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

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 copolyanilines [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 11 xylene was prepared in a 2-l reactor. The polymerization was then initiated by the addition of 9.36 g (0.04 mol) ammonium persulfate, (NH₄)₂S₂O₈, 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 31 acetone into the emulsion system, and this process made the polyaniline–DBSA complex precipitate. 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 cSt 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 (Viscotester 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.