obtained. Empirical formulas from mean field theory and the Mooney equation, which are applicable at high concentration of magnetic particles, are used to relate viscosity to particle concentration. The validity and physical meaning of these equations are discussed.

I. INTRODUCTION

When magnetic particles are immersed in fluid (Newtonian or viscoelastic), a dynamic coupling between the fluid and the particles is present. The suspended particles perturb the fluid and the fluid changes the dynamics of the particles, especially the orientation of the particles in hydrodynamic and/or magnetic fields. This dynamic coupling is experimentally observable either by studying the overall suspension (effective medium) behavior or by examining the dynamics of particle orientation. The overall suspension properties exhibit non-Newtonian behavior, as shown by thixotropy or shear thinning, and deviatoric normal stresses due to nonrandom ordering imparted by the external field. In the presence of significant magnetic interactions when the shape of the particles is non-spherical, understanding the complex dynamic coupling between the particles and the fluid is a challenging problem on a fundamental level and is very important to many technical applications, such as magnetic recording technology [1]. Although the particulate magnetic recording industry is mature, there still remain unsolved problem of rheological characterization and dispersion quality which plague any coating process involving unstable particle suspensions. Numerous papers on the suspension rheology of non-interacting particles have been published. However, the rheological properties of magnetic particle suspensions with strong interacting particles and various particles shapes are relatively unknown.

From a comparison of the intrinsic viscosity values at infinite shear rate, Smith and Bruce [2] characterized suspensions of nonmagnetic α-Fe_2O_3 and magnetic γ-Fe_2O_3 in ethylene glycol and showed that the particles existed as small stable flocs even at infinite shear rate. Nagashiro and Tsunoda [3] studied the effect of suspending media on the rheological properties of γ-Fe_2O_3 particle suspensions. In addition, Kuin [4] developed a theory for viscoelastic deformation of CrO_2 and γ-Fe_2O_3 particle suspensions. By fitting shear stress vs. shear rate data to their theory, they obtained yield stress, shear viscosity, stress coefficient, and relaxation time for elastic deformation.

In this paper, shape effects of magnetic particles, agglomeration phenomena at low concentration, shear induced breakage or agglomeration, and interaction between magnetic particles are investigated. In addition, effects of flocs in suspension are also investigated. Due to interparticle interactions, the primary particles in suspension usually form flocs. These flocs contain immobilized suspending fluid in their structures and thus the apparent increased particle concentration is expected to increase the effective viscosity of the suspension.

II. EXPERIMENTAL

For measurement of viscosity, the Wells-Brookfield LVT-D cone and plate viscometer with the C-42 cone type was employed. The C-42 cone type makes an angle of 1.565^{o} with the plate which has a radius of 2.5 cm. The plate serves as a sample cup with a built-in circulation channel and ports for a recirculant from a constant temperature bath. This specific cone and plate combination is designed to incorporate approximately 1 ml of sample. To maintain a constant temperature during the measurement, the jacket ports in the sample cup are connected to a recirculating loop of a constant temperature bath. For automatic data acquisition, the signal output receptacle of the viscometer and the thermocouples are multiplexed to a voltmeter which is interfaced to an IBM PC via a GPIB bus.

An approximately 150 ml master solution of each magnetic suspension having an approximate volume fraction of 0.05 was prepared by mixing the particle powder with ethylene glycol and then passing the suspension twice through a mini-Eiger motor mill at a speed of 1000 rpm. The volume concentration of the prepared master suspension was obtained using both TGA and the Rheomagnetic (RM) [5,6] concentration measurement device. More dilute samples were prepared by subsequent dilution of the concentrated master suspension. The test suspension is sheared for 3 minutes at a maximum shear rate of 115 sec^{-1} (30 rpm) to obtain a homogeneous dispersion, and then the suspension is stabilized for 2 minutes. After stabilization, the suspension is sheared at the highest shear rate for 2 minutes and then 20 measurements are performed between a 15 second intervals. A steady state viscosity is obtained by averaging the measured values. After this, the shear rate is decreased and the measurement is repeated. All measurements were performed at constant temperature by maintaining the temperature of the recirculating fluid at 25 ^{o}C.

