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SHORT COMMUNICATION

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Synthesis and electrorheological characterization of emulsion-polymerized dodecylbenzenesulfonic acid doped polyaniline-based suspensions

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Abstract The electrorheological (ER) properties of dodecylbenzenesulfonic acid (DBSA) doped polyaniline suspensions in silicone oil were investigated. In contrast to chemically polymerized polyaniline in an acidic aqueous medium by oxidation polymerization, we adopted an emulsion polymerization technique in which aniline is polymerized in an emulsion of water and a nonpolar (or weakly polar) organic solvent. The effects of electric field strength and particle concentration on the ER properties of DBSA-doped polyaniline suspensions in silicone oil were then examined. Rheological measurements were also carried out using a rotational rheometer with a high-voltage generator in both controlled shear rate and shear stress modes, and the results showed that the ER properties were enhanced by increasing the particle concentration and electric field.

Key words Electrorheological fluid · Polyaniline · Emulsion polymerization · Dodecylbenzenesulfonic acid · Suspension

Introduction

Electrorheological (ER) fluids are suspensions of polarizable particles in a non-conducting oil, which exhibit a dramatic change in rheological and electrical properties (e.g., viscosity, yield stress, viscoelasticity, and dielectric constant) in the presence of an electric field. This change originates from particle migration and formation of a chainlike or columnar structure oriented along the electric field direction over the gap between the electrodes [1–3].

There are many theories which attempt to explain ER fluid phenomena. The electrostatic polarization mechanism attributes the origin of the ER effect to the field-induced polarization of the disperse phase particles relative to the continuous phase [4]. The model of polarization of electric double layers has also been proposed [5, 6]. Each particle is surrounded by a diffuse counterion cloud that balances its charge. Under the applied field, this cloud will distort and overlap with the counterion clouds of its neighbors. This enhances the electrostatic repulsion between particles which must be overcome in order for the particles to flow past one another. In addition, ER effects due to water bridges between particles have also been suggested [7]. Among these various theories, the best is the dielectric polarization theory [4].

In the absence of an electric field, ER fluids exhibit Newtonian behavior. Under an imposed electric field, however, ER fluids suddenly become solidlike and possess a minimum yield stress, which is needed to break the chainlike or columnar structure under flow. This yield stress is the main characteristic of an ER fluid. Yield stress is primarily determined by electric field strength and particle concentration. By imposing a shear field, the structure is deformed, inclined, and then broken down. Flow will occur, and the fluid behaves in general as a Bingham fluid possessing a significant amount of yield stress [1, 9–11]. Note that Casson-like behavior has also been observed [12, 13].

Initial studies on this ER phenomenon covered various wet-base suspensions, such as corn starch, silica gel, and cellulose as dispersed phases [2, 14, 15]. In the wet-base systems with hydrophilic particles, the particle chain structure develops by the migration of ions in the absorbed water. However, this system has significant limitations in applications (e.g., thermal instability) because of the evaporation of water and corrosion. Recently, the use of dry-base systems employing aluminosilicate [16], carbonaceous material [17], zeolite [18], and polymer particles [8, 19–26] has yielded better rheological properties for application in broad temperature ranges by inducing a dipole moment within the particle itself [9]. Semiconducting polymers such as sulphonated poly(styrene-*co*-divinylbenzene) [8], acene quinone radical polymers [19, 20], polyaniline [21, 22] and copolyaniline [23, 24], and polymer–clay nanocomposites [25, 26] have been widely adopted as materials for dry-base, nearly anhydrous ER fluids. In this work, we investigated dodecylbenzenesulfonic acid (DBSA) doped polyaniline as a potential candidate for anhydrous particles in high-performance dry-base systems.

