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ORIGINAL CONTRIBUTION

Byoeng Seok Chae
Young Sil Lee
Myung S. Jhon

The scaling behavior of a highly aggregated colloidal suspension microstructure and its change in shear flow

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B.S. Chae · Y.S. Lee
Department of Chemical Engineering,
University of Delaware, Newark,
DE, 19716, USA

M.S. Jhon (✉)
Department of Chemical Engineering,
Carnegie Mellon University,
Pittsburgh, PA, 15213, USA
E-mail: mj3a@andrew.cmu.edu

Abstract The nature of the network structure and the evolution of structural change in shear flow were investigated for metal particle dispersions in terms of fractal aggregation of colloidal particles. Polymer-stabilized metal particle inks were prepared via a polyvinyl chloride coating dispersed in solvent. The fractal dimension of 1.74 was calculated with the scaling model based on the power law relationship between the elastic modulus and volume fraction. This scaling behavior can be explained by considering the deformable network structure of soft materials. While the elastic property of the floc was dominant, the limit of linearity was found at the inter-floc link, which is relatively weak and brittle. The steady shear results reveal two mechanisms that contribute to the breakdown of the microstructure in metal particle inks at increasing shear rate. Scaling of steady shear viscosity shows that these mechanisms are related to both inter-floc interactions and the elasticity of the floc itself. Further, these results suggest that individual flocs deform with weak inter-floc interactions and rupture into smaller flocs or aggregates at high shear stress, which is associated with the increased shear rate.

Keywords Colloidal suspension · Fractal dimension · Aggregation · Scaling · Magnetic particle

Introduction

Colloidal suspensions exhibit complex rheological properties, including viscoelastic properties that depend on particle volume fraction and particle-particle interactions. One of the determining factors in rheological properties of these colloidal suspensions is the formation of fractal aggregates. Concentrated suspensions form a complex microstructure; an association of particles to form sometimes an elastic network. A significant amount of research has been performed to study the suspension rheological properties of gels formed by fractal aggregation with spherical particles [1, 2, 3, 4] which result in non-Newtonian or viscoelastic behavior. The rheological properties can be tuned systematically by controlling the inter-particle interactions, the size and shape of the particles, and the particle volume fraction. When the inter-particle interaction is highly attractive, a gel structure is formed even at low particle volume fractions. In magnetic ink, strong attraction among particles exists, and the fractal structure is often found even for very low particle volume fractions.

Magnetic particle suspensions flocculate strongly because of their permanent magnetic moments. Relatively few experimental studies on the rheology of non-spherical, magnetic particle suspensions have been published [5, 6, 7, 8, 9, 10, 11]. Suspension microstructure depends on the polymer binder as well as the particle concentration. Inoue et al. [12] demonstrated that the adsorbed polymer layer acted as part of the magnetic particle in dispersion rheology. The magnetic particle dispersions are stabilized with polymers, but exhibit gel-like behavior without agitation [12, 13]. Yang et al. [5] examined the structure by investigating the yielding behavior of magnetic iron oxide suspensions in silicone oil. They found that the intrinsic viscosity became abnormally high even at high shear rates, indicating that the particles exist in clusters. Nagashiro et al. [6] and Kwon et al. [7] found that this abnormally high intrinsic viscosity at high shear rate indicated an alignment of particles into very long chains. Even at a relatively low particle concentration, it is believed that the magnetic particles form these microstructures as a result of their strong magnetic interaction [11, 14]. Despite many efforts to characterize the structure of magnetic inks, the equilibrium structure and its change during shear flow are not well understood. This is likely due to the non-spherical (typically acicular) shape, strong dipolar interactions, and dark color of the particle suspension, which makes optical characterization difficult.

Scaling behavior can be employed to examine the structure of dispersions [8, 15, 16]. The gel network is usually considered to be closely packed flocs. Kanai et al. [8] showed that the structure of a flocculated suspension can be characterized by a percolation exponent, which depends on the volume fraction. Mellema et al. [17] described various scaling models for gel structures formed by fractal aggregation. In this paper, we applied the fractal model developed by Shih et al. [18] to examine the rheological properties (including shear modulus) of magnetic ink.

