

Electrical and Rheological Behavior of the Anhydrous ER Fluids Based on Chitosan Derivatives as the Dispersion Phases

Ung-su Choi^{*}

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

Abstract: The electrical and rheological properties pertaining to the electrorheological (ER) behavior of chitosan derivatives, chitosan, chitosan ammonium salt and chitosan phosphate suspensions in silicone oil were investigated. Chitosan derivative suspensions showed a typical ER response (Bingham flow behavior) upon application of an electric field. However, chitosan phosphate suspension exhibited an excellent shear yield stress compared with chitosan and chitosan ammonium salt suspensions. The difference in behavior results from the difference in the conductivity of the disperse phases due to the difference of their polarizability. The shear stress for the chitosan, chitosan ammonium salt and chitosan phosphate suspensions exhibited a linear dependence on the volume fraction of particles and 1.18, 1.41 and 1.67 powers of the electric field. On the basis of the experimental results, the newly synthesized chitosan derivative suspensions found to be an ER fluid.

Keywords: Chitosan derivatives, ER effect, bingham flow, ER fluid

Introduction

Electrorheological (ER) fluids consist of highly polarizable particles in an insulating fluid and have the ability to control with electric field mechanical devices such as shock absorbers, dampers, clutches and engine mounts [1,2]. The ER behavior is characterized by a rapid and reversible increase in apparent viscosity due to the formation of particle chains upon application of an electric field [3-5].

Since the ER effect was discovered by Winslow in 1947, the hydrous ER fluids composed of cellulose [6] and corn starch [7] as the organic disperse phases have been widely used and have some problems, durability, dispersion stability, corrosion and limited temperature in actual use.

Recently the anhydrous ER fluids which do not contain water in the organic disperse phases have been introduced, which compose of polyaniline [8] and polyurethane [9] as the organic disperse phase. However, they also have some problems such as dispersion stability, durability and adhesion to electrical cell in spite of their high ER performance. Basically, because they have the polar groups such as hydroxy (-OH) and amino (-NH₂), respectively, suspensions of these particles provide the ER effect upon application of the field. The chemical structure of the organic materials as the disperse phases is therefore important in the ER effect.

To solve these problems, chitosan derivatives as the new organic disperse phases of the anhydrous ER fluids have been synthesized and the electrical and rheological properties of the suspensions in silicone investigated.

Chitosan as the base material is a natural organic polymer

from chitin by N-deacetylation and composed of poly D-glucosamine and has been widely used in the fields of biochemistry, pharmacology, enzymology, microbiology, agriculture and environment as a natural biocompatible organic polymer [10]. Chitosan suspension provides ER effect upon the application of the electric field due to the polarizability of the branched amino group [11].

The objectives of this paper are: (a) to describe the ER behavior of chitosan derivative suspensions (b) establish the ER mechanism and (c) to investigate the possibility as new ER fluids.

Experimental

Materials

The base liquid was silicone oil provided by Dow Corning with a specific gravity of 0.97, a kinematic viscosity of 50cst at 40°C and a dielectric constant of 2.61 at 25°C. The chitosan used as the base material was commercial powder provided by Jae-kwang Co. (Korea). Chitosan phosphate and chitosan ammonium salt as the chitosan derivatives were synthesized. Their particle sizes were 25 μm average diameter. Prior to mixing in silicone oil, the chitosan, chitosan phosphate and chitosan ammonium salt particles were dried for 5h at 150°C... and the silicone oil for 3h at 130°C... to remove water. Chitosan derivative suspensions were then prepared at volume fractions. Following vigorous mixing, the suspensions were stored in a desiccator to maintain the dry state.

Electrical tests

The dc current density J and the conductivity σ of the silicone oil and of the chitosan, chitosan phosphate and chitosan ammonium salt suspensions were determined at room temperature by measuring the current passing through the fluid

^{*}Corresponding author; Tel: 82-2-958-5657. Fax: 82-2-958-5659
E-mail: uschoi@kist.re.kr

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 $1M\Omega$ 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 $\sigma = J/E_0$.

Rheological Tests

The rheological properties of the suspension were investigated under a dc field using the Physica Couette-type rheometer with a 1 mm 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. The shear stress for the suspensions was measured under shear rates of 0.1 to 300 s^{-1} , electric fields of 0 to 3 kV/mm and volume fractions of 0.1 to 0.3. All data were obtained at constant shear rate.