Results and Discussion

Typical dependence of steady shear viscosity on particle volume concentration is presented in Fig. 1 for CrO_2 particle suspensions. For all particle suspensions, the viscosity of suspension increased exponentially with particle concentration, irrespective of shear rate. Hence, the viscosity for a concentrated suspension is often written as a series by [7]

$$\eta = \eta_0 (1 + k_1\phi + k_2\phi^2 + \cdots) \qquad (1)$$

Application of Eq. (1) is limited to the dilute concentration regime. An approach overcoming the drawbacks of the series expression for concentrated suspensions is the model based on mean field (MF) theory [8]. In this model, the incremental viscosity increases by additionally introducing a $d\phi$ volume concentration of particles into the suspension of viscosity, η, and volume fraction, ϕ [7]. It can be expressed as[9]

$$\eta = \eta_0 (1 - \phi/\phi_\infty)^{-[\eta]\phi_\infty} \qquad (2)$$

Here, $[\eta]$ is the intrinsic viscosity.

Another expression widely used for the concentration dependence of viscosity was developed by Mooney [10]. In his development, the relative viscosity of the suspension is assumed to be governed by $\eta/\eta_0 = H(\phi)$, where the function H depends solely upon ϕ. He assumed $H = \exp[2.5\phi/(1 - K\phi)]$ as a solution for spherical particle suspensions with K being the crowding factor. A straight forward extension of his expression on spheres yields an expression for nonspherical particles:

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{[\eta]\phi}{1 - \phi/\phi_\infty} \qquad (3)$$

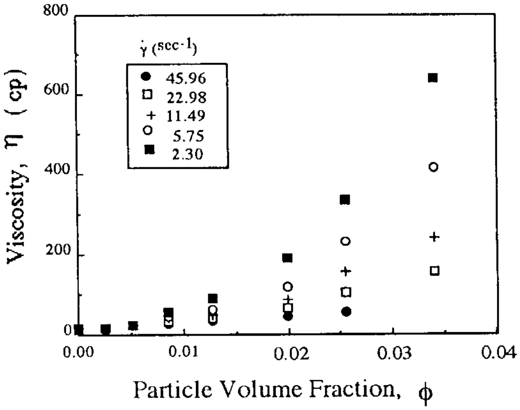

Fig. 1 Typical dependence of measured viscosity on particle volume fraction. Measured viscosity showes nonlinear dependence on particle volume concentration. Due to the concentration effects, the theory for dilute suspension is not directly applicable. The data were obtained for CrO_2 particle suspensions.

In order to obtain information on the state of the suspension over the concentration ranges, the measured viscosity is fitted with predictions incorporating concentration effects. For this purpose we choose the mean field and Mooney theories, given by Eqs. (2) and (3), respectively. Fig. 2 shows plots of viscosity vs. particle concentration for γ-Fe_2O_3 particle suspensions. Two parameters, $[\eta]$ and ϕ_∞ are determined from the fitting of the experimental data in terms of the theories. For example, with Mooney's equation given by Eq. (3), the curve fitting parameters, $[\eta]$ and ϕ_∞, are determined through the intercept, $-[\eta]^{-1}\phi_\infty^{-1}$ and slope, $[\eta]^{-1}$ in the $1/\ln(\eta/\eta_0)$ vs. ϕ^{-1} curve as illustrated in Fig. 3. However, as shown in the figure, both the slope and the intercept range are typically $O(10^{-2})$ and therefore it seems difficult to accurately obtain ϕ_∞ with limited data; because small changes in slope lead to large changes in the intercept, which affects ϕ_∞. Thus, we assume an ideal packing of spherical particles and approximate $\phi_\infty = 0.65$. We then determine only the dependence of $[\eta]$ although in practice ϕ_∞ is reported to be dependent upon particle shape and shear rate.

