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Synthesis and Electrorheological Effect of the Suspensions Composed of Nano Sized Hollow Polyaniline Derivatives

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Abstract: The electrorheology of hollow PANI derivative suspensions in silicone oil was investigated by varying the electric fields and shear rates, respectively. The hollow PANI derivative susepnsions showed a typical electrorheological (ER) response caused by the polarizability of an amide polar group and shear yield stress due to the formation of chains upon application of an electric field. The shear stress for the hollow PANI succinate suspension exhibited an electric field power of 0.67. On the basis of the experimental results, the newly synthesized hollow PANI derivative suspensions were found to be an anhydrous ER fluid.

Keywords: ER fluid, Hollow polyaniline derivative, Bingham fluid, Amide polar group

1. Introduction

Since Winslow's discovery of the ER effect in 1947 [1], many researchers have investigated ER performance for hydrous and anhydrous ER fluids and demonstrated the polarization models based on the polarization particle chains which are formed by interactive force between the polarized particles in a dielectric fluid upon application field. The polarization model of ER fluids can be described by the equation mentioned below [2,3,4,5].

$$\tau_E \propto \phi K_f E^2 \beta^2 \tag{1}$$

where τ is the shear stress, ϕ the volume fraction of particles, K_f the dielectric permittivity of the base fluid, E the electric field and β is the relative polarization at dc or low frequency at ac fields given by [3,6].

$$\beta = (\sigma_p - \sigma_f)/(\sigma_p + \sigma_f) \tag{2}$$

where σ_p is the conductivity of particles and σ_f the conductivity of base fluid [6].

Generally, electrorheological (ER) fluids are composed of electrically polarizables particles in a dielectric fluid and their ER performance are characterized by a rapid and reversible increase in apparent viscosity due to the formation of particle chains upon application of an electric field and depend on the electrical properties of the disperse phases. They are classified by the hydrous ER fluids and anhydrous ER fluids. The hydrous ER fluids composed of cellulose [7] and corn starch [8] as the disperse phases have been widely used and studied for a long time. Their ER performance is dependent upon the activation of a low molecular solvent and mostly frequently water under an electric field. But they have lots of problems, including dispersion stability, durability, corrosion and a limited temperature in actual use. Recently, anhydrous ER fluids composed of polyaniline [9], polyurethane [10], chitosan [11] and PMMA [12] as the disperse phases , which do not contain water or polar solvent in the particles, have been introduced. However, they also have certain problems, such as dispersion stability and adhesion to the cell inspite of their high ER performance.

In this paper, we are to introduce nano sized hollow polyaniline (PANI) derivatives as the disperse phase. Hollow PANI succinate sphere particles as the disperse phase were synthesized by chemical reactions between hollow PANI and succinic acid and the electrical and rheological properties of the synthesized hollow PANI succinate sphere particles in silicone oil were investigated. The suspensions provided an ER performance under an electric field due to the polarizability of the branched amide group.

This study is to describe the ER behavior of the synthesized hollow PANI succinate suspension and to investigate the possibility of an anhydrous ER fluid.

2. Experimental

2.1. Synthesis of hollow PANI succinate salts form

Hollow PANI succinate salts particles were prepared by synthesizing in the four step procedure. Monodispersed polystyrene (PS) spheres were synthesized by emulsion polymerization using a free radical initiator potassium persulfate (KPS, 99%, Aldrich) according to Menno *et al.* [13]. Ammonium persulfate (APS) was dissolved in the polyvinyl alcohol stabilized PS particles in a screw-cap bottle with magnetic stirring. The reaction mixture was acidified to pH 0.7 for APS, and the initial oxidant/monomer molar ratios were fixed 1.25. Aniline was added via syringe, and the polymerization was allowed to proceed for 24 h at 0°C. The pH value was maintained at 0.7 using a pH stat with 1 N HCl aqueous solution during the polymerization. And the HCl-doped PS-PANI

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composite particles were converted to the emerladine base form by treating it with NH_4OH aqueous solution for 12 h.

