

THE NONLINEAR BEHAVIOR OF SURFACTANT-ACTIVATED ELECTORRHEOLOGICAL SUSPENSIONS

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Abstract—The nonlinear electrorheological (ER) behavior of nonionic surfactant-activated ER suspensions is investigated. The influence of three nonionic surfactants (Brij*30, GMO, and GTO) on the electrorheological (ER) response of various alumina/silicone oil suspensions shows similar behavior. The prevalent feature common to all formulations is that the yield stress, τ_0 , initially increases with surfactant concentration, passes through a maximum, then decreases with surfactant concentration. The nonlinear behavior observed at large surfactant concentrations (i.e., $\tau_0 \approx E^n$, where $n < 2$) arises from field-induced phase separation of a surfactant-rich phase as opposed to field-dependent conductivity of a homogeneous continuous phase.

Key words: Electrorheology, Surfactants, Colloid

INTRODUCTION

The electrorheological (ER) response is defined as the dramatic change in rheological properties of a suspension of small particles due to the application of a large electric field transverse to the direction of flow. ER suspensions are typically composed of nonconducting or semiconducting particles dispersed in a nonconducting continuous phase. A large ER effect was first reported by Winslow in 1949, and has been reviewed in several publications [Shulman et al., 1981; Weiss and Carlson, 1993; Deinega and Vinogradov, 1984; Block and Kelly, 1988; Gast and Zukoski, 1989; Jordan and Shaw, 1989]. The simplicity of engineering designs based on ER materials has facilitated the development of specifications for a broad range of devices, such as dampers, clutches, and adaptive structures [Shulman et al., 1981]. Although many ER devices have been brought successfully to the prototype stage, and despite much industrial activity in the U.S. and abroad, the anticipated commercialization of these devices has yet to be realized. The main limitation of ER technology development is a lack of effective fluids [Weiss and Carlson, 1993]. Most applications require fluids that possess a large field-induced yield stress, are stable to settling and irreversible aggregation, are environmentally benign, and draw limited current. Our inability to design such acceptable fluids stems largely from a lack of a fundamental understanding of the mechanisms that control ER behavior.

Surfactants are often used to promote colloidal stability, which is necessary to keep particles from irreversibly flocculating, and to control rheological properties in the absence of the electric field. Surfactants can also be used to "activate" suspensions. Enhancing ER activity with surfactants offers advantages over other approaches, such as adding water which severely limits the allowable temperature range of operation, promotes

corrosion, and increases suspension conductivity and power consumption. Furthermore, additional independent variables (i.e., type and amount of surfactants) give flexibility to designing desired properties that is not possible by simply varying the materials of the disperse and continuous phases. The influence of several nonionic surfactants on ER suspension properties was investigated. At small concentrations, surfactants increase the dynamic yield stress by increasing the particle polarizability via enhanced interfacial polarization. At large surfactant concentrations, the yield stress decreases approximately with the electric field strength [Kim, 1996].

In this paper, the underlying mechanism at large surfactant concentrations is investigated. A surfactant-rich phase is formed at large surfactant concentrations under the applied electric field. The mechanism is similar to that proposed in Ref. [Felici et al., 1994] in that the yield stress is limited by increased conductance in the interparticle gap. The mechanism proposed here differs, however, in that the increased conductance does not arise from a field-dependent continuous phase conductivity, but rather from the field-induced phase separation of a more conducting phase (the conductivity of each phase is independent of field strength). This phenomenon is likely to occur in many ER formulations that contain surfactants.

MATERIALS AND METHODS

1. Suspension Preparation

Three different types of activated alumina particles were employed: acidic, neutral, and basic (Aldrich, $\rho_p = 3970 \text{ kg/m}^3$, average pore diameter = 58 Å). The alumina particles were approximately spherical and sieved to obtain diameters in the range of 63–90 μm . Nonionic surfactants investigated were glycerol monooleate (GMO, Chemical Service), glycerol trioleate (GTO, Chemical Service), and Brij*30 [$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OH}$, Aldrich]. The particles were either used as received ("nondried" suspen-

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sions), were dried for 3 hours under vacuum (-10 psig) at 58°C ("dried" suspensions), or were dried for 4 hours under vacuum (-10 psig) at 160°C ("highly dried" suspensions).

