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Electrorheological Performance of Chitosan Sebacicate Suspension as an Anhydrous ER Fluid

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Abstract : The electrorheological (ER) performance of a chitosan sebaciate suspension in silicone oil was investigated by varying the electric fields, volume fractions of particles, and shear rates, respectively. The chitosan sebacicate susepnsion showed a typical ER response caused by the polarizability of an amide polar group and shear yield stress due to the formation of multiple chains upon application of an electric field. The shear stress for the suspension exhibited a linear dependence on the volume fraction of particles and an electric field power of 1.88. On the basis of the results, the newly synthesized chitosan sebacicate suspension was found to be an anhydrous ER fluid.

Key words : ER fluid, amid polar group, multiple chains, chitosan sebacicate suspension

Introduction

Electrorheological (ER) fluids consist of highly polarizable particles in an insulating fluid and their ER mechanism is characterized by the formation of particles upon application of an electric field [1,2,3].

Since Winslow's discovery of the ER effect in 1947 [1], hydrous ER fluids composed of cellulose [7] and corn starch [8] as the organic disperse phases and silica gel [9] and zeolite [10] as the inorganic 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, plus they have lots of problems, including dispersion stability, durability, corrosion, abrasion, and a limited temperature in actual use.

Recently, anhydrous ER fluids, which do not contain water or polar solvent in the disperse, have been introduced composed of synthetic polymer, polyaniline [11], and polyurethane [12] as the organic disperse phases. However, they also have certain problems, such as dispersion stability and adhesion to the cell inspite of their high ER performance.

The current study attempted to solve the basic problems of conventional ER fluids and introduced a chitosan derivative based on a natural biocompatible polymer, as the organic disperse phase [13,14]. Chitosan sebacicate as the disperse phase was synthesized by chemical reactions between chitosan and sebacic acid under the catalysis, and the electrical and rheological properties of the synthesized chitosan sebacicate in silicone oil were investigated. The chitosan sebacicate suspension provided an ER performance under an electric field due to the polarizability of the branched amide group.

This study describes the ER performance of the synthesized chitosan sebacicate suspension and estabilishes the ER mechanism to investigate the possibility of an anhydrous ER fluid.

Experimental

Materials

The base fluid used was silicone oil (Dow Corning Co.) with a specific gravity of 0.97, kinematic viscosity of 50cst at 40°C, and dielectric constant of 2.61 at 25°C. The chitosan as a raw material was a commercial powder (Jaekwang Co., Korea) with a nitrogen content of 4.8wt% and molecular weight of 100,000. The sebacic acid was provided by Sigma Aldrich. The chitosan sebacicate was synthesized by an amide reaction between chitosan and sebacic acid under the catalysis of TPP (Triphenyl phosphine) and DEAD (Diethyl azodicarboxylate). The synthesized particle size was on average 25 μm in diameter. Prior to mixing in silicone oil, the chitosan sebacicate particles were dried for 5 h at 150°C and the silicone oil for 3 h at 130°C to remove any moisture in the vacuum oven. The chitosan sebacicate suspension were then prepared at volume fraction of 0.1 to 0.4.

Electrical Tests

The dc current density of the chitosan sebacicate suspension was determined at room temperature by measuring the current passing through the fluid upon application of an electric field E_0 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 MΩ resistor in series with the metal cell containing the oil using a voltmeter with a sensitivity of 0.01 mV.

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Rheological Tests

The rheological properties of the suspension 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 to 0.4, respectively.

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. The current densities of chitosan adipicate suspensions for the volume fraction ($\phi = 0.3$) with mol ratios of sebacic acid (0.25 to 2.0) under the electric field are given in Figure 1. As seen in Figure 1, the current density of the chitosan sebacicate suspensions increased with an increasing mol ratio of sebacic acid and then showed a decreasing trend over a mol ratio of 0.5. This appeared to result from the polarizability of the polar group, an amide radical, and the saturation of the reacted amide group between chitosan and sebacic acid over a mol ratio of 0.5.

Rheological Properties

The effect of the chitosan sebacicate suspensions with mol ratios of sebacic acid (0.25 to 2.0) on the rheological properties were investigated by varying the shear rates, electric fields, and volume fractions. The effect of the shear rate on the shear stress for the chitosan sebacicate suspension is illustrated in Figure 2. The suspensions exhibited a Bingham flow behavior upon application of the electric field (E = 3 kV/mm) and the shear stress of the suspensions increased with an increasing mol ratio of sebacic acid with a decreasing trend above a mol ratio of 0.5. Above mentioned, it is deduced to result from the saturation of the reacted amide group between chitosan and sebacic acid over a mol ratio of 0.5. The optimal mol ratio of sebacic acid therefore was found to be 0.5 for the amide reaction between chitosan and sebacic acid.

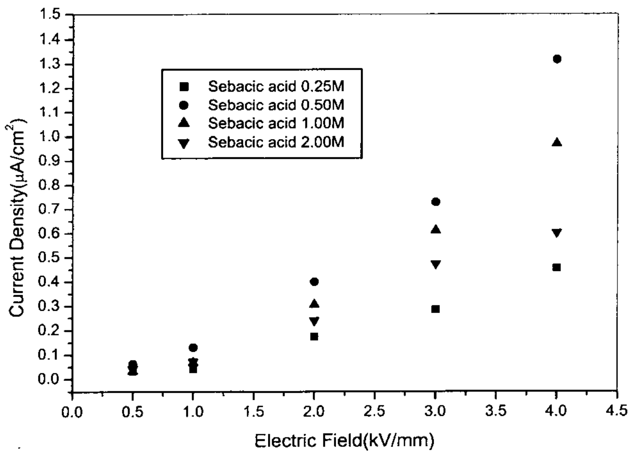

Fig. 1. Effect of electric field on current density relative to mol ratio of sebacic acid (ϕ=0.3).