The extraction of PS particle from PS-PANI composite particle with tetrahydrofuran (THF) under stirring at room temperature for 7 days was produced. 1 M succinic acid solution was prepared for salt form. This solution and hollow PANI capsules were stirred for 5 h at room temperature. The morphology and size distribution of the particles was examined by SEM and STEM. The synthesized particle size was on average 100-300 nm in diameter. Prior to mixing in silicone oil, the synsized particles were dried for 5 h at 130°C and the silicone oil for 3 h at 130°C to remove any moisture in the vacuum oven.

2.2. Electrical and rheological tests

The dc current density of the suspensions was determined at room temperature by measuring the current passing through the fluid upon application of an electric field E_o and then dividing the current by the area of the electrodes in contact with the fluid. The current was determined from the voltage drop across a 1 $M\Omega$ resistor in series with the metal cell containing the oil using a voltmeter with a sensitivity of 0.01 mV. DC conductivity was taken to be ($\sigma = J/E_0$).

The rheological properties of the suspensions were investigated in a dc field using a Physica Couette-type rheometer with a 1mm gap between the bob and the cup. The resistance to shear produced by the suspension was measured as the torque on the drive shaft and then converted to shear stress and viscosity. The shear stress for the suspensions was measured under shear rate of 1 to 300 s^{-1}, electric fields of 0 to 3 kV/mm, and volume fractions of 0.1, respectively.

The experimental cell was assembled by mounting two parallel copper electrodes with 1mm gap on the Teflon slide in which a drop of well mixed suspensions was dispersed and observed by a viedo camera attached to an optical microscope for ER effect.

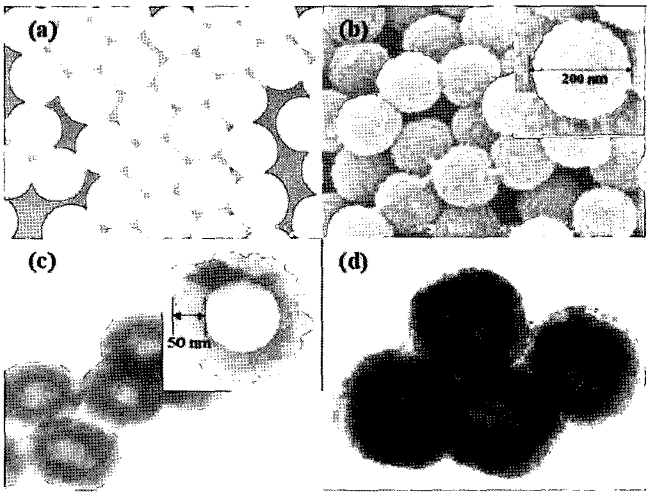

Fig. 1. SEM image showing (a) 100 nm PS cores, (b) 200 nm PANI spheres coated PS seed, (c) hollow PANI spheres, and (d) hollow PANI succinate spheres.

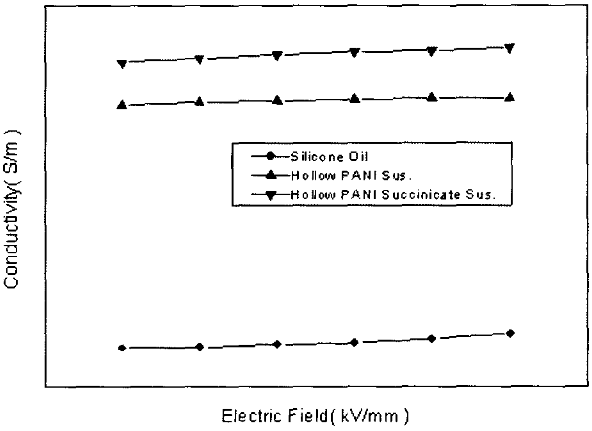

Fig. 2. Effect of electric field on conductivity for suspensions.

3. Results

The morphologies of the resulting samples as dispersed phase for ER fluids synthesized in a four-step procedure are shown in Fig. 1.