Theoretical considerations

To characterize structure, de Gennes [19] introduced scaling concepts that have been successfully applied to polymer gels. Since the colloidal gels are very similar to polymer gels, as both are viscoelastic and have similar aggregation processes, Shih et al. [18] extended de Gennes' concept to flocculated colloidal aggregation. They found that the scaling behavior of the critical strain for nonlinearity and the plateau modulus for colloidal gels depend on the strength of interactions between the flocs compared to within the flocs. They considered the gel network as closely packed, fractal flocs. This concept worked very well in a protein gel structure [15] and has been used previously by several researchers [20, 21]. The elasticity of dispersion is dominated by either the flocs or the interlink between flocs. The elastic constant (K) of the individual flocs depends on the floc size (ξ) and backbone fractal dimension (x) as follows:

$$K \propto K_0/\xi^{2+x} , \quad (1)$$

where K_0 is the local bending constant between two neighboring springs that belong to the effective backbone of a floc. The fractal dimension is defined by the ratio between the number of self-similar pieces to the magnification factor which breaks a feature.

When the links between flocs have a higher elasticity than those within the flocs, the macroscopic elastic constant (G) as a function of ϕ is dominated by K. The dependence of G on ϕ is derived from the relationship:

$$G \propto (L/\xi)^{d-2}K. \quad (2)$$

Here, d is the fractal dimension and L is the system size.

In this case, which is known as a "strong-link regime", the limit of linearity (γ_c) and G are related to ϕ as

$$\gamma_c \propto \phi^{-(1+x)/(3-d)} \quad (3)$$

$$G \propto \phi^{(3+x)/(3-d)} . \quad (4)$$

In this regime, bond breakage occurs within a floc. γ_c decreases with increasing ϕ because the flocs become more brittle with decreasing size [18]. When the flocs are more rigid than the inter-floc links, which is known as a "weak-link regime", the elastic behavior of the gel network is dominated by the elastic constant of the inter-floc links. Bond breakage occurs when strain increases at the inter-floc link. γ_c in this regime is expected to increase with increasing ϕ. In contrast to the strong-link regime, γ_c and G are related to ϕ as

$$\gamma_c \propto \phi^{1/(3-d)} \quad (5)$$

$$G \propto \phi^{1/(3-d)} . \quad (6)$$

Materials and methods

The magnetic inks were prepared by dispersing metal particles in a polymer solution by milling. A polyvinyl chloride (PVC) copolymer (MR110, $M_n = 12{,}000$, Nippon Zeon), containing 0.7 wt% SO_4 and 0.5 wt% OH functional groups, was used as a wetting resin. The PVC copolymer was adsorbed on the surface of the magnetic particles (MP) to provide steric stabilization. The solvent was cyclohexanone, chosen for its low volatility, and metal particles were dispersed in the solvent. These metal particles were metallic iron with a passive outer shell, which are typically used in high-density recording media, having an acicular shape with an aspect ratio of 8 and a long axis length of 150 nm. The particle density was 4.8 g/cm^3. The inks were simulated to meet commercial formulations. The weight ratio of polymer to metal particles was fixed at 0.175 for all magnetic particle ink samples.

The magnetic dispersion is believed to aggregate and form a structure due to strong interactions among magnetic particles. Since the structures can easily be broken even at relatively low shear stresses, a rheometer capable of accurately measuring small shear stresses is required to examine these effects. Since the yielding behavior for these systems is of interest, a Haake RS-100 controlled stress rheometer was used to measure the rheological properties of the magnetic ink. The rheological properties were measured via dynamic oscillatory and steady shear experiments.

All tests were performed with a 4^o cone with 35-mm-diameter parallel plates at a 0.135-mm gap. The temperature was maintained at 20 ± 0.1 ^{o}C via a constant-temperature water bath. In dynamic oscillatory shear tests, a sinusoidal stress $\tau = \tau_0 \sin(\omega t)$ was imposed on the sample, and the dynamic moduli were calculated from the measured strain and shifted phase angle. For every measurement, the sample was subjected to a pre-shear rate of 100 s^{-1} for 50 s and left at rest for 10 min. The moduli for the magnetic inks showed no time dependence, confirming that the initial conditions before the measurements did not affect the rheological data.