Alumina suspensions were prepared by first adding the desired amount of surfactant to silicone oil (SF96, General Electric, $\eta_c=0.0968$ Pa·s, $\rho_c=968$ kg/m³). The particles were then added to the surfactant solution and stored in a desiccator to minimize contact with air. Suspensions were allowed to equilibrate for at least 24 hours before experiments. The silicone oil was used as received for all rheological and dielectric measurements, and stored for more than 1 week over molecular sieves (Aldrich, 4-8 mesh beads) prior to Brij*30 and water adsorption experiments. Surfactants were used as received.

2. Rheological Measurements

Rheological experiments were performed at 23°C on a Bohlin VOR rheometer fitted with parallel plates, and modified for the application of large electric fields (a schematic diagram of the modified rheometer is presented in Fig. 1). Potential differences were supplied by a function generator (Stanford Research Systems, model DS345) and amplified with a Trek amplifier (model 10/10). Experiments were conducted with an electric field frequency of 500 Hz (except for the frequency sweep experiments).

The influence of surfactants on ER activity was determined by their effect on the dynamic yield stress. Samples were placed between the parallel plates and sheared for one minute at a large shear rate (>40 s⁻¹) and zero field strength to insure a uniform particle distribution. The desired electric field was then applied for one minute with no shear prior to measurements. Rheological measurements were performed by shearing the suspensions at a constant shear rate under the applied electric field, and recording the shear stress transmitted by the suspension. Experiments were performed with decreasing and then increasing shear rates, to obtain plots of shear stress as a function of shear rate. Values for the dynamic yield stress, τ_0 , were determined by extrapolating the shear stress-shear rate data to zero shear rate, using data over the range of shear rates, 0.01 s⁻¹ $< \dot{\gamma} < 0.1$ s⁻¹.

3. Dielectric and Conductivity Measurements

Suspension capacitance and loss were measured using a Gen-

eral Radio GR 1689M RLC Digibridge, which probes frequencies in the range of 12 Hz to 100 kHz, and operates with potential differences in the range of 0.01-1.0 V (rms). A three-terminal, guarded dielectric cell was employed. Suspension dielectric constants and loss tangents were determined for decreasing and increasing field frequencies. The samples' dc conductivities were measured with a picoammeter (Keithley 4853), with blocking circuitry to allow measurements at large electric field strengths.

4. Adsorption Measurements

The adsorption isotherm of Brij*30 on neutral alumina particles in SF96 was obtained spectrophotometrically using the difference method (using a Beckman DU Series 60 Spectrophotometer). A characteristic adsorption peak for Brij*30 was found at a wavelength of 276 nm. 5 wt% dried neutral alumina suspensions with various Brij*30 concentrations were sealed and equilibrated for 24 hours. Suspensions were then put in test tubes and centrifuged at 1550 rpm for 30 minutes. UV spectra of the supernatants were obtained, and the adsorbed amount determined by difference.

RESULTS

1. Rheological Data

The dependence of the dynamic yield stress on Brij*30, GMO, and GTO concentration is presented in Fig. 2 for 20 wt % dried neutral alumina suspensions. For all cases, the yield stress initially increases with surfactant concentration and then passes through a maximum; the surfactant concentration at the maximum is insensitive to the applied electric field strength, E , especially at large field strengths, but does depend on the surfactant type. It was also observed that, at low surfactant concentrations, the RE response depends on water and ion content,

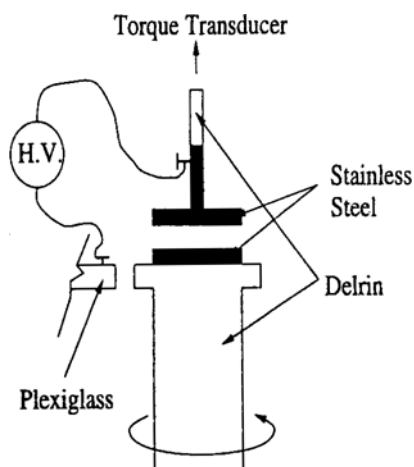


Fig. 1. Schematic diagram of the rheometer modified for the application of large electric fields.