Typically, a polyaniline is chemically synthesized in an acidic aqueous medium in which an oxidant is added [27–29]. In contrast to this chemical oxidation polymerization, we synthesized DBSA-doped polyaniline using an emulsion polymerization technique. This polymerization is carried out in nonpolar or weakly polar solvents in the presence of a functionalized protonic acid that acts simultaneously as a surfactant (or emulsifier) and as a protonating agent (dopant) for the resulting electrically conducting polyaniline [30].

Rheological properties of these ER fluids (DBSA-doped polyaniline in silicone oil) were then measured using a rotational equipped with a high-voltage generator.

Experimental

For the emulsion polymerization of DBSA-doped polyaniline, a solution composed of 19.52 g (0.2 mol) aniline, 97.92 g (0.3 mol) DBSA and 1 l xylene was prepared in a 2-l reactor. The polymerization was then initiated by the addition of 9.36 g (0.04 mol) ammonium peroxysulfate, $(NH_4)_2S_2O_8$, in 80 ml distilled water, which was added over a period of 30 min in order to avoid overheating the reaction mixture. The polymerization temperature was kept at 25 °C, and the total polymerization time was 24 h. The polymerization was terminated by pouring 3 l acetone into the emulsion system, and this process made the polyaniline–DBSA complex precipate. A dark-green powder of the synthesized polymer particle was recovered, filtered, and washed three times with 600 ml acetone, three times with 600 ml distilled water, and three more times with 600 ml acetone, sequentially. After these filtering and washing procedures, the polyaniline particles were ground using a pearl mill and passed through a 38-μm sieve to control the particle size and distribution.

Furthermore, to obtain semiconducting polyaniline for our ER study, we adopted the polyaniline particles by reducing the pH of the aqueous medium to pH 10 using an aqueous NaOH solution. The pH of the aqueous polyaniline suspension was kept constant for 1 day. The pH-controlled particles were again filtered and washed using distilled water, ethanol, and cyclohexane to remove oligomer and excess monomer and to make the particle surface hydrophobic.

Finally, the products were dried in a vacuum oven at 25 °C. The conductivity of the polyaniline was measured to be 1.78×10^{-10} S/cm by the two-probe method using compressed disks.

ER fluids were then prepared by dispersing the synthesized DBSA-doped polyaniline particles in silicone oil, which was dried in a vacuum oven and stored with molecular sieves prior to use. The density and kinematic viscosity of the silicone oil were 0.956 g/ml and 50 cS at 25 °C, respectively. The ER fluids were stored in a desiccator prior to use.

Rheological properties were measured using a Physica rotational rheometer (MC 120, Germany) with Couette geometry (Z3-DIN and Z4-DIN), a high-voltage generator (HVG 5000), and an oil bath (Viscotherm VT 100) for temperature control. The gaps of Z3-DIN and Z4-DIN were 1.06 mm and 0.59 mm, respectively. Their maximum and minimum stresses were 1141 Pa and 11.4 Pa for Z3-DIN and 6501 Pa and 65.0 Pa for Z4-DIN. The temperature could be controlled from −40 to 150 °C. To start a run, the ER fluid was placed in the gap between the stationary outer measuring cup and the rotating measuring bob, and a direct current (d.c.) voltage was applied to the cup. The electric field was applied for 3 min in order to obtain equilibrium chainlike or columnar structures before applying shear. The HVG 5000 could supply a d.c. voltage up to 5 kV/mm within ± 10 μA of electric current. In order to obtain reproducible data, the ER fluid was redispersed before each experiment and the measurements were carried out at least two or three times. The available shear rate was varied from 1.0 to 1000 s^{-1}. The rheological properties were obtained using two different modes, namely, controlled shear rate (CSR) and controlled shear stress (CSS), at 25 ± 0.1 °C. The static yield stress was measured using CSS mode with electric fields.

