Sulfonated polystyrene nanoparticles coated with conducting polyaniline and their electro-responsive suspension characteristics under electric fields

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ABSTRACT

Core-shell structured conducting polyaniline (PANI)-coated polystyrene (PS) composite nanospherical particles were synthesized and assessed as a candidate for electrorheological (ER) materials. Mono-disperse PS nanospheres were initially synthesized by a dispersion polymerization process and their surface was modified using concentrated sulfuric acid. This allowed the aniline monomer to be adsorbed easily on the sulfonated PS nanosphere and polymerized further by forming a PS/PANI nanosphere. The ER performance of their suspension dispersed in silicone oil was examined using a rotational rheometer under a variety of electric field strengths. The Bingham fluid model was used to analyze their flow curves to understand the interrelation between shear stress and shear rate. The relationship between the yield stress and electric field strength showed a slope of 2.0 following a polarization model. The dielectric spectra showed a good correlation with the ER performance of the ER fluid.

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1. Introduction

Electrorheological (ER) fluids are a family of intelligent material systems that are typically composed of semiconducting or polarizable particles suspended in insulating liquids, where their rheological characteristics can be controlled by an electric field [1—4]. Under the application of an electric field, the particles dispersed in the ER fluids are polarized and connected with each other to construct chain-like structures with a strong dipole—dipole interaction along the applied electrical field direction. Therefore, ER fluids undergo a phase transition from liquid-like to solid-like under the application of an electric field, and return reversibly to a liquid state when the electric field is removed [5—9]. Through this rapidly controllable process, the rheological properties, such as shear stress, shear viscosity, and dynamic modulus, can be changed simultaneously. Therefore, ER fluids have attracted considerable attention in many areas with a wide range of industrial applications based on their phase-transitions, such as automobile components, mechanical polishing, damper systems, tactile displays, and efficient energy production [10—13].

In recent years, there has been extensive research on the fabrication of electro-responsive materials. A variety of inorganic (e.g. zeolite, TiO$_2$, silica, etc.) [14—16] and organic materials have been proposed to be applicable in ER fluids. Conducting polymers, whose electrical conductivity can be adjusted by doping/dedoping processes, such as polyaniline (PANI) and its derivatives [17—21], poly (3, 4-ethylenedioxythiophene) [22], polythiophene [23], and polypyrrole [24,25], are also applied as anhydrous ER materials. Among them, PANI has been applied widely in ER fluids owing to its low cost, easy synthesis, and remarkable thermal and chemical stability [26—28]. In addition, core-shell structured conducting-polymer-incorporated particles have been reported to be good ER candidates via facile physical adsorption or chemical interactions to control the composite particle size, shape (sphere, rod, tube and even urchin-like form), and density [29—32].

In the present study, PANI-coated polystyrene (PS) core-shell nanosphere particles were synthesized. A better PANI coating onto PS was expected by sulfonating the surface of PS spheres using concentrated sulfuric acid than the previously reported technique of the simple π—π stacking interactions [33]. This could allow the aniline monomer to be adsorbed easily on the sulfonated PS nanosphere and polymerized further by forming a better PS/PANI nanosphere. These monodispersed PS/PANI core/shell particles were dispersed in silicone and their ER performance was investigated under various electric field strengths using a rotational

rheometer. The Bingham fluid model was used to analyze the resulting flow curves to understand the interrelationship between the shear stress and shear rate. The relationship between the yield stress and electric field strength was investigated further using a power-law relation.

2. Experimental

2.1. Preparation of PS and sulfonated PS nanospheres

Monodisperse PS nanospheres were synthesized using a typical dispersion polymerization technique. A 15 g sample of styrene monomer (99% purity, Sigma-Aldrich) was dissolved in 270 mL of methanol containing 3 g of polyvinylpyrrolidone (PVP) (Mw = 360,000 g/mol, Sigma-Aldrich) as a stabilizer with stirring under a N_2 atmosphere and heated to 60 °C. The reaction was initiated by adding the solution into the reactor, in which 0.25 g of 2,2′-azobisisobutyronitrile (AIBN, 98% purity, Junsei Chemical Co.) was dissolved in 30 mL of methanol, and polymerization continued for 24 h. Following the reaction, the PS nanospheres were centrifuged with methanol and deionized water, and then dried under vacuum. For their surface treatment, according to the procedures reported by Dai et al. [34], 3 g of the resulting PS nanospheres were dispersed in 200 mL of concentrated sulfuric acid and warmed to 40 °C, the sulfonation reaction was allowed to proceed for 6 h with stirring at 150 rpm. The sulfonated PS nanospheres were collected by repeated centrifuging and washing 3 times.

