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Electrorheological Properties of Chitin and Chitosan Suspensions

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Abstract: The electrorheological properties pertaining to the electrorheological (ER) behavior of chitin and chitosan suspensions in silicone oil were investigated. Chitosan suspension showed a typical ER response (Bingham flow behavior) upon application of an electric field, while chitin suspension acted as a Newtonian fluid. The difference in behavior results from the difference in the conductivity of the chitin and chitosan particles, even though they have a similar chemical structure. The shear stress for the chitosan suspension exhibited a linear dependence on the volume fraction of particles and a 1.18 power of the electric field. The experimental results for the chitosan suspension correlated with the conduction model for ER response.

Key words: Chitin, Chitosan, ER behaviour, conduction model

Introduction

Electrorheological (ER) fluids are suspensions which have the ability to control with electric field mechanical devices such as shock absorbers, dampers, clutchs 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]. Following discovery of the ER effect by Winslow [3] in the late 1940s, 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 host liquid [6,7], were proposed to explain the behavior. Recently, the importance of the conductivity of the host liquids which is strongly dependent on the electric field, has been demonstrated leading to the conduction model. The conduction model considers that the ER effect with a dc field is induced by the mismatch of the conductivity of the particles and the base fluid, given by the ratio of the conductivity of particles to that of the host liquid, $\Gamma s = \sigma_p/\sigma_f(0)$. The conduction model was originally proposed by Foulc *et al.* [8], Felici *et al.* [9] and Atten *et al.* [10] and modified by Davis and Ginder [11], Tang *et al.* [12] and Wu and Conrad [13]. In these models the conductivity of the base fluid is presumed to be given by a simplified expression for Onsager's [14] electric field-enhanced ionic dissociation theory, namely

$$\sigma_f(E) = \sigma_f(0)[(1 - A) + A \exp(E/E_c)^{1/2}] \qquad (1)$$

where $\sigma_f(0)$, A and E_c are constants which depend on the base fluid and E is the electric field. Taking Eq. (1) for the conductivity of the base fluid, the conduction model gives for the yield stress of ER fluids

$$\tau_E \propto \phi K_f\, f(E_0, \Gamma_\sigma, A, E_c) \qquad (2)$$

where ϕ is the volume fraction of particls, K_f the dielectric permittivity of the host liquid, $\Gamma_\sigma = \sigma_p/\sigma_f(0)$ and f a complex function of the indicated parameters.

ER fluids consist of highly polarizable particles in an insulating fluid and the disperse phase plays an important role in the ER phenomenon. Cellulose [15], corn starch [3,16] and polyaniline [4,17] have been widely used as the organic disperse phases in the formulation of ER fluids. Because they have the polar groups such as hydroxy (-OH) and amino ($-NH_2$), respectively, suspensions of these particles provide the ER effect upon application of the field. The chemical structure of the organic materials is therefore important in the ER effect.

Chitin consists of β-(1,4)2-acetamido-2-deoxy-D-glucose units. This natural organic polymer called poly N-acetyl-D-glucosamine can be formally considered to be a derivative of cellulose where the C-2 hydroxy groups have been completely replaced by acetamido groups. Further, chitosan is also a natural organic polymer from chitin by N-deacetylation and composed of poly D-glucosamine. Chitin and chitosan have been widely used in the fields of biochemistry, pharacology, emzymology, microbiology, agricurture and environment as a natural biocompatible organic polymer [18].

The objectives of this paper are: (a) to describe the ER behavior of chitin and chitosan suspensions, (b) estabilish the ER mechanism and (c) to investigate the possibility of a new ER fluid.

Experimental

Materials

The host liquid 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 chitin and chitosan used as the disperse phases were commercial powders

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provided by Shin-yang Co. (Korea) and contained nitrogen contents of 7.40 and 6.40 wt%, respectively. The particle sizes were 25 μm average diameter. Prior to mixing in silicone oil, the chitin and chitosan particles were dried for 5 h at 150°C and the silicone oil for 3 h at 130°C to remove water. Chitin and chitosan suspensions were then prepared at volume fractions of 0.1 to 0.3. Following vigorously mixing, the suspensions were stored in a dessicator to maintain the dry state.

Electrical tests

The dc current density J and the conductivity σ of the silicone oil and of the chitin and chitosan suspensions 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 $\sigma = J/E_0$.