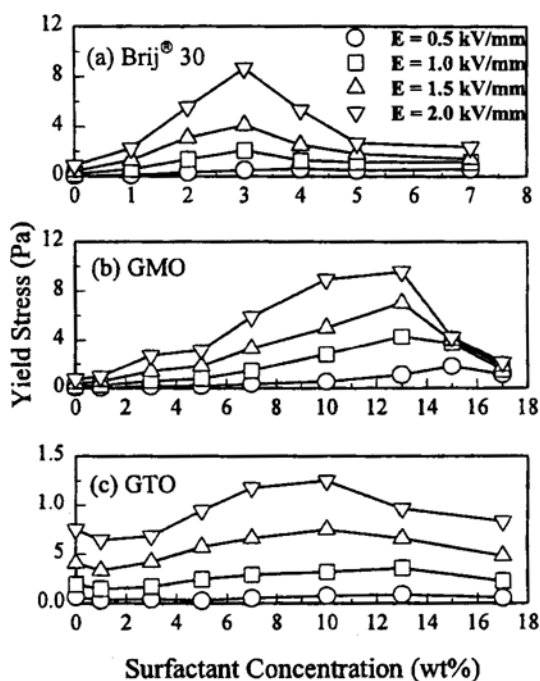


Fig. 2. Yield stress as a function of surfactant concentration for 20 wt% dried neutral alumina suspensions in silicone oil ($f_c=500$ Hz). (a) Brij*30, (b) GMO, and (c) GTO.

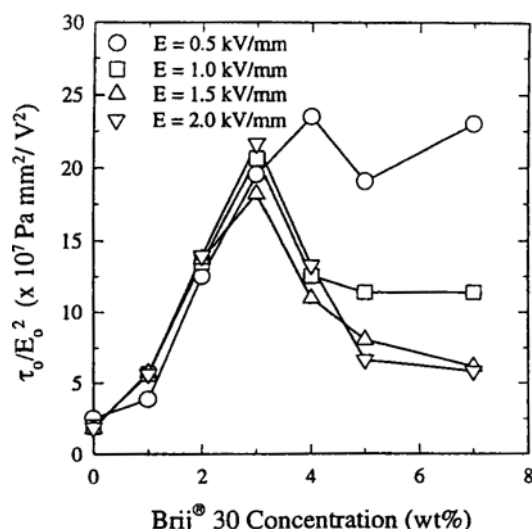


Fig. 3. Yield stress divided by the electric field strength squared as a function of Brij*30 concentration for 20 wt% dried neutral alumina suspensions in silicone oil ($f_e=500$ Hz).

electric field frequency, particle surface area [Kim, 1996].

A typical dependence of the yield stress on the electric field strength is depicted in Fig. 3. Here, the yield stress divided by the field strength squared is plotted against Brij*30 concentration ($f_e=500$ Hz). At small Brij*30 concentrations, the curves at different electric field strengths superpose and the yield stress scales with E^2 (linear polarization region). The ER response in the linear region arises from the enhanced interfacial polarization [Kim, 1996]. However, for Brij*30 concentrations >3 wt%, the yield stress deviates from the E^2 dependence, increasing approximately linearly with field strength (nonlinear polarization region).

2. Surfactant Adsorption

The Brij*30 adsorption isotherm for the dried neutral alumina particles in dried SF96 (23°C) is presented in Fig. 4. Brij*30 adsorption increases with surfactant concentration and reaches a plateau at large concentrations. Assuming that the adsorbate area is 46 \AA^2 (reported for adsorption at the air-water interface [Rosen, 1989]), monolayer coverage corresponds to approximately $3.5 \times 10^{-6} \text{ gmole/m}^2$. The pore volume of the neutral alumina particles is approximately $0.225 \text{ cm}^3/\text{g}$; the amount of Brij*30 ($\rho_{\text{surf}}=0.95 \text{ g/cm}^3$, $\text{MW}=362.56$) required to fill the pores is approximately $3.8 \times 10^{-6} \text{ gmole/m}^2$. Comparison with Fig. 4 clearly indicates that Brij*30 forms aggregates or multilayers on the particle surface at large concentrations (≥ 3 wt% Brij*30). Aggregate formation may arise from dipole-dipole and/or hydrogen bonding interactions between the hydroxyl groups [Zhu and Gu, 1991]. However, whether adsorption within the pores is monolayer or multilayer is uncertain.