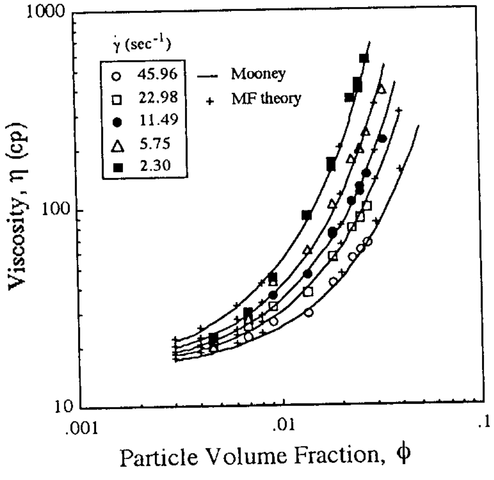

Fig. 2 Measured viscosity dependence on particle volume fraction in γ-Fe_2O_3 particle suspension. Measured viscosity fits well with mean field (MF) theory and Mooney equation. Intrinsic viscosity is obtained as fitting parameter.

Further analysis of the intrinsic viscosity [η] in terms of suspension viscosity theory gives, in principle, information on the microstructures in suspension. We find that $[\eta] \approx 100$ for rod-like particles corresponds to $p > 35$ and $[\eta] \approx 80$ corresponds to $p < 0.02$ for plate-like Ba-Ferrite particles. These aspect ratio values imply that in the case of rod-like particles, more than four primary particles are in end-to-end flocculation and in the case of plate-like Ba-Ferrite, more than 25 particles are in edge-to-edge flat flocculation.

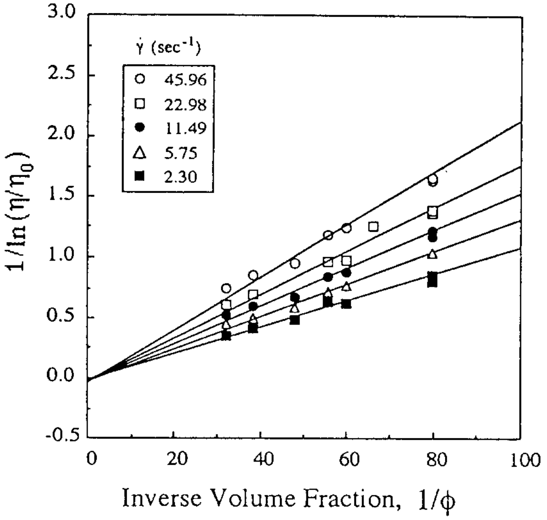

Fig. 3 $1/\ln(\eta/\eta_0)$ vs. ϕ^{-1} curve fitting based on Mooney's equation. [η] and ϕ_∞ are determined through the intercept, $-[\eta]^{-1}\phi_\infty^{-1}$ and slope, $[\eta]^{-1}$. In practice, however, the intercept is too sensitive to determine ϕ_∞ accurately. Illustrated data were obtained for γ-Fe_2O_3.

This seems unrealistic since some theoretical and experimental studies have shown that rod-like magnetic particles are more stable in side-by-side flocculation [11] and plate-like Ba-Ferrite is well known for face-on-face stacking flocculation [12]. However, it is difficult to claim that end-to-end flocculation of rod-like magnetic particles is totally infeasible. According to the description on the flocculation mechanism of rod-like magnetic particles [13], the particles are preferably approaching each other in an end-to-end configuration and when they are close enough, a particle flips around onto the other establishing a side-by-side aggregate. A contrasting view by some authors proposes the end-to-end configuration based on their rheological observations [3]. We suggest the side-by-side configuration viewpoint from the electronmicrographs of dry particle powder; furthermore side-by-side flocculation is more stable in terms of van der Waals attractions. In addition, the configuration can be stable in terms of magnetic attraction by forming closed magnetic flux loops in the microstructure. Therefore, we consider that the observed high intrinsic viscosities were due to the existence of flocs which contain immobilized suspending fluid in their structures, and the effective particle volume fraction is increased. Considering effects of flocs on viscosity, Smith[14] found that the most probable shape of a floc is nonspherical and therefore the viscosity of a suspension in infinite dilution can be expressed as :

