Electrorheological Properties of Monodispersed Submicron-sized Hollow Polyaniline Adipate Suspension

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Abstract: The electrorheological (ER) fluids are composed of a colloidal dispersion of polarizable particles in insulating oil, and it's the rheological property changes by the applied electric field. These changed are reversible and occur fast within a few milliseconds. The ER properties of the ER fluid such as increment of viscosity and yield stress come from the particle chain structure induced by electric field. When formulating the ER fluid for a specific application, some requirement must be satisfied, which are high yield stress under electric field, rapid response, and dispersion stability. While this characteristic makes valuable ER fluids in various industrial applications, their long term and quiescent application has been limited because of problems with particle sedimentation. In an effort to overcome sedimentation problem of ER fluids, the anhydrous ER materials of monodispersed hollow polyaniline (PANI) and adipate derivative respectively with submicron-sized suspension providing wide operating temperature range and other advantages were synthesized in a four-step procedure. The ER fluids were characterized by FT-IR, TGA, DLS, SEM, and TEM. Stability of the suspensions was examined by an UV spectroscopy. The rheological and electrical properties of the suspension were investigated Couette-type rheometer with a high voltage generator, current density, and conductivity. And the behavior of ER suspensions was observed by a video camera attached to an optical microscope under 3kV/mm. The suspensions showed good ER properties, durability, and particle dispersion.

Keywords: Electrorheological fluid, nano particle, hollow sphere, polyaniline, polyaniline adipate

Introduction

The electrorheological (ER) fluids [1] undergo a large, rapid alternation of rheological properties when subjected to an external electric field. First discovered by Winslow [2] in 1949, most ER fluids consist of a suspension of small, polarizable particles dispersed in a nonpolar liquid. They can switch from a liquid-like material to a solid-like material within a millisecond with the aid of an electric field, and this phenomenon is called the ER effect. The unique feature of the ER effect is that ER fluids can reversibly and continuously change from a liquid state to a solid state, and stress is required to break the chainlike or columnar structure and make it flow. When an electric field is imposed, the rheological properties of the fluid vary, showing a characteristic fibrillation; the strings of the particles are oriented along the direction of the electric field. This structure is known to be induced by a mismatch of the dielectric constants of the suspended particles and non-conducting oil. In the absence of an electric field, the fluid exhibits either a Newtonian or non-Newtonian fluidlike behavior, depending on the particle concentration. This stress, referred to as yield stress, is field-dependent and is the main characteristic of the ER fluid. The ER fluids also show increases in their shear viscosities of several orders of magnitude at low shear rates. Application of an electric field

induces the formation of chains of particles along the field direction; these chains are responsible for the increased resistance to flow perpendicular to the chains. Because of their controllable viscosity and short response time, the ER fluids are regarded as potential smart materials for active devices, such as brakes, clutches, shock absorbers, and actuators. But some of the shortcomings of these materials, such as low shear stress, poor temperature stability, easy sedimentation and high cost, have greatly restricted their industrial development [3]. This lack severely impedes the development of new fluid formulations with improved properties. In an effort to overcome disadvantages of suspension the ER fluids, recent research interests have been mainly concentrated on anhydrous ER system providing wide operating temperature range and other advantages. The anhydrous ER material, which possess advantages of a wide working temperature range, reduced device abrasion, and a relatively low current density, have intrinsic charge carriers in either the bulk particles or their surfaces that can move locally under an applied electric field. Among anhydrous ER materials, conducting polymers studied are based on a π-conjugated system constituting the polymer backbone. Polymers with conjugated π-electron systems display unusual electronic properties, including high electron affinities and low ionization potentials. The local electron distribution of particles induces the ER effect under the applied electric field.

By comparison with other ER fluids, polyaniline (PANI) has been widely used in ER materials due to its synthetic versatility

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and other advantages such as a relatively low density, environmental stability, and good thermal stability. Furthermore, electrical properties of PANI can be easily controlled by varying oxidation state, dopant type, and polymerization conditions. However, most electrically conducting polymers are insoluble in their doped, conducting state and hence suffer from poor processability. Recently, an ER fluid made of PANI derivatives particle has been investigated.

In this study, we synthesized new compounds of ER material of monodisperse submicron-sized hollow PANI adipate particles having low density and functional group, and prepared ER fluids by dispersing these particles into silicone oil. The suspensions showed good ER properties, durability, and particle dispersion. Specifically, modified PANI having carboxyl groups as the dispersed phase showed good yield stress and electrical stability.