DISCUSSION

At large surfactant concentrations, above the maximum in the yield stress (Fig. 3), the yield stress scales as E^n where $n \approx 1$, a feature that is not captured by enhanced linear interfacial polarization. Possible explanations for the nonlinear ER behavior are (1) nonuniform electric fields and (2) field-dependent

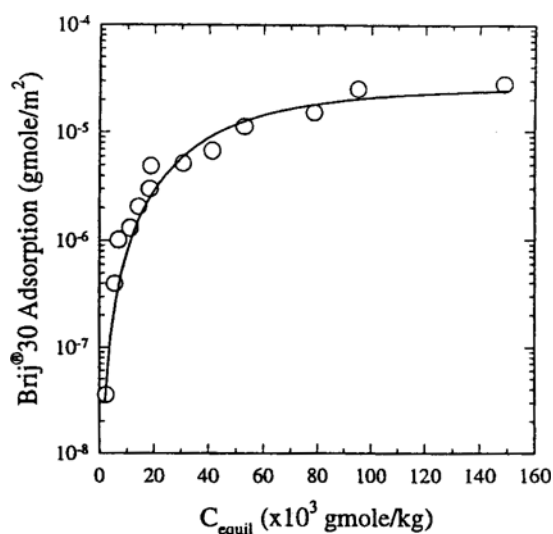


Fig. 4. Brij*30 adsorption isotherm on dried neutral alumina particles in SF96 (C_{equil} is the equilibrium surfactant concentration in the continuous phase).

dielectric properties.

For suspensions with zero conductivity, the electrostatic potential averaged over a volume containing many particles (but small relative to the electrode gap dimensions) will decrease linearly from the high to low potential electrodes. As the suspension conductivity increases, as observed at large surfactant concentrations, space charge layers may build up near the electrodes, screening the electric field near the center of the electrode gap. Within the framework of the electrostatic polarization model, the decreased electric field strength would lead to a decreased yield stress, and an apparent field strength scaling less than quadratic. However, it was found that the electric field across the ER suspensions, even at high surfactant concentrations, is uniform above an electric field frequency of 100 Hz [Kim, 1996], indicating that the effect of electrode polarization on the ER response is negligible at 500 Hz.

The nonlinear ER behavior does not arise from dramatic changes in the suspension dielectric properties with surfactant concentration at small electric fields. Dielectric properties (ϵ' , ϵ'') of neutral alumina suspensions increase smoothly with surfactant concentration, showing no abnormal behavior [Kim, 1996]. This result suggests that the enhanced interfacial polarization should provide enhanced stress transfer even at large surfactant concentrations, if there are no other impeding phenomena.

Indeed, nonlinear behavior is only observed at small shear rates. Fig. 5 shows the shear stress as a function of shear rate for 20 wt% dried neutral alumina suspensions with varying Brij*30 concentrations. At large shear rates, the shear stress at large surfactant concentrations is larger than at smaller surfactant concentrations. Here, the shear stress is proportional to E^2 , indicating that polarization is linear and that the increased stress transfer with increasing surfactant concentration arises from enhanced interfacial polarization. However, at small shear rates, the shear stress at large surfactant concentrations (>3 wt% Brij*30) decreases below that for suspensions with smaller sur-

