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Dual Rheological Responses in Ag Pastes

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ABSTRACT: Highly concentrated suspensions have complex structures that complicate their characterization and study. Highly concentrated suspensions of Ag particles in ethyl cellulose solutions (Ag pastes) were thus studied and dual rheological responses were observed. Under rotational shear, the unpredicted enhancement of shear moduli occurred in the low frequency regime, showing that rheological responses of Ag pastes were strongly influenced by fillers. Under large-amplitude oscillation, the hydrodynamic-induced enhancement effect was observed over the whole frequency range, showing that rheological responses of Ag pastes were dominated by the binder solutions. Further studies showed that this dual behavior arose from the dual nature of structures in Ag pastes. The different shear types promoted the development of different structures in rheological experiments. Rotational shear promoted cluster formation, resulting in the unpredicted enhancement; while large-amplitude oscillation broke the clustering, leading to the hydrodynamic enhancement. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1328–1333, 2013

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INTRODUCTION

Ag pastes are high loading suspensions of Ag particles in polymer binder solution; where the Ag particles offer electrical conductivity and the polymer binder affords processability. As a conductive adhesive, Ag pastes are widely used in the electronics industry.[1] Recently, Ag pastes have received much research attention due to their potential applicability in printed circuits and solar cells.[2,3] Economic and environmental considerations are driving the development of more efficient printing techniques (e.g., screen printing and roll printing), which provide directly written complex and fine patterns on substrates.[4] Such processes are required to produce fine lines of high aspect ratio, something that strongly depends on the shear-thinning characteristics of the Ag paste.[5] Other rheological properties, such as viscosity and modulus, also have significant influences on the printing behaviors of Ag pastes. Rheological investigations of Ag pastes are therefore necessary. Previous investigations have focused on determining optimal formulations through monitoring various rheological properties, but there is insufficient physical insight into the rheological behavior of Ag pastes.[1]

The rheological behaviors of simple, dilute suspensions, and a few typical concentrated suspension models are relatively well understood physically.[6,7] However, highly concentrated suspensions, such as Ag pastes, have received less attention due to their complex structures and behaviors.[8] Generally, various elements of various sizes (such as bubbles, droplets, clay particles, polymer, sand, and metal particles) are closely packed in highly concentrated paste suspensions. Consequently, they form complex interactions and structures that make structural characterization difficult. Various complex flow phenomena occur in such highly concentrated suspensions, such as aging, yielding, shear banding, and avalanching.[8,9] However, understanding these behaviors is not enough—the complex structures also contribute to the lack of understanding of these materials.

Previous studies of highly concentrated suspensions have shown that only two common qualitative characteristics may be easily distinguished:[8,10] disorder and crowding. No specific arrangements can be present in most pastes, and consequently they can be arbitrarily deformed without loss of mechanical properties. Although, neighboring elements may interact significantly because of the high loading, leading to solid behavior. Therefore, any attempt to link structural changes to bulk rheology becomes difficult; in both experimental and computer characterizations.[9,10] This work is a rheological study of Ag pastes. Rheology is the study of matter's flow and deformation: primarily in the liquid state, but also in "soft solids" under conditions that allow plastic flow. Although it observes bulk phenomena, rheological parameters are the manifestation of microscopic variables.[11] Therefore, rheological study can efficiently provide

Table I. EC Binder Solutions and Ag Pastes

Sample	EC (wt %)	BCA (wt %)	Ag particles (wt %)
EC15	15.0	85.0	
EC20	20.0	80.0	
PA15	2.4	13.6	84.0
PA20	3.2	12.8	84.0

information of the complex structures of highly concentrated suspensions, such as Ag pastes. This work reports the rheological behaviors of Ag pastes and compares then with corresponding ethyl cellulose (EC) solutions. Unlike simple EC solutions, Ag pastes showed dual rheological responses. This dual response was found to arise from variations of the paste's structure.

EXPERIMENTAL

Materials and Methods

EC ($M_w = 159{,}900$, PDI = 9.6, $\rho = 1130$ kg/m^3) was purchased from Dow Chemical. 2-(2-Butoxyethoxy)ethyl acetate (BCA, $\rho = 977$kg/m^3) and Ag powder ($\rho = 10{,}530$ kg/m^3)of average size 3.5 μm were provided by Samchun Pure Chemical and Chang Sung Corporation, Korea, respectively. Other solvents and reagents were purchased from Sigma-Aldrich and used without further purification. The pastes' morphologies were investigated by a Hitachi S-4800 field emission scanning electron microscope at 10 kV acceleration voltage.