2.2. Synthesis of PANI coated PS

The conducting PANI shell was coated on the sulfonated PS surface using the following procedure. The resulting sulfonated PS nanospheres (1 g) were dispersed in water (150 mL) with vigorous stirring of 200 rpm. Subsequently, 0.75 g of aniline monomer (DC Chemical, Korea) in 20 mL of a 1 M HCl (35%, OCI Co., Korea) solution was added to the above suspension. The aniline monomer can be adsorbed on the sulfonated PS nanosphere and polymerized further on the PS surface to form a PS/PANI nanosphere [35,36]. An aqueous solution containing 2.3 g of ammonium persulfate (APS) (Daejung Co., Korea) was added, and the mixture was allowed to react at 0 °C for 24 h. The PS/PANI nanospheres obtained were collected by washing with ethanol and water, and finally dried using a freezing-drier with 24 h. Fig. 1 presents a schematic diagram of the entire experimental process of PS/PANI.

2.3. Preparation of ER fluid

The electrical conductivity of the PS/PANI hybrid nanospheres fabricated was measured to be 10^{-3} S/cm using a resistivity meter. Because this electrical conductivity is too high for direct application to ER materials, it is important to tune the electrical conductivity. This is because a high electrical conductivity would lead to damages to the rheometer by an electric short circuit. The obtained PS/PANI nanospheres were dispersed in di-water, and their pH in the dispersion was maintained at 9 by adding a 1 M NaOH solution. The dedoped PS/PANI nanospheres were then filtered and dried. The electrical conductivity of the final obtained PS/PANI nanospheres was decreased to 10^{-8} S/cm. As for the relationship between electrical conductivity and ER performance, Plachy et al. [37] recently reported the higher ER effect for the samples with higher conductivity. But the critical conductivity for the ER effect was 10^{-7} S/cm. For the ER fluid in this study, the PS/PANI nanospheres (10 vol% particle concentration) were milled carefully in a mortar and added to 50 cSt silicone oil for the ER test.

2.4. Characterization

The morphology of the PS/PANI nanospheres was observed by scanning electron microscopy, (SEM, SU 8010, Hitachi) and transmission electron microscopy (TEM, CM200, Philips). The chemical structure of the prepared samples was examined by Fourier transform-infrared (FT-IR) vacuum spectrometry (VERTEX 80V, Bruker). The thermal properties were analyzed by thermogravimetric analysis (TGA, TG209F3, Tarsus) in air. The ER behaviors of the PS/PANI nanosphere-based ER fluid were investigated using a rotational rheometer (Physica MCR 300, Stuttgart) equipped with a DC high voltage generator. To examine the interfacial polarization of the ER fluids, the dielectric spectra were analyzed using a LCR meter (HP 4284A Precision) with a Liquid Test Fixture (HP 16452A) for liquids, in which the frequency of the AC electric fields was varied from 20 Hz to 1 MHz.

3. Results and discussion

The morphologies of both PS and PS/PANI nanospheres were observed by SEM. As shown in Fig. 2(a), the spherical pure PS particles had relatively smooth surface and a uniform size with a mean particle diameter of 360 nm. In contrast, the PS/PANI particles have a much rougher surface than the PS particles, as shown in Fig. 2(b). The PS/PANI particles maintained a spherical shape but particles were larger than the PS particle diameter with a mean particle size of approximately 500 nm. This indicates that the coating thickness of the PANI layer is approximately 70 nm.

Fig. 3 presents TEM images of pure PS and core-shell structured PS/PANI nanospheres at different magnifications. Compared to pure PS (Fig. 3 (a), (b)), a dense and rough PANI shell wrapped the PS surface, in which the internal black core (PS) was coated with an external gray shell (PANI), as shown in Fig. 3 (c), (d). The mean thickness of the PANI shell was approximately 70 nm.

Fig. 4 shows the thermal stability of the pure PS and PS/PANI nanospheres. TGA was carried out from 25 °C to 800 °C at a heating rate of 10 °C/min in air. The TGA curve of the pure PS revealed a sharp weight loss at approximately 280 °C and continuing to 430 °C due to the large-scale thermal degradation of PS. In the case of the PS/PANI particles, the slight weight loss before 100 °C was possibly attributed to the adsorbed moisture in the particles before the TGA measurement even though the trace water in the particles has been removed completely during the particle synthesis. The PS/PANI showed a second weight loss of approximately 23% between 280 °C and 410 °C which is in accordance with the complete decomposition of the pure PS particles. Furthermore, the 70% weight loss from 410 °C to 650 °C corresponds to the thermal degradation of PANI. The thickness of the PANI shell was calculated based on the weight loss of PANI using the following equations [38]:

$$\frac{V_2 \rho_2}{V_1 \rho_1 + V_2 \rho_2} \times 100 = m \tag{1.1}$$

$$V_1 = \frac{4}{3} \pi R^3 \tag{1.2}$$

$$V_2 = \frac{4}{3} \pi \left[(R+d)^3 - R^3 \right] \tag{1.3}$$

where m is the PANI weight ratio and R is the radius of the PS sphere; d is the thickness of the PANI shell. V_1 and V_2 represent the volume of the PS and PANI; ρ_1 and ρ_2 represent the density, respectively. The density of PS increased after the PANI coating to 1.13 g/cm^3 from 0.98 g/cm^3 of pure PS while the density of PANI was 1.36 g/cm^3, which was measured using a pycnometer. The