Results and discussion

Dynamic oscillatory measurement

To characterize the viscoelastic properties of magnetic inks, the frequency-dependent moduli of MP inks were measured at four different particle concentrations in the linear viscoelastic regime and were plotted in Fig. 1. For $\phi > 0.007$, the storage modulus, G', is almost independent of the frequency, ω, in our experimental range, allowing us to identify a plateau modulus, G_0. The loss modulus, G'' , exhibits a minimum at intermediate frequency [11]. The shape of the data is similar to that of soft glassy materials [22, 23, 24], which suggests the existence of a gel-like structure. The soft glassy materials, such as foams, dense emulsions, and pastes, show qualitative similarities to the glass transition with the possibility of deformation and flow. Data for smaller ϕ exhibit a significantly different behavior as shown for $\phi = 0.007$. The G' and G'' scaled as ω^2 for G' and ω for G'', i.e., purely viscous. This liquid-like behavior is expected for a dilute suspension indicating no existence of a network structure.

The dependence of the G'' on strain amplitude, γ, is shown in Fig. 2 at a frequency of 6.28 rad/s. As strain amplitudes become smaller than the limit of linearity ($\gamma \le \gamma_c$), the G' is independent of strain, indicating a gel structure. γ_c is the critical strain for nonlinearity. On the other hand, for large strains ($\gamma > \gamma_c$), the G' decreases rapidly with increasing strain. However, for $\phi = 0.007$ the decrease is not found as expected. From these results we believe that the magnetic particles form a solid network structure with a highly elastic modulus above $\phi = 0.007$. Further, γ_c increases with increasing ϕ, suggesting that the inter-floc links become more flexible with increasing ϕ (weak-link regime). The inset of Fig. 2 shows the slope (in log scale) of γ_c and ϕ and the evaluated fractal dimension, d, from Eq. 5, is 1.74. The floc fractal dimension of 1.74 is an indication of highly aggregated structures, implying diffusion-limited aggregation, where the probability of contact between diffusing particles is very high [25, 26]. The same fractal dimension is obtained from the relationship between G_0 and ϕ. However, the dependence of G_0 on ϕ in Fig. 3 has an exponent of 3.4, implying that the dependence of G_0 on ϕ is described by the strong-link regime.

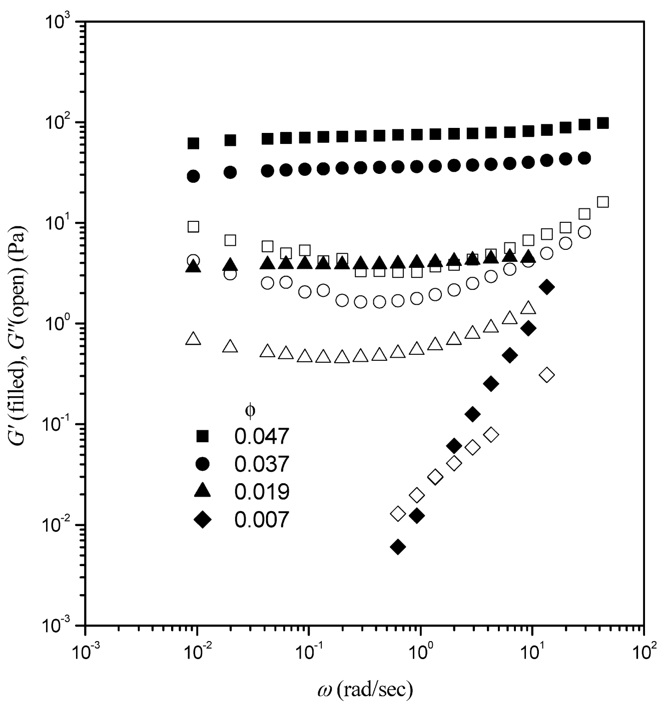

Fig. 1 G' and G'' vs. ω at four different volume fractions for the MP inks: $\phi = 0.047$ (*square*), 0.037 (*circle*), 0.019 (*triangle*), and 0.007 (*diamond*). *Filled symbols* indicate G' while *open symbols* indicate G''