Formulation of Ag Pastes

Binder solutions were prepared by dissolving EC in BCA. This was facilitated by heating and stirring. Ag pastes were prepared by mixing Ag particles with EC/BCA solutions for 0.5 h using a three-roll mill. Table I summarizes the formulations of EC binder solutions and Ag pastes.

Rheological Measurements

Rheological tests were performed on a Physica MCR 301 rheometer (Anton Paar Germany GmbH) equipped with 25 mm diameter parallel plates set 0.3 mm apart at 25°C. Strain amplitude sweeps were conducted at an angular frequency of 10 rad/s in the overall amplitude range of 0.1–100%, which determined the linear viscoelastic ranges of materials. Results showed that the linear viscoelastic response occurred at strains of <10% for EC binder solutions (<1% for Ag pastes). Dynamic frequency sweeps were undertaken at fixed amplitude of 0.5% for EC binder solutions (0.3% for Ag pastes). Shear-dependent behaviors of Ag pastes were studied, which involved measuring time-dependent changes of the shear moduli in oscillatory and rotational shear modes, respectively. In step I, small oscillations were applied to obtain the shear moduli of the initial state. Here, the time sweep for 100 s was taken at an angular frequency of 10 rad/s and fixed amplitude of 0.3%. In step II, high shear was applied to break the initial state. Here, the rotational shear was used in the rotational shear mode, and the large amplitude oscillation (the strain amplitude was 100%) was applied in the oscillatory shear mode. Then, the progression of G' and G'' with small oscillations was monitored in step III, where the applied perturbation (the strain amplitude was 0.3%) was in the linear response range and hence the microstructure's recovery to its original was not influenced by the perturbations. All samples were aged for ca. 24 h before tests. The samples were kept at rest for 15 min before measurements to reduce the influences of the mechanical treatment associated with the deposition of the samples into the rheometer.

RESULTS AND DISCUSSION

Frequency-Dependent Behaviors

Dynamic frequency sweeps in the Ag pastes and corresponding EC solutions were undertaken [Figure 1(a)]. Compared to the EC solutions, a marked increase of G' and G'' was observed in Ag pastes over the indicated frequency range. For these sweeps, the Reynolds number ($\mathrm{Re}_{\dot{\gamma}} \approx 10^{-15} \sim 10^{-11} <<1$) was very small and the Peclet number ($Pe_{\dot{\gamma}} \approx 10^{2} \sim 10^{6} >>1$) was quite large, implying that the moduli and viscosity of suspensions mainly depend on filler loading.[12,13] Note that the Pe $\rightarrow \infty$ limit implies strong shear flow where colloidal particles experience hydrodynamic interactions with each other by generating

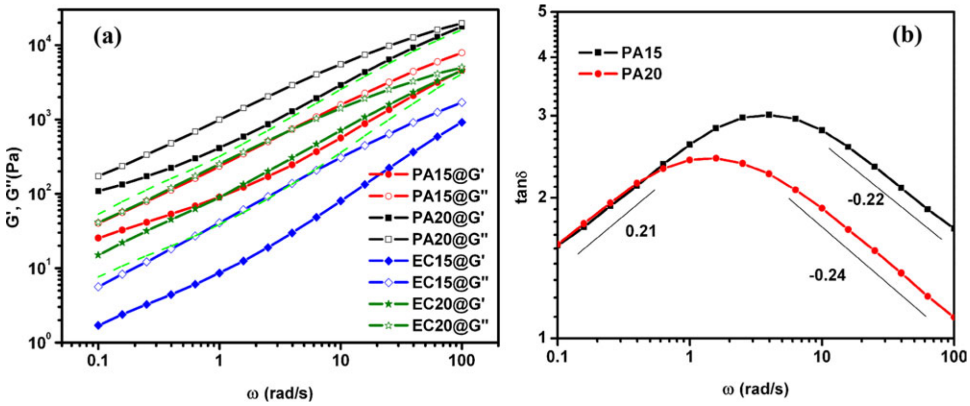

Figure 1. Frequency dependence of shear moduli (G' and G'', a), and loss tangent (tan δ, b) of Ag pastes and corresponding EC solutions obtained in the linear viscoelastic regime. The dashed lines in panel (a) were obtained based on eq. (1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Enhancements of Shear Moduli in Ag Pastes After Different Treatments

