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Enhanced electrorheological activity of polyaniline coated mesoporous silica with high aspect ratio

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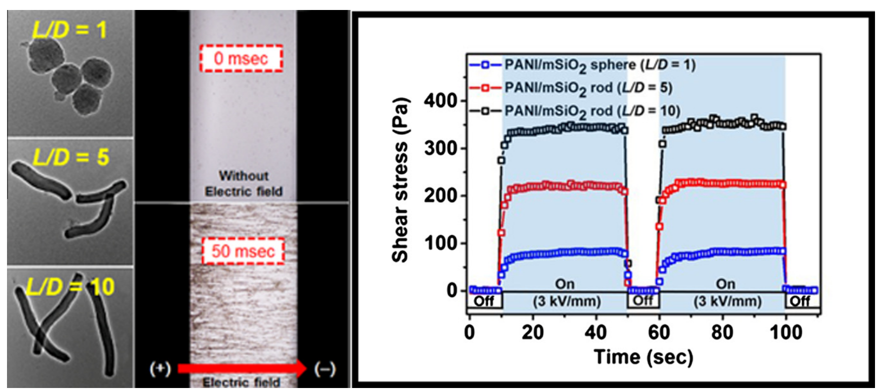
HIGHLIGHTS

- Mesoporous silica particles having various aspect ratios (*L/D* = 1, 5, and 10) were fabricated as multi-gram scales to investigate geometric effects on electrorheological activity.
- Electrorheological performance of the polyaniline coated mesoporous silica materials was significantly enhanced with increasing aspect ratio.
- Geometric effects on the electrorheological activity were illustrated by various factors including flow resistance, mechanical stability and dielectric properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyaniline-coated mesoporous silica (PANI/mSiO_2) materials with different aspect ratios (*L/D* = 1, 5, and 10) were fabricated by a vapor deposition polymerization (VDP) method to investigate the geometric effect on electrorheological (ER) activity. The PANI/mSiO_2 materials were dedoped by a facile NH_4OH treatment to reduce the conductivity to a level appropriate for ER applications. Notably, the PANI/mSiO_2-based ER fluids exhibited enhanced ER performance with increasing aspect ratio. In particular, the PANI/mSiO_2 material with the highest aspect ratio manifested the highest ER activity, which was attributed to geometric effects on flow resistance and mechanical stability. Moreover, the ER materials with higher aspect ratios showed improved dielectric properties of large achievable polarizability and short relaxation time. Hence, the synergistic contribution of geometric effects and dielectric properties resulted in enhanced ER activity. Consequently, this study provides insight into an effective method to improve ER performance by simple manipulation of the particle geometry.

1. Introduction

Electrorheological (ER) fluids are colloidal suspensions of polarizable materials dispersed in an insulating medium such as silicone oil and mineral oil [1–3]. These ER materials are able to transform their structure from a randomly dispersed state to a fibril-like state under an applied electric field. Such a transition creates versatile characteristics of rapid response time, reversibility, and simple mechanics [4–6]. Hence, ER fluids are applied in various fields like dampers, shock absorbers, torques, and transducers [7,8]. For practical applications, a variety of polarizable particles have been investigated as ER materials including organic, inorganic, metallic, polymeric, and hybrid materials [9–13].

Among them, silica (SiO_2) has been widely studied as a typical ER material because it can be produced in large quantities with

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high uniformity [14]. It is known that SiO_2 can be used as pristine forms, but its composites like core/shell structure and derivative forms are widely studied in various fields [3,7]. In particular, mesoporous silica ($mSiO_2$) is a good candidate for ER applications owing to its additional advantages of low density and high surface area [15,16]. Compared to pristine SiO_2, ER fluids containing $mSiO_2$ particles showed improved dispersion stability and dielectric properties, which greatly enhanced the ER performance [17–20]. However, usage of $mSiO_2$ in the ER field is still limited because of its low electrical conductivity [21]. An external coating or doping process is necessary to enhance its conductivity. Coating materials include metals, carbonaceous materials, and semiconducting polymers, which can exert a strong particle interaction due to increased polarizability [22–24].

Polyaniline (PANI) has often been selected as a coating material for ER applications because of its environmental stability, low cost, and facility for conductivity control by doping and dedoping [25–27]. For example, Choi et al. fabricated PANI-doped MCM–41 to enhance ER activity [28]. Additionally, Sasidharan et al. improved ER performance by covalently grafting PANI onto SBA–15 [29]. Other researchers have enhanced ER activity by methods including controlling the size and morphology of the ER materials and using different coating methods [30–34].

It has recently been reported that high aspect ratio ER materials can increase ER performance. For instance, Shin et al. demonstrated the enhanced ER activity of symmetrical dimer particles compared with spherical material [35]. Lee et al. improved ER performance by increasing the aspect ratio of graphene oxide-coated silica rods [36]. However, there have been few reports regarding on the series of geometric effect arising from various aspect ratios on the ER performance. Hence, a more comprehensive study is required to clarify the geometric influence on the ER activity and related underlying mechanisms.