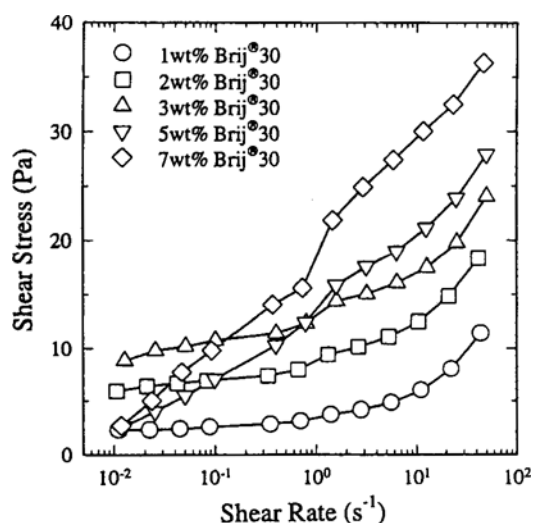


Fig. 5. Shear stress as a function of shear rate for 20 wt% dried neutral alumina suspensions with varying Brij®30 concentrations ($E=2.0$ kV/mm and $f_e=500$ Hz).

factant concentrations. Here, the response is nonlinear at large surfactant concentrations.

Small and large shear rates differ primarily in the state of aggregation. At sufficiently large shear rates, particles are well-dispersed and hydrodynamic forces degrade large aggregates. At small shear rates, particles form large columnar aggregates due to the strong electrostatic polarization interactions. Within the aggregates, particles remain in close contact. The electric field strength in an interparticle gap can be much larger than the nominal field strength. These features suggest that the mechanism producing nonlinear ER behavior arises from the large electric fields between closely-spaced particles.

A promising explanation for nonlinear ER behavior is nonlinear, nonhomogeneous conduction. Conductivities of many fluids may increase at field strengths comparable to those expected between particles in ER fluids due to field-enhanced dissociation of electrolytes [Brosseau, 1991; Felici, 1985]. Felici et al. [1994] have shown that increased conductivity due to field-enhanced dissociation in the fluid between conducting particles under dc electric fields can lead to electrostatic interactions and yield stresses that increase slower than E^2 .

However, this model assumes that the continuous phase is homogeneous. In contrast, we have found that under large electric fields, surfactants in solution can phase separate, forming a surfactant-rich phase which appears in the interparticle gap. As discussed below, this leads to nonlinear conduction only on a macroscopic scale—conduction within each phase appears to be independent of field strength. Thus the mechanism for nonlinear ER behavior, with yield stresses increasing slower than E^2 , arises from a different mechanism than that proposed in Refs. [Felici et al., 1994].

1. Field-Induced Formation of a Surfactant-Rich Phase

The formation of the surfactant-rich phase between fixed glass beads under ac electric fields was also observed. Two glass beads (420 μm diameter) were glued to a microscopic slide at a separation of ≈ 12 μm , and between electrodes separated by 8 mm. The glass beads are non-porous and hence most sur-

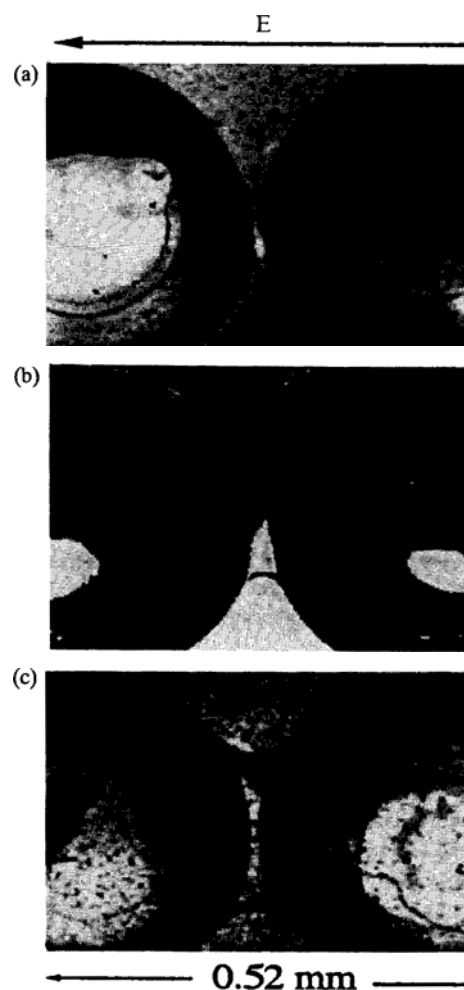


Fig. 6. Surfactant structure formation between two glass beads in surfactant solutions under an applied electric field of 513 V/mm ($f_e=500$ Hz); (a) 1 wt%, (b) 3 wt%, and (c) 7 wt% Brij®30.