	(G''/G_0'')@100 rad/s		(G'/G_0')@0.1 rad/s	
	Experimental	Prediction	Experimental	Prediction
Pristine PA15	5.02	3.53	15.0	3.53
Sheared PA15	5.15	3.53	48.2	3.53
Oscillated PA15	3.09	3.53	4.04	3.53
Pristine PA20	3.77	3.56	7.2	3.56
Sheared PA20	4.06	3.56	15.8	3.56
Oscillated PA20	2.54	3.56	2.84	3.56

and reacting to a fluid's local velocity. Hence, the enhancement effect was tested using the following equation:[14,15]

$$G^* \equiv G_0^*(1-\phi/\phi_m)^{-2.5\phi_m} \tag{1}$$

where G^* and G_0^* are the moduli of the dispersions and the matrix, ϕ, volume fraction of filler, and ϕ_m, is the critical packing fraction, 0.58.[10] It is derived from the strong hydrodynamic effect in high-concentration suspensions.[11] This equation has been applied to analyze particulate-filled rubber's response to shear/tensile deformation.[14,15] As shown in Figure 1(a), predictions are in good agreement with experiments in the high (> ca. 10 rad/s) frequency regime while they are much lower than experiments in the low (< ca. 1 rad/s) frequency regime (Table II lists data from the mechanical enhancement). Such consistency in the high frequency regime indicates that enhancement was the result of the hydrodynamic effect in this region. In the low frequency, however, another factor was present in addition to the simple hydrodynamic effect, which caused the unpredicted enhancement. Moreover, the loss peaks were observed for PA15 and PA20 in the frequency range of interest [Figure 1(b)]. Two different relaxation regions can thus be distinguished between 0.1 and 100 rad/s: one low (< ca. 1 rad/s) and one high (> ca. 10 rad/s) frequency regime. As above suggested, different enhancement effects occurred in the two relaxation regions.

Shear-Dependent Behaviors

The temporal evolution of various properties (viscosity, moduli, etc.) after the cessation of shear allows the evaluation of pastes' printing behaviors. More importantly, they can establish the structures of pastes as well as their structural changes.[16] Figure 2 shows the temporal evolutions of G' and G'' in the Ag pastes and corresponding EC solutions under rotational and oscillatory shear modes, respectively.

At low shear rates (e.g., 1–10 s^{-1}), PA20 [Figure 2(a)] and EC20 [Figure 2(b)] can regain their initial moduli, suggesting little structural change. At high shear rates (e.g., 100–1000 s^{-1}), PA20 and EC20 cannot regain their initial moduli, indicative of structural changes. An opposite trend was observed after the structural changes: PA20 had higher moduli while EC20 had reduced G' and G''. Similar was observed in PA15 and EC15, although they showed smaller changes. The decrease of moduli in EC20 was likely the result of the partial breakup of the microstructure, and the increase of G' and G'' in PA20 should be ascribable to hydrodynamic clustering. Hydrodynamic clustering involves a shear-induced flocculation of particles, which increases viscosity with increasing shear stress as the dynamical clusters become larger.[17,18] Under rotational shear [Figure 2(a)], G' and G'' often increased and then decreased with time during recovery (except when $\dot{\gamma} = 1000\ s^{-1}$ and $t = 3\,s$). This suggests a shear-induced reversible flocculation. As aforementioned, the samples were not able to return to their prior states before the high rate shear, indicative of irreversible flocculation.

In Figure 2(c), the EC solutions showed trivial changes after large-amplitude oscillation, especially EC 15. However, marked and irreversible decreases of G' and G'' occurred in PA15 and PA20 when large-amplitude oscillation was applied. In a particulate-reinforced elastomer/rubber, such an irreversible decrease is referred to as the Mullins effect,[19] where an instantaneous and irreversible stress softening occurs whenever the load increases beyond its prior maximum value. This effect is