Experimental

Preparation of hollow PANI adipate

The overall procedure for preparing monodisperse submicron-sized hollow polyaniline adipate sphere suspensions as dispersed phase for ER fluids is depicted in Fig. 1.

Materials

The monomers, styrene (99%), aniline (99.9%), from Aldrich, were purified through distillation under reduced pressure, and stored before use in a fredge at −20°C. The other components, initiator, potassium persulfate (KPS, 99%), ammonium persulfate (APS, 98%) and the surfactant, polyvinyl alcohol (PVA, Mw = 85,000~146,000, 98% hydrolyzed), from Aldrich, were used received. Hydrochloric acid (HCl, 37%), ammonium hydroxide (NH$_4$OH, 28% NH$_3$ in water, 99.99%), tetrahydrofuran (THF, 99.5%), adipic acid (99%), triphenyl phospine (TPP, 99%), and diethyl azo dicarboxylate (DEAD) were used as received from Aldrich. Deionized water used in all experiments.

Synthesis of PS sphere

Monodispersed polystyrene was synthesized by emulsion polymerization using a free radical initiator KPS according to Menno et al. [4]. The styrene polymerization was allowed to proceed at 70°C, under a N$_2$ atmosphere for 24 h, in four-necked round reactor equipped with a stirrer rotating at 350 rpm.

Preparation of PANI-coated PS

APS was dissolved in the PVA stabilized PS latex in a screw-cap bottle with magnetic stirring. The latex was acidified to pH 0.7 for APS, respectively, and the initial oxidant/monomer molar ratio was fixed at 1.25. Aniline was added via auto-syringe, and the polymerization was allowed to proceed for 24 h at room temperature. And the HCl-doped PS-PANI composite particles were converted to the emeraldine base form by treating NH$_4$OH solution for 12 h. The resulting PANI-coated PS latexes were purified by repeated centrifugation/redispersion cycles, to remove the oligomers and the inorganic byproducts of the aniline polymerization.
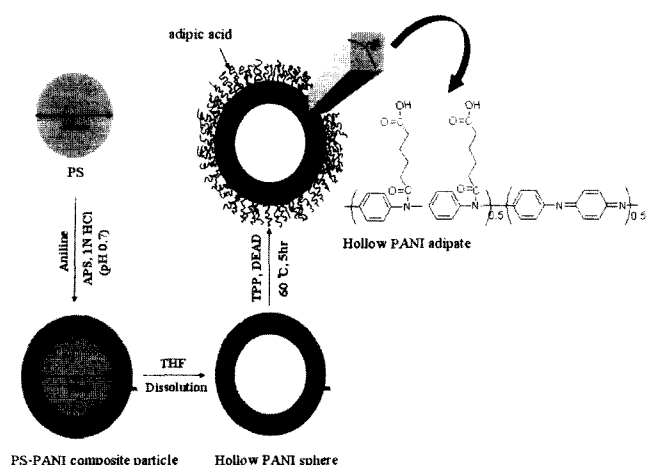

PS-PANI composite particle   Hollow PANI sphere

Fig. 1. Schematic illustration of the formation mechanism of hollow polyaniline adipate spheres.

Preparation of Hollow PANI capsule

Excess THF was added to dried PANI-coated PS latexes at room temperature. This solution was left 7 days. The resulting black residues were filtered, washed with THF, and dried under freezing dryer.

Synthesis of Hollow PANI adipate particles

Dried hollow PANI capsules, adipic acid (1mol), TPP (0.01 mol), DEAD (0.01 mol), and distilled water (500 ml) were put into a round flask under N$_2$ purging and reacted at a 75°C oil bath for 5 h with magnetic stirring. After a reaction hollow PANI adipate was distilled water and dried under freezing dryer.

Particle characterizations
Chemical characterizations

The morphology and size distribution of the particles was examined by SEM, TEM, and DLS. FT-IR spectroscopy was used to identify the chemical structure of the synthesized particles. The thermal stability and degree of dissolution of core in core-shell composite particles was confirmed TGA.

