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Electrorheology of Amine Dispersant Coated Chitosan Phosphate Suspension

Ung-su Choi† and Young-gun Ko

Tribology center, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul, Korea

Abstract : The electrorheological (ER) behavior of amine coated chitosan phosphate suspension in silicone oil is investigated. Amine coated chitosan phosphate suspension shows a typical ER response (Bingham flow behavior) upon application of an electric field due to the polarizability of phosphoryl polar group. The shear stress for the suspension exhibits a linear dependence on an electric field power of 1.94. The values of structure factor, A_s obtains 2 for amine coated chitosan phosphate suspension and it may be due to the formation of multiple chains upon application of the electric field. Throughtout the experimental results, amine coated chitosan phosphate suspension shows good dispersion stability and found to be an anhydrous ER fluid.

Keywords : Electrorheological fluid, amine coated chitosan phosphate, structure factor

Introduction

ER fluids are nonaqueous suspensions composed of electrically polarizable particles dispersed in a dielectric fluid and especially, the disperse phase plays an important role in the ER phenomenon [1-3]. The organic polymers, polyaniline [4] and polyurethane [5] as the disperse phases have been widely used for the formulation of anhydrous ER fluids. Because they have the polar groups such as amino(-NH_2) and amino-cyan(-NHCN) radicals, respectively, suspensions of these particles provide the ER effect upon application of the electric field. Therefore, the chemical structure of the organic polymers is important in the ER effect.

Chitosan as the base material is a natural organic biocompatible polymer from chitin by N-deacetylation and composed of poly D-glucosamine. It has been widely used for applications to the fields of biochemisry, pharmacology, emzymology, microbiology, agricurture and environment [6]. As the new anhydrous ER suspension, chitosan suspension provided the ER behavior upon application of an electric field due to the polarizability of the branched amino group [7]. And also a chitosan derivative suspension composed of the anhydrous disperse phase, chitosan phosphate synthesized by phosphorylation reactions between chitosan and phosphorous acid introduced and its ER behavior investigated. Chitosan phosphate suspension showed execllent ER performance under the electric field due to the phosphoryl polar group [8].

However, it has certain problem, such as dispersion stability inspite of its high ER performance and nonadhesion to the electric cell. To solve this problem, amine dispersant coated chitosan phosphate as the disperse phase has been prepared and the electrical and rheological properties of the suspension investigated. The amine dispersant coated chitosan phosphate suspension provides the ER effect under the electric field and also stable dispersion stability.

This study is to describe the ER behavior of amine dispersant chitosan phosphate suspension and to investigate the possibility of a newly anhydrous ER fluid.

†Corresponding author; Tel: 82-2-958-5657, Fax: 82-2-958-5659
E-mail: uschoi@kist.re.kr

Experiments

Materials

The base fluid is 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. Chitosan used as the raw material is a commercial powder provided by Shin-yang Co. (Korea) and contained nitrogen content of 4.8 wt%. Chitosan phosphate as the disperse phase is synthesized by phosphorylation reactions between chitosan and phosphorous acid (2 mole soln) and contained phosphorous content of 9.5 wt%. After the reaction, chitosan phosphate is dispersed in 3% dioctyl amine aceton solution for 1hour. And then amine coated chitosan phosphate is dryed in oven. Its particle sizes is in 5 μm average diameter. Prior to mixing in silicone oil, amine coated chitosan phosphate particle is dried for 5 h at 150°C and the silicone oil for 3 h at 130°C to remove moisture in vacuum oven. Amine coated chitosan phosphate suspensions are then prepared at volume fractions of 0.1 to 0.3. After vigorous mixing, the suspensions are stored in a dessicator to maintain the dry state.

Tests

The dc current density J and the conductivity σ of the silicone oil and of amine coated chitosan phosphate suspensions are 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 is determined from the voltages drop across a 1MW resistor in series with the metal cell containing the oil using a voltmeter with a sensitivity of 0.01 mV. This method gives a current measuring sensitivity of 0.01 nA. The dc conductivity is taken to be $\sigma = J / E_0$.

