

Rheology of Hollow Polyaniline Gutarate Suspension Under DC Electric Field

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Abstract: The electrical and rheological behavior of the hollow polyaniline glutarate suspension in silicone oil was investigated. Hollow polyaniline glutarate suspension showed a typical ER response (Bingham flow behavior) under a DC electric field. The shear stress for the suspension exhibited the dependence with a factor equals to 0.95 power on the electric field. The experimental results for the hollow polyaniline glutarate suspension behaved as an ER fluid.

Keywords: ER fluid, bingham flow, hollow polyaniline glutarate, conductivity, yield stress

1. Introduction

Electrorheological (ER) fluids are nonaqueous suspensions composed of electrically polarizable particles dispersed in an insulating fluid such as the silicone oil and the disperse phase plays an important role in the ER phenomenon. The flow behavior of ER fluids is characterized by a rapid and reversible increase in apparent viscosity due to the formation of particle chains upon application of an electric field and behaved as Bingham flow[1-5]. Since the ER effect was discovered by Winslow in 1947, many researchers have investigated ER phenomenon for a variety of ER fluids

The anhydrous ER fluids which do not contain water in the disperse phase have been introduced, which compose of polyaniline[6], polyurethane [7] and chitosan[8] as the organic disperse phases. These have several problems about durability, limited temperature and dispersion stability in actual use.

As a new organic disperse phase of the ER fluid, nano-sized hollow polyaniline(PANI) glutarate has been synthesized and the electrical and rheological properties pertaining to the ER behavior of hollow PANI glutarate suspension in silicone oil were investigated. The synthesized suspension provides the ER response upon application of an electric field.

This study describes the ER behavior of hollow PANI glutarate suspension and the possibility of its use as a new ER fluid.

2. Experimental

2.1. Materials

The base fluid was silicone oil provided by Dow Corning with a specific gravity of 0.97, a kinematic viscosity of 50 cSt at 40 °C, and a dielectric constant of 2.61 at 25°C. Hollow PANI glutarate used as the disperse phase was synthesized through four steps. Monodispersed polystyrene (PS) spheres were

synthesized by emulsion polymerization using a free radical initiator potassium persulfate (KPS, 99%, Aldrich) according to Menno et al [9]. 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 composite particles were converted to the emeraldine base form by treating it with NH₄OH 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. 1M glutaric 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 100nm in diameter. Prior to mixing in silicone oil, hollow PANI glutarate particles were dried for 5 h at 130 °C and silicone oil for 3h at 130°C to remove moisture in vacuum oven. The suspensions were then prepared at volume fractions of 0.1. After vigorous mixing, the suspensions were stored in a dessicator to maintain the dry state.

2.2. Electrical and rheological tests

The dc current density J and the conductivity s of the silicone oil and the hollow PANI glutarate suspension were 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. The current was determined from the voltages drop across a 1M Ω resistor in series with the metal cell containing the oil using a voltmeter with a sensitivity of 0.01mV. This method gave a current measuring sensitivity of 0.01nA. The dc

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conductivity was taken to be $\sigma = J / E_0$.

The rheological properties of the suspension were investigated in a dc field using the Physica Couette-type rheometer with a 1mm gap between the bob and cup. The resistance to shear produced by the suspensions was measured as a torque on the drive shaft and then converted to shear stress and viscosity. The shear stress for the suspensions was measured under shear rates of 1 to 1000 s^{-1} , electric fields of 0 to 3.0 kV/mm and volume fractions of 0.1, respectively.

3. Results and discussion

3.1. Electrical properties

ER fluids consist of dielectric particles surrendered by an insulating fluid, and in a device they essentially function as leaky capacitors. The transfer of charge between particles results in an electric current through the fluid. The current density associated with a particular ER fluid is useful for estimating the power consumption of devices using the fluid. The electrical properties of ER fluids are therefore important for predicting the power requirements for the design of an ER device and also identifying the ER effect mechanism. Figures 1 and 2 shows the current density and the conductivity of the silicone oil and hollow PANI glutarate suspension with the electric field. The current density increases with increasing the electric field in Figure 1. As seen in Figure 2, the conductivity of hollow PANI glutarate suspension is about 3 orders of magnitude higher than that of the silicone oil.

3.2. Rheological properties

To investigate the effect of PANI glutarate suspension on the rheological properties, studies were carried out by varying shear rates, and electric fields. The effect of the shear rate on the shear stress for hollow PANI glutarate suspension under shear rate of 1-1000 s^{-1} , a volume fraction of 0.1 and electric field of 0-3kV/mm is illustrated in Figure 3. Hollow PANI glutarate suspension behaves as a Newtonian fluid without the electric field, but upon application of the electric field it exhibits a shear yield stress τ_E , which is followed by a

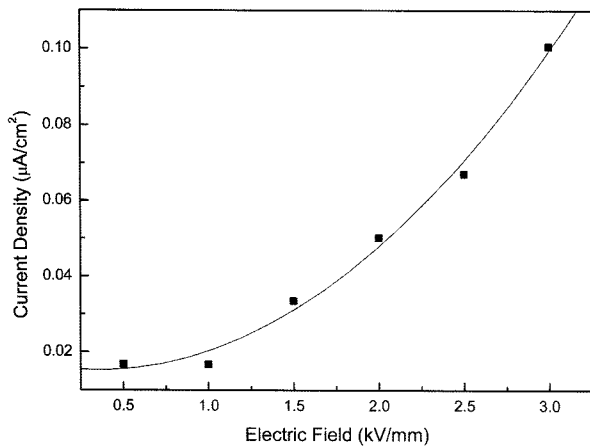


Fig. 1. Effect of electric field on current density for hollow PANI glutarate suspension