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 the current density and the conductivity of the silicone oil with the electric field. Evident is the non-ohmic character of the behavior. The conductivity parameters $\sigma_f(0)$, A and Ec of the silicone oil were calculated using Eq. (1) to give $\sigma_f(0) = 1.2 \times 10^{-13}$ S/m, A = 0.007 and Ec = 0.11 kV/mm. The conductivities of the silicone oil and the chitin and chitosan suspensions for a volume fraction $\phi = 0.3$ vs electric field are given in Fig. 2. This shows that the conductivities of the chitin and chitosan suspensions are non-ohmic in character similar to the silicone oil. Moreover, the conductivity of the chitosan suspension is about 1.5 orders of magnitude higher than that of the chitin suspension and about 3 orders higher than the silicone oil. The conductivity of the chitosan particles ϕ_p was calculated from the data in Figs. 1 and 2 assuming that the structure consists of single-row chains with number of chains per unit area $N_A = 3/2\ \phi/\pi a^2$:

$$\sigma_s = 3/2\phi\sigma_p + \sigma_f(1-3/2\phi) \qquad (3)$$

where ϕ is the volume fraction of particles. The results are presented in Fig. 3. The increase in the conductivity of the chitosan particles σ_p with field indicated here is considered to the result from the increase in the conductivity of the silicone oil film between the particles due to the order of magnitude greater field than the applied field existing there [13].

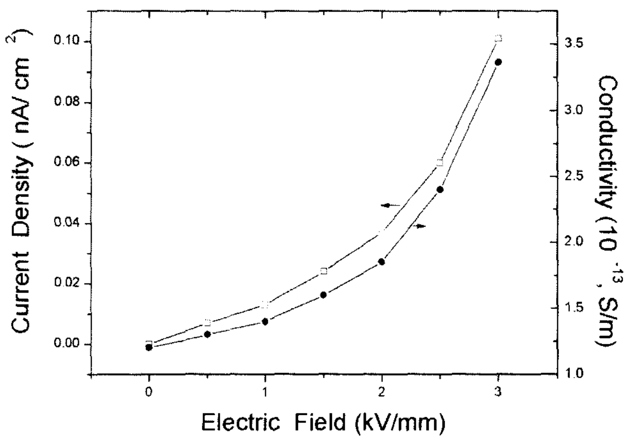

Fig. 1. Effect of the electric field on: current density and conductivity of silicone oil.

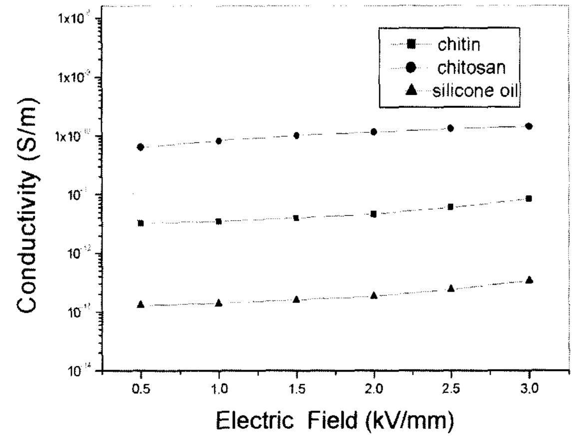

Fig. 2. Effect of the electric field on the conductivity for chitin and chitosan suspensions (vol. = 0.3).

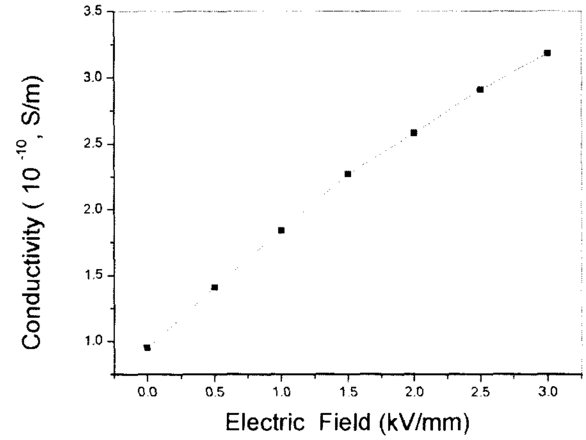

Fig. 3. Effect of the electric field on the conductivity of chitosan particles.

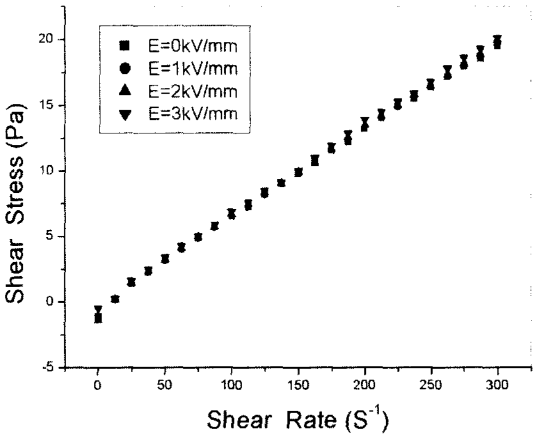

Fig. 4. Shear stress vs shear rate for silicone oil.