The rheological properties of the suspension are 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 is measured as a torque on the drive shaft and then converted to shear stress and viscosity. The shear stress for the suspensions is 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 to 0.3 , respectively.

The dispersion stability of the suspension is monitored on time for sedimentation of the disperse phase within glass tube at room temperature and represented as the sedimentation degree:

$$\text{Sedimentation degree (\%)} = a / (a + b) \times 100 \quad (1)$$

where a is the oil layer separated from the suspension and b the disperse layer of the suspension.

Results and Discussion

The electrical properties of ER fluids are important for predicting the power requirements for the design of an ER device and also identifying the ER mechanism. The conductivities of the chitosan phosphate and amine coated chitosan phosphate suspensions for a volume fraction ($\phi = 0.3$) vs electric field are given in Fig. 1. The results in Fig. 1 indicate that the conductivity of amine coated chitosan phosphate suspension is about 1 order of magnitude lower than that of chitosan phosphate suspension and about 3 orders higher than the silicone oil. The decrease in conductivity of amine coated chitosan phosphate suspension is considered to result from the lower ploarizability caused by the insulation effect of dioctyl amine coated chitosan phoaphate particles.

To investigate the effect of amine coated chitosan phosphate suspension on the rheological properties, studies are carried out by varying shear rates, electric fields and volume fractions. The effect of the shear rate on the shear stress for amine coated chitosan phosphate is illustrated in Fig. 2. As seen in Fig. 2, the rheological behavior of the amine coated chitosan phosphate suspension behaves as a Newtonian fluid without the electric field, but upon application of the electric field, it exhibits a yield stress τ_E, that is, this suspension approximates a Bingham-type behavior, which is described by the equation

$$\tau = \tau_E(E, \gamma) + \eta\gamma \quad (2)$$

And the resulting amine coated chitosan phosphate suspension shows excellent ER response upon application of the electric field due to phosphoryl polar group. Figure 3 shows a log-log plot of the shear stress versus the square of the electric field for the amine coated chitosan phosphate suspension. The results in Fig. 3 indicate that the shear stress was proportional to an electric field power of 1.94, that is, $\tau \propto E^{1.94}$.

The sedimentation degree of amine coated chitosan phosphate suspension is investigated for dispersion stability of the suspension and the results are illustrated in Fig. 4. The results in Fig. 4 show that sedimentation degree slowly increases until 5% on time and then becomes constant over 10 days.

To explain the ER behavior of amine coated chitosan phosphate suspension, we will examine the results obtained with the assumption that the base fluid and particles behave as

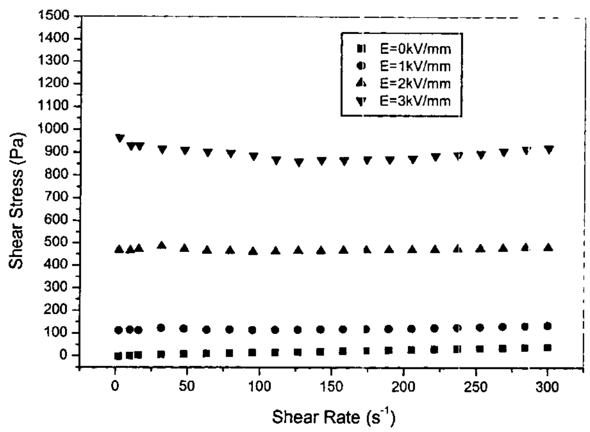

Fig. 2. Effect of shear rate on shear stress for amine coated chitosan phosphate suspension ($\phi = 0.3$).

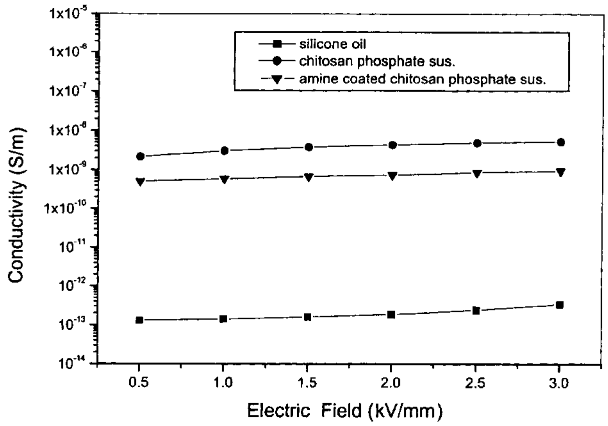

Fig. 1. Effect of electric field on conductivity for silicone oil and chitosan phosphate suspensions.