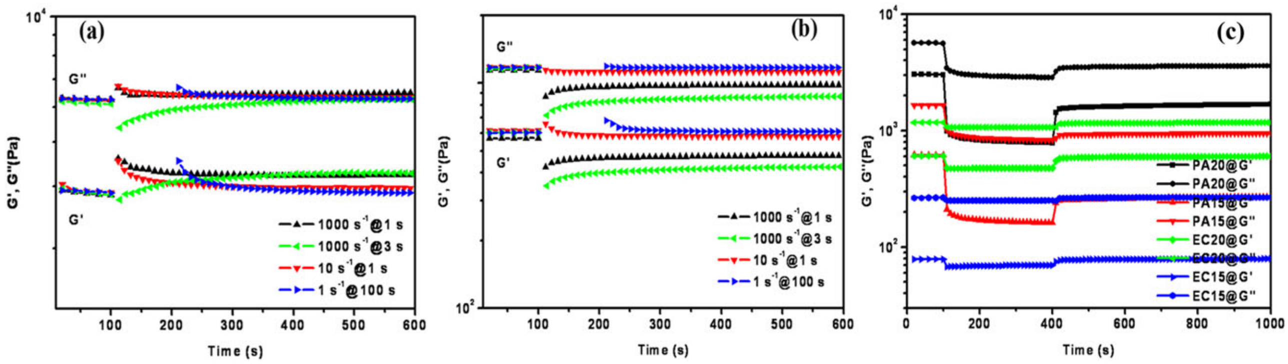

Figure 2. The shear moduli (G' and G'') *versus* time curves for Ag pastes and corresponding EC solutions. PA20 (a) and EC20 (b) were tested using a rotational shear mode. The shear rate and shear time are labeled. Panel (c) used an oscillatory shear mode. The strain amplitude and oscillation time were 100% and 300 s in step II, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

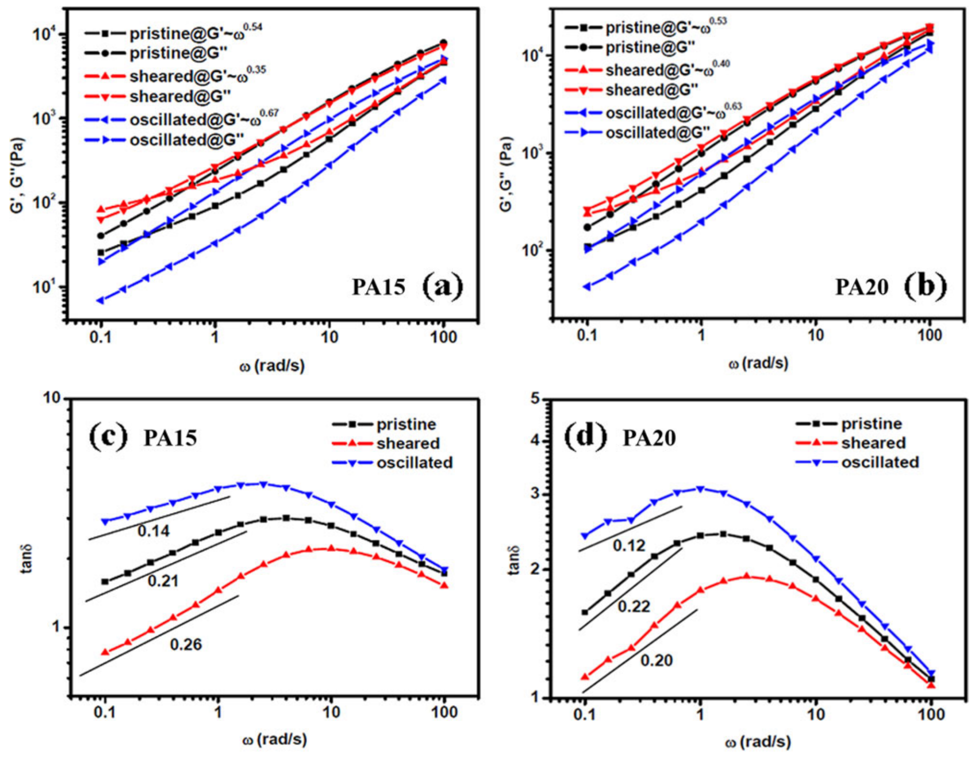

Figure 3. Frequency dependence of the shear moduli (G' and G'', a and b), and loss tangent (tan δ, c and d) in the pristine, sheared, and oscillated Ag pastes. The sheared and oscillated samples are from the recovery experiments of Figure 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

attributable to the breaking of filler clusters or filler-matrix decoupling.[19] Results from large-amplitude oscillations thus suggest the breakup of Ag particle-EC coupling or filler clusters.