ER characterizations

ER fluids were prepared by dispersing the hollow PANI adipate particles into silicone oil whose viscosity was 50 cS at 25°C. The particle concentration was fixed at 10% volume fraction. The rheological properties of the suspension were investigated in a static DC field using a Physica Couette-type rheometer with a high voltage generator. The shear stress for the suspensions was measured under shear rate of 10^{-1} to 10^3 s^{-1} and electrical fields of 0-3 kV/mm. The dc current J of PANI hollow adipate particle suspensions was determined at room temperature by measuring the current passing through the fluid upon application of the electric field E$_0$ and dividing the current by the area of the electrodes in contact with the fluid.

Dispersion stability test

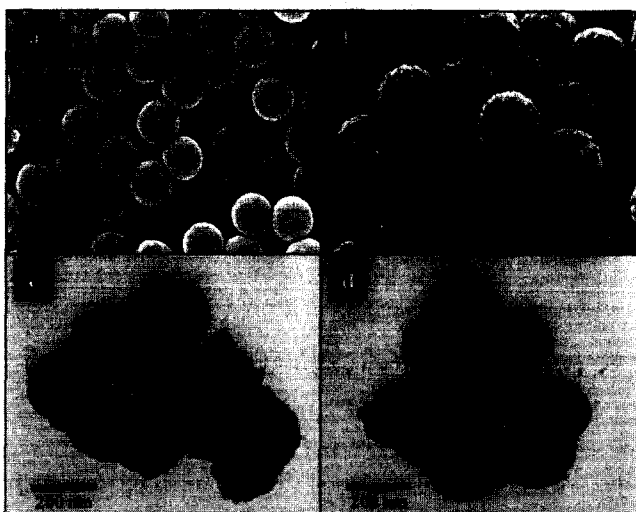Stability of the hollow polyaniline sphere and adipate suspension

Fig. 2. Morphologies of the (a) PS, (b) PS-PANI spheres, (c) hollow PANI particles, and (d) hollow PANI adipate compounds.

were examined by method such as an UV absorption test and a sedimentation ratio test at 0.525% concentration hollow particles and checked up sedimentation degree more than 1000 h. In the UV absorption test, changes in the absorbed UV ray passed through a given spot of the prepared sample were measured in accordance with time. A decrease in the absorbance with time at a given point implies that sedimentation of the colloidal system is occurring.

Results and Discussion

Chemical properties

The morphologies of the resulting samples as dispersed phase for ER fluids synthesized in a four-step procedure are shown in Fig. 2.

Monodispersed and stable seed particles were obtained by emulsion polymerization. Fig. 2(a) and (b) shows the SEM images of PS particles with an average diameter of 100 nm and PANI-coated PS spheres with an average diameter of 200 nm. The coated spheres are as monodisperse as the PS spheres is very uniform. And the TEM image of hollow PANI spheres is shown in Fig. 2 (c). In Fig. 2 (d), the TEM image of hollow PANI adipate particles was observed. All the particles were very clear and highly monodisperse with a particle size distribution. Proof of the chemical component of the synthesizing particles comprising PS coated with PANI and hollow capsule was provided by the FT-IR spectroscopy, as presented in Fig. 3.

In Fig. 3 (a), typical PS absorption bands at 3025, 2921, 1601, 1492, 754, and 695 cm⁻¹ can be seen clearly. These peaks are attributed to characteristic aromatic =C-H, -CH₂-, aromatic C=C, and monosubstituted ring. In Fig. 3 (b), the spectra of the PANI coated PS latexes showed that the ring stretching vibrations of the quinoid and benzoid forms in the polymer are observed at 1562 and 1478 cm⁻¹, respectively. The C-N stretching vibration, C-H stretching vibration, and out of plane C-H are observed at 1298, 1133, and 799 cm⁻¹. In Fig. 3 (c),
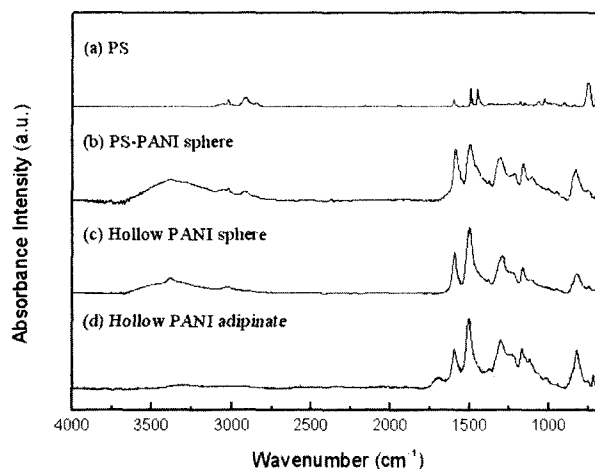