Results and discussion

Successful polymerization was confirmed by Fourier transform (FT) IR spectrum analysis. The FT-IR spectrum of the DBSA-doped polyaniline determined using KBr pellets is shown in Fig. 1. The peaks at 825 cm^{-1} originate from the out-of-plane H deformation

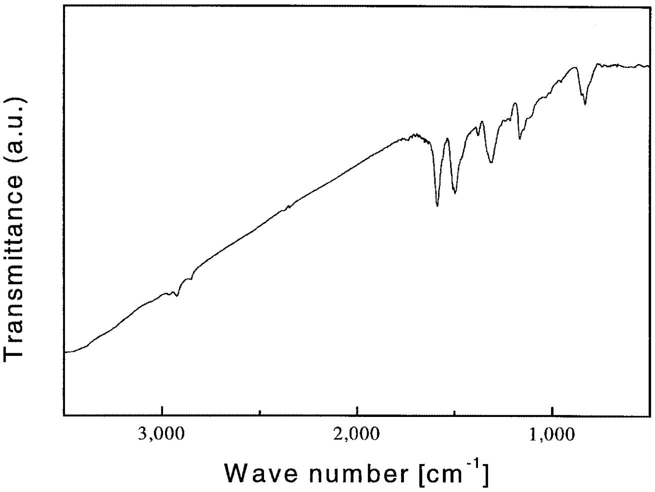

Fig. 1 Fourier transform IR spectrum of dodecylbenzenesulfonic acid (*DBSA*) doped polyaniline

of aromatic rings in polyaniline unit sequences, whereas the peaks at 1145 cm^{-1} and 1310 cm^{-1} are due to aromatic amine stretching and those at 1490 and 1590 cm^{-1} are the C-C stretching modes. The FT-IR spectrum shows that the DBSA-doped polyaniline synthesized for this study is similar to that of an emeraldine base [31].

Flow curves measured using the CSR mode for the 15 wt% DBSA-doped polyaniline particles in silicone oil with various electric field strengths are shown in Fig. 2. In the absence of an electric field, the fluid is similar to that of a typical concentrated shear-thinning suspension. Non-Newtonian, shear-thinning behavior is observed at zero electric field, since the slope (0.7) of the shear stress as a function of shear rate is less than 1 (which is the Newtonian fluid limit). Such non-Newtonian behavior even at zero electric field has also been observed for proton-doped polyaniline [32] and polyaniline–Na$^+$–montmorillonite nanocomposite [25] ER fluids. When an electric field was applied to this suspension, the shear stresses for the ER fluid rapidly increased and produced a yield stress. Shear stresses increase over the entire shear rate range with the increase in electric field strength. Furthermore, the shear stress exhibits either a plateau region or a slightly decreasing region depending on the applied electric field over the broad range of shear rate due to an interparticle interaction force [33]. Beyond this region, shear stress increased with shear rate similar to non-Newtonian fluids, implying that the hydrodynamic force begins to dominate the electrostatic force. To check the reproducibility of the data given here, all the measurements were repeated. Some fluctuations in the shear stress in this region might be due to properties such as the nonspherical shape and the nonuniform size of the ER particles [18, 34].

At low shear rates, shear stresses depend strongly on the electric field. On the other hand, at high shear rates, where the hydrodynamic force dominates, the electric field effect is somewhat reduced. The behavior at a low shear rate is probably due to the deformation, destruction, and reformation of the chainlike or columnar structure as the shear rate increased below the critical shear rate. Sprecher et al. [35] referred to this fluctuational shear stress behavior as a swirling motion and stated that particle motion occurred due to the electrohydrodynamic effect. This behavior might be due to the fact that an electrostatic interaction was still sustained below the critical shear rate at which the yield stress occurred. This value of the critical shear rate was observed to increase as the electric field strength increased.

Flow curves obtained using the CSR mode for DBSA-doped polyaniline in silicone oil with different particle concentrations at an electric field strength of 1.5 kV/mm are shown in Fig. 3. Shear stresses increase with an increase in the particle concentration over the entire shear rate range. To have a better understanding of either a plateau or a slightly decreasing region of the shear stress as in Fig. 2, error bars for the shear stress are given in Fig. 3.

