Electrorheological Effect of the Suspension Composed of Bismark Brown Chitosan Succinate as the Dispersed Phase

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Abstract: The electrorheological effect of the suspension composed of Bismark Brown chitosan succinate as the dispersed phase in silicone oil was investigated. Bismark Brown chitosan succinate suspension showed a typical ER response (Bingham flow behavior) upon application of an electric field. The shear stress for the suspension exhibited the dependence with a factor equals to 1.84 power on the electric field. The experimental results for the suspension correlated with the polarization model and Bismark Brown chitosan succinate suspension behaved as an anhydrous ER fluid. On the basis of the the results, Bismark Brown chitosan succinate suspension showed the ER flow behavior upon application of the electric field due to the polarizability of the branched amide and amine polar groups of the Bismark brown chitosan succinate particles.

Keywords: ER fluid, bingham flow, polarization model, bismark brown chitosan succinate, ER effect

1. Itroduction

Electrorheological (ER) fluids are nonaqueous suspensions composed of electrically polarizable particles dispersed in a dielectric fluid and smart materials which changed from a liquid-like material to a solid-like material under an electric field, and this phenomenon is called the ER effect. The disperse phases composed in ER fluids play a very important role in the ER phenomenon. Many kinds of organic polymers as the disperse phases which exhibit the ER behavior have been introduced and demonstrated. Cellulose [1], starch [2,3] and chitosan [4]) as the natural organic polymers provide a source of the disperse phases and are composed of the branched hydroxy (-OH) and amine ((-NH₂) polar groups. The synthetic organic polymers, polyaniline [5] and polyurethane [6] have been widely used as the disperse phases and also have the branched polar groups such as amino (-NH₂), and amino-cyan (-NHCN), respectively. The polar groups may affect on the ER behavior by playing a role of the electronic donors in the electric field. The chemical structure of the organic materials is therefore important in the ER effect.

ER fluids are characterized by a rapid and reversible increase in apparent suspension viscosity and a drastic change in suspension structure upon application of an electric field. Their flow behavior can be described by Bingham equation

$$\tau = \tau_E + \tau_V \tag{1}$$

where τ is the shear stress, τ_E the yield stress by electric induced field and termed the polarization component. τ_V is the flow stress at zero electric field termed the viscous component:

$$\tau_V = \eta\gamma \tag{2}$$

where η is the viscosity of the fluid and γ is the shear rate [2,7-9].

Since the ER effect was discovered by Winslow in 1947 [2], many researchers have investigated ER phenomenon for a variety of ER fluids and demonstrated the polarization particles chains which are formed by interactive force between the polarized particles in a dielectric fluid and also relative polarizability between the particles and the base fluid upon application of the electric field [10-12]. The polarization model of ER fluids can be described by the equation mentioned below

$$\tau_E \propto \varphi K_f E^2 \beta^2 \tag{3}$$

where φ is the volume fraction of particles, K_f the dielectric permittivity of the base fluid, E the electric field and β the relative polarizability of a single spherical particle with relative dielectric constant K_p and conductivity σ_p dispersed in a base fluid of relative dielectric constant K_f and conductivity σ_f can be written as [7,11]

$$\beta = (\sigma_p - \sigma_f)/(\sigma_p + 2\sigma_f) \text{ at dc or low-frequency ac fields}$$
$$= (K_p - K_f)/(K_p + 2K_f) \text{ at high-frequency ac fields} \tag{4}$$

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

Chitosan derivatives as the new organic disperse phases of the ER fluid have been synthesized and their ER properties investigated [4]. Of these, in this study, electrorheology pertaining to the ER performance of Bismark Brown chitosan succinate suspension in silicone oil was investigated.

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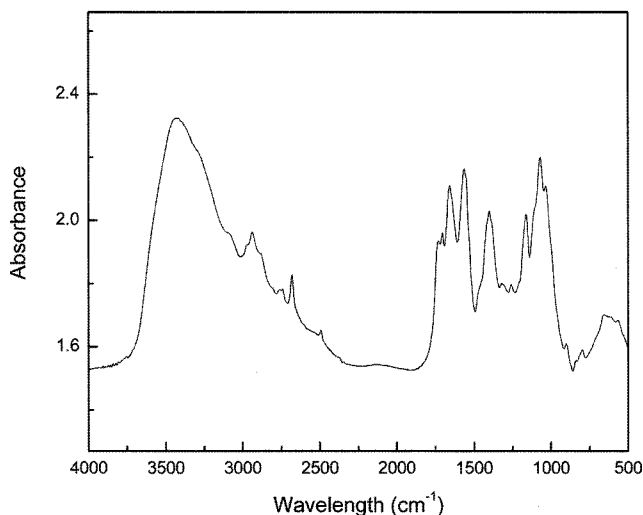Tel: +82-2-958-5657, Fax: +82-2-958-5659

Fig. 1. FT-IR spectra of Bismrak Brown chitosan succiniate.