Results

Electrical Properties

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. Figure 1 shows that the conductivities of the chitosan, chitosan phosphate and chitosan ammonium salt suspensions are non-ohmic in character similar to the silicone oil. Moreover, the conductivity of the chitosan phosphate suspension is about 2 orders of magnitude higher than that of the chitosan suspension and about 1 and 5 orders higher than the chitosan ammonium salt suspension and the silicone oil. The difference in the conductivity of the chitosan derivative suspensions is considered to the result from the difference of polarizability of the branched groups.

Rheological Properties

The effect of the shear rate on the shear stress for chitosan, chitosan phosphate and chitosan ammonium salt suspensions is illustrated in Fig. 2. In Fig. 2, it is seen that the chitosan,

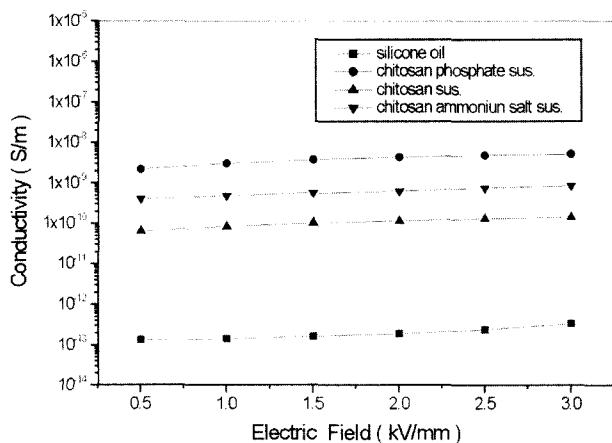


Fig. 1. Effect of electric field on conductivity for silicone oil and chitosan derivative suspensions.

chitosan phosphate and chitosan ammonium salt suspensions behave as a Newtonian fluid without electric field, but upon application of the electric field they exhibit the yield stress τ_E . The chitosan derivative suspensions approximate a Bingham-type behavior, which is described by the equation

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

Figure 3 gives a log plot of τ_E vs E^2 for the chitosan, chitosan phosphate and chitosan ammonium salt suspensions. The results are obtained under a shear rate of 2 s^{-1} and a volume fraction of 0.3.

Figure 3 indicates that the shear yield stress is proportional to 1.18, 1.67 and powers of the electric field i.e., $\tau_E \propto E^{1.18}$ for chitosan suspension, $\tau_E \propto E^{1.67}$ for chitosan phosphate suspension and $\tau_E \propto E^{1.41}$ for chitosan ammonium salt suspension. The effect of the volume fraction of chitosan, chitosan phosphate and chitosan ammonium salt particles in the silicone oil on the shear stress is given in Fig. 4. The results were obtained at a shear rate of 2 s^{-1} and a electric field of 3 kV/mm. The shear stress increases in a linear fashion with the volume fraction of chitosan derivative particles.

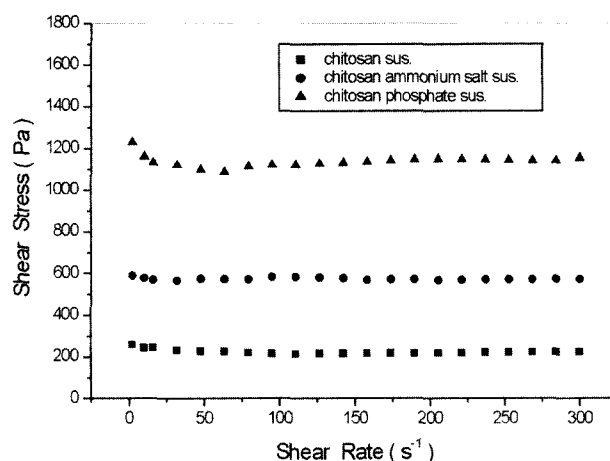


Fig. 2. Shear stress vs shear rate for chitosan derivative suspensions ($\phi = 0.3$, $E = 3$ KV/mm).