Fig. 3. FT-IR spectra of four samples: (a) PS spheres, (b) PS-PANI spheres, (c) hollow PANI spheres, and (d) hollow PANI adipate spheres.
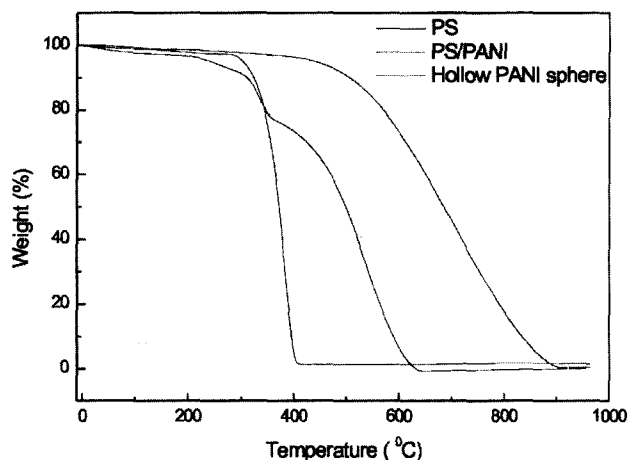

Fig. 4. TGA plots of (−) PS particle, (---) PANI-coated PS composite particle, and (···) hollow PANI sphere.

extinction in the amount of PS in the PS-PANI composite particles is reflected by a decrease in the intensity of the peaks near 695 and 795 cm⁻¹. FT-IR spectra of hollow PANI adipate particles are given in Fig. 3 (d). The bands observed at 1542 and 1453 cm⁻¹ in the PANI samples synthesized with adipic acid are due to C=N bonds of quinoid units and C-N bonds of benzoid units, respectively (Fig. 3 (c)). Figure 4 shows the result of TGA of the product. The weight loss processes of these samples were measured by heating them from 30 to 1000°C in the TGA with a heating rate of 10°C/min under argon gas. In Fig. 4, thermal degradation of PS sphere and PANI was observed at 310°C and 430°C. Also, degree of dissolution of core in core-shell composite particles was confirmed by analyzing TGA result. In Fig. 4, between 310 and 430, a weight loss of 21% is attributed to removal of the PS and the residual weight of 79% should be the weight of the PANI particles. This indicates the weight fraction of PS in the PS-PANI composite sphere should be calculated qualitatively. Also, these results showed thermal stability as ER materials.
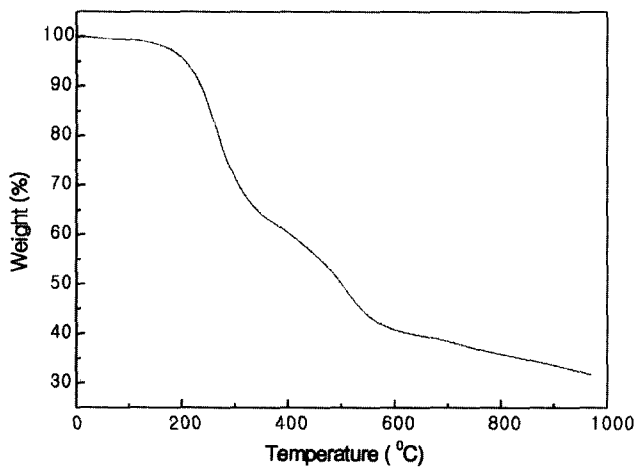
Figure 5 exhibits the thermograms of hollow PANI and

Fig. 5. TGA plots of PANI adipateparticles.

Fig. 6. Current density vs. electric field for hollow PANI and PANI adipate suspension.

Fig. 7. Dependence of the yield stress on the electric field for hollow PANI adipate and PANI suspension (10 vol.-%).

adipate samples taken between 30 and 1000°C. PANI has three stage weight losses in some of the samples synthesized with different acids. This can be explained as follows: The first weight loss of 11% observed up to 110°C is due to loss of water from the polymer [5-6]. The second stage observed within the temperature range of 110-310°C is related to removal of dicarboxyl group molecules from the polymer structure [7]. The weight loss observed between 310-580°C after the removal of the dicarboxyl group molecules corresponds to the degradation of the polymer chain [8]. The thermograms clearly show that PANI samples synthesized with dicarboxylic acids looses approximately 60% of their total weight at 800°C. The weight loss values at the critical temperatures such as 100, 180, 420, 880°C in Fig. 5 reveal that the type of carboxyl group employed affects the thermal properties of the resulting PANI.