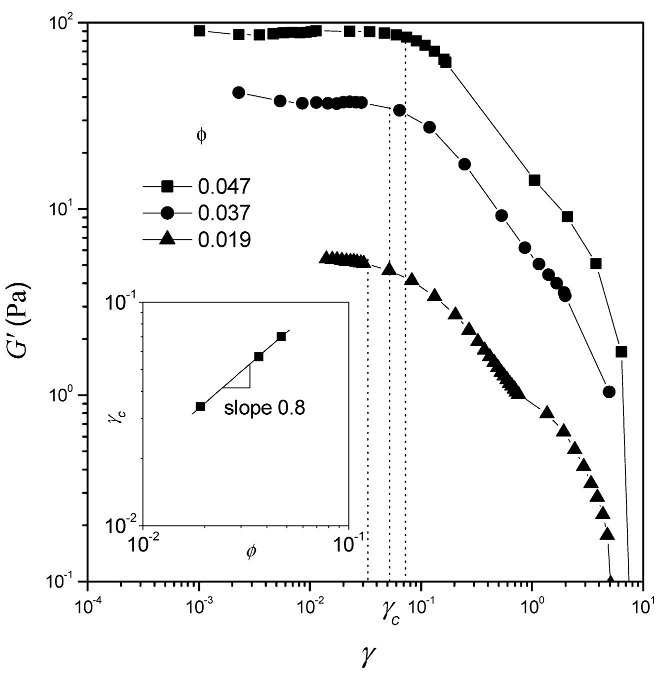

Fig. 2 G'' vs. strain amplitude at different volume fractions for the MP inks: $\phi = 0.047$ (*square*), 0.037 (*circle*), and 0.019 (*triangle*). The *inset* shows γ_c as a function of volume fraction. The log plot shows the slope of 0.8

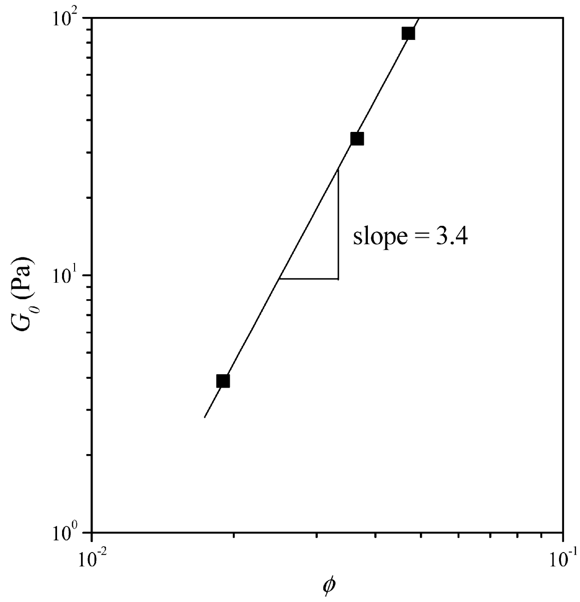

Fig. 3 The plateau modulus vs. volume fraction in a log plot

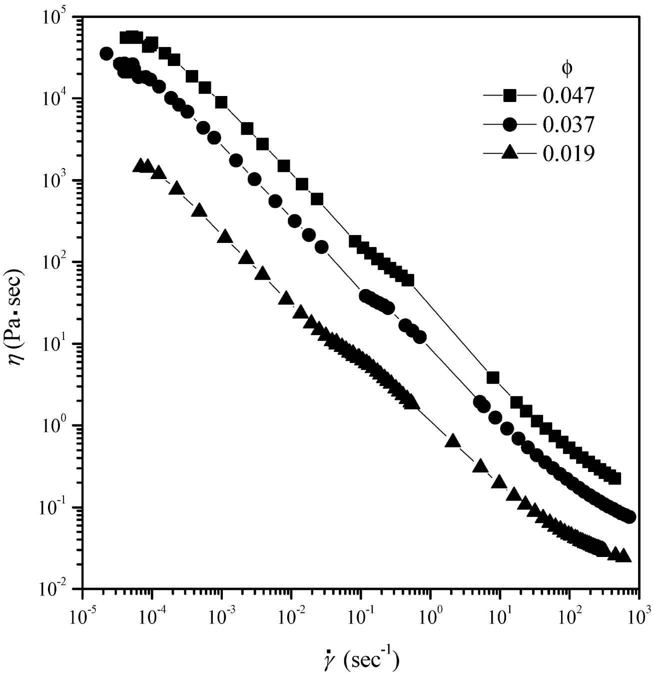

Fig. 4 Viscosity vs. shear rate at different volume fractions: $\phi = 0.047$ (*square*), 0.037 (*circle*), and 0.019 (*triangle*)

Assuming the same fractal dimension, the backbone fractal dimension is calculated as $x = 1.3$ (see Eq. 4). This value is inevitable with the high exponent of 3.4, since x is greater than 1.