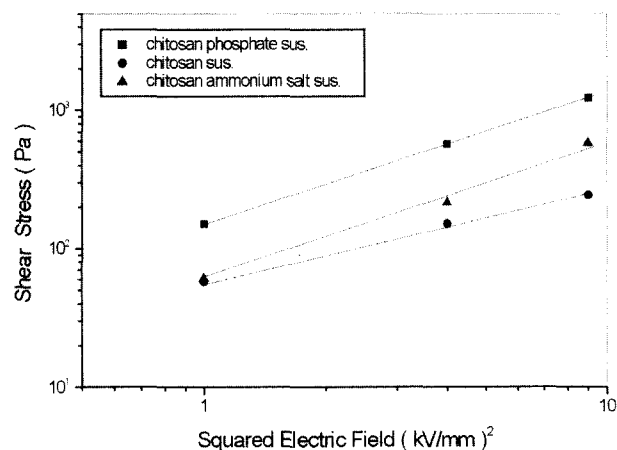


Fig. 3. Shear stress vs squared electric field for chitosan derivative suspension ($\phi = 0.3$, $\dot{\gamma} = 2$ s^{-1}).

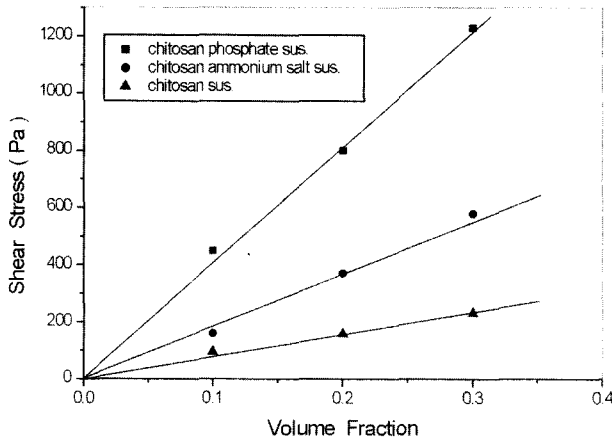


Fig. 4. Shear stress vs volume fraction for chitosan derivative suspensions ($E = 3 \text{ kV/mm}$, $\dot{\gamma} = 2 \text{ s}^{-1}$).

Discussion

To explain the ER behavior of chitosan, chitosan phosphate and chitosan ammonium salt suspensions, we will examine the results obtained with the assumption that the base fluid and particles behave as ideal dielectric materials, and particles are aligned in chains or columns between electrodes. With these assumptions, the rheological analysis of Conrad *et al.* [12] gives for the polarization component of the yield stress

$$\tau_E = 44.1 A_s \psi \epsilon_0 K_f (\beta E)^2 \left| \exp\left\{\left[14.84 - 6.165(R/a)\right]\beta\right\} \right| \times \left[1/(R/a)^8 - 4(R/a)^{10}\right]^{0.5} \left| \max \right. \quad (2)$$

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 be 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 particles 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. (2), that is, $A_s = \tau_{\text{meas.}}/\tau_{\text{calc.}}$. We obtain $A_s = 1, 2$ and 4 for chitosan, chitosan ammonium salt and chitosan phosphate suspensions at a shear rate of 2 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 single low chains for chitosan suspension and of multi-chains aligned between electrodes for chitosan ammonium salt and chitosan phosphate suspensions.

Conclusion

This study was conducted to deduce the ER behavior of

chitosan derivatives, chitosan, chitosan ammonium salt and chitosan phosphate suspensions and to investigate the possibility as an ER fluid.

(1) Chitosan derivatives, chitosan, chitosan ammonium salt and chitosan phosphate suspensions in silicone oil showed the ER response upon the application of the electric field. The chitosan phosphate suspension exhibited an excellent shear yield stress compared with chitosan and chitosan ammonium salt suspensions. This results from the large difference in the conductivity of the dispersed phases due to the difference of polarizability.

(2) The shear yield stress of the chitosan, chitosan ammonium salt and chitosan phosphate suspensions increased linearly with the volume fraction of the particles and the 1.18, 1.41 and 1.67 powers of the electric field.

(3) The value of structure factor, A_s obtained 1, 2 and 4 for chitosan, chitosan ammonium salt and chitosan phosphate suspensions and it may be due to the formation of single-row chains and multi-chains upon application of the electric field.

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