The static yield stress versus the electric field strength for three different weight fractions of DBSA-doped polyaniline using a CSS mode measurement is shown in Fig. 4. The CSS mode was to measure the static yield stress. In contrast to a CSR mode, in which a shear rate is applied to the ER fluid and then the resulting shear stress is measured giving a dynamic yield stress, the ER fluid is stressed by an applied mechanical torque until the particle chain structure is perfectly broken so that the shear occurs. Thereby the shear rate is observed

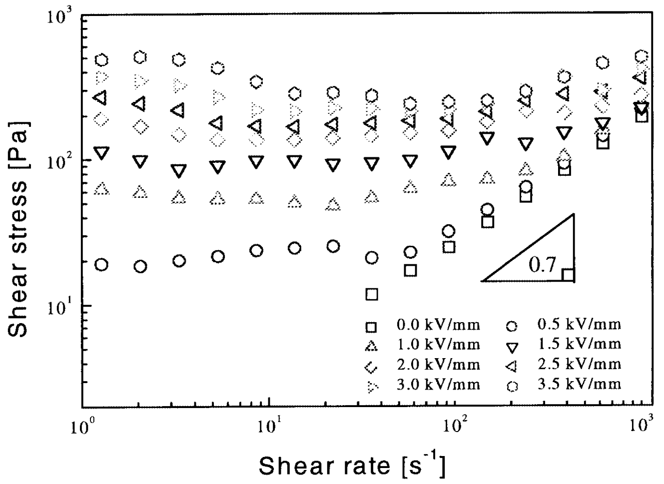

Fig. 2 Shear stress versus shear rate measured using the controlled shear rate mode at various electric field strengths (DBSA-doped polyaniline 15 wt% in silicone oil)

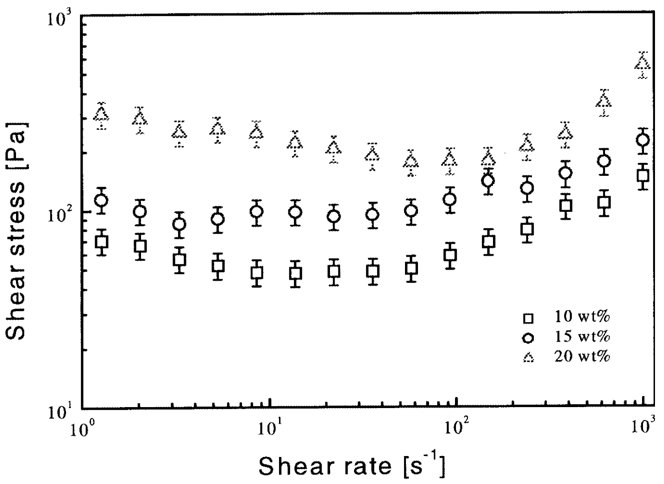

Fig. 3 Shear stress versus shear rate measured using the controlled shear rate mode at three different particle concentrations (electric field strength = 1.5 kV/mm)

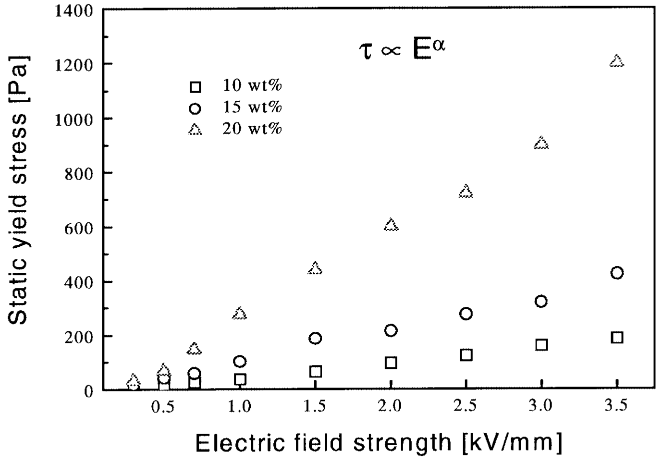

Fig. 4 Static yield stress versus electric field strength measured using the controlled shear stress mode at three different particle concentrations