Scheme 1. Chemical structure of Bismark Brown chitosan succiniate.

2. Experimental

2.1. Materials

The base fluid used 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 succinate as the organic disperse phase was synthesized by amide reaction between chitosan (Jaekwang Co., 5 μm) and succinic anhydride (Sigma Aldrich) with the catalysis of TPP (Triphenyl phosphine) and DEAD (Diethyl azodicarboxylate) in dimethyl sulfoxide (500 ml, DMSO, Aldrich Co.) solution at a 60°C oil bath for 5 hr with stirring. After a reaction, chitosan succinate was washed with DMSO and distilled deionized water and dried at a 40°C vacuum oven. Bismark Brown chitosan succinate was synthesized by the following method. Synthesized chitosan succinate, Bismark Brown (Aldrich Co.), and dimethyl sulfoxide (500 ml) were put into a round flask under N_2 purging and reacted at a 80°C oil bath for 24 hr with stirring. After a reaction, reagent was washed with DMSO and distilled deionized water and dried at a 40°C vacuum oven. The synthesized Bismark Brown chitosan succinate was conformed by FT-IR analysis and its spectra and chemical structure are shown in Figure 1 and scheme 1.

Prior to mixing in silicone oil, Bismark Brown chitosan succinate particles were dried for 5 h at 150°C and silicone oil for 3 h at 130°C to remove moisture in vacuum oven. The 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.

2.2. Electrical tests

The dc current density and conductivity of the silicone oil and of the Bismark Brown chitosan succinate suspension were measured at room temperature. The current density of silicone oil and Bismark Brown chitosan succinate suspension was determined by measuring the current and dividing by the area of the electrodes in contact with the fluid. The current density
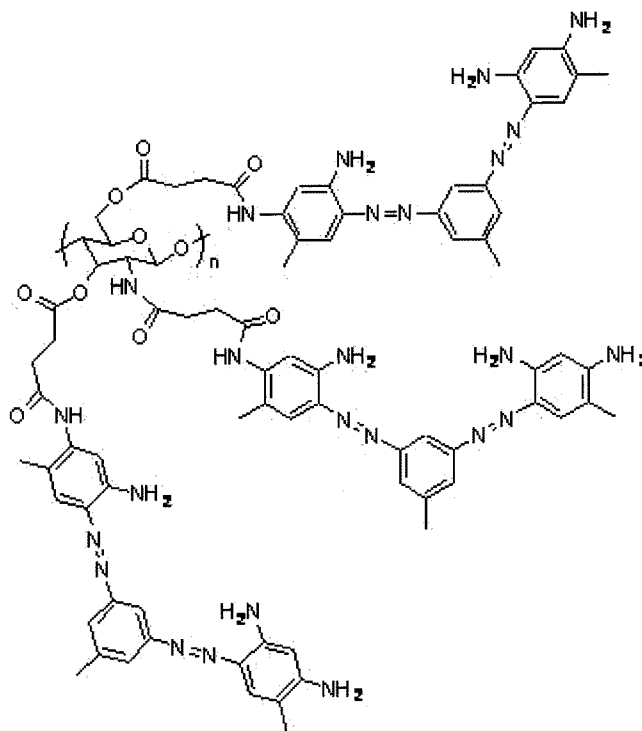
was measured by means of the voltage drop across a 1 MΩ resistor in series with the metal cell containing the oil using a voltmeter with a sensitivity of 0.01 mV. This method gave a current measuring sensitivity of 0.01 nA. The conductivity was taken as the relationship of the current density with respect to the electric field, i.e., $\sigma = J/E_0$.

2.3. Rheological tests

The rheological properties of the suspension were investigated using the Physica Couette-type rheometer with a 1 mm gap between the bob and cup in a dc field. The resistance to shear produced by the suspension was measured as a torque on the drive shaft and then converted to the data points of shear stress and viscosity. The shear stress for the suspension was measured under shear rates of 0.1 to 1000 s^{-1}, electric fields of 0 to 3 kV/mm, volume fractions of 0.3.