Electrical and rheological properties

In principle, the conducting mechanism of PANI type semiconductors is based on the flow of electrons or charge carriers along the conjugated π system PANI backbone [9-11]. With the adulteration of the dopant (Cl⁻), the delocalization of those charges carrier and the electrons charges. But doped PANI enhanced the conductivity of not only the inner part of the particles but also their outer layers. This defect of doping was then compensated by the method of the antidoping with ammonia solution as an antidopant.

Figure 6 shows the change of current density of the hollow PANI adipate nanocomposite ER fluids as a function of applied electric fields. The current density of the PANI adipate based ER fluids increases slightly as the electric field increases. In generally, the limitation of current density for commercial ER fluids is about 300 mA/m² at 6 kV/mm. Therefore, the current density of our ER system is much less than the commercial requirement, exhibiting better electrical stability. The conductivity of the hollow PANI and adipate suspensions are 2.23×10^{-10} and 3.37×10^{-10} S/m.

Also the resulting of dielectric constant (ε) was 2.84 and 3.09. In contrast with PANI, the PANI adipate is comparatively higher values of electrical tests due to the presence of carboxyl
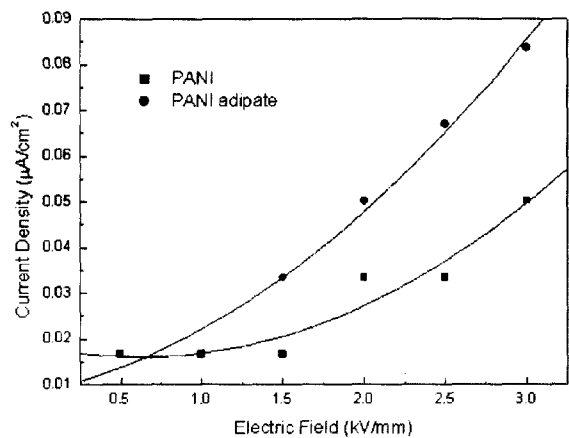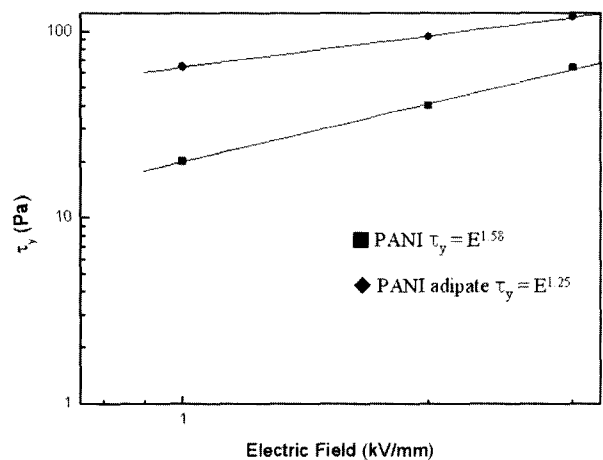
group.

The yield stresses obtained from various logarithmic shear stress versus shear rate curves also plotted as a function of electric field strength (E) for two kinds of ER fluids as shown in Fig. 7. The change of yield stress with different electric field can be represented by the following equation $\tau_y \propto E^a$. The a values of hollow PANI and adipate suspension are 1.58 and 1.25. The effect of dicarboxyl group with respect to enhancing the yield stress is distinctively large as compared with hollow PANI suspension.

Figure 8 shows changes in the structure in a dilute hollow PANI adipate sphere suspension under various electric fields, the chain-like particle structure could be observed. These partial fibrils are thought to contribute to the viscosity increase, since an attempt to move one electrode relative to the other would be hindered by the drag of the dangling fibrils. On the basis of the results, we may consider that the hollow PANI adipate spheres based ER fluid exhibit ER performance.