Dynamic measurements were undertaken after the sheared and oscillated samples were rested for 60 min. The “steady” state was thought to be reached after 60 min, since their moduli nearly reached a plateau in the above experiments. Figure 3 shows the results of the frequency sweeps, and Table II lists data from the mechanical enhancement. A significant change occurred in the low frequency regime [Figure 3(a,b)], as shown by the changes of tan δ [Figure 3(c,d)]. In the sheared samples, the enhancements of G' were much higher than predicted in the low frequency regime (Table II). As above suggested, the unpredicted enhancement should arise from hydrodynamic clustering. Rotational shear appeared to promote the formation of clusters. In the oscillated samples, the enhancements of G' and G'' became weaker in the low and high frequency regimes (Table II). In fact, predictions were in good agreement with experiment for the oscillated samples in the whole frequency range. This indicates that the mechanical enhancements in the oscillated samples were mainly due to hydrodynamic effects. Large-amplitude oscillation broke the non-hydrodynamic interactions between particles, which was called the clustering effect.

SEM Observation

SEM specimens were prepared by carefully drying pristine, sheared and oscillated samples. As the structural change of Ag pastes is very slow at rest, structural information is likely retained sufficiently long to allow SEM observation. Figure 4 shows the surface morphologies of Ag particles in each of the three samples. The oscillated samples had very rough and clean surfaces of Ag particles, suggesting that EC was barely adsorbed. In the pristine and sheared samples, the surfaces of Ag particles appeared dim, with EC films observed between the particles, suggesting good adsorption of EC. This implies that the large-amplitude oscillation led to desorption of EC from the Ag particles. Desorption can lead to weaker enhancements,[20] in agreement with the rheological results. Desorption of EC also suggests the breakup of particle clusters. Whether the intense rotational shear improved the adsorption of EC on Ag particles is not clearly known based on the SEM images. However, the adsorption of EC on Ag particles promoted hydrodynamic clustering (adsorption allowed EC to act as an adhesive holding particles together) when the intense rotational shear was applied, resulting in stronger enhancements of the shear moduli.

Rheophysics of Pastes

Pastes are generally classifiable, by the interactions between the elements,[8–10] into colloidal and granular pastes. In colloidal pastes, colloidal particles (typically between 1 nm and 1 μm) interact at distance via van der Waals attractions and electrostatic repulsion, known as “soft” interactions. Therefore, leaving aside the hydrodynamic interactions during flow or deformation, the soft interactions determine the behavior of colloidal pastes. In granular pastes, interactions between non-colloidal particles (>1 μm) strongly differ from those between colloidal