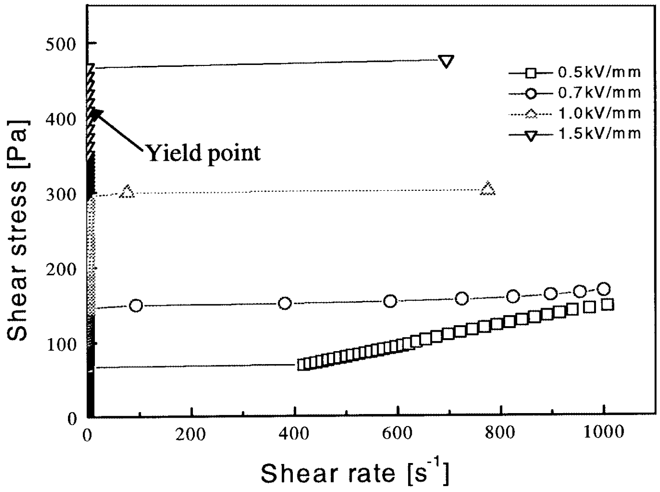

Fig. 5 Measurement of yield stress with different electric field strengths using the controlled shear stress mode. (DBSA-doped polyaniline 20 wt% in silicone oil)

when the flow of the ER fluid starts. The stress at this point is known as a static yield stress. Similar to many other ER fluid systems, the DBSA-doped polyaniline/silicone oil ER system also possesses the property that yield stress increase as particle concentration increases. The polarization forces between particles increase with both increasing electric field strength and particle concentration, which in turn develops the particles' chain structure, thus increasing the yield stress. When the particle concentration is too low there are few particle chains or fibrils owing to the small polarization forces and there is only a minute increase in the static yield stress.

Generally, the correlation of the static yield stress (τ_y) to the electric field strength (E) at a fixed concentration is expressed as follows [2, 5]:

$$\tau_y \propto E^{\alpha} \ .$$

The α values in this study were observed to range from 1.2 to 1.4. These values differed from 2.0 from the polarization model [36] as expected; the difference might be from the nonspherical particle shape, the particle size distribution, and the polarizability [3, 8].

This result from emulsion-polymerized DBSA-doped polyaniline-based ER suspensions can be compared with the correlation of τ_y to the electric field strength studied for the conventional chemically polymerized polyaniline in an acidic aqueous medium by oxidation polymerization [34]. Choi et al. [34] observed the α values for chemically polymerized polyaniline synthesized at 5 °C were 1.1–1.9. In the polarization model [3], the applied electric field induces electrostatic polarization interactions between the spheres themselves and between the spheres and the electrodes, owing to a difference in the dielectric constants of the disperse and continuous phase. In the point-dipole limit, each sphere is treated as a dipole only, located at the sphere center and aligned with the applied electric field, the magnitude of the dipole being given by that induced on an isolated dielectric sphere in a uniform electric field. Therefore, the polarization model with the point-dipole approximation is a rather ideal system compared to our real DBSA-doped polyaniline system.

Furthermore, Fig. 5 represents the measurement of static yield stress of DBSA-doped polyaniline ER fluids (20 wt%) with different electric field strengths. Shear stress was increased up to 1000 Pa, and then the change in shear rate was observed. A yield stress was obtained as soon as the flow occurs as given in Fig. 5. Note that the static yield stress from the CSS mode is known to be always larger than the dynamic yield stress from the CSR mode, and a difference between static and dynamic yield stress is found for our DBSA-doped polyaniline ER fluids from Figs. 3 and 4.

In conclusion, DBSA-doped polyaniline was synthesized as a suspended particle for ER fluids by emulsion polymerization and the yield stress was found to increase with both particle concentration and electric field strength.

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