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# Monodisperse conducting colloidal dipoles with symmetric dimer structure for enhancing electrorheology properties

Kyomin Shin [a], Daun Kim [a], Jun-Cheol Cho [a], Hyung-Seok Lim [a], Jin Woong Kim [b,*], Kyung-Do Suh [a,*]

[a] Division of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea
[b] Department of Applied Chemistry, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do 426-791, Republic of Korea

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ABSTRACT

This study introduces an electrorheological (ER) approach that allows us to obtain remarkably enhanced ER properties by using monodisperse colloidal dimer particles. Two sets of colloidal particles, which are spheres and symmetric dimers, were synthesized employing the seeded polymerization technique. The aspect ratio of dimer particles was ~1.43. Then, the surface of the particles was coated with polyaniline by using the chemically oxidative polymerization method. After preparation of the particle suspensions having the same particle volume and concentration, their ER behavior was investigated with changing the electric field strength. At the same experimental condition, both shear stress and shear yield stress of the dimer particle suspension remarkably increased, compared with those of the spherical particle suspension. This attributes to the fact that the shape anisotropy of suspending particles effectively led to increase in the dipole moment under the electric field, thus resulting in formation of a well-structured colloidal chains between the electrodes.



## 1. Introduction

The electrorheological (ER) fluid, which is generally composed of polarizable solid particles dispersed in insulating oil, behaves like a Bingham fluid under an applied electric field. When electric field strength in a range of kV $mm^{-1}$ is applied to this fluid, the polarized particles orient and connect to each other to form either colloidal chains or columns along the direction of electric field between the electrodes. The particle chains inhibit the fluid flow; hence, the fluid has enhanced viscoelastic shear stress and yield stress. On eliminating the electric field, the fluid returns to its initial state. This rapid and reversible behavior of ER fluid has been interested not only on academic researches but also on the industrial applications, such as electrical clutches, locks, valves and shock absorbers. Although the ER technology has great potentials, only a few devices have reached the marketplaces due to a fatal lack of effectiveness in fluidity control as well as quick responsiveness.

Many researchers have widely investigated chemical and physical features of dispersion systems to obtain sufficiently applicable ER effects. Major factors that determine the shear stress of ER fluids are the dielectric constant, the particle conductivity, the volume fraction of particles, as well as the nature of the applied electric field (frequency and magnitude) [1–4]. In principle, they are affected by material properties of suspending materials. Typically, anhydrous ER materials are polarized to intrinsically form dipoles under electric field. They include semiconducting polymer particles [5–9], carboneous materials [10–12] and metals [7,13–15]. Among them, polyaniline (PANi) has been widely attracted, since it can be obtained using a variety of synthetic methods and has excellent thermal stability [16–18]. The emeraldine form of PANi is a semi-conjugated π system that is easily polarizable. Once the ER materials are polarized in the fluid, their particle topology and uniformity critically affect the ER properties [19–23]. This is because the microstructure of suspending particles changes the ER response and electrostatic interaction.

Despite shape anisotropy of suspending particles can seriously affect their polarizability in the ER fluid, only a few studies have been made [24,25]. In order to clarify the shape anisotropy effect of polarizable particles on ER behaviors, in this study, we fabricate conducting PANi dimer particles with perfect symmetry as well as extreme uniformity in shape. The template dimer particles in micrometer length scales were synthesized using the seeded polymerization technique [27–29] and their surface was sulfonated to facilitate polymerization of PANi thereon. For comparison, we also synthesized spherical conducting particles having the identical particle volume and surface property. Finally, ER behaviors of those particles in fluids were characterized with changing control parameters, such as electric field strength and particle conductivity.

* Corresponding authors.
*E-mail addresses:* kjwoong@hanyang.ac.kr (J.W. Kim), kdsuh@hanyang.ac.kr (K.-D. Suh).

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## 2. Experimental

### 2.1. Materials

Styrene (St, Kanto Chemical Co.) and divinylbenzene (DVB, mixture of isomer; 55%, Aldrich Chemical Co.) were all reagent grade and used as received. 2,2′-Azoisobutyronitrile (AIBN, Junsei Chemical Co.) were recrystallized to remove an inhibitor from methanol before use. Another materials were used without further purification; polyvinylpyrrolidone (PVP, $M_w \sim 4.0 \times 10^4$ g mol$^{-1}$, Sigma Aldrich Chemical Co.), ethanol (Daejung Chemicals), dioctyl sodium sulfosuccinate (aerosol-OT, Wako Pure Chemicals), poly (vinyl alcohol) (PVA, $M_w$ is $8.8 \times 10^4$–$9.2 \times 10^4$ g mol$^{-1}$, 87–89% hydrolyzed, Sigma Aldrich), potassium persufate (KPS, Shinyo Chemical Co.), 2,2′-azobis (2,4-dimethyl valeronitrile) (ADVN, Wako), Tween 60 (Shinyo), ammonium hydroxide (25–28%, Daejung), hydrochloric acid (HCl, Daejung), aniline (99%, Daejung) and sulfuric acid (95%, Junsei). All aqueous solutions were prepared using distilled water.