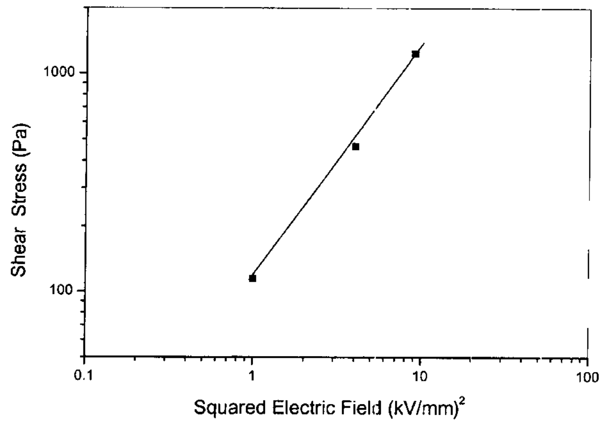

Fig. 3. Shear stress vs squared electric field for amine coated chitosan phosphate suspension ($\phi = 0.3$, $\gamma = 10\ s^{-1}$).

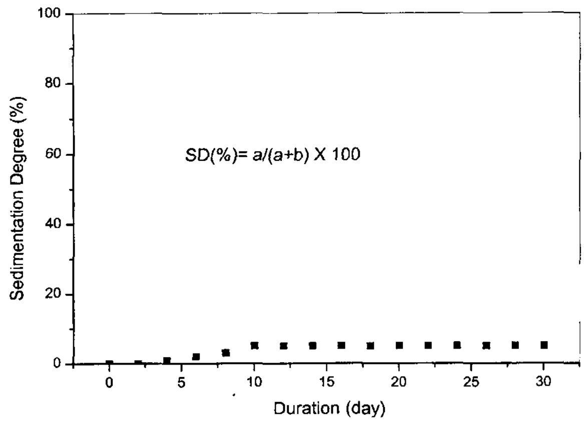

Fig. 4. Effect of duration on sedimentation degree for amine coated chitosan phosphate suspension ($\phi = 0.3$).

ideal dielectric materials, and particles are aligned in chains or columns between electrodes. With these assumptions, the theological analysis of Conrad *et al.* [9] gives for the polarization component of the yield stress

$$\tau_E = 44.1\, A_s\, \phi\, \varepsilon_0\, K_f\, (\beta E)^2\, I\{\exp[(14.84 - 6.165(R/a))\beta^2]\} \times [1/(R/a)^8 - 4/(R/a)^{10}]^{1/2} I_{max} \quad (3)$$

where A_s is taken to be a structure factor pertaining to the alignment of the particled. 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 ($\beta = 1$) and R/a the ratio of the separation of the particles center to their radius ($R/a \cong 2.05$). The structure factor, A_s is obtained from the ratio value of measured to calculated shear stress using Eq. (3), that is, $A_s = \tau_{meas.}/\tau_{calc.}$. We obtain $A_s = 2$ for amine coated chitosan phosphate suspension under the test conditions at a shear rate of 10 s^{-1}, the electric fields of 1 to 3 kV/mm and a volume fraction of 0.3. It may be due to the formation of multiple chains aligned between electrodes for the suspension [9,10].

Conclusions

This study is conducted to investigate the electrorheological behavior of amine coated chitosan phosphate suspension and the following results are found;

(1) Amine coated chitosan phosphate suspension in silicone oil shows the ER response upon the application of the electric field due to the polarizability of phosphoryl polar group.

(2) The shear stress of amine coated chitosan phosphate suspension increases linearly with 1.94 power of the electric field.

(3) Amine coated chitosan phosphate suspension shows good dispersion stability.

(4)The values of structure factor, As were 2 for amine coated chitosan phosphate suspension and it may be due to the formation of multiple chains upon application of the electric field.

Acknowledgments

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