$$\frac{\eta-\eta_0}{\eta_0} = [\eta]\phi = 2.5\phi_{floc} + [\eta]_{pp}\phi_{pp} \qquad (4)$$

where $[\eta]_{pp}$ is the intrinsic viscosity for the primary particles in suspension and ϕ_{floc} and ϕ_{pp} are the volume fraction of flocs and primary particles in suspension, respectively. Rearranging, Eq. (4) yields:

$$\frac{\phi}{\phi_{floc}} = \frac{2.5}{[\eta]} + \frac{[\eta]_{pp}\phi_{pp}}{[\eta]\phi_{floc}} \qquad (5)$$

If flocculation tendency is strong enough, the second term of the r.h.s. of Eq. (5), will vanish to give $\phi/\phi_{floc} = 2.5/[\eta]$.

If we assume strong flocculation behavior and that most of the particles reside in flocs, estimation of the structure of flocs residing in suspension can be achieved by taking $\phi_{pp} \sim 0$ in Eq. (5). For a shear rate range, $\dot{\gamma} = 2.3 \sim 45.96 \text{sec}^{-1}$, the estimated fraction of particles in flocs, ϕ/ϕ_{floc}, ranged from 0.020 to 0.048 for γ-Fe_2O_3, 0.028 to 0.056 for α-Fe_2O_3, 0.021 to 0.045 for CrO_2, and 0.033 to 0.079 for Ba-Ferrite. These values imply that most flocs in suspension are composed of 92 ~ 98 vol.% suspending fluid. Physical stability of this kind of flocculation structure is questionable. However, the results suggest that the flocs in suspension contain a significant amount of immobilized liquid leading to an increase in effective particle volume fraction. In addition, it is noted that this analysis reveals somewhat expected trends of particle flocculation behavior: increased shear rate yields more compact floc structures, and that flocculation structures of Ba-Ferrite particles are more compact compared to those of rod-like particles.

Intrinsic viscosity values obtained from MF theory were smaller than those obtained by Mooney's equation. However, these values are still higher compared to the theoretically predicted intrinsic viscosity values by dilute suspension theory. As was the case for the results obtained from Mooney's equation, interpretation based on the MF theory also reflects the presence of flocs containing a significant amount of immobilized liquid. The underestimated intrinsic viscosity values compared to those obtained from Mooney's equation occur because we arbitrarily used $\phi_\infty = 0.65$ for fitting the data. Here, we attempt to obtain an approximate value for ϕ_∞ by assuming that the equation and the MF theory are equivalent. This assumption is made since the physical meaning of ϕ_∞ is basically the same in both theories. By introducing intrinsic viscosity values determined by Mooney's equation into MF theory and then fitting the same viscosity data, we obtained $\phi_\infty \approx 0.96$-0.99 for all the particle suspensions. This range of ϕ_∞ is peculiarly high and seems unrealistic considering typical values reported for various nonmagnetic particle shapes, i.e. $\phi_\infty = 0.2$-0.7 [7]. As discussed, particles in suspension form flocs containing significant amounts of immobilized suspending medium and therefore ϕ_∞ are actually expected to be somewhat lower. The high values were obtained because the intrinsic viscosity values obtained from Mooney's equation are too high for the MF theory. This can be attributed to either an existing incompatibility between the MF theory and the Mooney's equation or an overestimation of the intrinsic viscosity by the Mooney's equation. It is not clear which factor is responsible for the higher ϕ_∞. Future studies are necessary since both the Mooney and the MF predictions are so frequently used in interpreting suspension viscosity and ϕ_∞ values.