3. Results and Discussion

3.1. Synthesis of electrorheological materials

Bismark Brown chitosan succinate was synthesized from chitosan succinate and Bismark Brown. Figure 1 and Scheme 1 show FT-IR spectra and chemical structure of Bismark Brown chitosan succinate. After coupling of Bismark Brown on chitosan succinate, peaks of C = O (amide group, 1658 cm^{-1}), NH (amide group, 1563 cm^{-1}), N = N (1401 cm^{-1}) and NH$_2$ (1578 cm^{-1}) shown in Fig. 1. and also several peaks appeared between 3000-2490 cm^{-1} due to triazine structure of Bismark Brown.
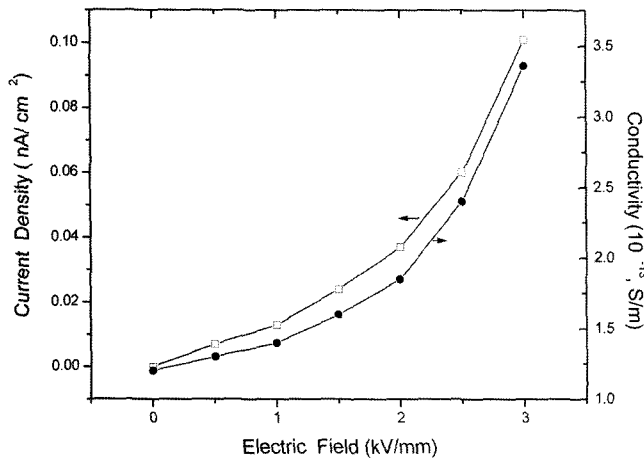
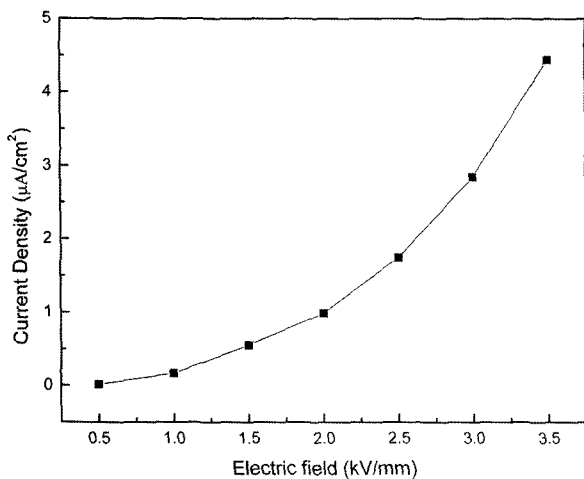Fig. 2. Effect of the electric field on the current density and the conductivity of silicone oil.

Fig. 3. Effect of the electric field on the current density for the suspension.

Fig. 4. Effect of the electric field on the conductivity for the suspension.

Fig. 5. Shear stress vs shear rate for silicone oil.

3.2. Electrical properties

The electrical properties of ER fluids are important to predict the power requirements for the ER device design and also to identify the ER mechanism. Figure 2 shows the current density and the conductivity of the silicone oil in the electric field. Evident in Fig. 2 is the non-Ohmic character of the behavior.

The current density and the conductivity of the Bismark Brown chitosan succinate suspension for a volume fraction of 0.3 vs electric field are given in Figures 3 and 4. As shown in Figs. 3 and 4, the current density and the conductivity of the Bismark Brown chitosan succinate suspension increase with the electric field intensity and moreover the conductivity of the suspension is about 7 order of magnitude higher than that of the silicone oil.

3.3. Rheological properties

To investigate the effect of silicone oil and Bismark Brown chitosan succinate suspension on the rheological properties, studies were conducted by varying shear rates,and electric field intensity. Figure 5 shows a plot of the shear stress vs shear rate for silicone oil. There is no effect on the shear stress of the
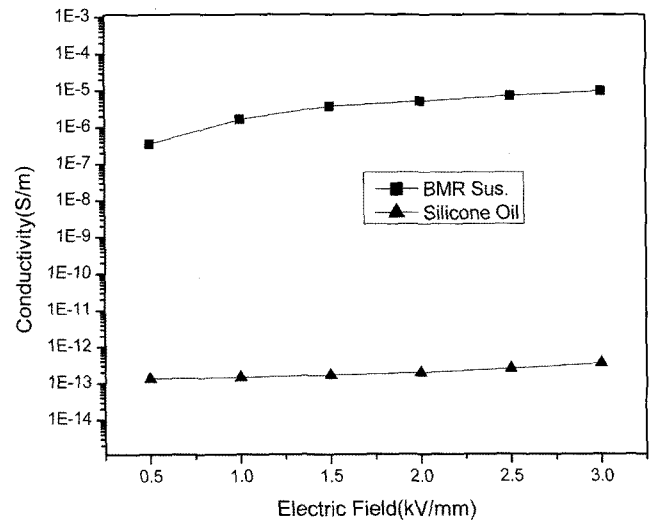
silicone oil with the electric field. The shear stress, τ_v is proportional to the shear rate, γ in accord with a Newtonian fluid as given in Eq. (2).