Following Shih et al. [18], our results show that the critical strain is a function of inter-floc links, and the plateau modulus is the result of the behavior of the floc itself. This indicates that the inter-floc links are weaker, but more rigid and brittle, than the bonds inside the flocs, which are known as the intra-floc links. Shih's scaling theory only considers the hard sphere system as a function of floc size, which depends only on particle concentration. To compare our data with their model, we hypothesized that the flocs have stronger internal bonds and behave like deformable spheres. The viscoelastic responses of our samples support this hypothesis. These properties are not easily found in hard sphere suspension systems, but are very close to those of soft glassy materials [22, 23, 24].

Steady shear measurement

The dependence of steady shear viscosity η of MP inks on shear rate γ and volume fraction ϕ is shown in Fig. 4. The Newtonian plateau region does not exist in our experimental range and shear thinning behavior was found in the entire shear rate range, which suggests a continuous structure change. The power law index in Fig. 4 can be obtained by the simple relationship

$$\eta \propto \dot{\gamma}^{1-n} . \qquad (7)$$

Note that Silbert et al. [27] simulated the flow behavior of colloidal gels and obtained a shear thinning exponent (1-n) of 0.84, which is identical to our measured exponent.

Strong shear thinning can be explained by solving an anomalous diffusion equation for the fractal structure of the complex system [28]. The dynamic or complex viscosity can be obtained as:

$$\eta * (\omega) = \eta'(\omega) - i\eta''(\omega) \propto (1 - i)\omega^{-\alpha}, \qquad (8)$$

where $\eta'(\omega)$ and $\eta''(\omega)$ are defined by G''/ω andG'/ω, respectively. The shear thinning exponent can be introduced by $\alpha = d/2$. In their study on magnetic particle suspensions, Chae et al. [9] found the shear thinning exponent for steady shear viscosity as a function of shear rate should correspond to that of dynamic viscosity as a function of frequency. We found the fractal dimension is 1.68 from our shear thinning exponent. This value is close to the fractal dimension 1.74 obtained from the relationship between the elastic constant and the volume fraction (Eq. 4). According to the analysis of the shear thinning exponent at low shear rates, the microstructure of magnetic ink in equilibrium can be related to the change of microstructure during shear flow.

Yielding behavior is indicated in Fig. 5, which demonstrates the relationship between shear viscosity and shear stress for three different particle volume fractions. To avoid collecting transient values for each measurement, we set a minimum criterion in our rheometer. Also

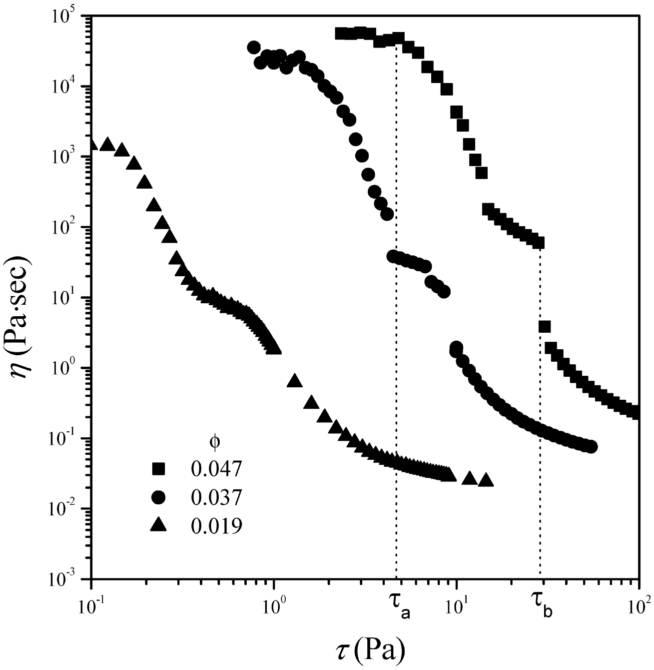

Fig. 5 Viscosity of MP inks as a function of shear stress at different volume fractions: $\phi = 0.047$ (*square*), 0.037 (*circle*), and 0.019 (*triangle*). The yielding behaviors are found at τ_a and τ_b