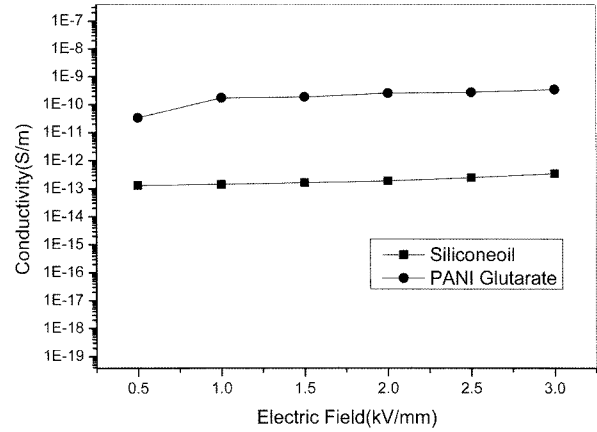


Fig. 2. Effect of electric field on conductivity for suspensions

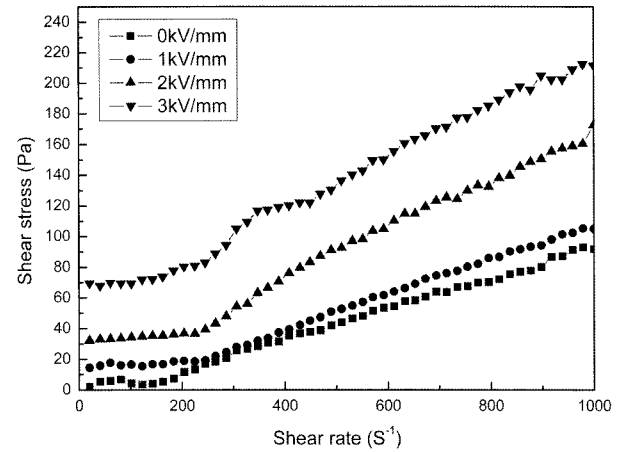


Fig. 3. Effect of shear rate on shear stress for hollow PANI glutarate suspension

increase in flow stress. This suspension approximates a Bingham flow behavior, which is described by the equation

$$\tau = \tau_E(E_0, \gamma) + \eta \dot{\gamma} \quad (1)$$

Figure 4 shows a plot of $\log \tau$ vs $\log E_0$ for the suspension under a shear rate of 10 s^{-1} and a volume fraction of 0.1. The results in Figure 4 indicate that the shear stress is proportional to 0.95 power of the electric field.

To describe the status of ER behavior of the hollow PANI glutarate suspension, the examination process for obtaining the results will be conducted with the assumption that the base fluid and particles behave as ideal dielectric materials, and the particles are aligned in chains or columns between electrodes. With these assumptions, the theoretical analysis of Conrad et al.[19] gives for the polarization component of the yield shear stress

$$\tau_E = 44.1 A_s \phi \epsilon_0 K_f (\beta E)^2 \left\{ \exp \left[(14.84 - 6.165 (R/a)) \beta^2 \right] \right\} \times 1 / (R/a)^4 (1 - 4 / (R/a)^2)^{1/2} \Big|_{\max} \quad (2)$$

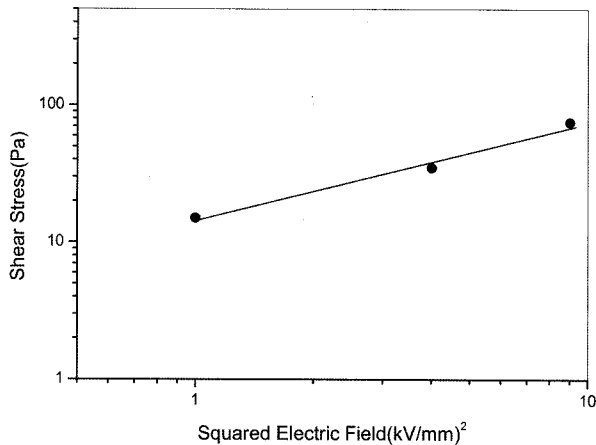


Fig. 4. Effect of squared electric field on shear stress for hollow PANI glutarate suspension

where A_s is taken to be a structure factor pertaining to the alignment of the particles. It is equal to one for perfectly aligned single- row chains and may have a value of the order of ~ 10 for multiple chains or columns. K_r is the dielectric constant, β the relative polarizability ($\cong 1$) and R/a the ratio of the separation of the particle center to their radius (≥ 2.05). The structure factor, A_s , is obtained from the ratio value of measured- to- calculated shear stress using Eq.(4), that is, $A_s = \tau_{\text{meas}} / \tau_{\text{calc}}$. We obtain $A_s = 1$ for all of the test conditions at the shear rate of 10 s^{-1} , the electric fields of 1 to 3 kV/mm and the volume fraction of 0.1, and it may be resulted the above mentioned conclusion due to the experimental output in relation with the formation of multiple aligned between electrodes[10].

4. Conclusions

This study was investigated the electrorheological behavior of the hollow PANI glutarate suspension and the following conclusions were found:

- (1) A hollow PANI glutarate suspension showed the ER response upon the application of the field and it behaved as a Bingham flow.
- (2) The shear stress of the hollow PANI glutarate suspension increased the 0.95 power of the electric field and the conductivity of hollow PANI glutarate suspension is about 3 orders of magnitude higher than that of the silicone oil.
- (3) The value of the structure factor, A_s , in the conduction model was 1 and it may be resulted due to the formation of chains upon application of the electric field.

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