Monodispersed and stable seed particles were obtained by emulsion polymerization. Fig. 1(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. 1 (c). In Fig. 1 (d), the TEM image of hollow PANI succinate salt particles was observed. All the particles were very clear and highly monodisperse with a particle size distribution.

The electrical properties of ER fluids are important for predicting the power requirements for the design of an ER device and also to identify the ER mechanism. The current density and conductivity of the hollow PANI and hollow PANI succinate suspensions for the volume fraction ($\phi = 0.1$) under the electric field are given in Fig. 2. In Fig. 2, the conductivity of the hollow PANI succinate suspension increased with an increasing the electric field and moreover, the conductivity of the suspension is about 1 and 8 orders of magnitudes higher than those of the hollow PANI suspension and the silicone oil. This appeared to result from the polarizability of the polar amide group.

To determine the effect of hollow PANI and hollow PANI succinate suspensions on the rheological properties, studies were conducted by varying the shear rates and electric fields. The effect of the shear rate on the shear stress for the hollow PANI and hollow PANI succinate suspensions is illustrated in Figs. 3 and 4. As seen in Figs. 3 and 4, the suspensions exhibited a Bingham flow behavior upon application of the electric field and also hollow PANI succinate suspension showed higher than hollow PANI suspension. This is caused by polarizability of the polar amide group in hollow PANI succinate suspension.

Figure 5 shows a log-log plot of the shear stress versus the square of the electric field for hollow PANI and hollow PANI

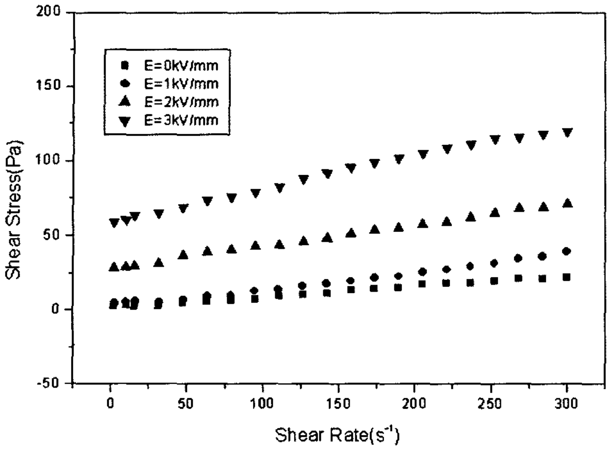

Fig. 3. Effect of shear rate on shear stress for hollow PANI suspension.

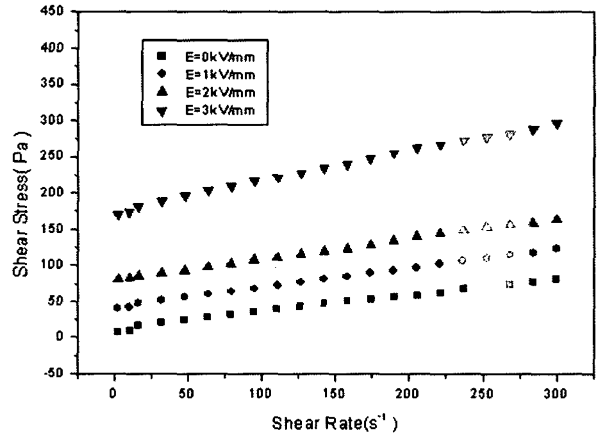

Fig. 4. Effect of shear stress on shear rate for hollow PANI succinate suspension.

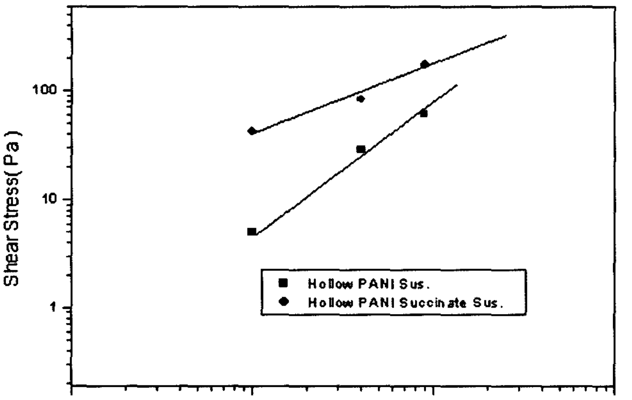

Fig. 5. Effect of squared electric field on shear stress for suspensions.