Herein, we fabricated polyaniline coated mesoporous silica (PANI/$mSiO_2$) particles having different aspect ratios (L/D = 1, 5, and 10) to investigate the geometric effect on ER activity. The core $mSiO_2$ template material was synthesized by a modified Stöber method [37]. Then, the PANI was coated onto the template by a vapor deposition polymerization (VDP) method. Dedoping was conducted by base treatment to avoid electrical short-circuits during ER measurements. The ER activity of the resulting materials was examined under various experimental conditions such as shear rate, on-off test, and electric field strength. Furthermore, the dielectric properties of the ER materials were investigated using an electrostatic polarization model to clarify the relationship between the particle geometry and ER activity.

2. Materials and methods

2.1. Materials

Hexadecyltrimethylammonium bromide (CTAB), Tetraethyl orthosilicate (TEOS, 98%), triblock copolymer Pluronic F127, iron chloride (97%), aniline (>99.5%), and silicone oil [poly (methylphenylsiloxane), viscosity = 100 cSt] were purchased from Aldrich Chemical Co. Ammonium hydroxide (28–30%), and absolute ethanol (ethyl alcohol, 99.5%) were purchased from Samchun Chemical Co. (Korea) All chemicals were used without further purification.

2.2. Synthesis of mesoporous silica ($mSiO_2$) with various aspect ratios (L/D)

The $mSiO_2$ particles with different aspect ratios were fabricated according to the modified Stöber method [37]. To synthesize rod-like $mSiO_2$ particles, CTAB (0.3 g), Pluronic F127 (0.12 g), absolute ethanol (3 mL) and ammonium hydroxide (1 mL) were dissolved in distilled water (30 mL) with vigorous stirring. Subsequently, TEOS was added and the mixture was stirred at room temperature for 3 h. The $mSiO_2$ particles with different aspect ratios were made by changing the amount of added TEOS. Specifically, $mSiO_2$ particles with the aspect ratios of 5 and 10 were synthesized by adding 1.0 and 0.5 mL of TEOS, respectively. Spherical $mSiO_2$ (L/D = 1) particles were fabricated by the same procedure but without addition of Pluronic F127 and at 40 °C. The product was collected by centrifugation and dried at 80 °C. All of the $mSiO_2$ materials were calcined at 500 °C to remove any residual surfactants. In addition, the fabrication of the $mSiO_2$ can be scaled up to 10 times and the resulting product maintained the structural characteristics compared to original method.

2.3. Fabrication of polyaniline coated mesoporous silica (PANI/$mSiO_2$)

The PANI layer was coated onto the $mSiO_2$ using a VDP method [38]. Firstly, $mSiO_2$ (0.2 g) was dispersed in distilled water (40 mL) and $FeCl_3$ (0.6 g) was added with vigorous stirring for 6 h. The $FeCl_3$-soaked $mSiO_2$ was collected by centrifugation and dried in a vacuum oven at 25 °C. To introduce the PANI onto the $mSiO_2$, aniline monomer (0.1 mL) was carefully injected using a syringe into a vacuum chamber containing the $FeCl_3$-soaked $mSiO_2$. Thereafter, the chamber was placed in an oven at 80 °C for 6 h to obtain yellow PANI/$mSiO_2$ powder. The conductivity of the PANI coated $mSiO_2$ (PANI/$mSiO_2$) was reduced to prevent the electrical short-circuits during the ER measurement by following dedoping process. The PANI/$mSiO_2$ (0.2 g) was dissolved in distilled water (30 mL). Ammonium hydroxide (1 mL) was then added to the PANI/$mSiO_2$ solution with stirring for 2 h. The color change of the solution from yellow to dark blue indicated the successful dedoping process for the PANI/$mSiO_2$ [39]. The final dedoped PANI/$mSiO_2$ was isolated by centrifugation and dried overnight.

2.4. Characterization

The structural image of the particles was taken by TEM (JEM–200CX, JEOL) and FE-SEM (JSM–6700F, JEOL). The HR-TEM (JEOL JEM–2010F) images were taken to determine the thickness of PANI layer. Elemental mapping was displayed by STEM (Tecnai F20, FEI) with a Gatan image filter (Gatan, Inc.). The N_2-sorption isotherm and BJH pore size distribution were measured with an ASAP 2010 analyzer (Micrometrics). The elemental weight percentages were obtained with FE-SEM (JSM–6700F, JEOL) installed with an EDS spectrometer (INCA energy). Fourier-transform Infrared (FT-IR) spectra were recorded on a spectrometer (Bomem MB 100). TGA thermograms were obtained using a thermogravimetric analyzer (TA Q–500). Dielectric properties were determined by an impedance analyzer (Solartron 1260) combined with a dielectric interface (Solartron 1296).

2.5. Investigation of electrorheological (ER) activity

To investigate the ER activity, dried $mSiO_2$ (0.3 g) and PANI/$mSiO_2$ (0.3 g) powders were well dispersed in silicone oil (10 mL, poly[methylphenylsiloxane], viscosity = 100 cSt) using a sonicator and stirrer. All of the ER fluids were equally set to 3.0 wt%, and no additives were added. The ER properties were measured using a rheometer (AR 2000 Advanced Rheometer, TA Instruments) equipped with a cup (radius = 15.0 mm, height = 30.0 mm), a concentric cylinder conical geometry (radius = 14.0 mm, height = 30.0 mm), a high-voltage generator (Trek 677 B), and a temperature controller. To start the measurement, the ER fluids were placed in the gap between the cup and rotor. After loading