Dispersion stability test

In previous study, the sedimentation test was investigated through naked-eye observation of sedimentation or flocculation
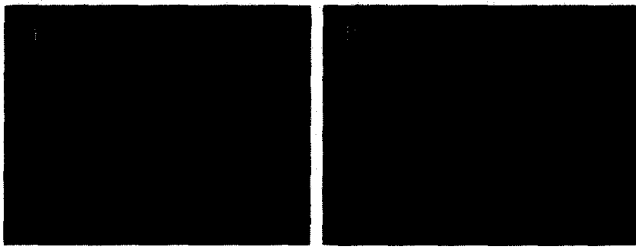
Fig. 8. (a) Optical microscopy image of hollow PANI adipate suspensions. (b) Same portion of the suspension after application of a 3 kV/mm dc electric field.
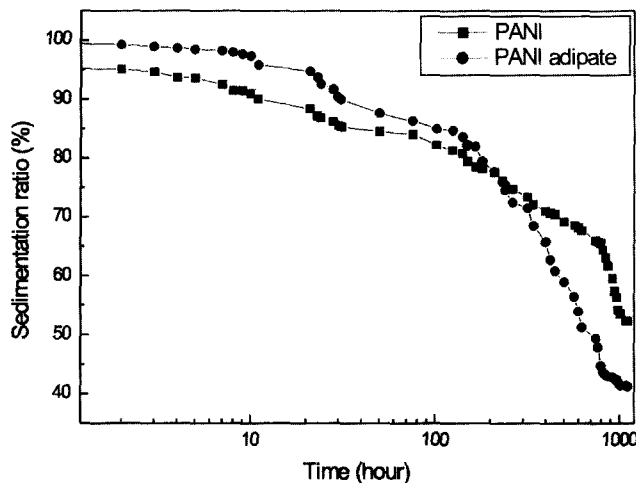

Fig. 9. Sedimentation ratio as a function of the time for 0.525 % (v/v) hollow PANI adipate in silicone oil (50 cS).

of suspensions [12-13]. The experimental samples were placed in capped test tubes and observed within a given period of time. During this time, the height of the phase separation between the particle-rich phase and the relatively clear oil-rich phase was measured as a function of time. Then, the sedimentation ratio, defined by the height percentage of the particle-rich phase, relative to the total suspension height, can be readily evaluated. This method was not qualitative but quantitative. Also sedimentation test was estimated only a few days.

On the other hand, we are estimated by using UV spectra. In the UV absorbance test, changes in the absorbed UV light passed through the Hollow PANI sphere suspension with different concentrations were measured over 1000 h. The experimental sample was prepared by dispersing 3 different low volume fraction of hollow PANI sphere in silicone oil. If experimental sample concentration is deep, UV light can not absorb sufficiently sample tube. According to synthesized emeraldine base PANI particle color was dark violet, concentration of PANI particle was prepared below 10 % (v/v). A decrease in the absorbance with time at suspensions implies that sedimentation or flocculation of the colloidal system is occurring. Through these results, the relatively colloidal stability of the hollow PANI sphere suspensions can be estimated, at qualitatively. In Figure 9, the sedimentation ratio is plotted as a function of time at various concentrations of hollow PNAI and adipate

particles in silicone oil, respectively. This figure shows that tiny small (submicron-sized) and porous particle has good dispersibility for a long time. The hollow PANI and adipate suspensions were visible a similar tendency of sedimentation ratio. However, hollow PANI particles showed better dispersion stability than PANI particles having carboxyl group.

Conclusion

In the present study, the ER fluid was prepared by dispersing semi-conductive polymer PANI particles and their derivative having dicarboxyl group with submicron-sized hollow sphere in silicone oil to improve sedimentation problems and ER performance on ER response.

The PS-PANI composite particles are nearly mono-dispersed with spherical particles 200 nm in diameter. Since the PS latex particle before coating PANI was 100 nm, the thickness of the PANI layer 50 nm. Also, hollow PANI synthesized successfully with adipic acid.

The alignment of ER particles like fibrils on an electric field was confirmed by using optical microscope in this experiment. Monodispersed, submicron-scale hollow PANI adipate suspension showed better ER performance and stable under various electric fields than PANI suspensions. Also, the ER material indicated stable thermal and electrical properties.

An UV-light absorbance test and sedimentation ratio test for the colloidal stability exhibited that submicron-sized hollow PANI sphere and adipate suspension observed more stable dispersibility in silicone oil for along while.

The hollow PANI particle and derivatives suspensions as ER fluid could decrease the sedimentation problem maintaining ER properties and proposed the method in which sedimentation ratio was estimated qualitatively.

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