The effect of shear stress on the shear rate for Bismark Brown chitosan succinate suspension is illustrated in Figure 6. The results were obtained at the electric fields of 0 to 3 kV/mm, a volume fraction of 0.3, shear rates of 0.1 to 1000 s^{-1} and a temperature of 25°C. Bismark Brown chitosan succinate suspension behaves as a Newtonian fluid without the electric field, but it does not flow below a certain shear stress upon application of the electric field. This suspension, therefore, approximates a Bingham fluid behavior in the electric fields. Figure 7 shows a log-log plot of the shear stress vs the squared of the electric field for the Bismark Brown chitosan succinate suspension. The shear stress exhibited the dependence with a factor equals to 1.84 power on the electric field , i.e., $\tau \propto E^{1.84}$. It follows from the fact that the interaction force for dipole in an electric field is proportional to the electric field intensity.

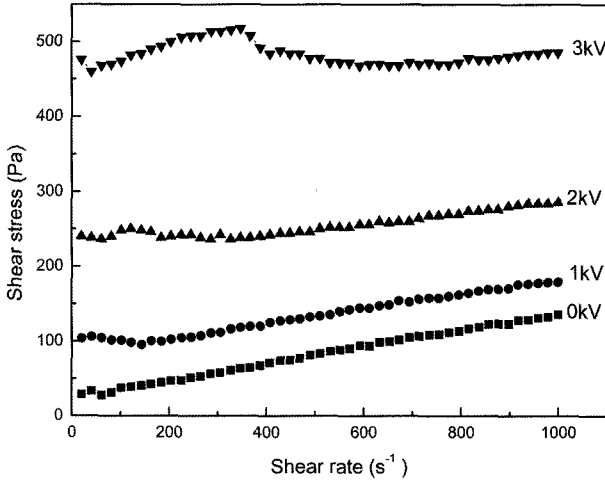The general flow behavior of ER suspensions upon application

Fig. 6. Shear stress vs shear rate for Bismark Brown chitosan succiniate suspension.
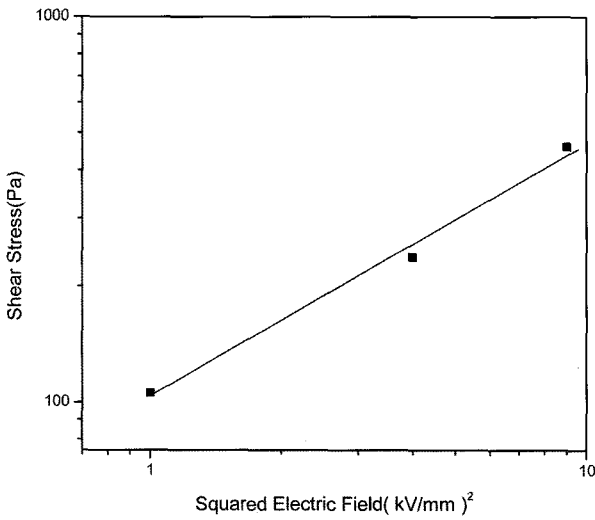

Fig. 7. Effect of the squared electric field on shear stress for Bismark Brown chitosan succiniate suspension.

of the electric field may be described using the Bingham plastic equation and polarization model given by Eq. (3). According to Eq. (3), it is reported that the shear strength of ER fluids is controlled by the polarizability β. Generally, the relative polarizability β of a single spherical particle with relative dielectric constant K_p and conductivity σ_p dispersed in a base fluid of relative dielectric constant K_f and conductivity σ_f can be written as [7,12]

$$\beta = (\sigma_p - \sigma_f)/(\sigma_p + 2\sigma_f) \text{ at dc or low-frequency ac fields}$$
$$= (K_p - K_f)/(K_p + 2K_f) \text{ at high-frequency ac fields} \quad (5)$$