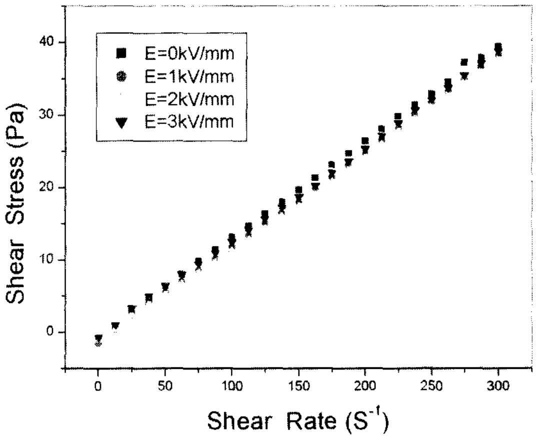

Fig. 5. Shear stress vs shear rate for chitin suspension (vol. = 0.3).

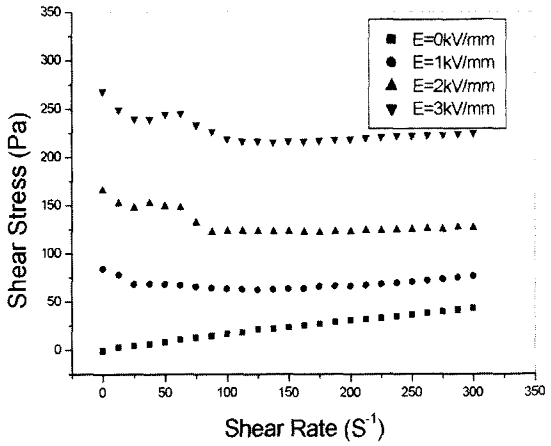

Fig. 6. Shear stress vs shear rate for chitosan suspension (vol. = 0.3).

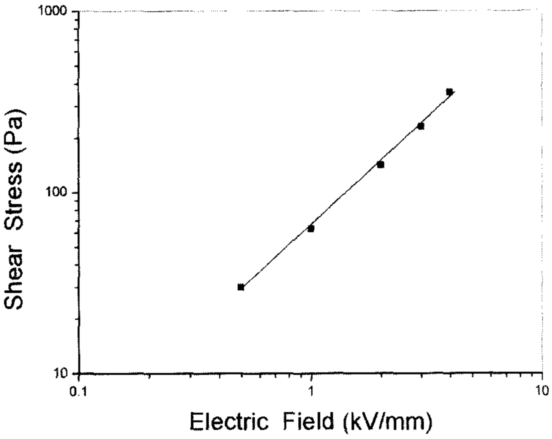

Fig. 7. Effect of the electric field on shear stress for chitosan suspension.

Rheological properties

Figure 4 shows a plot of the shear stress vs the shear rate for the silicone oil. The electric field has no effect on the shear stress of silicone oil. The shear stress, τ is proportional to the shear rate, γ in accord with a Newtonian fluid, which is given by the equation

$$\tau = \eta\gamma \tag{4}$$

The effect of the shear rate on the shear stress for chitin and chitosan suspensions is illustrated in Figs. 5 and 6, respectively. As seen in Fig. 6, the rheological behavior of the chitin suspension exhibits a trend similar to that of silicone oil, i.e., it also acts as a Newtonian fluid. In Fig. 6, it is seen that the chitosan suspension behaves as a Newtonian fluid without electric field, but upon application of the electric field it exhibits a yield stress τ_E, which is followed by a decrease in flow stress, ultimately reaching a relatively constant shear stress. This suspension approximates a Bingham-type behavior, which is described by the equation

$$\tau = \tau_E(E, \gamma) + \eta\gamma \tag{5}$$

The results in Fig. 6 indicate that τ_E initially decreases with shear rate and then becomes constant at γ 200 s^{-1}. Figure 7 gives a plot of log τ_E vs logE for the chitosan suspension. The results are for a shear rate of 2 s^{-1} and a volume fraction of 0.3. Fig. 7 indicates that the shear yield stress is proportional to 1.18 power of the electric field i.e., $\tau_E \propto E^{1.18}$. The effect of the volume fraction of chitosan particles in the silicone oil on the shear stress is given in Fig. 8. The results were obtained at a shear rate of 2 s^{-1}. The shear stress increases in a linear fashion with the volume fraction of chitosan particles.