#### 2.1.1. Synthesis of semi-IPN seed particles

Monodisperse crosslinked seed particles were prepared by using the seeded polymerization technique. All reactions were carried out in a 500 mL four-neck glass reactor equipped with a mechanical stirrer, a refluxing condenser and a nitrogen injection system. At first, linear PS seed particles were dispersed in 1 wt% PVA solution by applying ultrasonic for 30 min. The monomer mixture of styrene, DVB, AIBN was emulsified by ultrasonic homogenizing in the PVA solution for 2 min and poured into the reactor. After completely disappearance of monomer emulsion, the swollen seed particles were stabilized with a PVA aqueous solution (1 wt%). Then, the reactor was submerged into a preheated oil bath on 70 °C for 12 h. The reaction mixture was stirred with speed of 120 rpm. The synthesized, semi-interpenetrating polymer network (IPN) particles were centrifuged at 3600 rpm for 10 min. The supernatant solution was decanted and the remaining semi-IPN seed particles were repeatedly washed with several centrifugation/redispersion cycles in a methanol/water mixture. Finally, the semi-IPN seed particles were dried under a vacuum at room temperature.

### 2.2. Synthesis of colloidal dimer particles

To synthesize colloidal dimer particles with exact dimer structure, the seeded polymerization was carried out again with the semi-IPN seed particles. First, the semi-IPN PS seed particles were completely dispersed in 1 wt% PVA solution and swollen with an emulsified monomer solution, consisting of styrene, DVB, and ADVN (2 wt% based on total weight of monomers). The monomer swelling ratio was controlled to exactly form symmetric dimer particles after polymerization. In this this system, the seed-to-monomer swelling ratio was 1 to 4 by weight. To observe the effect of particle shape, spherical particles with the same particle volume were also synthesized by using the seeded polymerization [27,28]. The particles were treated with sulfuric acid to induce effective coating of PANi on their surfaces [26].

### 2.3. Coating of PANi layer on particle surface

The sulfuric acid treatment of PS particles generates sulfonate groups on their surface. The sufonate groups enhance grafting polymerization of PANi chains. The PS particles baring sulfonate groups were dispersed in 1.2 M HCl aqueous solution with Tween 60 (0.25 wt%) at room temperature. KPS (0.1 M based on the weight of aniline) was added under vigorous magnetic stirring. Then, the aniline in 1.2 M HCl aqueous solution was slowly dropped into the reactor. Aniline content was controlled by using different concentration (to 30 wt%) based on the weight of particles. Polymerization reaction was continued for 24 h at room temperature. After polymerization, PANi/PS particles were recovered by centrifugation and continuously further treated with 3 wt% ammonia hydroxide solution for 1 h to reduce the particle conductivity. The synthesized composite particle was obtained after drying under a vacuum at room temperature, followed by several times washing with ethanol/water mixture and consecutive centrifugation.

### 2.4. Characterization of particles

The shape of the particles was observed using a scanning electron microscope (SEM, JSM-6300, JEOL). FT-IR spectroscopy (Magna-IR 760 Nicolet) was utilized to analyze the chemistry of PANi-coated particles. In order to measure the thickness of PANI layer on the surfaces of composite particles, more than 100 particles were analyzed from the SEM images. Relative coating mass of PANi on the particles was determined by using a thermal gravimetric analyzer (TGA, TA Instrument). The heating rate was adjusted to 10 °C/min in the range 0–800 °C under the atmosphere of air. The conductivity of the particles was calculated by using the four-probe measurement based on the van der Pauw technique [30].

### 2.5. Rheology measurement of ER fluids

ER suspensions with 5 wt% solid content were prepared by completely dispersing the conducting particles in silicone oil (KF-96, 50 cS, Shinetsu). Rheological behavior of the ER suspensions was measured with a concentric cylindrical rheometer (ARES4, Rheometric Scientific, Inc.) equipped with a high-voltage power generator (EL5P8L, Glassman High Voltage Inc.). The ER fluids were placed in the gap between the rotating outer cup and the stationary inner bob. An electric field was applied for 3 min to obtain an equilibrium structure before applying the shear and the flow curves were obtained with the rheometer operating in the controlled shear rate (CSR) mode.

## 3. Results and discussion

Symmetric dimer particles were synthesized by employing the seeded polymerization technique, as illustrated in Fig. 1 [27–29]. This technique is truly advantageous in that the phase separation in the uniform monomer drops, induced by elastic stress generated from the crosslinked polymer network at elevated temperatures, can provide shape anisotropy to the particles, while maintaining their extreme uniformity in shape. By simply manipulating the monomer swelling ratio, the symmetry of bulbs in a particle can be controlled. In this study, when the swelling ratio of monomers to the semi-IPN seed particles was 4 to 1 by weight, symmetric dimer particles were produced in the micrometer length scale. In the absence of the elastic stress, no phase separation occurs, thereby producing spherical particles. As the seed particles were swollen by the same amount of monomers and the monomers were polymerized at the same reaction conditions, all the final particles, regardless of particle shapes, had the same volume. After preparation of the spherical and dimer particles as templates, respectively, their surfaces were treated with sulfuric acid to create sulfonate groups. These sulfonate groups on the surface aid chemical grafting of PANi chains while carrying out the chemically oxidative polymerization method. Eventually, the PANi layer is able to give particles polarizability.