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Electrorheology of Hollow Polyaniline Pimelate Suspension by Conduction Model

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Abstract: The electrorheological behavior of the hollow polyaniline pimelate suspension in silicone oil was investigated. Hollow polyaniline pimelate suspension showed a typical ER response (Bingham flow behavior) upon application of an electric field. The shear stress for the suspension exhibited the dependence with a factor equals to 0.84 power on the electric field. The experimental results for the hollow polyaniline pimelate suspension correlated with the conduction models of Tang *et al.*, and this suspension behaved as an ER fluid.

Keywords: ER fluid, Bingham flow, Conduction model, Hollow polyaniline pimelate suspension

1. Introduction

The flow behavior of electrorheological (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 [1-3]. Since the ER effect was discovered by Winslow in 1947, many researchers have investigated ER phenomenon for a variety of ER fluids and demonstrated the polarization models based on the point-dipole approximation, with focus on the mismatch between the real components of the dielectric permittivities of the particles and base fluid [4,5].

Recently, the importance of the conductivity of the base fluid which is strongly dependent upon the electric field, has been demonstrated and the conduction model was proposed. The conduction model considers that the ER effect in a dc field is induced by the mismatch of the conductivity of the particles and the base fluid. The conductivity of the base fluid is presented by a simplified expression for Onsager's electric-enhanced ionic dissociation theory [6]. The conduction model was originally proposed by Foulc *et al.* [7] in 1992 and modified by Davis and Ginder [8], Tang *et al.* [9] and Wu and Conrad [10]. It gives the following expression for the yield shear stress of ER fluids.

$$\tau_E \propto \phi K_f f(E_0, \Gamma_\sigma, A, E_c) \quad (1)$$

where ϕ is the volume fraction, K_f the dielectric permittivity of the base fluid, E_0 the electric field, Γ_σ the ratio of the conductivity of particles to that of the base fluid ($\sigma_p/\sigma_f(0)$), and A, $\sigma_f(0)$ and E_c are the constants which depend on the base fluid.

ER fluids are nonaqueous suspensions composed of electrically polarizable particles dispersed in a dielectric fluid and the disperse phase plays an important role in the ER phenomenon. The anhydrous ER fluids which do not contain water in the disperse phase have been introduced, which compose of polyaniline [11] and polyurethane [12] as the organic disperse phases. These have several problems about durability, limited temperature and stability in actual use.

To solve these problems, nanosized hollow polyaniline (PANI) pimelate as a new organic disperse phase of the ER fluid has been synthesized and the electrical and rheological properties pertaining to the ER behavior of hollow PANI pimelate 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 pimelate 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 pimelate 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.* [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 composite particles were converted to the emerladine base form by treating it with NH_4OH aqueous solution for 12 h.

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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 pimelic 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, hollow PANI pimelate particles were dried for 5 h at 130°C and silicone oil for 3 h 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 σ of the silicone oil and the hollow PANI pimelate 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 1 MΩ resistor in series with the metal cell containing the oil using a voltmeter with a sensitivity of 0.01 mV. This method gave a current measuring sensitivity of 0.01 nA. The dc 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 300 s^{-1}, electric fields of 0 to 3.0 kV/mm and volume fractions of 0.1, respectively.

3. Results and discussion

3.1. Eelctrical 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 pimelate suspension with the electric field. The non-Ohmic character of the behavior is evident. The conductivity parameters, A, $\sigma_f(0)$ and E_c of the silicone oil were calculated using Onsager's equation to give A = 0.007, $\sigma_f(0) = 1.2 \times 10^{-13}$ S/m and $E_c = 0.11$ kV/mm. As seen in Fig. 2, the conductivity of hollow PANI pimelate suspension increases with the electric field and moreover, the conductivity of the suspension is about 8 orders of magnitude higher than that of the silicone oil.

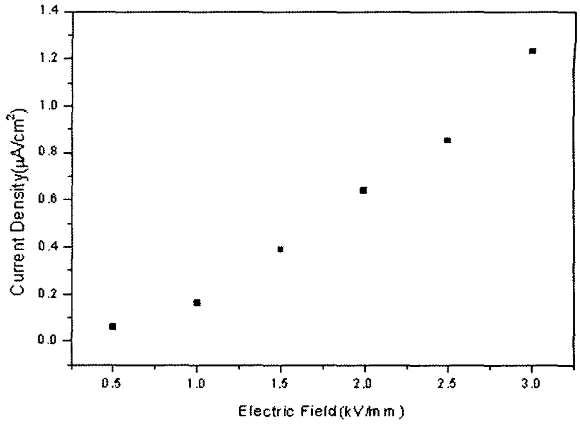

Fig. 1. Effect of electric field on current density for hollow PANI pimelate suspension.