In addition, magnetic particle suspensions typically showed shear shinning behavior as shown in Fig. 4 for CrO_2 particle suspensions. In order to investigate the dependence of viscosity on shear rate, we fitted the measured viscosity of CrO_2 particle following Casson equation in Fig. 5.

$$\tau^{1/2} = \tau_0^{1/2} + \eta_\infty^{1/2}\dot{\gamma}^{1/2} \qquad (6)$$

For all types of particle suspensions, the Casson equation agreed well with the measured viscosity. From the slope of the Casson equation fit, we also obtained the intrinsic viscosity at infinite shear rate, $[\eta]_\infty$, for various particle concentrations and the results are presented in Fig. 6. For all types of particle suspensions, $[\eta]_\infty$ ranged from 3 to 80 and showed a decreasing trend with particle concentration. From this study, it was found that the concentration dependence of viscosity was well represented by both Mooney's equation and the MF theory. The intrinsic viscosities of all the types of particle suspensions exceeded the predictions of hydrodynamic theory for dilute suspensions and supported the existence of flocs containing significant amounts of immobilized suspending medium in the microstructures. In addition, shear rate dependence of viscosity was well characterized by the Casson equation.

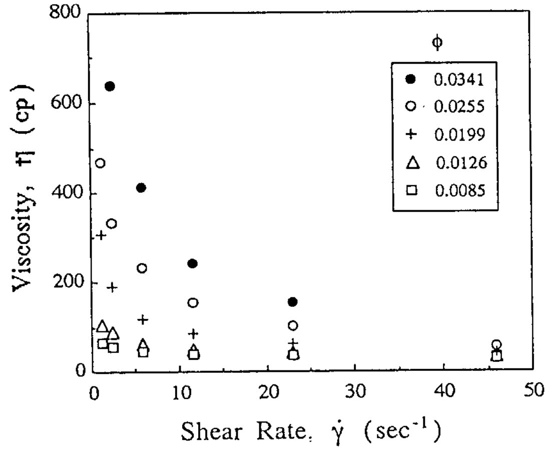

Fig. 4 Typical dependence of measured viscosity on shear rate. the measured viscosity shows shear thinning of the suspensions. Data werre obtained for CrO_2 particle suspensions.

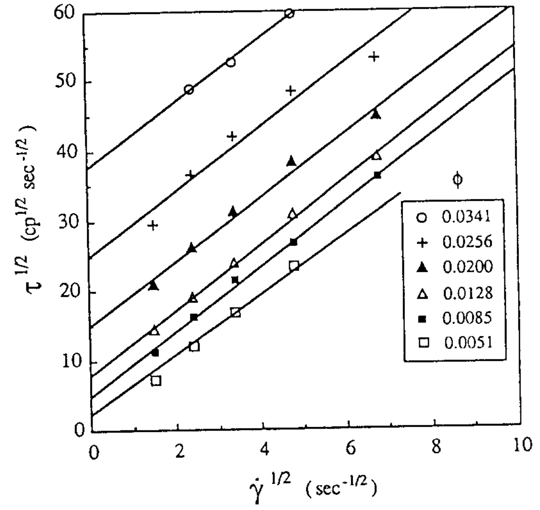

Fig. 5 $\tau^{1/2}$ vs. $\dot{\gamma}^{1/2}$ plot for CrO2 particle suspensions. The intercept and slope of the curve are related to the yield strress and the viscosity at infinte shear rates, respectively.

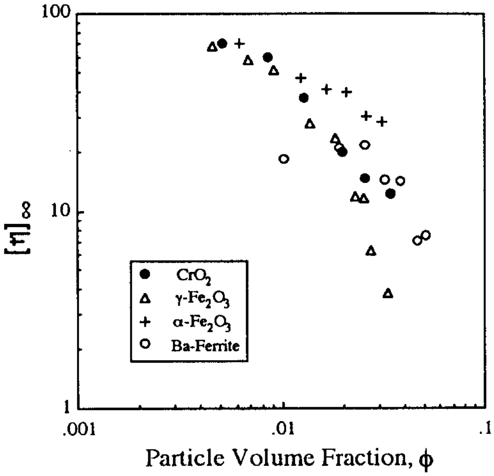

Fig. 6 Dependence of the intrinsic viscosity at infinite shear rate on particle concentration. Trends were determined from the Casson equation fitting.

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