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Electrorheology of the Suspension Based on Chitosan Adipate as a New Anhydrous ER Fluid

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Abstract : The electrorheology of the chitosan adipnate suspension in silicone oil was investigated. Chitosan adipnate suspension showed a typical ER response (Bingham flow behavior) upon application of an electric field. The shear stress for the chitosan adipnate suspension exhibited a linear dependence on the volume fraction of particles and an electric field power of 1.88. The experimental results for the chitosan adipnate suspension correlated with the conduction models and this suspension was found to be an anhydrous ER fluid.

Key words : Electrorheological fluid, bingham flow, conduction model, chitosan adipate

Introduction

Electrorheological (ER) fluids are smart materials which have the ability to control the electric field mechanical devices such as shock absorbers, dampers, clutchs and engine mounts under the effect of electric field [1,2]. Their flow 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, 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 [6,7].

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 [8]. The conduction model was originally proposed by Foulc *et al.* [9] in 1992 and modified by Davis and Ginder [10], Tang *et al.* [11] and Wu and Conrad [12]. It gives the following expression for the yield shear stress of ER fluids

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

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. Cellulose [13], starch [4,14], silica [11], zeolite [15] and titanium oxide [16] have been widely utilized as the disperse phases in the formulation of the hydrous ER fluids, which have several problems about durability, corrosion, limited temperature and dispersion stability in actual use. Recently, the anhydrous ER fluids which do not contain water in the disperse phase have been introduced, which compose of polyaniline [17] and polyurethane [18] as the organic disperse phases. However, they also have some problems ,such as dispersion stability and adhesion to the cell inspite of their high ER performance.

To solve this problem, chitosan derivatives as the new organic disperse phases of the ER fluid have been synthesized [19]. Of these, in this study, electrorheology pertaining to the ER behavior of chitosan adipnate suspension in silicone oil was investigated. The synthesized chitosan adipnate suspension provides the ER response upon application of an electric field. This study describes the ER behavior of chitosan adipnate suspension and the possibility of its use as a new ER fluid.

Experimental

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. The chitosan adipnate as the organic disperse phase was synthesized by amide reaction between chitosan (Jaekwang Co., 5 μm) and adipic acid (Sigma Aldrich) under the catalysis of TPP (Triphenyl phosphine) and DEAD (Diethyl azodicarboxylate). Its chemical reaction mechanism and chemical structure is

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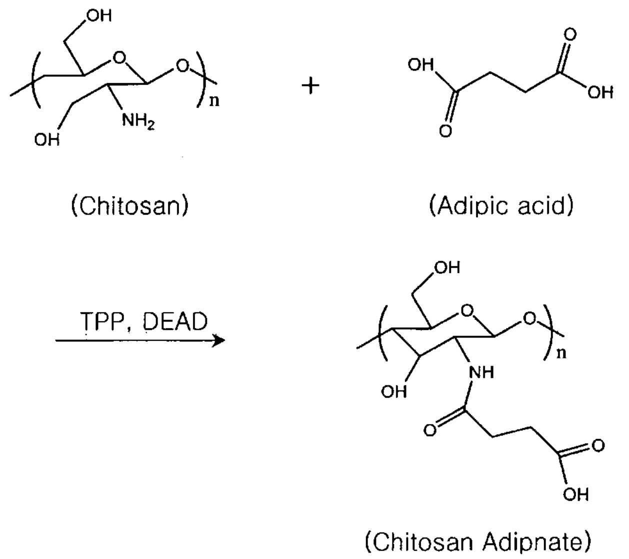

Scheme 1. Chemical reaction mechanism and chemical structure of chitosan adipnate.

shown in Scheme 1. Prior to mixing in silicone oil, chitosan adipnate particles were dried for 5 h at 150°C and silicone oil for 3 h at 130°C to remove moisture in vacuum oven. Chitosan adipnate suspensions were then prepared at volume fractions of 0.1 to 0.3. After vigorous mixing in ball mill, the suspensions were stored in a dessicator to maintain the dry state.

Electrical and rheological tests

The dc current density (J) and the conductivity (σ) of the silicone oil and the chitosan adipnate 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 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 and viscosity. The shear stress for the suspensions was measured under shear rates of 1 to 200 s^{-1}, electric fields of 0 to 3 kV/mm and volume fractions of 0.1 to 0.3, respectively.

Results and Discussion

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. 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.The conductivity of chitosan adipnate suspension for a volume fraction of 0.3 vs electric field is given in Fig. 1. As seen in Fig. 1, the conductivity of chitosan adipnate suspension increases with the electric field and moreover , the conductivity of the suspension is about 1 and 3 orders of magnitude higher than those of the chitosan suspension and the silicone oil. Figure 2 shows a plot of the conductivity of chitosan adipnate particles vs electric field. The conductivity of chitosan adipnate particles, σ_p can be calculated from the data in Fig. 1 assuming that the structure consisted of single-row chains with numbers of chains per unit area

$$N_A = 3/2\ \phi/\pi a^2:$$
$$\sigma_s = 3/2\sigma_p \phi + \sigma_f(1 - 3/2_p \phi) \qquad (2)$$

where f is the volume fraction of particles.