Discussion

To explain the ER behavior of chitosan suspension, the conduction model given by Eq. (2) is applied, wherein the conductivity parameters affecting the ER behavior are Γ_σ, A, E_c and $\sigma_f(0)$. We will compare the experimental values of the shear stress with those predicted by the conduction models of Tang *et al.* [12], Davis and Ginder [11] and Wu and Conrad [13]. The conduction model of Tang *et al.* [12] gives the following expression for the shear stress

$$\tau_E = K_f\tau_0\phi E_0^2 \tag{6}$$

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

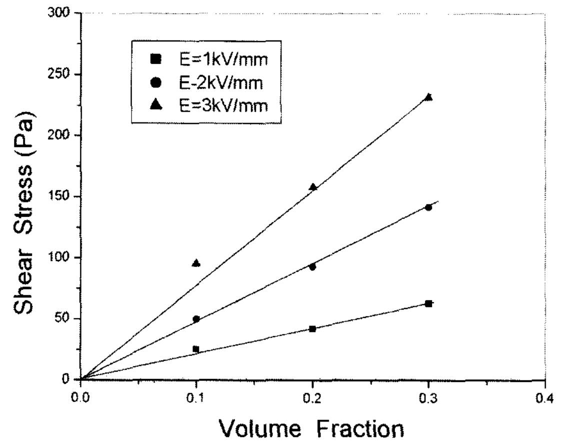

Fig. 8. Effect of volume fraction on the shear stress for the chitosan suspension.

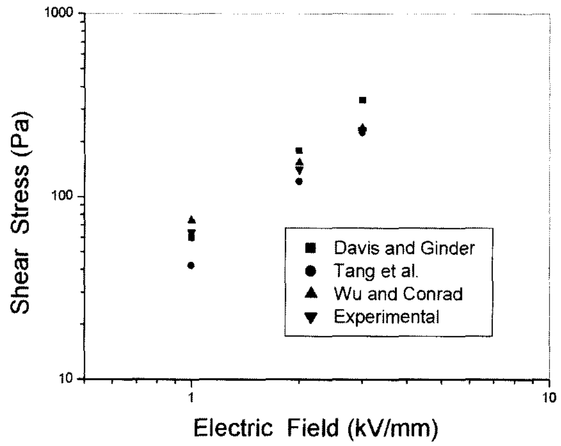

Fig. 9. Comparision of the predicted shear stresses with that measured for chitosan suspension.

$$\tau_0 = m_1(E_c/E_0)^{0.6} / 1 + m_2(E_c/E_0)^{0.6} \tag{7}$$

with

$$m_1 = 63.5 \log(0.0222\Gamma_\sigma/A) \tag{8}$$

and

$$m_2 = 0.54 + 25.9\ A^{-0.25}\ \Gamma_\sigma^{-1}. \tag{9}$$

The conduction model of Davis and Ginder[11] gives the following equation

$$\tau_E = 4/\sqrt{3}\ \varepsilon_f \phi E_0^{3/2}\ \sqrt{E_m} \tag{10}$$

where E_m is the saturation field and according to Wu and Conrad [13] is equal to

$$30(\Gamma_\sigma/A)^{0.1}(E_c/E_0)^{0.9}. \tag{11}$$

The conduction model of Wu and Conrad [13] gives

$$\tau_E = 3/2\ K_f \phi \varepsilon_0\ E_0^2\ F\ \gamma/(1 + \gamma^2)^{1/2} \tag{12}$$

where

$$F = 66(\Gamma_\sigma/A)^{0.1}(E_c/E_0)^n \tag{13}$$

when $E_c = 0.1 \sim 0.3$, $n = 1$ and the shear strain, $\gamma \sim 0.3$ at maximum attractive force between particles. The predicted values were calculated using Eqs. (6), (!0) and (12) and compared with experimental values for the chitosan suspension. The results are given in Fig. 9. The experimental results were obtained at a shear rate of 2 s^{-1}, a volume fraction of 0.3 and electric fields of 1 to 3 kV/mm. As seen in Fig. 9, the predicted values of all three conduction models are in accord with the experimental values.

Figs. 5 and 6 show that the ER behavior of chitosan suspension differs from that of chitin suspension. This results from the fact that there is a difference in the conductivity of the two suspensions in Fig. 2 even though their chemical structure is similar.

Summary

(1) A chitosan suspension in silicone oil showed different response to a dc electric field compared to a chitin suspension. The chitosan suspension exhibited a yield stress, whereas the chitin suspension behaved as a Newtonian fluid. This results from the large difference in the conductivity of the two dispersed phases even though they have a similar chemical structure.

(2) The shear yield stress of the chitosan suspension creased linearly with the volume fraction of the particles and the 1.18 power of the electric field.

(3) There is reasonable agreement between the predicted and experimental values of the yield stress for the chitosan suspension and the conduction models.

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