factants are initially in the continuous phase. A nominal electric field strength of 513 V/mm ($f_e=500$ Hz) was applied for different Brij®30 concentrations and video images were acquired. Representative images are presented in Fig. 6 for the beads immersed in solutions of 1 wt%, 3 wt%, and 7 wt% Brij®30. Without the applied electric field, all solutions are homogeneous. Upon applying the electric field, the solutions phase-separate and droplets move to the glass bead surfaces. The droplets move along the surface, accumulate in the interparticle gap, and form a surfactant-rich "bridge" between the particles. The volume of the surfactant-rich bridge increases with surfactant concentration.

Video images of surfactant bridge formation in 1 wt% Brij®30 solutions under the various electric field strengths are also presented in Fig. 7. Without an electric field and up to a certain field strength, bridges do not form [Fig. 7(a)]. Above a critical field strength ($190 < E_c < 250$ V/mm), surfactant-rich droplets accumulate on the particles and migrate to form a bridge between the glass beads. The bridge grows with increasing electric field strength [Fig. 7(b) and (c)].

Bridge formation between small alumina particles (63-90 μm diameters) is difficult to image. However, evidence of bridges

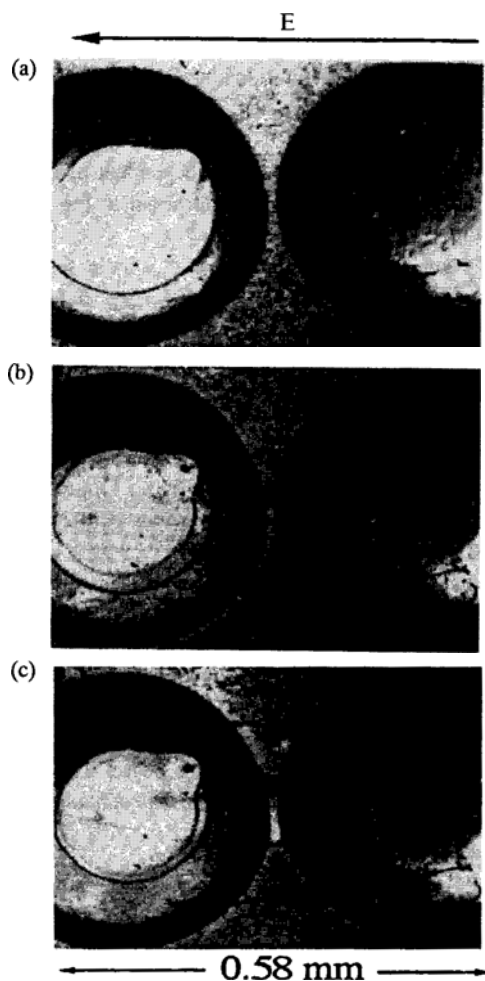


Fig. 7. Surfactant structure formation between two glass beads in a 1 wt% Brij*30 solution for different electric field strength ($f_e=500$ Hz); (a) $E=0$ V/mm, (b) $E=256$ V/mm, and (c) $E=641$ V/mm.

can be obtained from elasticity measurements, where suspensions with particles held together by such bridges display elasticity in the absence of an electric field. The storage modulus of 20 wt% dried neutral alumina suspensions containing 1 and 7 wt% Brij*30 were measured with and without an electric field (oscillation frequency=10 Hz, strain amplitude=3 %). The results are presented in Fig. 8 where the storage moduli are plotted as a function of time. For an electric field strength of 2 kV/mm, both suspensions possess large storage moduli. When the field is removed, the modulus of the 1 wt% Brij*30 suspension decreases rapidly, while the modulus of 7 wt% Brij*30 suspension initially increases, and then decreases slowly, consistent with a surfactant-mediated force holding the field-induced structure together. This result indicates the formation of surfactant-rich bridges between small alumina particles at large surfactant concentrations, consistent with the observations with large glass beads.

Below, it is shown that the surfactant bridges have a larger conductivity than the continuous phase, decreasing electrostatic particle interactions and shear stresses, thus producing a nonlinear ER response.