The results in Fig. 2 show that the conductivity of chitosan adipnate particles is one order of magnitude higher than that of chitosan adipnate suspension. The increase in the conductivity of chitosan adipnate particles σ_p with field is considered to result from the increase in the conductivity of the silicone oil film between the particles due to the field which is an order of magnitude greater than in the bulk [12].

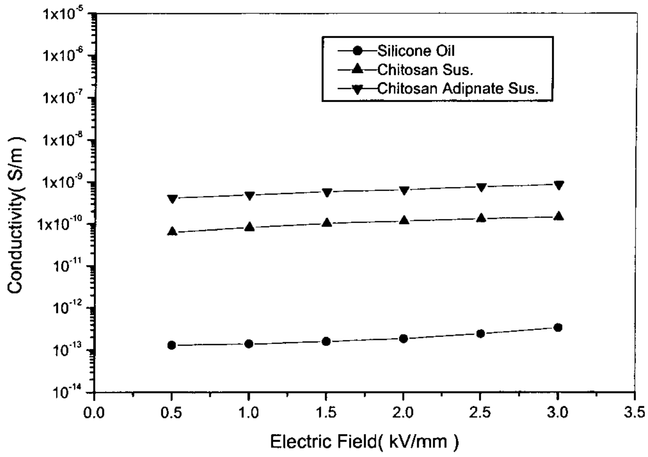

Fig. 1. Effect of electric field on conductivity for suspensions.

Rheological properties

To investigate the effect of chitosan adinate suspension on the rheological properties, studies were carried out by varying shear rates, electric fields, and volume fractions of particles. The effect of the shear rate on the shear stress for chitosan adipnate suspension is illustrated in Fig. 3. Chitosan adipnate 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. This suspension approximates a Bingham

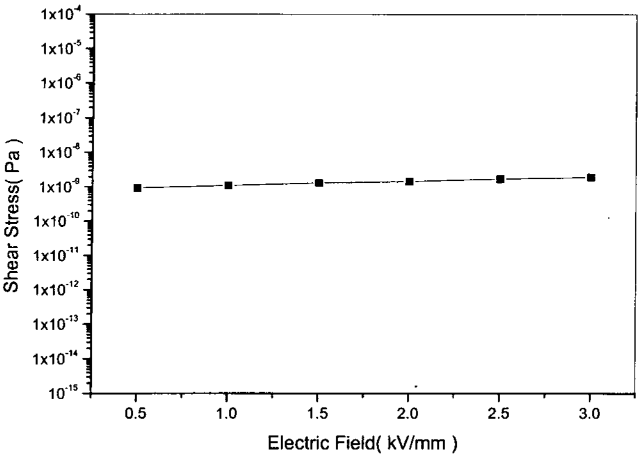

Fig. 2. Effect of electric field on conductivity of chitosan adipnate particles.

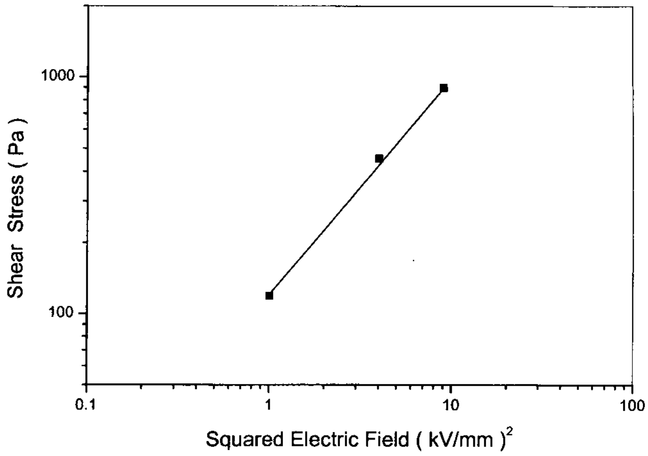

Fig. 4. Shear stress vs squared electric field for chitosan adipnate suspension(ϕ=0.3, $\dot{\gamma}$=10s^{-1}).

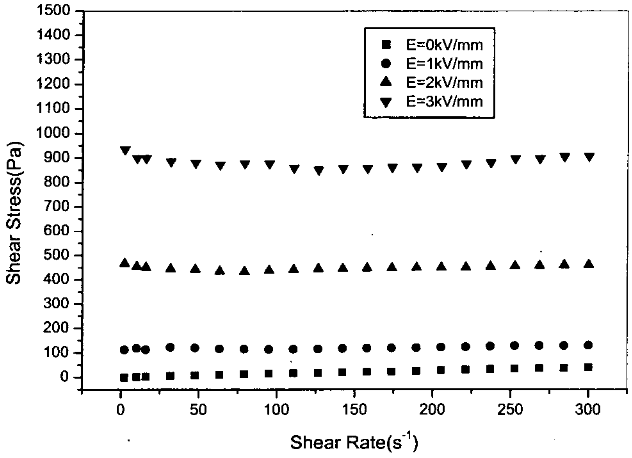

Fig. 3. Effect of shear rate on shear stress for chitosan adipnate suspension (ϕ=0.3).