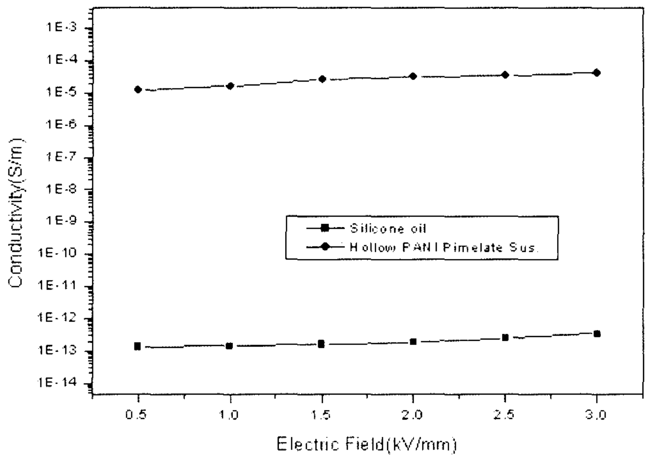

Fig. 2. Effect of electric field on conductivity for suspensions.

3.2. Rheological properties

To investigate the effect of cellulose phosphate ester 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 pimelate suspension is illustrated in Fig. 3. Hollow PANI pimelate 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 increase in flow stress, ultimately reaching a relatively constant shear stress. This suspension approximates a Bingham flow behavior, which is described by the equation.

$$\tau = \tau_E(E_0, \gamma) + \eta\gamma \quad (3)$$

Figure 4 gives a plot of log τ 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 0.84 power of the electric field.

To describe the status of ER behavior of the hollow PANI pimelate 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

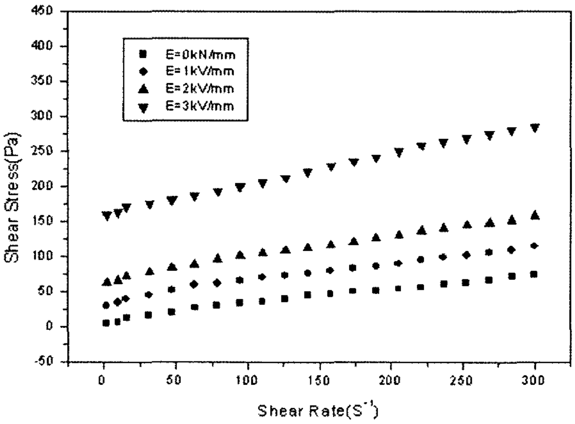

Fig. 3. Effect of shear rate on shear stress for hollow PANI pimelate suspension.

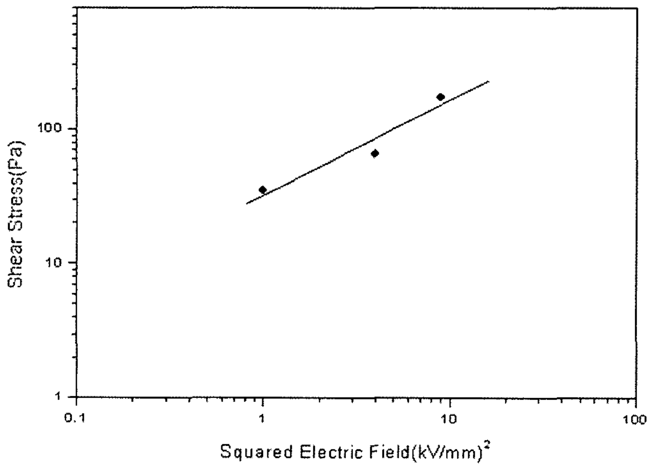

Fig. 4. Effect of squared electric field on shear stress for hollow PANI pimelate suspension.

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.

$$\tau_E = 44.1\ A_s\ \phi\ \varepsilon_0\ K_f(\beta E)^2 \mid \{\exp[(14.84 - 6.165(R/a))\beta^2]\} \times 1/(R/a)^4 (1 - 4/(R/a)^2)^{1/2} \mid_{max} \quad (4)$$

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 a value of the orders of ~10 for multiple chains or columns. K_f is the dielectric constant, β the relative polarizability (≅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, $A_s = \tau_{meas}/\tau_{calc}$. We obtain $A_s = 1$ for all of the test conditions at the shear rate of 10 s^{-1}., the elelctric fields of 1 to 3 kV/mm and the volume fraction of 0.1, and it maybe be resulted the above mentioned conclusion due to the experimental output in relation with the formation of multiple aligned between electrodes [14].

We will compare the experimental values of the shear stress with those predicted by the conduction models of Tang *et al.*

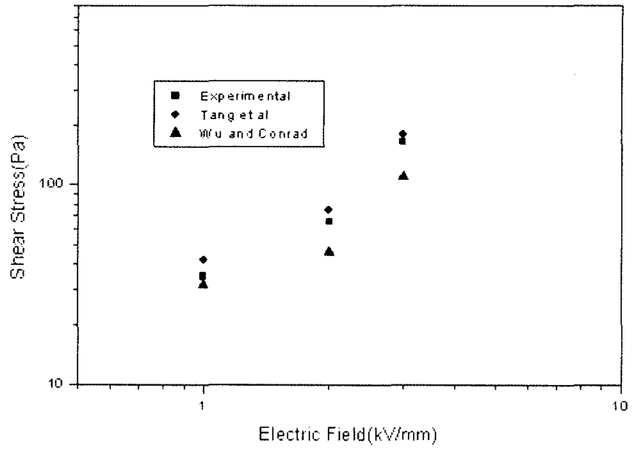

Fig. 5. Comparison of the predicted shear stress with that measured for hollow PANI pimelate suspension ($\phi = 0.1, \gamma = 10s^{-1}$).