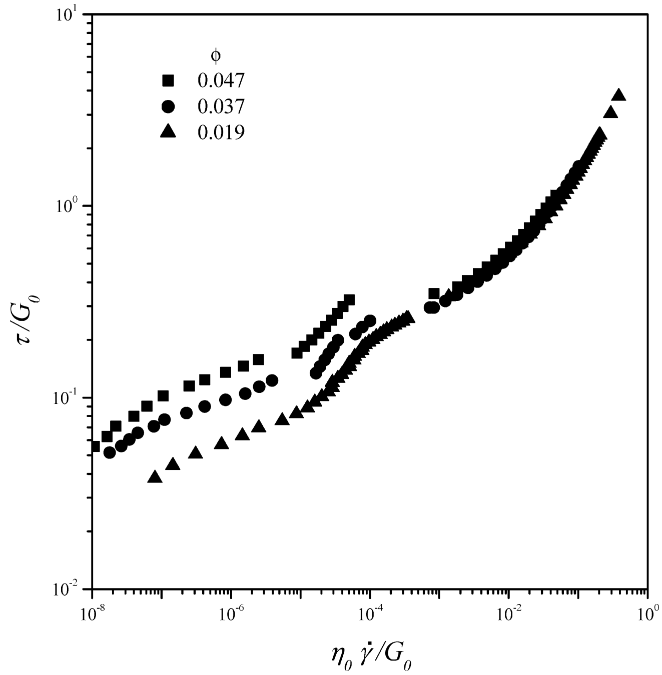

Fig. 6 Dependence of scaled shear stress with G_0 on the scaled shear rate with the elastic constant and viscosity for MP inks at different volume fractions: $\phi = 0.047$ (*square*), 0.037 (*circle*), and 0.019 (*triangle*)

in that criterion, we confirmed the shear viscosity reaches a steady state value. This type of yielding behavior has been previously reported [5, 27] and implies an abrupt change in the flow mechanism and a rupture of structure connectivity. The yielding behavior was not pronounced for $\phi = 0.007$. We actually found two critical stresses, denoted as τ_a and τ_b, in our experimental range, indicating that the structure formation in MP inks has two different mechanisms as the shear develops. Before the first yielding, τ_a, shear thinning is not significant and the stress exhibits a plateau value. It is believed that in this regime, the magnetic particles and the network structure are continuously broken and rearranged, thus providing an equilibrium state under steady shear.

A scaling of the shear stress (τ) with G_0 and the shear rate with G_0/η_0, which is the ratio of the plateau modulus of a colloidal suspension to the continuous phase viscosity, is shown in Fig. 6. G_0 is considered to be strongly dependent on the inter-particle interactions and particle volume fraction. To remove explicit effects of the interaction and/or particle volume fraction on shear stress as a function of shear rate, we plotted the normalized shear stress vs. $\eta_0\gamma/G$. η_0/G_0 is a characteristic relaxation time of a particle in a suspension [29, 30]. This scaling enables us to examine the microstructure in shear flow [29, 30]. Here, it suggests that flow properties should correlate with one another when τ/G_0 is plotted as a function of $\eta_0\gamma/G_0$. Figure 6 reveals that the model agrees with our data at high shear rate. However, the scaling at low shear rate does not collapse into a single curve. Since the assumption in this scaling is that the yielding is related to the dislocation of particles related to linear elastic models, the failure of the collapsing at low shear rate is an indication of the existence of significantly large clusters. Chow et al. [29] and Fagan et al. [30] also found that this scaling does not collapse beyond the shear thickening point, where large aggregates are formed. As $\eta_0\gamma/G_0$ becomes higher than 10^{-3} (the corresponding shear rate is a second yielding point, τ_b) all curves, except $\phi = 0.007$, coincide. This implies that after a second yielding point, flow behavior does not depend on the particle volume fraction or floc size, but does depend on the plateau modulus of each floc or structure breakage. Since the G_0 represents the elasticity of intra-floc links, the result shows that the individual floc structure is dominant after a second yielding. This indicates that the second yielding is responsible for breaking the inter-floc links and rupturing the floc into smaller ones, which is consistent with the above explanation. Similar behavior was also shown by Wessel et al. [4], who studied the effects of shear rate on the fractal structure of flocculated emulsion drops, showing that the size of the flocs usually decreases with an increase in the shear stress, and that the flocs often split into primary particles at high shear rates. Further, van Marle et al. [31] showed that the breakup mechanisms of yogurts depended on the type of structures in shear flow.