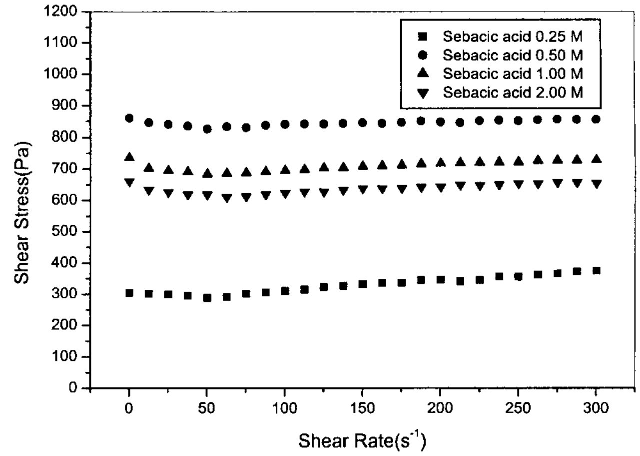

Fig. 2. Effect of shear rate on shear stress for chitosan sebacicate suspension relative to mol ratio of sebacic acid (ϕ=0.3, E=3 kV/mm).

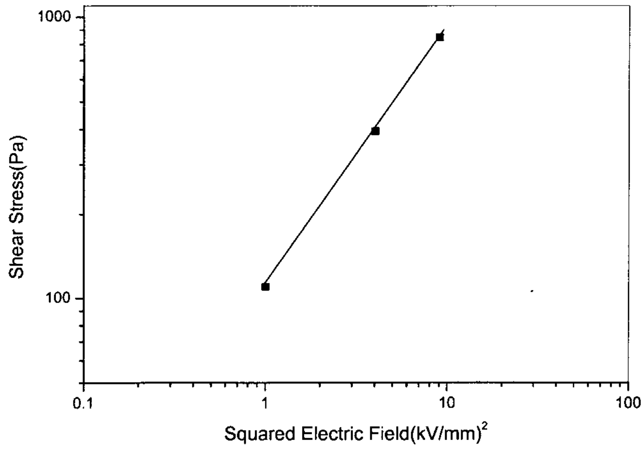

Fig. 3. Effect of squared electric field on shear stress (ϕ=0.3, M=0.3, γ=10 s^{-1}).

Figure 3 shows a log-log plot of the shear stress versus the square of the electric field for the chitosan sebacicate suspension. The results in Figure 3 indicate that the shear stress was proportional to an electric field power of 1.88, that is, $\tau \propto E^{1.88}$. This follows from the fact that the interaction force for the dipole in an electric field is proportional to the electric field intensity. The effect of the volume fraction of the chitosan sebacicate particles in the silicone oil is shown in Figure 4. The shear stress increased linearly with the volume fraction of the chitosan sebacicate particles. This was caused by the structure which mainly consisted of particle chains.

Discussion

The general flow behavior of ER fluids upon application of an electric field can be described using the Bingham plastic equation and the polarization model. Polarization models based on a point-dipole approximation, with a focus on the

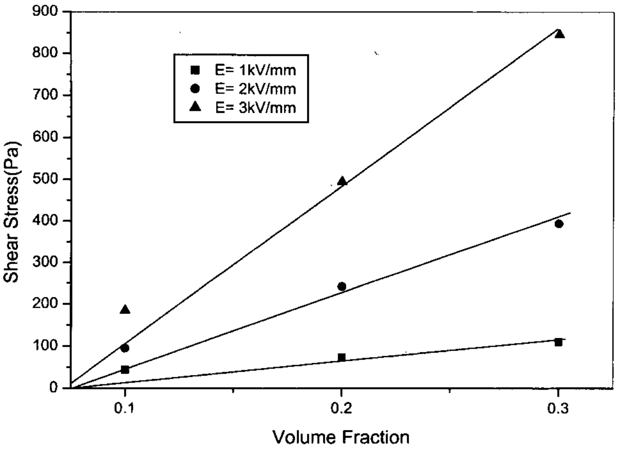

Fig. 4. Effect of volume fraction on shear stress ($\dot{\gamma}$=10 s^{-1}).

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 the equation [3,4,5]

$$\tau \propto \phi K_f E^2 \beta^2 \qquad (1)$$

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

$$\beta = (\sigma_p - \sigma_f) / (\sigma_p + 2\sigma_f) \qquad (2)$$

where σ_p is the conductivity of the particles and s_f the conductivity of the base fluid.

To explain the ER mechanism of the chitosan sebacicate 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

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

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($\geq$ 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= 2 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 0.3, which may have been due to the formation of multi-chains aligned between the electrodes [3,15].

Conclusions

This study was conducted to deduce the ER performance of a chitosan sebacicate suspension, to estabilish the ER mechanism, and to investigate it's potential as an ER fluid. The following is a summary of the results:

1. A chitosan sebacicate suspension in silicone oil showed an ER response upon the application of an electric field and the suspension exhibited a Bingham flow behavior. This was considered to result from the polarizability of the branched polar group, an amide radical.
2. The optimal mol ratio of sebacic acid was 0.5 for the amide reaction between chitosan and sebacicate acid.
3. The shear stress of the chitosan sebacicate suspension increased linearly with the volume fraction of particles and an electric field power of 1.88.
4. The value of the structure factor, A_s was 2 and this may have been due to the formation of multi-chains aligned between the electrodes upon the application of an electric field.
5. Chitosan sebacicate supension was found to behave as an anhydrous ER fluid

Acknowledgments

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