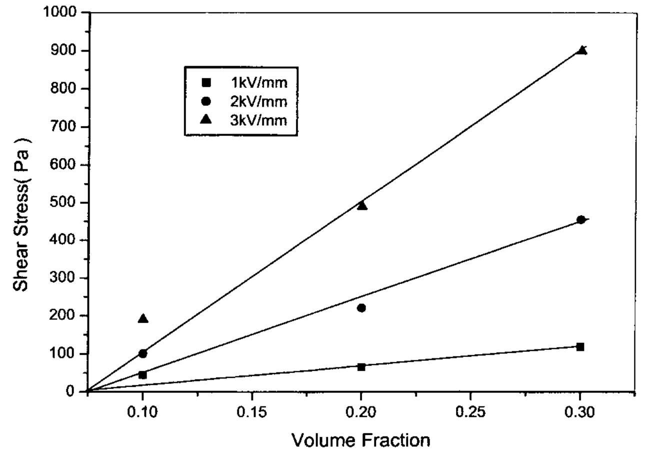

Fig. 5. Effect of volume fraction on shear stress for chitosan adipnate suspension($\dot{\gamma}$=10s^{-1}).

flow behavior, which is described by the equation

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

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 0.3. The results in Fig. 4 indicate that the shear stress is proportional to 1.88 power of the electric field, that is $\tau \propto E^{1.88}$. The effect of the volume fraction of chitosan adipnate particles in silicone oil on the shear stress is illustrated in Fig. 5. The results were obtained at a shear rate of 10 s^{-1}. The shear stress increases in a linear trend with the volume fraction of chitosan adipnate particles. This was caused by the structure which mainly consisted of particle chains.

To describe the status of ER behavior of the chitosan adipnate 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.* [20] gives for the polarization component of the yield shear stress

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

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, b the relative polarizability($\cong$1) and R/a the ratio of the separation of the particle center to their radius ($\geq$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 $A_s = 2$ 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 0.3, and it maybe be resulted the above mentioned conclusion due to the experimental output in relation with the formation of multiple aligned between electrodes [15,19].

We will compare the experimental values of the shear stress with those predicted by the conduction models of Tang *et al.* [11] and Wu and Conrad [12]. The conduction model of Tang et al. gives the following expression for the shear stress

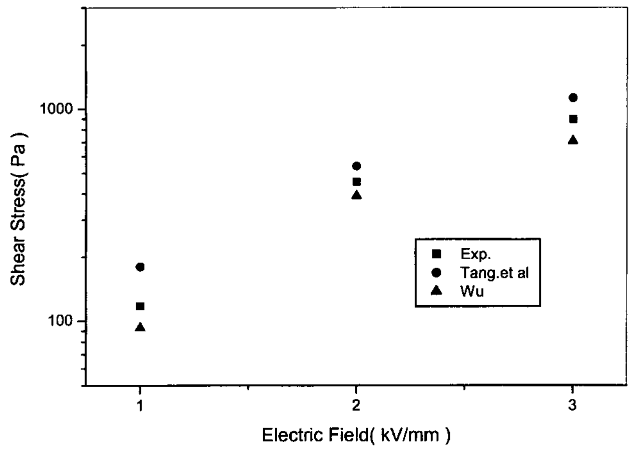

Fig. 6. Comparision of the predicted shear stress with that measured for chitosan adipnate suspension(ϕ=0.3, γ=10s^{-1}).

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

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

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

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

When $E_c = 0.1\sim0.3$, $n = 1$ and the shear strain, $\gamma\sim0.3$ at maximum attractive force between particles. The predicted values were calculated using Eqs. (5) and (6) , and compared with experimental values for the chitosan adipnate suspension. The results are given in Fig. 6. The experimental results were obtained at a shear rate of 10 s^{-1}, a volume fraction of 0.3 and the electric fields of 1 to 3 kV/mm. As seen in Fig. 6, the predicted values of conduction models are in agreement with the experimental values.

Conclusions

This study was conducted to investigate electrorheological behavior of the chitosan adipnate suspension and the following conclusions were found:

(1) The chitosan adipnate 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 chitosan adipnate suspension increased linearly with the volume fraction of particles and the 1.88 power of the electric field.

(3) The value of the structure factor, A_s was 2 and it may be resulted due to the formation of multiple 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 suspension by the conduction models.

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