[9] and Wu and Conrad [10]. The conduction model of Tang *et al.* gives the following expression for the shear stress.

$$\tau_E = A_s K_f \tau_0\ \phi\ E_0^2 \quad (5)$$

where τ_0 is given as follows for $\Gamma_\sigma > 10^3$

$$\tau_0 = m_1(E_c/E_0)^{0.6}/1 + m_2(E_c/E_0)^{0.6}$$

with $m_1 = 63.5 \log(0.0222\Gamma_\sigma/A)$ and $m_2 = 0.54 + 25.9\ A^{-0.25}\ \Gamma_\sigma^{-1}$.

The conduction model of Wu and Conrad gives

$$\tau_E = 3/2\ A_s K_f \tau_0\ \phi\ E_0^2 F\gamma/(1+\gamma^2)^{1/2} \quad (6)$$

where $F = 66(\Gamma_\sigma/A)0.1(E_c/E_0)^n$

When Ec = 0.1~0.3, n = 1 and the shear strain, γ~0.3 at maximum attractive force between particles.

The predicted values were calculated using Eqs. (5) and (6) and compared with experimental values for the cellulose phosphate ester suspension. The results are given in Fig. 5. The experimental results were obtained at a shear rate of 10 s^{-1}, a volume fraction of 0.1 and the electric fields of 1 to 3 kV/mm. As seen in Fig. 5, the predicted values of Tang *et al.* of two conduction models are in agreement with the experimental values.

4. Conclusions

This study was conducted to investigate the electrorheological behavior of the hollow PANI pimelate suspension and the following conclusions were found:

(1) A hollow PANI pimelate suspension showed the ER response upon the application of the field and it behaved similar to a Bingham flow.

(2) The shear stress of the hollow PANI pimelate suspension increased the 1.41 power of the electric field.

(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.

(4) There is a reasonable agreement between the predicted and experimental values of the yield shear stress for the hollow PANI pimelate suspension when using the conduction model of Tang *et al.*.

References

1. Winslow, W. M., Induced Fibration of Suspension, J. Appl. Phys., Vol. 20, pp. 1137-1140, 1949.
2. Block, H. and Kelly, J.P., Electrorheology, J. Phys. D:Appl. Phys., Vol. 21, pp. 1661-1667, 1988.
3. Klingberg, D. J. and Zukoski, C. F., Studies on the Steady-Shear Behavior of Electrorheological Suspensions, Langmuir, Vol. 6, pp. 15-24, 1990.
4. Conrad, H. and Chen, Y., Electrorheological Properties and the Strength of Electrorheological Fluids, Progress in Electrorheology, edited by K. O. Havelka and F. E. Filisko (Plenum Press, New York), pp. 55-65, 1995.
5. Gow, C. J. and Zukoski, C. F., The Electrorheological Properties of Polyaniline Suspension, J. Colloid Interface Sci., Vol. 136, pp. 175-188, 1990.
6. Onsager, L., Deviation from Ohm's Law in Weak Electrolyst J. Chem. Phys., Vol. 2, pp. 599-615, 1934.
7. Foulc, J. N., Felici, N. and Atten, P., C. R. Acad. Sci. Paris 107. 1995.
8. Davis, L. C. , Polarization Forces and Conductivity Effects in Electrorheological Fluids, J. Appl. Phys. Vol. 72, pp. 1334-1340, 1992.
9. Tang, X., Wu, C. and Conrad, H., On the Conductivity Model for the Electrorheological Effect, J. Rheol. Vol. 39, pp. 1059-1073, 1995.
10. Wu, C. and Conrad, H., A Modified Conduction Model for the Electrorheological Effect, J. Phys. D: Appl. Phys., pp. 3147-3153, 1996.
11. Block, H. and Kelly, J. P., Materials and Mechanism in Electrorheology, Langmuir, Vol. 6, pp. 6-14, 1990.
12. Bloodworth, R. and Wendt, E., Electrorheological Effect of Polyurethan Suspension, Progress in Electrorheology, edited by K. O. Havelka and F. E. Filisko (Plenum Press, New York), pp. 185-192, 1995.
13. Menno, G. D., Alain, G., Colloid Polym. Sci. Vol. 281, pp. 105, 1992.
14. Conrad, H.,Chen, Y. and Sprecher, A., The Strength of Electrorheological Fluids, J. of Modn. Phys. B, Vol. 16, pp. 2575-2583, 1992.