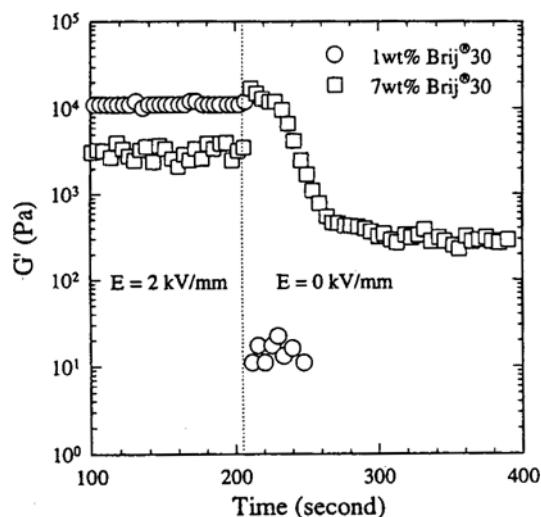


Fig. 8. Storage modulus as a function of electric field strength for 20 wt% dried neutral alumina suspensions with 1 wt% and 7 wt% Brij*30 (the oscillation frequency is 10 Hz, the edge shear strain is 2.4×10^{-4} (1 wt% Brij*30) and 1.3×10^{-4} (7 wt% Brij*30), and $f_e=500$ Hz).

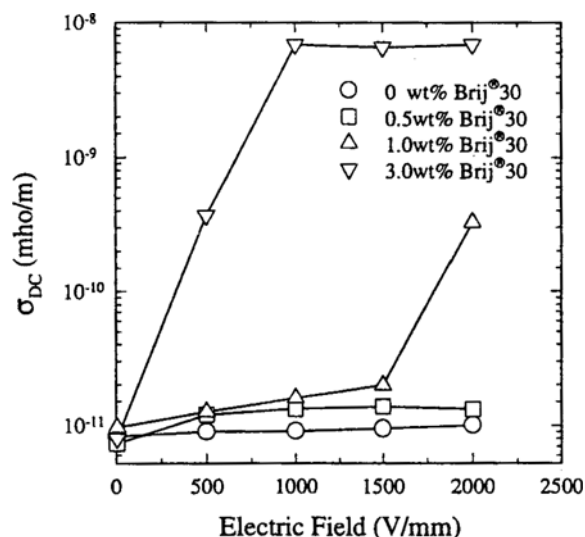


Fig. 9. DC conductivity as a function of the electric field strength for 20 wt% dried neutral alumina suspensions with varying Brij*30 concentrations.

2. Electrical Properties of Solutions and Suspensions with a Surfactant-Rich Phase

The conductivity of pure Brij*30 was found to be independent of field strength up to 2.0 kV/mm. Therefore, the conductivity increase with increasing field strength for the Brij*30 solutions is caused by the formation of surfactant-rich fibers, with the conductivity within each phase evidently independent of field strength.

The dc conductivities of 20 wt% dried neutral alumina suspensions with different surfactant concentrations were measured before, during, and after the application of large electric fields. Typical results are presented in Fig. 9. The dc conductivity with 1 wt% Brij*30 increases with the application of the electric field. Upon removal of the field, the conductivity returns to

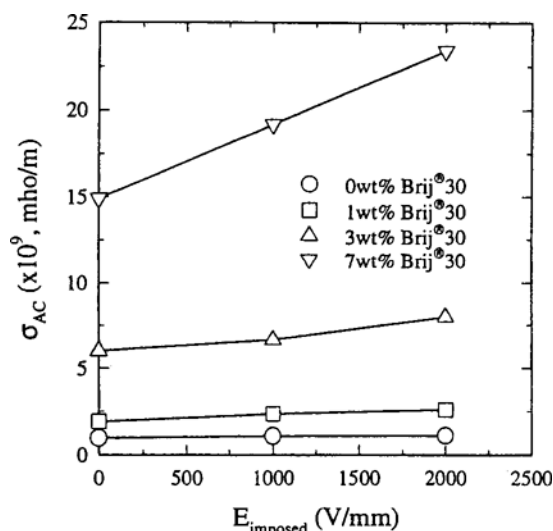


Fig. 10. AC conductivity as a function of the imposed electric field strength for 20 wt% dried neutral alumina suspension with 0 wt%, 1 wt%, 3 wt%, and 7 wt% Brij*30, respectively ($f_e=500$ Hz).