Previous theoretical studies on the polarization model of ER fluids show that there is a close relation between the polarizabiliy of the particles and the attractive force between them [9,13]. Equation (6) gives two extreme cases pertaining to the polarizability of a particle. At dc and low-frequency ac fields, β depends only on the conductivity mismatch between the particles and the base fluid. However, at high-frequency ac
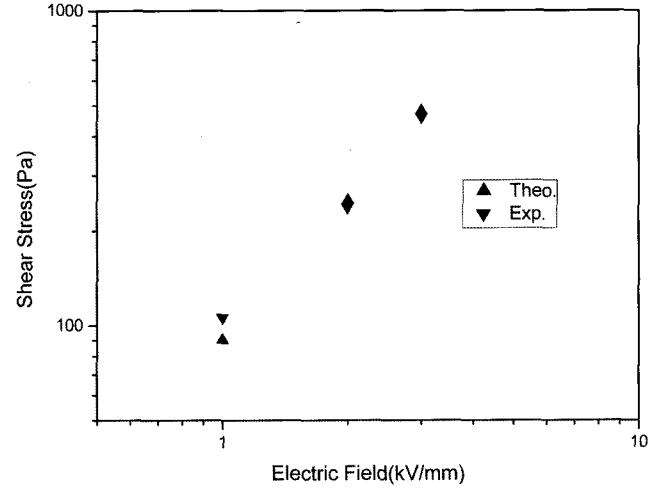
fields the dielectric constant mismatch is dominant.

The interaction force between two close-positioned particles can be scaled in term of β^2 [9]

$$F_r = 12\pi a^2 \varepsilon_0 K_f \beta^2 E^2 f_r \quad (6)$$

where f_r is a function of the relative position of the adjacent particles, a the radius of the particles and ε_0 the dielectric constant of free space. Even when the many body effect is considered and the particles align into a single row chain, the attractive force between particles gives [13]

$$F_s = 37.74\pi a^2 \varepsilon_0 K_f \beta^2 E^2 \exp\{[14.84 - 6.16(R/a)]\beta^2\}$$
$$\times [1/(R/a)^8 - 4/(R/a)^{10}]^{1/2} \quad (7)$$

where R is the center to center spacing and R/a 2.05.

As a first approximation, the shear yield stress τ_E is proportional to the force $F_{s\,max}$ to rupture a chain times the number of chains per unit area N_A, i.e.

$$\tau_E = A_s N_A F_{s\,max} \quad (8)$$

where A_s is a constant which represents the structure, i.e., the deviation of the geometric arrangement of the particles from single row chains and N_A is given by

$$N_A = 3\chi\varphi/2\pi a^2 \quad (9)$$

where χ is the fraction of particles that lie in the chains parallel to the electric field, $\chi = \pi/4 \sim \pi/6$ depending on the size and size distribution of the particles, and Φ is the volume fraction of particles.

Taking $\chi = \pi/4$ and substituting Eqs. (7) and (9) into Eq. (8) we get

$$\tau_E = 44.1\varphi A_s \varepsilon_0 K_f \beta^2 E^2 \exp\{[14.84 - 6.16(R/a)]\beta^2\}$$
$$\times [1/(R/a)^8 - 4/(R/a)^{10}]^{1/2} \quad (10)$$

Here A_s is equal to one for perfectly aligned single row chains [12]. The measured value for the melaminated chitosan succinate suspension is compared with the predicted value by Eq. (10) and the data are given in Figure 8. The experimental

Fig. 8. Comparision of the predicted shear stress with that measured for Bismark brown chitosan succiniate suspension.

results were obtained at a shear rate of $2\ s^{-1}$, a volume fraction of 0.3. As shown in Figure 8, there is good agreement between the measured and predicted values. It follows from Eq. (1) that at low shear rates the electric polarization force dominates, while at high shear rates the viscous shear force becomes dominant. The low shear rate regime has been termed quasi-static and the high shear rate regime dynamic. Many researches have been conducted under the quasi-static regime, considerably less attention having been given to the more complex behavior in the dynamic regime. By these reasons, the results for the Bismark Brown chitosan succinate suspension in Figs. 7 and 8 were obtained at a shear rate of $2\ s^{-1}$ in the quasi-static regime.

On the the results, Bismark Brown chitosan succinate suspension showed the ER flow behavior upon application of the electric field due to the polarizability of the branched amide and amine polar groups of the Bismark brown chitosan succinate particles.

4. Conclusion

The electrorheological effect of the Bismark Brown chitosan succinate suspension was investigated. The following is a summary of the results:

(1) Bismark Brown chitosan succinate suspension showed the ER response upon application of the electric field. It can be caused by the polarizablility of the branched amino and amide polar groups of the Bismark Brown chitosan succinate particles.

(2) The shear stress for the suspension exhibited the dependence with a factor equals to 1.84 power on the electric field.

(3) There is a good agreement between the measured and the predicted values of shear yield stress.

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