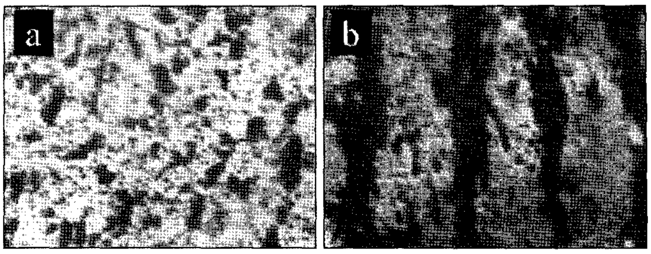

Fig. 6. The formation structure of particles chains without (a) and with (b) an electric field.

succinate suspensions. The results in Fig. 5 indicate that the shear stress was proportional to an electric field powers of 1.46 and 0.64 in hollow PANI and hollow PANI succinate suspensions, those are, $\tau \propto E^{1.46}$ and $E^{0.67}$. This follows from the fact that the interaction force for the dipole in an electric field is proportional to the electric field intensity. Figure 6 shows changes in the structure in a dilute hollow PANI suspension without (Fig. 6-a) and with (Fig. 6-b) electric field and In Fig. 6-b, 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 electride 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 suspension acts as ER behavior.

4. Discussion

Polarization models based on a point-dipole approximation, with a focus on the mismatch between the real components of the dielectric permittivities of the particles and the based fluid, have been proposed to explain the behavior and can be described by Eq. (1).

To explain the ER mechanism of the hollow PANI succinate suspension under an electric field, the results obtained with the suspension were examined based on the assumption that the base fluid and particles behaved as ideal dielectric materials, and the particles were aligned in chains or columns between electrodes. Using these assumptions, the theological analysis of Conrad *et al.* [3] for the polarization component of the shear yield stress gives.

$$\tau_E = 44.1\, A_s \phi \varepsilon_o K_f (\beta E)^2 \Big| \{\exp[(14.84 - 6.165(R/a))\beta^2]\} \times 1/(R/a)^8 (1 - 4/(R/a)^{10})^{1/2} \Big|_{\max} \qquad (3)$$

where A_s is taken to be the structure factor pertaining to the alignment of the particles. This is equal to one for perfectly aligned single-row chains and can have a value of the order of ~10 for multi-chains or columns. K_f is the dielectric constant, β the relative polarizability ($\cong 1$), and R/a the ratio of the separation of the particle center to the radius (≥ 2.05). The structure factor, A_s is obtained from the ratio value of the measured to the calculated shear stress using Eq. (3), that is, $A_s = \tau_{meas.}/\tau_{calc.}$. $A_s = 1$ was obtained for all the test conditions at a shear stress of 10 s^{-1}, electric fields of 1 to 3 kV/mm, and a volume fraction of 0.1, which may have been due to the formation of chains aligned between the electrodes [14].

5. Conclusions

This study was conducted to deduce the ER behavior of hollow

PANI and hollow PANI succinate suspensions, estabilished the ER mechanism, and investigated their potential as an ER fluid. The following is a summary of the results:

Hollow PANI and hollow PANI succinate suspensions in silicone oil showed an ER response upon the application of an electric field and the suspension exhibited a Bingham flow behavior. The hollow PANI succinate suspension showed higher than hollow PANI suspension. This was considered to result from the polarizability of the branched polar amide group.

The shear stress of the hollow PANI and hollow PANI succinate suspensions increased the electric field powers of 1.46 and 0.67.

The value of the structure factor in hollow PANI succinate suspension, A_s was 1 and this may have been due to the formation of chains aligned between the electrodes upon the application of an electric field.

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