its original value, indicating that there is no significant bridge formation between particles. The dc conductivity with 3 wt% Brij*30 decreases when the large field is removed, but does not return to its original value, indicating that surfactants form some bridges between particles. The dc conductivity with 7 wt% Brij*30 remains essentially at its large field value when the field is removed, suggesting that the surfactant structure between particles is fully developed at this surfactant concentration.

The ac conductivities of 20 wt% dried neutral alumina suspensions were measured after imposing large electric fields. The results are presented in Fig. 10 for different Brij*30 concentrations. The experiments were performed by imposing the desired field strength ($f_e=500$ Hz), and then waiting 1 minute after removing the electric field before measuring $\sigma_{AC}=\epsilon_0 \epsilon'' \omega$. For the suspensions with 0 wt% and 1 wt% Brij*30, the conductivities are essentially independent of the imposed field strength, indicating that there is no significant surfactant structure formation between particles. For 3 wt% Brij*30, the conductivity depends weakly on the imposed electric field strength. The conductivity of the 7 wt% Brij*30 suspension increases with the imposed field strength, indicating that surfactant bridges form between particles. These results are consistent with the dc conductivity behavior described above (Fig. 10).

The connection between surfactant bridge formation and nonlinear ER behavior can be determined by considering the role of the conductivities of each phase on the interparticle forces. Interparticle forces are determined by conductivity differences between the particles and the continuous phase [Anderson, 1992; Davis 1992]. When the particle conductivity (σ_p) is much greater than the fluid conductivity in the interparticle gap (σ_{gap}), the field strength in the gap between nearly-touching particles is much greater than the applied field strength; pair electrostatic interactions are dominated by the large field strength in this region [Anderson, 1994]. The yield stress is determined directly by the particle interactions [Klingen and Zukoski, 1990], and is

thus influenced strongly by the field intensification between particles.

At low surfactant concentrations, surfactants and water are located primarily in the particles. Therefore, $\sigma_p \gg \sigma_{gap}$ and the yield stress is relatively large. Since the conductivities of the disperse and continuous phases are independent of field strength, the field strength in the gap is proportional to the applied field strength and $\tau_0 \approx E^2$.

At large surfactant concentrations, σ_{gap} increases due to the presence of the surfactant bridges. The gap field strength is thus reduced, which reduces the particle interactions and the yield stress. The gap field intensification and yield stress decrease with further increases in surfactant concentration as the bridges continue to grow and the gap conductance further increases. The bridge volume also increases with increasing field strength; the field strength in the gap is no longer proportional to the applied field strength, and thus the particle interactions and yield stress increase slower than E^2 .

We note that this mechanism for nonlinear ER behavior is similar to that proposed in Refs. [Felici et al., 1994] in that the yield stress is limited by an increase in gap conductance with field strength. The mechanism proposed here differs in that the increase in conduction does not arise from nonlinear conduction within a homogeneous phase, but rather results from phase separation of a more conducting phase. This mechanism can occur in a variety of ER systems that contain components in addition to particles and a pure oil.

CONCLUSIONS

We have investigated the nonlinear ER behavior at large surfactant concentrations where yield stresses increase slower than E^2 . The nonlinear behavior observed at large surfactant concentrations (i.e., $\tau_0 \approx E^n$, where $n < 2$) arises from field-induced phase separation of a surfactant-rich phase which forms conductive interparticle bridges. This mechanism for nonlinear ER is similar to that proposed by Felici et al. [1994], in that the yield stress is limited by an increase in conductance in the interparticle gap. In contrast, the mechanism proposed here differs in that the conductance increase in the gap does not arise from a field-dependent continuous phase conductivity, but rather from phase separation of a more conducting phase. Each phase apparently possesses a field-independent conductivity, but the relative volumes of each phase depend on the field strength and surfactant concentration. This phenomenon is likely to occur in many ER suspensions that contain surfactants.

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