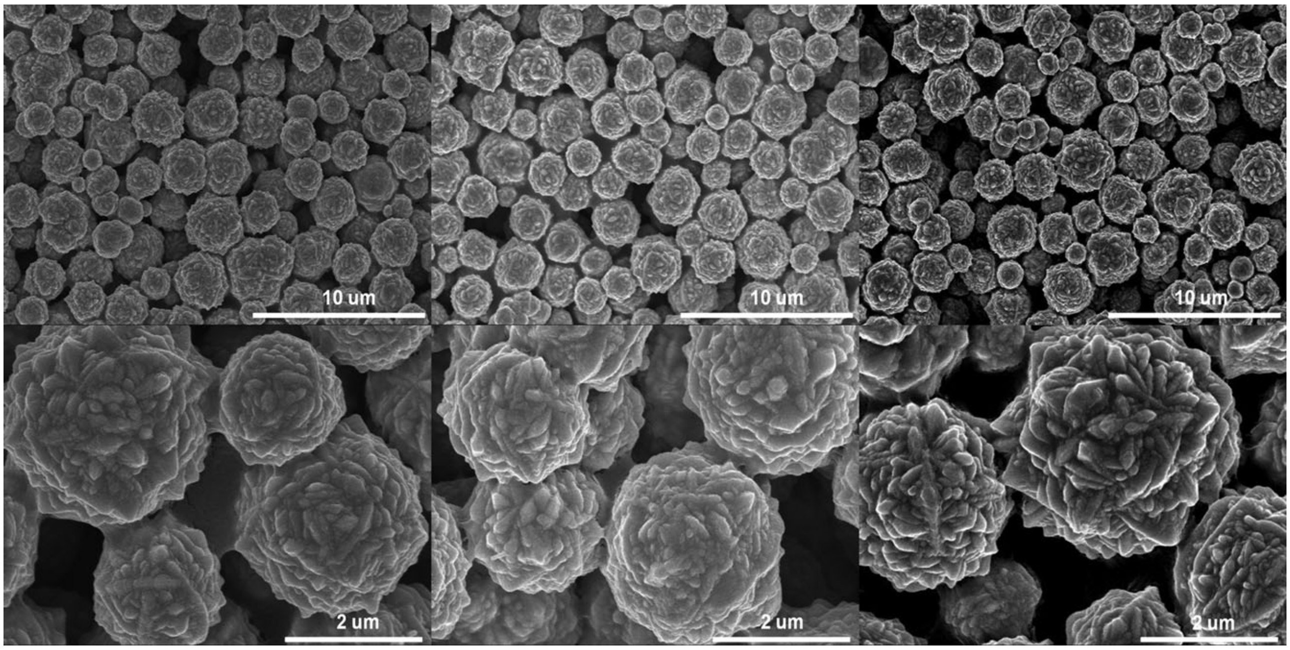

Figure 4. SEM images of pristine (left), sheared (middle) and oscillated (right) PA20.

particles. At rest, their interactions at distance are negligible, but when they are in contact, the normal force between them can increase greatly; therefore it is known as "hard" interaction. The Ag pastes studied here were granular pastes.

In the Ag pastes, the volume fraction of Ag particles was ca. 34%—far from the critical volume fraction, $\phi_c = 0.5–0.58$, suggested by experimental and numerical results about uniform spheres.[10,21] When the packing fraction is close to or above ϕ_c, complex interactions between particles, including friction, lubrication and collisions, dominate the flow behavior of granular pastes.[8–10] Otherwise, only the hydrodynamic effect is present, and consequently the rheological behavior of the pastes should be governed by their binder solutions.[8–10] The rheological behaviors of the Ag pastes studied here showed many attributes of EC solutions, especially for the oscillated pastes. However, differences in the rheological behaviors were also observed, especially for the sheared pastes. Hence, dual responses occurred in this paste system.

The differences in paste behavior should intuitively depend on the particle–particle interactions induced by flow when the different shear types are applied. In concentrated suspensions, flow, especially fast flow, often causes friction and lubrication between filling particles.[10,22] At higher shear rates, hydrodynamic forces become larger than the Brownian force (here $\mathrm{Re}_{\dot\gamma} \approx 10^{-7} \sim 10^{-6} << 1$, and $Pe_{\dot\gamma} \approx 10^{10} \sim 10^{11} >> 1$). So, when the particles are driven close together by rotational shear, lubrication hydrodynamics strongly couple the particles' relative motion.[23] Consequently, particle clusters or strings form. Hence, rotational shear led to cluster formation. However, large-amplitude oscillation likely provided additional energy to separate contacting particles, since oscillation is a back and forth movement (during a cycle, oscillation possibly produced near zero effect on the many-particle configuration[12,13]). In this way, hydrodynamic-induced clustering would be broken by oscillation. As a result, the paste behavior depended on the binder solution. In this way, the dual responses of Ag pastes can be explained. Although such dual behavior was observed after the prior structure was broken by different shear methods, the discussion suggests that this was attributable to the dual nature of the prior state, which was supported by the dynamic frequency sweeps (Figure 1).

CONCLUSIONS

The rheology of Ag pastes and corresponding EC binder solutions was studied. Dynamic frequency sweeps showed that the Ag pastes had two different relaxation regions in the frequency range of 0.1–100 rad/s. Different enhancements of the shear moduli were observed in these regions. Enhancement at high frequencies (> ca. 10 rad/s) was consistent with predictions from the hydrodynamic effect, while at low frequencies (< ca. 1 rad/s) higher than predicted enhancement was observed, due to clustering in the Ag pastes. Moreover, shear-dependent behaviors of Ag pastes were studied. Increase of moduli was found under rotational shear, due to hydrodynamic clustering; however, marked decrease of moduli was observed under oscillatory shear, due to the breakup of clusters. Further studies showed that rotational shear promoted cluster formation, causing that rheological responses of pastes were strongly influenced by fillers; while large-amplitude oscillation broke the clustering, causing that rheological responses of pastes were dominated by the binder solutions.

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