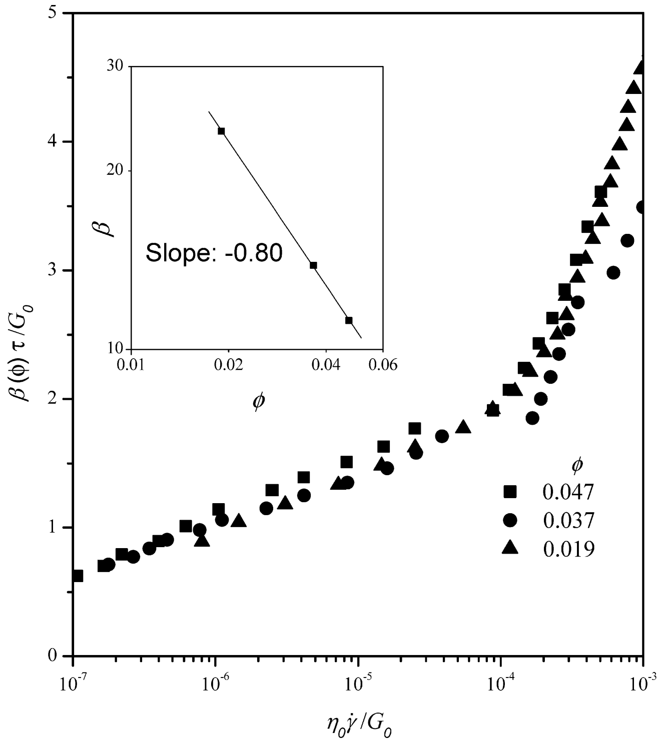

Fig. 7 Scaling curve for shear stress and shear rate for MP inks. The curves shift with β from the data in Fig. 6. We only examined the data before the second yielding point

Before the second yielding, the curves in Fig. 6 show a slight divergence. This implies that the modulus of the floc, which is represented by G_0, is not the only contribution before the second yielding. Since the scaling τ/G_0 is expected to be a weak function of concentration and particle interactions [30], we propose a role for another type of interaction before the second yielding. In Fig. 7, we attempt a superposition of the curves before the second yielding point using the data in Fig. 6 by shifting the vertical axis with the vertical shift factor, $\beta(\phi)$. The inset of Fig. 7 shows that the value of β relates to the volume fraction, i.e., $\beta \propto \phi^{-0.80}$. This relationship can be described from Eq. 6 as $\beta \propto 1/G_{0\text{-}int} \propto \phi^{-0.80}$, where $G_{0\text{-}int}$ is the plateau modulus of the inter-floc as described in Eq. 6. This implies that the other structure contributions prior to the second yielding can be the result of inter-floc links. This indicates that the interaction between flocs remains significant before the rupture of the flocs. The equilibrium structure cannot persist at a high shear rate. However, the long-range magnetic interaction between flocs is still significant and affects the inter-floc structure. This long-range interaction depends on the floc size and therefore, the particle volume fraction and was described by the modulus of inter-floc links in the weak-link regime. In this shear rate range, shear thinning occurs as shown in Fig. 4 due to the deformation of flocs.

From these results, we propose the following mechanisms of the structural change in MP inks with shear rate:

i) The network structure is continuously rearranged at very low shear rates or shear stress regions.
ii) As the shear rate increases, the equilibrium structure is broken, but the long-range interactions maintain the inter-floc structure. In this regime, the flocs can deform or rotate causing shear thinning behavior.
iii) At a high shear rate, the long-range interactions are insufficient to maintain flocs, as explained by Figs. 6 and 7. The floc is broken into smaller ones with increasing shear rate (i.e., shear thinning behavior).

Conclusion

We have shown that the magnetic inks have a network structure formed by the magnetic particles. The nature of this network structure was examined via scaling laws. From the viscoelastic experiments we proposed a floc structure. The inter-floc interaction and intra-floc interactions were examined in terms of linear viscoelastic and flow properties. From the scaling behavior, we showed that the floc is deformable and the non-linearity is due to the breakage of inter-floc structures. This model was consistently explained by the steady shear experiment. We showed that both yielding behaviors in steady shear data are due to different breakage mechanisms. We found that each yielding corresponded to the breaking of inter-floc links and the intra-floc interactions, respectively. The shear thinning behavior was successfully explained by these structural changes.

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